

## ANTIMONY

## ANNUAL SURVEY COVERING THE YEAR 1985

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Except for our Annual Survey covering the year 1983, no book or review devoted exclusively to organoantimony compounds was published in 1985. A number of review articles have appeared, however, in which certain aspects of organoantimony chemistry were briefly examined. Thus, the structures, dipole moments, and electronic spectra of tri-arylamines, -phosphines, -arsines, -stibines, and -bismuthines have been reviewed in the Russian literature [1]. Organoantimony compounds have also been mentioned in a review of the ligand behavior of derivatives of phosphorus, arsenic, antimony, and bismuth in which the Group V atom was multiply bonded and had a coordination number of one, two, or three [2]. Some interesting reactions of primary and secondary stibines have been discussed in a review article on the addition of the arsenic-hydrogen and antimony-hydrogen functions to unsaturated systems [3]. Information about organoantimony compounds has been included in surveys of recent work on the main-group elements of Group V [4] and on organic derivatives of arsenic, antimony, and bismuth [5]. In addition, organoantimony compounds have been very briefly mentioned in review articles on the following subjects: metal-ligand bond energies in organometallic compounds [6], substitution reactions of metal carbonyls with Group V and Group VI ligands [7], diffraction studies of organometallic compounds [8], and the organometallic chemistry of the main-group elements [9].

The first organic compound that has been shown to contain a ring of six antimony atoms has been prepared in 16% yield by the slow air oxidation of a solution of bis(trimethylsilyl)phenylstibine in 1,4-dioxane [10]:

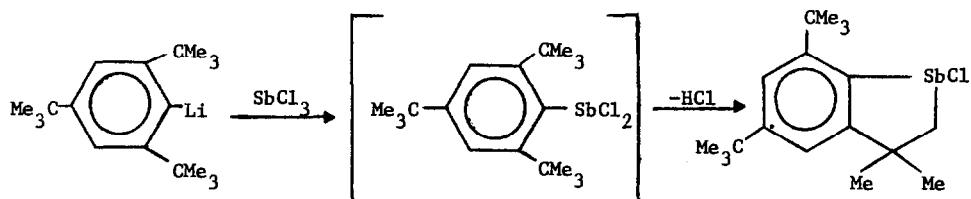


In the solid state, the yellow crystalline substance thus obtained was remarkably inert towards oxygen. In solution, however, the substance (which was slightly soluble in chloroform or toluene) reacted rapidly with air to form a colorless solid. When a toluene solution of the cyclic compound was warmed and then cooled, a black-brown solid

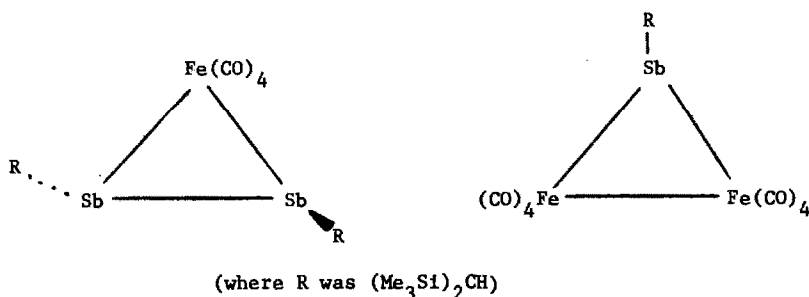
\*Previous survey see *J. Organomet. Chem.*, 298(1986)37-66.

(believed to be a polymeric "phenylantimony") was obtained. An X-ray crystal structure of the cyclic compound showed the presence of isolated centrosymmetric  $(\text{PhSb})_6$  molecules. The  $\text{Sb}_6$  rings had a chair conformation, and the phenyl groups were equatorial. There appeared to be no specific interactions between the dioxane molecules and the antimony atoms. The Sb-Sb distances, 2.836–2.839(1)Å, were similar to those found in distibines; and the Sb-C distances, 2.16–2.17(1)Å, were in the usual range found for organoantimony compounds. When the oxidation of bis(trimethylsilyl)phenylstibine was conducted in benzene instead of dioxane, orange-yellow crystals of composition  $(\text{PhSb})_6 \cdot \text{PhH}$  were obtained in 20% yield. This substance appeared to be similar to the "phenylantimony" earlier [11] prepared by the interaction of phenylstibine and styrene in benzene.

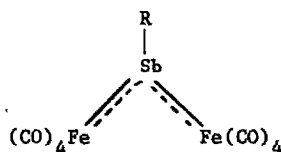
The synthesis of the dichlorostibines  $\text{RSbCl}_2$ , where R was 2,4,6- $(\text{Me}_3\text{C})_3\text{C}_6\text{H}_2$ ,  $(\text{Me}_3\text{Si})_3\text{C}$ , or  $(\text{Me}_3\text{Si})_2\text{CH}$ , has been investigated in connection with their potential usefulness in preparing distibene and stibinidene complexes of iron [12]. The attempted synthesis of 2,4,6-tri-*tert*-butylphenyldichlorostibine via the corresponding organolithium reagent, however, resulted in intramolecular dehydrochlorination and formation of an antimony heterocycle:



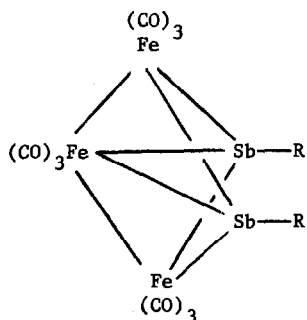
On the other hand, the reactions of antimony trichloride with tris(trimethylsilyl)methyl lithium or bis(trimethylsilyl)methylmagnesium chloride did yield the desired dichlorostibines. Tris(trimethylsilyl)methyldichlorostibine proved to be extremely sensitive to light and, as a consequence, bis(trimethylsilyl)methyldichlorostibine became the reagent of choice. The structure of the latter compound was determined by single-crystal X-ray diffraction. The geometry around the antimony atom was found to be clearly pyramidal. The average Sb-Cl bond length, 2.366(2)Å, and the Sb-C bond length, 2.136(4)Å, were close to the sums of the corresponding single bond covalent radii. The interaction of the dichlorostibine with the disodium salt  $\text{Na}_2[\text{Fe}(\text{CO})_4]$  resulted in the formation of a mixture of a distibene complex and a "closed" bridging stibinidene complex:



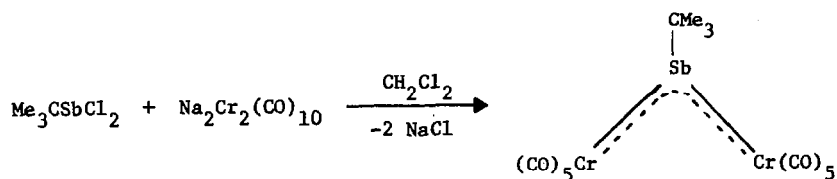
The structures of both substances were established with the aid of X-ray crystallography and high resolution mass spectroscopy. The Sb-Sb bond length in the distibene complex was  $2.774(1)\text{\AA}$ , a value slightly less than a typical Sb-Sb single bond length and possibly suggestive of a small amount of multiple bond character. The geometry around the iron atom was considered as being trigonal-bipyramidal with the distibene occupying a single equatorial site. The existence of a "closed" structure in the stibinidene complex was consistent with the observed pyramidality of the antimony atom (the sum of the bond angles was  $287.1^\circ$ ). Although the Fe-Fe separation,  $2.801(1)\text{\AA}$ , exceeded the usual single-bond range, it was concluded that the iron atoms were bonded to one another. Unlike comparable "open" complexes, the "closed" stibinidene complex acted as a Lewis base. Thus, it was readily protonated by reaction with the acid  $\text{HBF}_4 \cdot \text{OEt}_2$  to form an unstable cation. Treatment of the distibene complex with nonacarbonyldiiron yielded the "closed" stibinidene complex plus two new antimony compounds. One of these appeared to exist in hexane solution as the "open" stibinidene complex:



In the solid state, however, the properties of this substance were identical to those of the isomeric "closed" stibinidene complex. The structure of the other new antimony compound could not be determined by X-ray diffraction because of severe disorder problems. Other methods (IR, NMR, and fast-atom bombardment mass spectrometry), however, led to the following structural assignment:

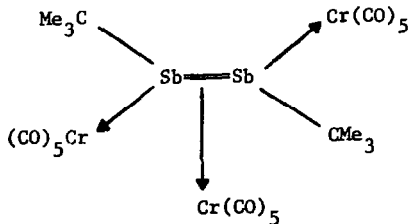


An "open" stibinidene complex has been obtained by the following reaction [13]:

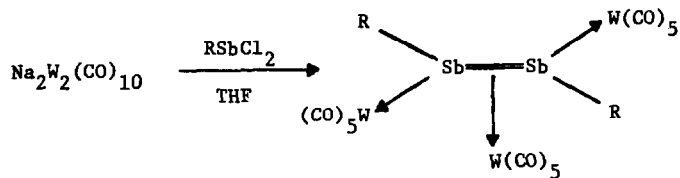


(where the dotted line represents  $\pi$ -delocalization of the antimony lone pair electrons)

The following distibene complex was also isolated from the reaction mixture:

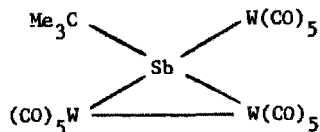


Similar distibene complexes of tungsten were prepared in an analogous manner:



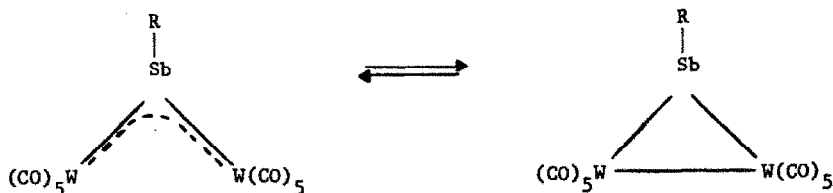
(where R was Me, Ph, or Me<sub>3</sub>C)

In addition to a distibene complex, the reaction with *tert*-butyldichlorostibine yielded the trinuclear derivative I:

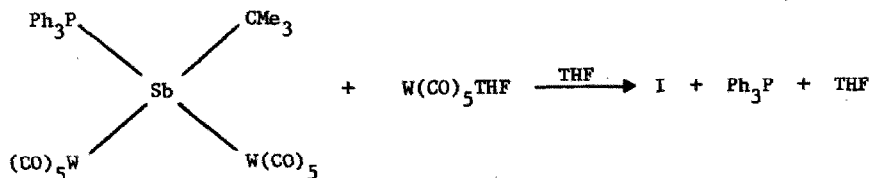


I

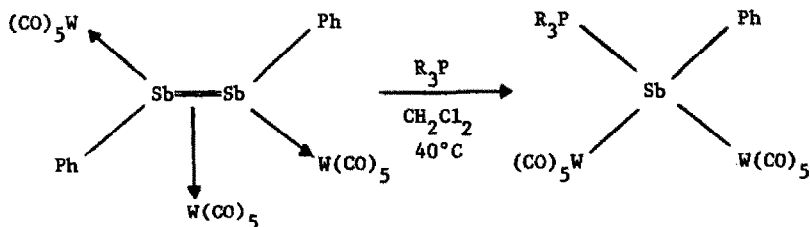
It was suggested that the reactions of the dichlorostibines with  $\text{Na}_2\text{W}_2(\text{CO})_{10}$  gave stibinidene intermediates that exhibited the following type of valence tautomerism:



The "open" form was said to be a Lewis acid, while the "closed" form (with a lone pair localized on the antimony atom) showed Lewis base behavior. The distibene complexes of tungsten presumably arose from interaction of the two forms. As mentioned in the next paragraph, the trapping of stibinidene intermediates by Lewis bases has been observed. One of these adducts was converted to the trinuclear derivative I:



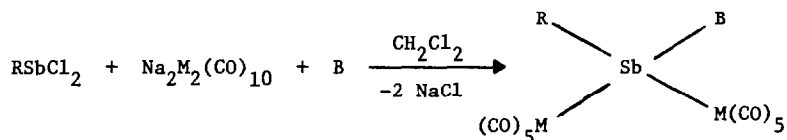
Phosphine adducts of a stibinidene complex were also obtained from a distibene complex:



(where R was Ph or Bu)

The various new compounds prepared for this investigation were characterized by elemental analysis and by IR, UV, and PMR spectroscopy. The distibene complex of chromium and the trinuclear derivative I were subjected to X-ray structural analysis; the C-Sb distances in the former compound were 2.25(2)Å and 2.26(3)Å, and the C-Sb distance in the latter compound was 2.25(6)Å.

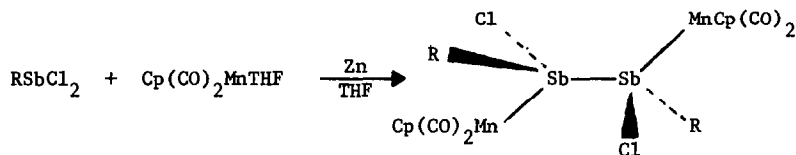
The following type of reaction has been employed for the preparation of base adducts of stibinidine complexes [14]:



(where R was Me, Me<sub>3</sub>C, or Ph, B was (MeNH)<sub>2</sub>C=S, and M was Cr or W; where R was Me or Me<sub>3</sub>C, B was Ph<sub>3</sub>P, and M was Cr or W; where R was Ph, B was Bu<sub>3</sub>P, and M was Cr or W; and where R was Ph, B was Ph<sub>3</sub>P, and M was W)

The adducts were obtained in good yields as yellow or orange solids, which were stable in air at room temperature for several hours. They were characterized by elemental analysis, IR, and PMR spectroscopy; <sup>31</sup>P NMR was used for the adducts of the tertiary phosphines. An X-ray structure was obtained for the adduct in which R was Me, B was Ph<sub>3</sub>P, and M was W; the C-Sb distance was 2.26(2)Å.

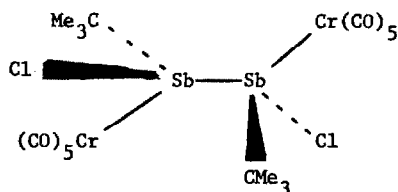
Chlorine-containing distibene complexes of manganese have been prepared by the following type of reaction [15]:



(where R was Me, Me<sub>3</sub>C, or Ph)

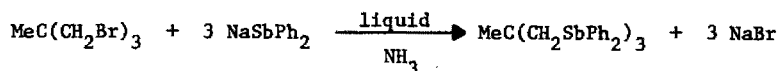
The complexes were isolated as blackberry-colored crystals. Their intense color was surprising and could not be ascribed to a solid-state effect, since the color was unchanged in solution. Their PMR spectra indicated that in solution a *meso* form and an enantiomeric pair were present. Thus, two signals were observed in C<sub>6</sub>D<sub>6</sub> for the Cp protons; the more intense signal probably was due to the sterically favored *meso* form. The PMR signals of the alkyl groups in the methyl and *tert*-butyl complexes were broad singlets; the configuration of the stereoisomers presumably had only

a slight influence on the chemical shifts of the alkyl protons. The PMR spectrum of the phenyl-substituted complex in acetone- $d_6$  exhibited four Cp signals. These were assumed to arise from some type of association between the complex and the solvent; the nature of this association was not elucidated. It was also discovered that the interaction of *tert*-butyldichlorostibine and the disodium salt  $\text{Na}_2\text{Cr}_2(\text{CO})_{10}$  in THF yielded the following chlorine-containing distibine complex (in addition to the "open" stibinidene and the distibene complexes discussed in an earlier paragraph):

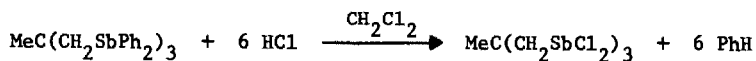


This chromium complex was obtained as an orange, crystalline solid. Like the manganese-distibine complexes, it was characterized by elemental analyses and by IR and PMR spectroscopy. In addition, it was studied by X-ray diffraction, which showed that the chromium complex had the *meso* configuration. The Sb-Sb distance was  $2.901(2)\text{\AA}$ , a value similar to that found in tetraalkyldistibines. The C-Sb distance of  $2.20(1)\text{\AA}$  was also not unusual.

Although treatment of the trichloride  $\text{MeC}(\text{CH}_2\text{Cl})_3$  with sodium diphenylstibide in liquid ammonia has been found to convert the stibide to tetraphenyldistibine, the interaction of the tribromide  $\text{MeC}(\text{CH}_2\text{Br})_3$  and the stibide gave not only the distibine but also a tri-tertiary stibine in 20-25% yield [16]:



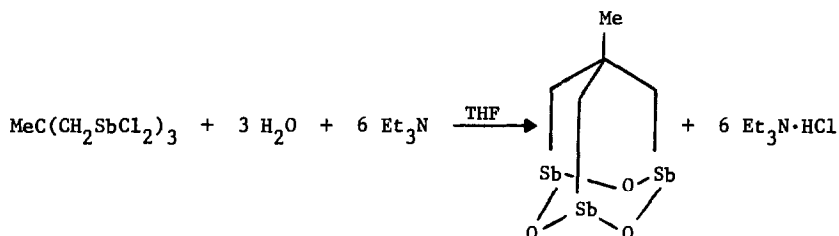
This substance was then converted to 4-methyl-1,2,6-tristibatricyclo-[2.2.1.0<sup>2,6</sup>]heptane by the following sequence of reactions:



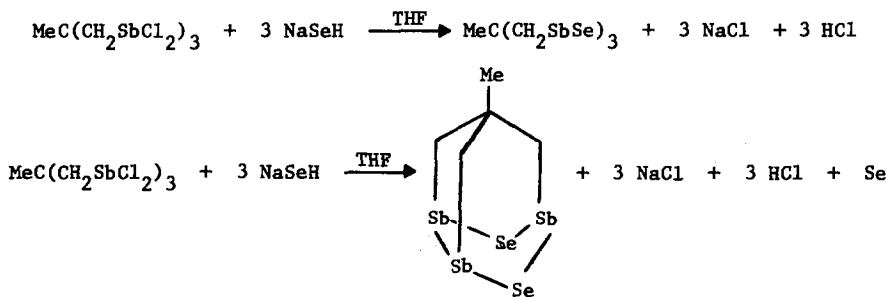
The composition and structure of the deep-orange all-*cis* cyclic tri-stibine was established by elemental analysis, spectroscopy (UV, PMR, IR,

Raman, and mass), and X-ray diffraction. The average intramolecular Sb-Sb distance was found to be  $2.80\overset{\circ}{\text{Å}}$ , while the average intermolecular  $\text{Sb}\cdots\text{Sb}$  contact was  $3.96\text{--}4.00\overset{\circ}{\text{Å}}$ . This latter value was significantly shorter than the sum of the van der Waals radii ( $4.40\overset{\circ}{\text{Å}}$ ). The cyclic trisbicine was sublimable at  $216\text{--}218^\circ\text{C}$ . It was readily soluble in THF and gave a pale yellow-orange solution; it was moderately soluble in dichloromethane and chloroform but insoluble in other common organic solvents. When a pentacarbonyl complex of the type  $\text{M}(\text{CO})_5\text{THF}$  (where M was Cr, Mo, or W) was generated by the UV irradiation of a THF solution of a hexacarbonyl complex of the type  $\text{M}(\text{CO})_6$  and then added to a THF solution of the cyclic trisbicine, dark-red adducts of the type  $\text{MeC}(\text{CH}_2\text{Sb})_3\cdot\text{M}(\text{CO})_5$  were obtained. These adducts were characterized by elemental analyses and by PMR, IR, Raman, and mass spectroscopy; each one was shown to contain an M-Sb bond.

Treatment of the tris(dichlorostibinomethyl) derivative mentioned in the above paragraph with 6 moles of water and 6 moles of triethylamine has been found to yield an adamantane-like substance [17]:



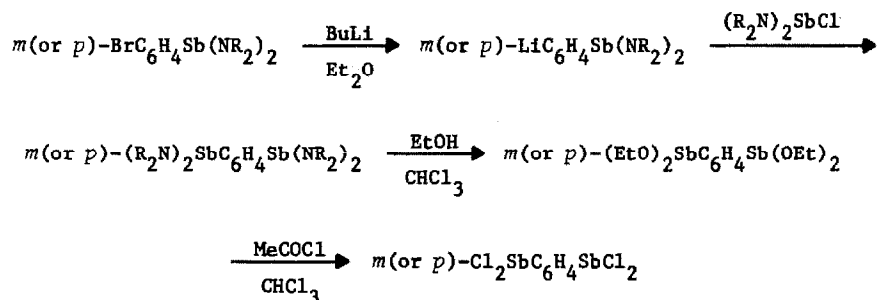
When a large excess of water and ammonia were used, however, only tetra-antimony hexoxide was isolated. The interaction of the tris(dichlorostibinomethyl) derivative and hydrogen sulfide in the presence of triethylamine gave the sulfur analog of the above adamantane. When sodium hydrogen selenide was used, two cage compounds were formed, *viz.* a triselenatristibaadamantane (in 60% yield) and a diselenatristibanoradamantane (in 20% yield):





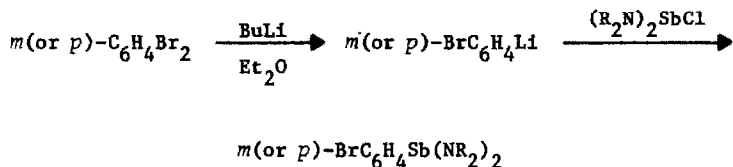
Several attempts to prepare an adamantane or noradamantane that contained antimony and tellurium were unsuccessful. Sodium telluride was found to reduce the tris(dichlorostibinomethyl) derivative to 4-methyl-1,2,6-tristibatricyclo[2.2.1.0<sup>2,6</sup>]heptane (*cf.* above paragraph). Oxidation of the latter compound in THF by air gave tetraantimony hexoxide. The new compounds prepared in this investigation were characterized by elemental analysis, by mass, IR, and Raman spectroscopy, and in some cases by PMR.

The preparation of *m*- and *p*-phenylenebis(dichlorostibine) has been accomplished by the following series of reactions [18]:

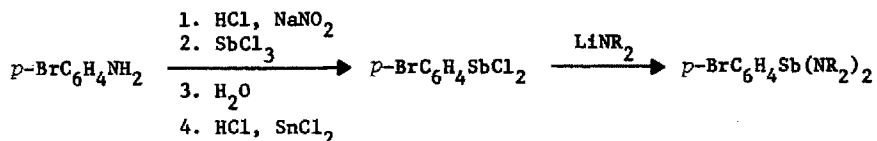


(where R was Me<sub>2</sub>CH)

Both *m*- and *p*-bromophenylbis(diisopropylamino)stibines could be obtained via organolithium reagents:

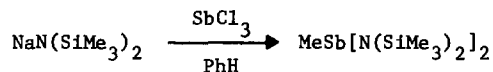


*p*-Bromophenylbis(diisopropylamino)stibine was also prepared from a dichlorostibine:

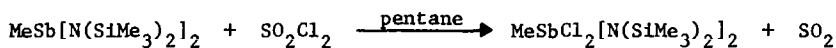


All of the organoantimony compounds were characterized by elemental analysis and by PMR and IR spectroscopy. In addition, the mass spectra of the phenylenebis(dichlorostibines) were reported.

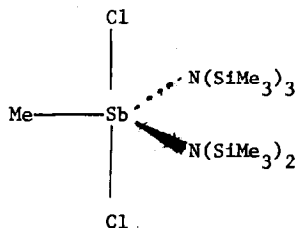
The interaction of one mole of antimony trichloride and three moles of the sodium salt of bis(trimethylsilyl)amine has unexpectedly been found to give a 20-30% yield of a compound containing a Me-Sb bond [19]:



The stibine was a colorless liquid and was very sensitive to air and moisture; it gave a normal cryoscopic molecular weight in benzene. Treatment with sulfuryl chloride resulted in oxidative dichlorination:

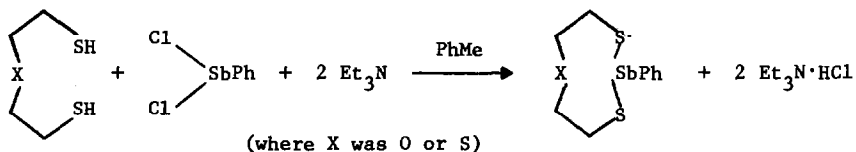


The dichloride was a white solid, which was also shown by cryoscopic measurements to be monomeric in benzene. The structures of both new organoantimony compounds were clearly established by elemental analysis and by NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ), IR, and Raman spectroscopy; the mass spectrum of the stibine was also reported. The X-ray structure of the dichloride showed that the antimony atom possessed slightly distorted trigonal-bipyramidal coordination in which the chlorines occupied the apical positions while the methyl group and the nitrogens were equatorial:



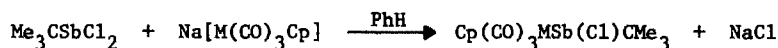
The Cl-Sb-Cl angle was  $174.8(1)^\circ$ , the N-Sb-N angle was  $120.1(3)^\circ$ , and the Me-Sb-N angles were  $118.5(4)^\circ$  and  $121.4(4)^\circ$ . The C-Sb distance of  $2.116(11)\text{\AA}$  was not unusual. There were four monomeric units per cell.

Oxadithia- and trithiastibocanes have been synthesized by the interaction of a dithiol and phenyldichlorostibine [20]:



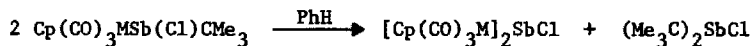
When the triethylamine was omitted, the phenyl group in the stibocanes was replaced by a chlorine atom. The phenyl-substituted products were colorless solids, which were stable in dry air at room temperature. They were investigated by thermogravimetric analysis and by  $^{13}\text{C}$  NMR, mass, IR, and Raman spectroscopy. X-ray crystal structures were also obtained. The oxadithiastibocane exhibited a chair-chair conformation. There were two independent molecules in the crystal structure of the trithiastibocane; both molecules exhibited boat-chair conformations with the phenyl groups differently twisted. In each case there was significant 1,5-transannular interaction that expanded the valence shell of the antimony atom. There were also important intermolecular contacts. Thus, in the oxadithiastibocane, there was partial bonding between the antimony atom of one molecule and the two sulfur atoms of the  $\text{SbS}_2$  group of another molecule. The resulting coordination of the antimony in this compound was described as being  $\psi$ -monocapped octahedral. The crystal structure of the trithiastibocane exhibited chains of four molecules. The antimony atoms in the two molecules in the middle of the chain also possessed  $\psi$ -monocapped octahedral coordination. In the two molecules at the ends of the chain, however, each antimony atom was partially bonded to only one sulfur atom of the  $\text{SbS}_2$  group of a neighboring molecule. These antimony atoms were said to be  $\psi$ -octahedral. The C-Sb distances were  $2.164(6)\overset{\circ}{\text{A}}$  in the oxadithiastibocane,  $2.169(4)\overset{\circ}{\text{A}}$  in the  $\psi$ -monocapped octahedral trithiastibocane, and  $2.158(4)\overset{\circ}{\text{A}}$  in the  $\psi$ -octahedral trithiastibocane.

The nucleophilic metalation of *tert*-butyldichlorostibine has been accomplished by the following type of reaction [21]:

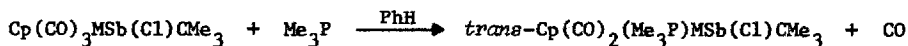


(where Cp was  $\eta^5$ -cyclopentadienyl and M was Mo or W)

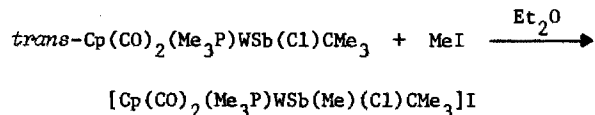
The organoantimony compounds thus obtained were found to disproportionate on standing in solution at room temperature:



On being treated with trimethylphosphine, they lost one mole of carbon monoxide:

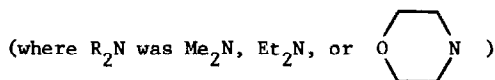
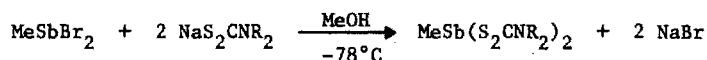


The trimethylphosphine complex in which M was W was easily quarternized:

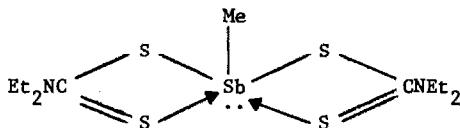


The resulting complex salt was a yellow crystalline powder and was quite soluble in THF and acetonitrile. All of the new compounds prepared in this investigation were characterized by spectroscopy (IR and NMR) and by elemental analysis.

Three methylbis(dialkyldithiocarbamato)stibines have been obtained by the following type of reaction [22]:



After recrystallization from ethanol or a mixture of dichloromethane and petroleum ether, all three compounds were light yellow solids. They were relatively air-stable, hardly sensitive to hydrolysis, and they gave normal molecular weights in benzene solution. They were quite soluble in moderately polar solvents such as dichloromethane, chloroform, or benzene. In more polar solvents like alcohols or ether they were difficultly soluble, while in nonpolar solvents like saturated hydrocarbons they were insoluble. Their PMR spectra exhibited the expected signals, and their IR spectra suggested that the dialkyldithiocarbamato ligands were bidentate. The chelating ability of these ligands was clearly demonstrated by an X-ray diffraction study of methylbis(diethyldithiocarbamato)stibine:



The antimony atom was almost exactly in the plane of the four sulfur atoms and the methyl-antimony bond was nearly perpendicular to this plane. The C-Sb bond distance was  $2.152(8)\text{\AA}$ , a value similar to that reported for other organoantimony compounds. Two of the Sb-S distances ( $2.960(2)$  and  $2.904(2)\text{\AA}$ ) were significantly longer than the other two ( $2.544(2)$  and  $2.538(2)\text{\AA}$ ). The crystal structure of this compound showed no special intermolecular interactions. In contrast to this result,

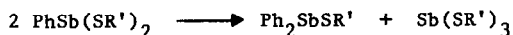
both the analogous bismuth compound  $\text{MeBi}(\text{S}_2\text{CNET}_2)_2$  and the xanthatostibine  $\text{MeSb}(\text{S}_2\text{COEt})_2$  had earlier been shown to form dimeric units in the crystalline state. Intermolecular interactions, however, had not been observed in the crystal structure of phenylbis(diethyldithiocarbamato)-arsine.

Eight dithiolatostibines have been prepared by the following type of reaction [23]:



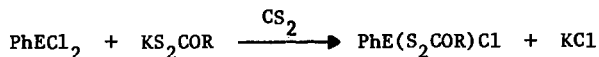
(where R was Me or Ph and R'SH was pyrimidine-2-thiol, 2-mercapto-4,5-thiazoline, 2-mercapto-1-methylimidazole, or 5-mercapto-1-phenyl-1,2,3,4-tetrazole)

The compounds thus obtained were yellow or white solids, which were only moderately soluble in polar solvents such as methanol or ethanol. On the other hand, they were quite soluble in donor solvents such as acetone or DMSO. The phenyl-substituted compounds were not completely free of ethanol (which was used as the reaction medium) even after they were dried *in vacuo* for several hours. All eight compounds were characterized by elemental analysis, PMR spectroscopy, and differential thermoanalysis. The compound obtained by the interaction of phenyldiethoxystibine and 2-mercapto-1-methylimidazole disproportionated exothermally at 88°C in accordance with the following equation:

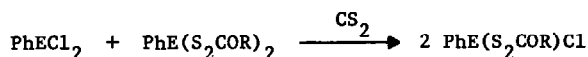


The thiolatodiphenylstibine formed in this reaction was isolated, and its structure was established by mass and PMR spectroscopy.

Two methods have been employed for the preparation of mixed chloride xanthates of the type  $\text{PhE}(\text{S}_2\text{COR})\text{Cl}$ , where E was As or Sb and R was Me, Et, Pr, or  $\text{Me}_2\text{CH}$  [24]. One method involved the interaction of phenyldichloroarsine or phenyldichlorostibine and a potassium xanthate at ambient temperatures:



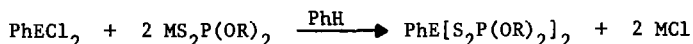
The other method involved the following type of disproportionation reaction at ambient temperatures:



The chloride xanthates thus obtained were either light yellow liquids

or crystalline solids and were monomeric in refluxing chloroform. They were highly soluble in carbon tetrachloride, chloroform, benzene, carbon disulfide, and similar solvents, and they did not volatilize under reduced pressure. Their IR spectra exhibited bands in the expected regions. Their PMR spectra displayed the characteristic resonances due to the alkyl and phenyl protons. The signals were sharp and did not show splitting indicative of structural rigidity on the PMR time scale. The mass spectrum of the chloride xanthate in which E was Sb and R was Et showed a weak molecular ion peak and no peaks arising from a higher molecular weight species or a polyantimony species. The mass spectral results therefore supported the conclusion that the chloride xanthate molecules were not associated.

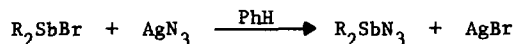
Dithiophosphates of arsenic and antimony have been obtained in quantitative yields by the following type of reaction [25]:



(where E was As or Sb, M was Na or  $\text{NH}_4$ , and R was Et, Pr,  $\text{Me}_2\text{CH}$ , or Ph)

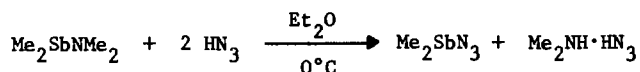
The compounds were crystalline solids or colorless liquids. They were soluble in common organic solvents and were monomeric in refluxing benzene; they were non-volatile even under reduced pressure. IR and NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$ ) spectral data were used to investigate plausible structures; and fragmentation pathways were suggested from mass spectral data. The X-ray crystal structures of the two compounds of type  $\text{PhE[S}_2\text{P(OCHMe}_2\text{)}_2\text{]}_2$  were also determined. It was found that the dithiophosphate ligands were bidentate and that they chelated the central arsenic or antimony atom. The overall geometry was octahedral with a nonbonded pair of electrons occupying an axial position *trans* to the phenyl group. The Sb-C bond distance was  $2.152\text{\AA}$ , a value similar to that found in other organo-antimony compounds.

Two azidostibines have been prepared by the following type of reaction [26]:



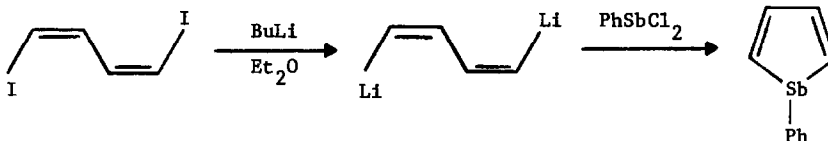
(where R was Me or Et)

The reactions required about one week and had to be conducted in the absence of light. Dimethylazidostibine was obtained in a substantially faster manner by the following procedure:



It was quite soluble in aprotic solvents like benzene, toluene, or diethyl ether. It underwent decomposition on exposure to light, heat, or moisture. Both azidostibines gave normal cryoscopic molecular weights in benzene. When the crystal structure of dimethylazidostibine was determined by X-ray diffraction data collected at  $-67^\circ\text{C}$ , however, it was found that the compound was polymeric. The antimony atoms were linked via the  $\alpha$ -nitrogen atoms to form endless zig-zag chains in which the Sb-N-Sb angles were  $126.0(1)^\circ$ . If the lone pair of electrons were included, the coordination about the antimony could be described as distorted trigonal-bipyramidal, with azido groups occupying the apical positions. The N-Sb-N angle of  $169.6(1)^\circ$  and the C-Sb-C angle of  $93.36(7)^\circ$  did deviate significantly from the "ideal" angles,  $180^\circ$  and  $120^\circ$ , respectively. The C-Sb distance of  $2.140(3)\text{\AA}$  was not unusual. The Sb-N bonds alternated between two different lengths,  $2.322(3)\text{\AA}$  and  $2.434(3)\text{\AA}$ . It was suggested that the longer Sb-N bond was cleaved when the compound was dissolved in a solvent. The IR and Raman spectra of both dimethyl- and diethylazidostibine in the solid state were also described and analyzed. In addition, NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{15}\text{N}$ ) and mass spectra were reported for the dimethyl compound, while  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{15}\text{N}$  NMR spectra were reported for the diethyl compound.

1-Phenylstibole has been prepared in low yield by the following series of reactions [27]:



The compound was isolated as a yellow oil by Kugelrohr distillation at  $70^\circ\text{C}$  (0.005 torr). It proved to be rather labile. On standing at  $25^\circ\text{C}$  under an inert atmosphere, it darkened and slowly resinified. The stibole was characterized by mass and UV spectroscopy and by comparing its  $^1\text{H}$  and  $^{13}\text{C}$  NMR parameters with those of the corresponding nitrogen, phosphorus, and arsenic compounds.

Aldehydes and ketones have been selectively reduced to the corresponding alcohols by the interaction of the carbonyl compound with diphenylstibine in the presence of a Lewis acid and subsequent hydrolysis of the reaction mixture with dilute sulfuric acid or sodium hydroxide [28]. In the absence of a Lewis acid, diphenylstibine did not react with aldehydes or ketones. Even in the presence of a Lewis acid, the second-

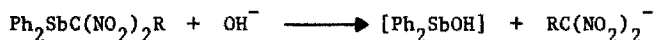
ary stibine did not attack esters, acid chlorides, alkyl halides, or olefins. Reduction of the carbonyl group of  $\alpha,\beta$ -unsaturated open-chain aldehydes or ketones was also observed.  $\alpha,\beta$ -Unsaturated cyclic ketones, however, gave 1,2 or 1,4 reduction products. Four Lewis acids were found to be effective in promoting the reduction of aldehydes and ketones with diphenylstibine; the order of effectiveness was  $\text{AlCl}_3, \text{TiCl}_4 > \text{SnCl}_4 > \text{ZnCl}_2$ . When a mixture of an aldehyde and a ketone was allowed to react with diphenylstibine, the aldehyde was reduced preferentially.

Tertiary stibines have been obtained by the interaction of diphenylchlorostibine with silver or potassium salts of trinitromethane or 1,1-dinitroethane [29]:



(where M was Ag or K and R was  $\text{NO}_2$  or Me)

In all cases the reactions went to completion after a few hours at 0-20°C. Both tertiary stibines were crystalline compounds, which were sensitive to atmospheric moisture and gradually decomposed at about 20°C. The purity of these substances was shown by TLC, and their structures were confirmed by UV and IR spectroscopy. Treatment with aqueous ammonia or alkali in aqueous alcohol resulted in hydrolysis:



The same C-Sb bond was cleaved by chlorine at 0-20°C:



Metathetical reactions were observed when tetraphenylantimony bromide was treated with the silver salt of trinitromethane or 1,1-dinitroethane:

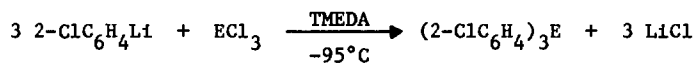


The UV spectra of the antimony(V) compounds thus obtained exhibited a band at 350 nm ( $\epsilon$ , 14,500) when R was  $\text{NO}_2$  and a band at 380 nm ( $\epsilon$ , 17,500) when R was Me; these bands were considered characteristic of the trinitromethyl and 1,1-dinitroethyl anions, respectively.

The thermal stability of 2-chlorophenyllithium in ether has been markedly increased by the addition of an equimolar quantity of tetramethylethylenediamine (TMEDA) [30]. The stabilized organolithium

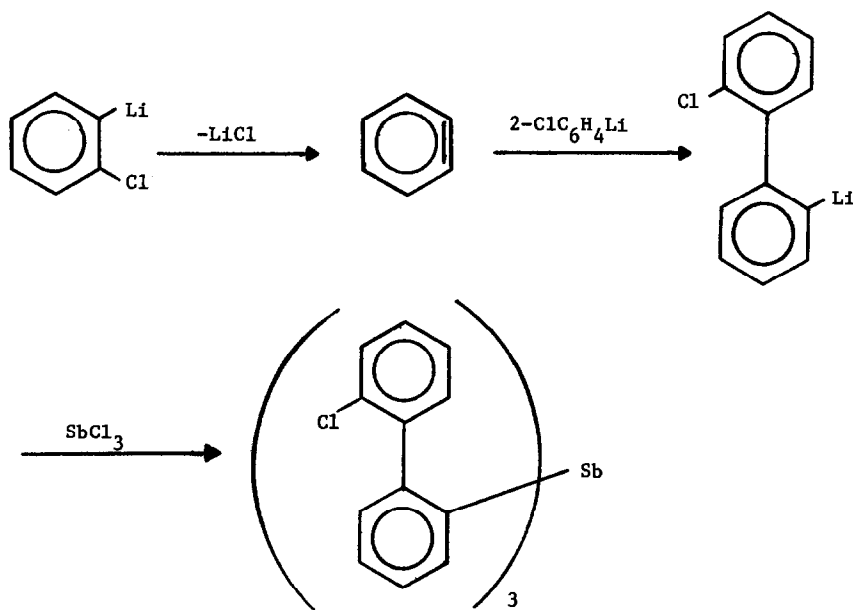


reagent thus produced was then used to obtain very good yields of tris(2-chlorophenyl)phosphine, -arsine, -stibine, and -bismuthine:

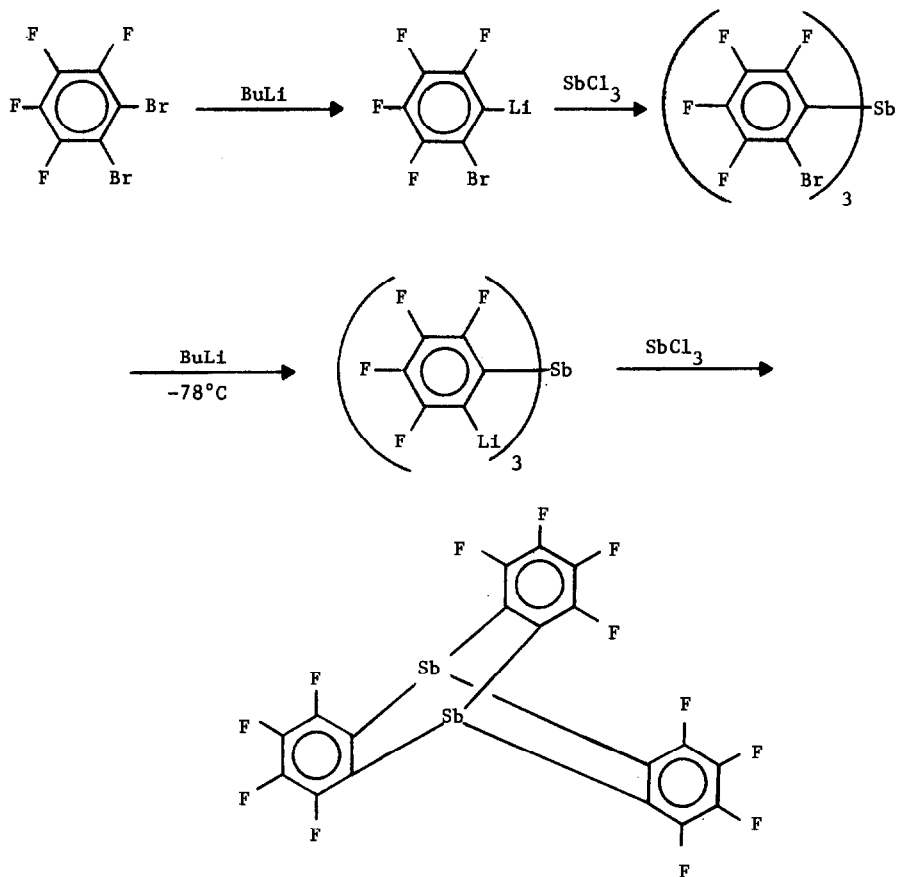


(where E was P, As, Sb, or Bi)

No tris(2-chlorophenyl)stibine was isolated when antimony trichloride was added to 2-chlorophenyllithium at  $-90^\circ\text{C}$  in the absence of TMEDA. A 5% yield of a tris(2'-chlorobiphenyl)stibine was the only product derived from the reaction mixture. This substance presumably was derived from benzyne formed by the elimination of lithium chloride from the organolithium compound:

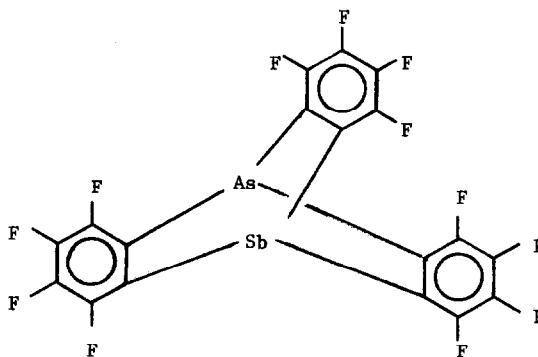


A new procedure for the synthesis of perfluoro-1,6-disubstituted triptycenes has been reported [31]. The compounds prepared in this investigation included the di-tertiary stibine II that was obtained by the following series of reactions:



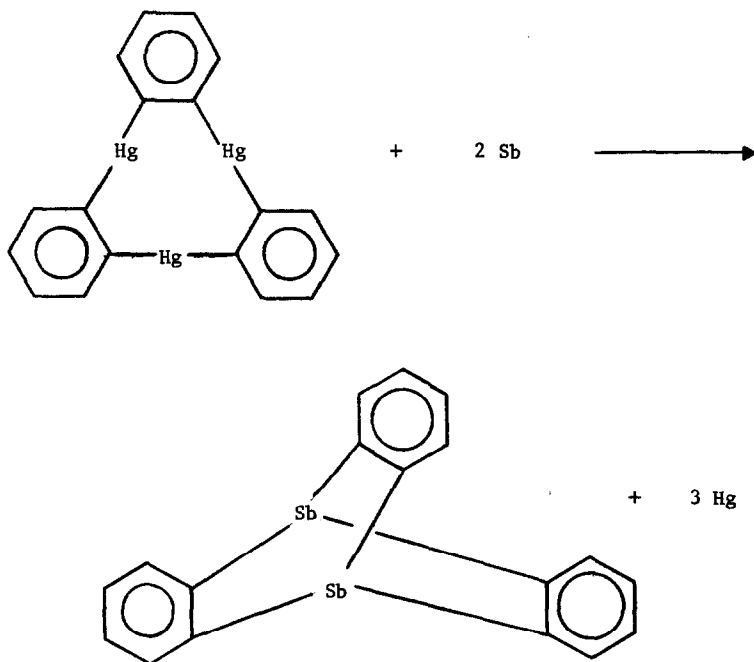
II

The substance isolated in low yield by this step-wise procedure was identical (mp, mixture mp, and IR spectrum) to the compound prepared earlier in the same laboratory by the direct reaction of antimony powder with 1,2-diodotetrafluorobenzene in a sealed tube at  $250^\circ\text{C}$ . When tris(2-lithiotetrafluorophenyl)arsine was treated with antimony trichloride, a small amount of a "mixed" arsenic-antimony species was obtained:



A similar procedure was presumably used for the preparation of an analogous phosphorus-antimony compound,  $\text{PSb}(\text{C}_6\text{F}_4)_3$ , but experimental details have not been published. The identity of all the perfluoro-1,6-disubstituted triptycenes included in this study was confirmed by elemental analysis, high resolution mass spectral measurements on their molecular ions, and  $\text{F}^{19}$  and  $\text{C}^{13}$  NMR spectra.

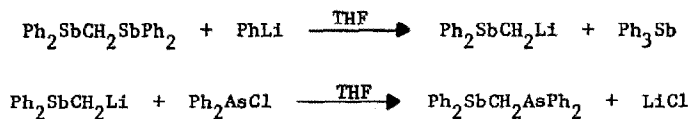
An attempt has been made to prepare 1,6-distibatriptycene by the type of procedure described in the above paragraph for the perfluoro derivative [32]. Tris(2-chlorophenyl)stibine could not, however, be converted to an organolithium reagent by treatment with lithium, butyllithium, or butyllithium plus TMEDA; temperatures ranging from  $-90^\circ\text{C}$  to the reflux point of ether were tried. When antimony powder was heated with 1,2-diiodobenzene (for 48 h) or 1,2-dibromobenzene (for 96 h) in a sealed tube at  $300^\circ\text{C}$ , the only product ever isolated was triphenylene. The desired compound was finally obtained in about 5% yield by the interaction of *ortho*-phenylenemercury trimer and antimony powder in a sealed, evacuated tube at  $260^\circ\text{C}$ :



The product separated from hexane with 0.5 mole of solvent per mole of 1,6-distibatriptycene. The main antimony-containing ions in the mass spectrum were  $\text{Sb}_2(\text{C}_6\text{H}_4)_3^+$ ,  $\text{Sb}(\text{C}_6\text{H}_4)_2^+$ ,  $\text{SbC}_6\text{H}_4^+$ , and  $\text{Sb}^+$ . The identity of the compound was confirmed by accurate mass measurements of the

three peaks present in the molecular ion cluster, *viz.*  $C_{18}H_{12}^{121}Sb_2^+$ ,  $C_{18}H_{12}^{121}Sb^{123}Sb^+$ , and  $C_{18}H_{12}^{123}Sb_2^+$ .

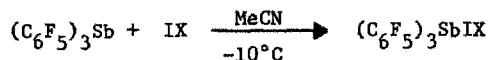
[(Diphenylstibino)methyl]diphenylarsine has been prepared by the following sequence of reactions [33]:



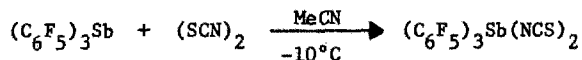
The compound was characterized by elemental analysis and by NMR ( $^1H$  and  $^{13}C$ ) and mass spectroscopy. Attempts to convert it to (diphenylarsino)-methyl lithium by treatment with phenyllithium were unsuccessful.

A study has been reported of the effect of certain metallic impurities on the purification of trimethylstibine by rectification [34]. The trimethylstibine was prepared by the interaction of triethylaluminum and antimony trichloride, and the impurities (compounds of tin, bismuth, and cadmium) were believed to be capable of forming alkyl-substituted derivatives. Radioactive isotopes of cadmium chloride, bismuth trichloride, and tin tetrachloride were used as the impurities.

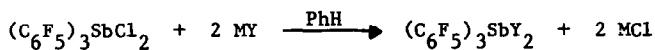
The synthesis, reactions, and physical properties of a considerable number of tris(pentafluorophenyl)antimony compounds has been reported [35]. One synthetic method involved the oxidative addition of an interhalogen, a halo-pseudohalogen, thiocyanogen, or sulfur to tris(pentafluorophenyl)-stibine:



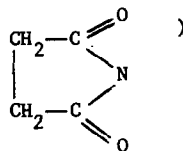
(where X was Cl, Br, N<sub>3</sub>, or NCO)



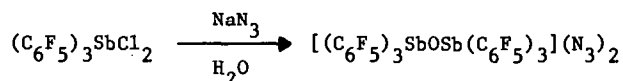
The reaction with sulfur was carried out in refluxing benzene or acetone in a dry nitrogen atmosphere. The stibine sulfide was also obtained by passing hydrogen sulfide into an alcoholic ammonia solution of tris(pentafluorophenyl)antimony dichloride. The molecular weight of the stibine sulfide (determined cryoscopically in benzene) indicated that it existed as a monomer. A second method of preparing various tris(pentafluorophenyl)antimony(V) derivatives consisted of the metathetical reaction of tris(pentafluorophenyl)antimony dichloride with a silver or sodium salt:



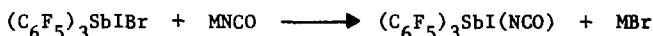
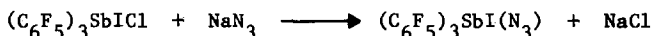
(where M was Ag and Y was NCO or NCS; or where M was Na and Y was  $\text{Me}_2\text{C}=\text{NO}$ ,  $\text{Ph}(\text{Me})\text{C}=\text{NO}$ ,  $4\text{-O}_2\text{NC}_6\text{H}_4\text{CO}_2$ , or



The reaction of the dichloride in ether with aqueous sodium azide yielded a binuclear oxo-bridged compound:

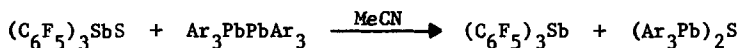


Selective replacement reactions were observed when a mixed tris(pentafluorophenyl)antimony dihalide was allowed to react with an equimolar amount of a metallic salt in benzene solution:

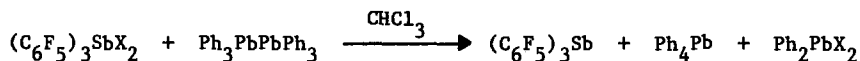


(where M was K or Ag)

Several of the antimony(V) compounds mentioned earlier in this paragraph were reduced with hexaaryldileads:

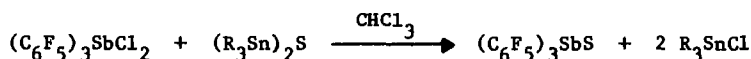


(where Ar was Ph or 4-MeC<sub>6</sub>H<sub>4</sub>)



(where X was Cl or NCO)

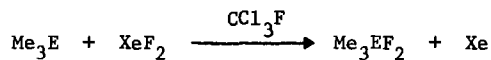
The reaction of the antimony dichloride with bis(tributyltin) sulfide or bis(triphenyltin) sulfide resulted in complete exchange of the anionic groups:



(where R was Bu or Ph)

The molar conductance of  $10^{-3}$  M acetonitrile solutions of the newly synthesized antimony(V) compounds ranged between 13 and 35  $\text{ohm}^{-1} \text{mol}^{-1} \text{cm}^2$ , values that indicated that the substances were non-electrolytes. Their IR spectra exhibited absorptions characteristic of the pentafluorophenyl group and of covalently bonded anionic groups. The binuclear oxo-bridged azide had a strong band at  $705 \text{ cm}^{-1}$ , which was assigned to the  $\nu(\text{Sb-O-Sb})$  vibration. It was concluded that the antimony(V) compounds had trigonal-bipyramidal structures in which the pentafluorophenyl groups occupied the equatorial positions.

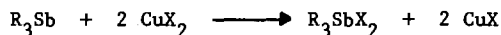
The usefulness of xenon difluoride for the oxidative difluorination of methyl derivatives of the *p*-block elements has been investigated [36]. Xenon difluoride was found to react explosively on contact with liquid trimethylphosphine, -arsine, or -stibine at or near ambient temperatures. When the trimethyl compound was diluted with 100 parts of trichlorofluoromethane, however, there was a smooth reaction in which one mole of xenon was quantitatively evolved for every mole of xenon difluoride consumed:



(where E was P, As, or Sb)

The compounds were free from any contaminants detectable by NMR ( $^1\text{H}$  and  $^{19}\text{F}$ ) spectroscopy, and they were isolated in greater than 90% yields based on the amounts of xenon difluoride used in the reaction. Deuteriochloroform solutions of the compounds gave rise to well-resolved NMR spectra at ambient temperatures.

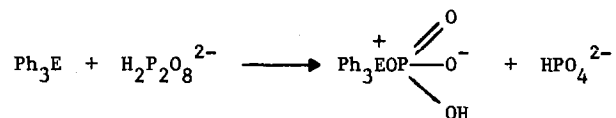
The oxidative dihalogenation of tricymanthrenylstibine has been accomplished with cupric chloride or bromide in acetone at  $50\text{--}60^\circ\text{C}$  [37]:



(where R was  $[(\text{CO})_3\text{MnC}_5\text{H}_4]$  and X was Cl or Br)

The antimony dichloride and dibromide were obtained as yellow crystals that decomposed at  $250^\circ\text{C}$  and  $220^\circ\text{C}$ , respectively. They were soluble in aromatic solvents but not in aliphatic hydrocarbons. An attempt to prepare the dichloride by the interaction of the stibine and chlorine led to decomposition, but details of this reaction were not described. A preliminary X-ray analysis of the dibromide indicated that the molecule had a trigonal-bipyramidal configuration. The apical positions were occupied by bromine atoms with markedly different Sb-Br bond distances, *viz.*  $2.617\text{\AA}$  and  $2.545\text{\AA}$ . The Br-Sb-Br bond angle ( $176.9^\circ$ ) deviated somewhat from the linear arrangement expected.

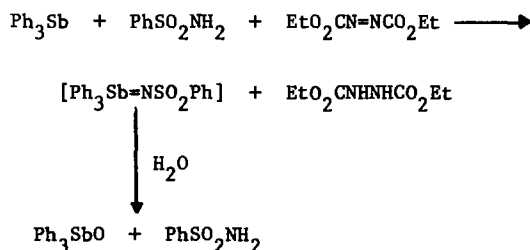
Rate coefficients have been determined for the oxidation of triphenylphosphine, triphenylarsine, and triphenylstibine by tetrapotassium peroxodiphosphate in 60% acetonitrile [38]. The reactions followed second-order kinetics: first order in the reductant and first order in the oxidant. The concentration of hydrogen ion (in the pH range of 1-3) had a pronounced accelerating effect on the reaction rate. The rate was also influenced by changing the ionic strength of the medium, but the addition of acrylonitrile had no effect. It was concluded that the rate-determining step involved the following type of nucleophilic displacement:



(where E was P, As, or Sb)

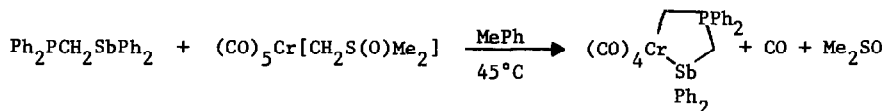
The relative order of the rates was  $\text{Ph}_3\text{P} > \text{Ph}_3\text{Sb} > \text{Ph}_3\text{As}$ . This order was attributed to two conflicting trends as the atomic number of E increases: the increased availability of *d* orbitals for  $\pi$ -bonding with peroxide oxygen and the decrease in E-O bond strength. The oxidation of the triphenylstibine in this investigation yielded a crystalline triphenylstibine oxide that did not melt even after heating to 280°C and that liberated iodine from potassium iodide in glacial acetic acid. These properties were believed to be consistent with the characteristics of a polymeric material previously prepared by the oxidation of triphenylstibine with hydrogen peroxide.

The reaction of equimolar quantities of triphenylstibine, benzene-sulfonamide, and diethyl azodicarboxylate in THF at 0°C has been found to yield triphenylstibine oxide and diethyl hydrazinedicarboxylate [39]. It was suggested that an adduct of the stibine and the sulfonamide was first formed and then was hydrolyzed by the inadvertent introduction of water:



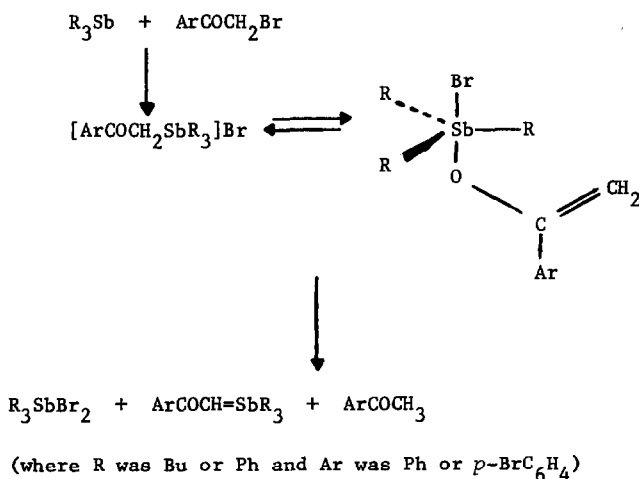
No information about the properties of the triphenylstibine oxide was given.

A cyclic ylid complex has been obtained by the thermal reaction of [(diphenylstibino)methyl]diphenylphosphine with a sulfur ylid complex [40]:



No ylid complexes resulted when the phosphine was replaced by bis(diphenylstibino)methane. The only product identified was the chromium complex  $(\text{CO})_5\text{CrSb}(\text{Ph}_2)\text{CH}_2\text{SbPh}_2$ . The structure of the cyclic ylid complex mentioned above was established by elemental analysis, an osmometric molecular weight determination in dichloromethane, and IR and mass spectroscopy.

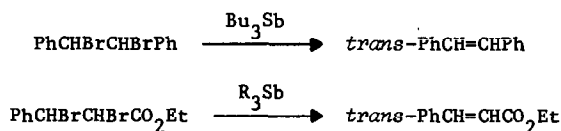
The debromination of phenacyl and benzylic bromides by the use of tributyl- or triphenylstibine has been investigated [41]. It was found that the reduction of phenacyl bromide with tributylstibine proceeded smoothly at room temperature to afford acetophenone in 67% yield; the addition of protic solvents (such as methanol) to the reaction mixture increased the yield to about 80%. The following mechanism was proposed for the interaction of a phenacyl bromide and a tertiary stibine:



It was also suggested that protonation of the antimony ylid formed in the last step led to an increased yield of ketone. When phenacyl chloride was allowed to react with tributylstibine, the yield of acetophenone was only 10% even in the presence of methanol. The reaction of the secondary bromide  $\text{PhCOCH}(\text{Br})\text{Me}$  with triphenylstibine gave the expected ketone  $\text{PhCOCH}_2\text{Me}$ . The tertiary bromide  $\text{PhCOC}(\text{Br})\text{Me}_2$ , however, did not react with triphenylstibine. The dibromide  $p\text{-BrC}_6\text{H}_4\text{COCHBr}_2$ , on reaction with triphenylstibine, gave a 10% yield of the bromoketone

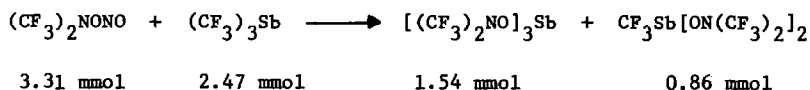


$p$ -BrC<sub>6</sub>H<sub>4</sub>COCH<sub>2</sub>Br and a 22% yield of  $p$ -bromoacetophenone. The interaction of a benzylic bromide with tributylstibine led to the precipitation of a quaternary antimony bromide of the type [ArCH<sub>2</sub>SbBu<sub>3</sub>]Br; refluxing these substances with ethanolic potassium hydroxide gave the desired ArCH<sub>3</sub> type of compound. In a few cases 1,2-elimination was observed when tributyl- or triphenylstibine was employed:

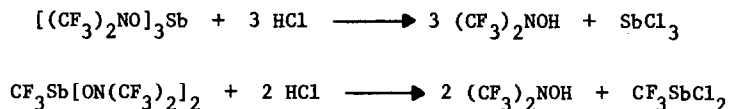


(where R was Bu or Ph)

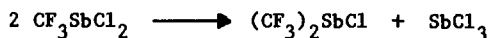
The interaction of tris(trifluoromethyl)stibine and  $O$ -nitrosobis-(trifluoromethyl)hydroxylamine at room temperature has been found to yield two trivalent antimony compounds [42]:



Mass balance studies showed that the (CF<sub>3</sub>)<sub>2</sub>NO groups that were bonded to the antimony in the products must have been derived from *both* reactants. Two mechanisms (both of which involved homolytic cleavage of CF<sub>3</sub>-Sb bonds) were suggested that appeared capable of explaining these results. On treatment with anhydrous hydrogen chloride, each product gave a stoichiometric amount of  $N,N$ -bis(trifluoromethyl)hydroxylamine:

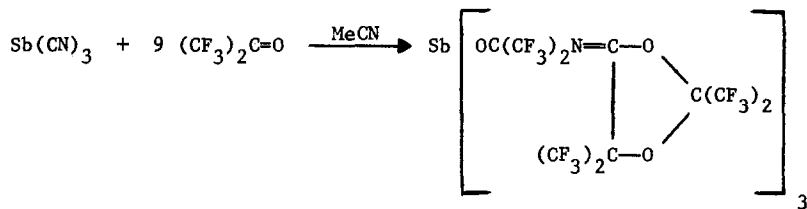


Only a 12% yield of the dichlorostibine was isolated from the latter reaction. It was suggested that most of this substance disproportionated in the following manner:



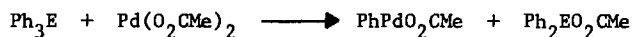
Antimony trichloride was in fact obtained, but the fate of the bis(trifluoromethyl)chlorostibine was not elucidated.

Hexafluoroacetone has been found to react under mild conditions with nitriles of several representative elements of Group V and VI [43]. The reaction of tricyanostibine with this ketone was catalyzed by triethylamine and proceeded as follows:



The structure of the substance thus obtained was established by elemental analysis, IR,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR, and high resolution mass spectra.

Stereospecific phenylation of alkenylsilanes of the type (E)- or (Z)- $\text{RCH}=\text{CHSiMe}_3$ , where R was Ph, Hex, or  $\text{MeOCH}_2$ , has been performed with phenylpalladium acetate generated *in situ* from various sources [44]. The reactions were accompanied by inversion of the starting geometry with respect to the R and  $\text{Me}_3\text{Si}$  groups. Palladium(II) acetate was used as a starting material in one method of obtaining the phenylpalladium acetate:



(where E was P or Sb)

Intermediates formed in the photolysis of triphenylamine, -phosphine, -arsine, -stibine, and -bismuthine have been studied by a combination of spin-trapping techniques, column chromatography, and ESR spectroscopy [45]. Except in the case of triphenylamine, the phenyl radical was identified as a product of the photolysis. It was concluded that the initial photochemical step for all five compounds could be described as a homolysis.

Charge-transfer complexes of tetracyanoethylene (TCNE) and triphenylarsine, -stibine, or -bismuthine in dichloromethane have been investigated by electronic spectroscopy [46]. It was found that weak 1:1 complexes of the type  $\text{Ph}_3\text{E}-\text{TCNE}$  (where E was As, Sb, or Bi) were present in these solutions and were in equilibrium with their components. Each of these complexes had two overlapping absorbance bands. The low wavelength bands (385-405 nm) arose from  $a_2$  orbitals, whereas the high wavelength bands (515-545 nm) arose from  $n$  orbitals energized by  $p_\pi-d_\pi$  conjugation. The  $\text{Ph}_3\text{Sb}-\text{TCNE}$  complex exhibited maxima at 395 nm ( $\epsilon$ , 457) and 525 nm ( $\epsilon$ , 131).

A polarographic technique has been used to study the effect on electrode reactions of the adsorption of triphenylphosphine, -arsine,

-stibine, and -bismuthine at the mercury/methanolic solution interface [47]. It was found that all four compounds were strongly adsorbed on the positively charged mercury electrode. The adsorption increased from the phosphine to the bismuthine. The presence of these substances at the mercury/solution interface catalyzed hydrogen evolution but inhibited the reduction of *o*-dinitrobenzene, oxygen, and the  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  cations. The catalytic effect was strongest for the bismuthine, somewhat less strong for the phosphine, and very weak for the arsine and stibine. The inhibition effects decreased in the order  $\text{Ph}_3\text{Bi} > \text{Ph}_3\text{Sb} > \text{Ph}_3\text{As} > \text{Ph}_3\text{P}$  and thus were correlated with the extent of adsorption on the mercury surface.

Triphenylstibine has been included in a study of exchange reactions between phenyllithium and organometallic or organometalloid reagents in THF at  $-78^\circ\text{C}$  [48]. The presence of the antimony compound did not significantly affect the rate of the reaction of the phenyllithium with chalcone or butyl iodide.

Triphenylstibine has also been included in a series of organometallic compounds used in a study of the fluorescence quenching of 9,10-dicyanoanthracene [49]. Other quenchers investigated consisted of a series of inorganic anions and a series of organic acceptors. The wide ranges of redox potentials for the three series of quenchers enabled the rigorous testing of current theories of electron transfer quenching.

A study of the polymerization of 1-phenyl-1-propyne by tantalum(V) chloride has shown that the polymer underwent degradation after all of the monomer had been consumed [50]. In contrast, no polymer degradation occurred when certain cocatalysts (*e.g.*, triethylsilane, tetrabutyltin, triphenylstibine, and triphenylbismuthine) were added in a 1:1 ratio to the tantalum compound. The use of one of these cocatalysts made it possible to obtain samples of poly(1-phenyl-1-propyne) that had weight-average molecular weights exceeding  $1 \times 10^6$ . Thus, the following beneficial effects of the cocatalysts were observed: (1) polymerization was accelerated; (2) degradation of the polymer (by the tantalum compound) was inhibited; and (3) the molecular weight of the polymer was higher than the maximum molecular weight attainable without a cocatalyst.

The rate of acrylonitrile photopolymerization in the presence of various electron donors as initiators has been investigated [51]. The electron donors included triphenylamine, -phosphine, -arsine, -stibine, and -bismuthine as well as diphenyl ether and diphenyl sulfide. It was found that the rate of the photopolymerization decreased in the order  $\text{Ph}_3\text{P} > \text{Ph}_2\text{S} > \text{Ph}_3\text{N} > \text{Ph}_2\text{O}$  and  $\text{Ph}_3\text{As} > \text{Ph}_3\text{Sb} > \text{Ph}_3\text{Bi}$ . A mechanism was proposed for the photopolymerization.

Iron and cobalt catalysts have been employed for the linear codimerization of 2-cyclopropyl-1,3-butadiene and methyl acrylate [52].

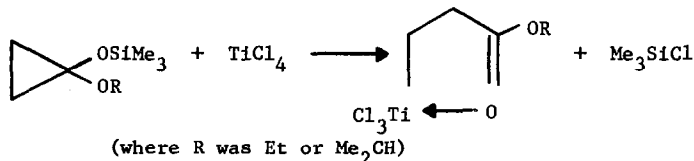
One of the catalysts studied was a 1:1:4 mixture of iron(III) acetylacetonate, triphenylstibine, and triethylaluminum.

Triphenylstibine has been used to help stabilize unsaturated polyesters [53] and to retard the oxidation of polyamide 12 [54]. It has also been suggested as a ingredient of fire-resistant polymers [55, 56], transparent conductive films [57], and corrosion inhibitors for ferrous metals exposed to acids [58]. The thermal decomposition of tripropylstibine has been employed in the preparation of high quality adherent dielectric films on gallium arsenide [59].

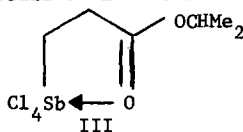
There have been numerous recent articles that mentioned the use of tertiary stibines as ligands in transition metal complexes. The metals coordinated to the antimony in these complexes included chromium [16, 40], gold [60-62], iron [63-66], molybdenum [16, 67], nickel [68, 69], osmium [66], palladium [70-72], platinum [73, 74], rhodium [75-77], ruthenium [66, 78, 79], and tungsten [16].

The stibonic acid  $p\text{-H}_2\text{O}_3\text{SbC}_6\text{H}_4\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$  was obtained by means of the Scheller reaction from  $p\text{-H}_2\text{NC}_6\text{H}_4\text{CH}(\text{NHAc})\text{CO}_2\text{H}$  and  $\text{SbCl}_3$  [80]. Esterification with EtOH and HCl gave  $p\text{-H}_2\text{O}_3\text{SbC}_6\text{H}_4\text{CH}(\text{NH}_2)\text{CO}_2\text{Et}$ . Neither the carboxylic acid nor the corresponding ethyl ester possessed schistosomicidal activity.

Nakamura and coworkers [81] have found that  $\text{TiCl}_4$  reacted with a 1-trimethylsiloxy-1-alkoxycyclopropane to yield a compound with a Ti-C bond:



The authors speculated that the presence of the two substituents on the cyclopropane ring stabilized the intermediate cation formed in the ring-opening reaction and thus facilitated the formation of the carbon-metal bond. Accordingly, they investigated the reaction of 1-ethoxy- or 1-isopropoxy-1-siloxycyclopropane with a wide variety of metal halides in the hope of finding a new method for forming carbon-metal bonds. It was found that the isopropoxy group was superior to the ethoxy group, and for this reason the majority of the reactions employed 1-isopropoxy-1-trimethylsiloxy-cyclopropane. Among the metal halides employed was  $\text{SbCl}_5$  in hexane solution. The compound III was obtained as a colored oil which could not be purified by distillation. It was characterized by NMR ( $^1\text{H}$

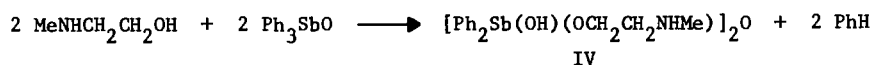


and  $^{13}\text{C}$ ) and IR spectroscopy. For the NMR results the reaction to form III was carried out in  $\text{CDCl}_3$  rather than in hexane. The yield of product in  $\text{CDCl}_3$  was 87%.

A number of papers on the crystal structures of organoantimony compounds from the laboratory of D. B. Sowerby in England have appeared in the chemical literature. The latest paper [82] concerns the structure of the compound  $\text{Ph}_2\text{SbBrO}$ . This compound was prepared by the air oxidation of  $\text{Ph}_2\text{SbBr}$  with the exclusion of moisture, or better by oxidation of the same compound with *tert*-butyl hydroperoxide in 1,2-dichloroethane. Bands in the IR spectrum at 650 and  $495\text{ cm}^{-1}$  were associated with Sb-O stretching vibrations. In a similar manner, oxidation of  $\text{Ph}_2\text{SbCl}$  gave  $\text{Ph}_2\text{SbClO}$ . However, pure compounds could not be obtained from the oxidation of either  $\text{PhSbBr}_2$  or  $\text{PhSbCl}_2$ . The crystal structure of  $\text{Ph}_2\text{SbBrO}$  was determined by x-ray diffraction. The compound was dimeric with a planar 4-membered ring of alternating Sb-O bonds. Of the two oxygen atoms attached to each antimony, one oxygen was axial and one was equatorial, and the two bromine atoms were in axial positions. Thus, the configuration of each Sb atom was that of a trigonal bipyramid.

The preparation of trichlorodiphenylantimony from readily available starting material ( $\text{SbCl}_5$  and  $\text{Ph}_4\text{Sn}$ ) has been described in *Inorganic Syntheses* [83]. The yield of  $\text{Ph}_2\text{SbCl}_3 \cdot \text{H}_2\text{O}$  by this procedure was 79-88%.

Based on the discovery by Goel and Ridley [84] that methanol condensed with  $\text{Ph}_3\text{SbO}$  to give  $\text{Ph}_3\text{Sb}(\text{OMe})_2$ , Nomura and coworkers [85] expected that  $\text{Ph}_3\text{SbO}$  would react with aminoalcohols to give the corresponding amino-substituted alkoxides. It was found, however, that 2-(methylamino)ethanol underwent reaction with  $\text{Ph}_3\text{SbO}$  at  $100^\circ\text{C}$  with loss of benzene and formation of the  $\mu$ -oxo compound IV:

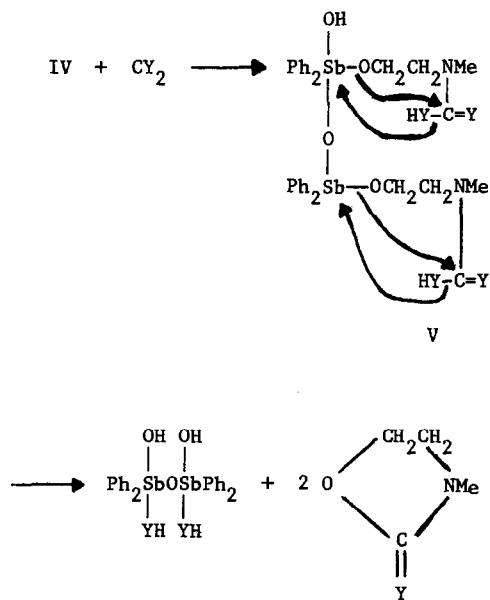


The yield of IV was 97.3%. It was also formed in 91% yield from:  $\text{Ph}_3\text{Sb}(\text{OMe})_2$  (formed *in situ* from  $\text{Ph}_3\text{SbO}$  and MeOH) and  $\text{MeNHCH}_2\text{CH}_2\text{OH}$ . IV was obtained as white crystals, m.p.  $286\text{--}287^\circ\text{C}$ . Its structure was determined by IR spectroscopy, PMR, molecular weight determinations, and elemental analysis. When a benzene solution of IV was heated under pressure with  $\text{CO}_2$  at  $160^\circ\text{C}$ , 3-methyl-2-oxazolidinone was obtained in 73.4% yield. The other product of the reaction was diphenylstibinic acid, obtained in quantitative yield.

The reaction of IV with  $\text{CS}_2$  to produce 3-methyloxazolidine-2-thione proceeded much more readily than the reaction with  $\text{CO}_2$ . Thus, when the two reactants, in the presence of a small amount of benzene, were allowed to react for 1 hour, a 79.1% yield of oxazolidine-2-thione was obtained

(together with traces of 3-methylthioazolidine-2-thione). It was then found unnecessary to isolate IV; the same two products were obtained when  $\text{Ph}_3\text{SbO}$ ,  $\text{MeNHCH}_2\text{CH}_2\text{OH}$ , and  $\text{CS}_2$ , together with some  $\text{MeOH}$ , were allowed to stand at room temperature for 1 hour. However, when  $\text{Ph}_3\text{SbO}$  in catalytic amounts was heated ( $100^\circ\text{C}$  for 6 hours) with  $\text{MeNHCH}_2\text{CH}_2\text{OH}$  and  $\text{CS}_2$ , the principal product was 3-methylthiazolidine-2-thione, with only small amounts of 3-methyloxazolidine-2-thione. Having discovered that  $\text{Ph}_3\text{SbO}$  was an efficient reagent for the condensation of 2-(methylamino)-ethanol with  $\text{CO}_2$  or  $\text{CS}_2$  to form heterocyclic products, the authors tried  $\text{Sb}_2\text{O}_3$  as a reactant rather than  $\text{Ph}_3\text{SbO}$ . It was found that  $\text{MeNHCH}_2\text{CH}_2\text{OH}$  and  $\text{Sb}_2\text{O}_3$  did not react, either at room temperature or at reflux temperature. However, when  $\text{CS}_2$  was added, reaction did occur at room temperature to give a 91.3% yield of an antimony thiocarbamate,  $\text{Sb}[\text{SC}(\text{S})\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{OH}]_3$ . When this thiocarbamate was refluxed in xylene for 6 hours it was converted to 3-methyloxazolidine-2-thione (80%) and 3-methylthiazolidine-2-thione (14%). Finally, the effect of  $\text{Ph}_3\text{SbO}$  as a catalyst for the reaction of amines with  $\text{CS}_2$  was investigated. It was found that  $\text{Et}_2\text{NH}$  and  $\text{CS}_2$  at room temperature, in the presence of  $\text{Ph}_3\text{SbO}$  (in acetonitrile), gave a 90% yield of  $\text{N,N,N',N'}$ -tetraethylthiuram disulfide.

A mechanism for the reaction of IV with  $\text{CO}_2$  or  $\text{CS}_2$  was suggested. This involved the formation of a C-N bond to yield the intermediate V which reacted further to give the heterocycle and (with  $\text{CO}_2$ ) diphenylstibinic acid:



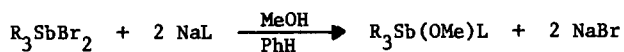
(where Y was O or S)

The reduction of a number of organic compounds by  $\text{Ph}_3\text{P}$ , catalyzed by  $\text{MoO}_2(\text{S}_2\text{CNEt}_2)_2$ , has been reported [86]. Among the compounds reduced by this method was  $\text{Ph}_3\text{SbO}$ . The reaction conditions used were mild, *e.g.*,  $40^\circ\text{C}$  for 20 hours.

The reaction of  $(\text{Me}_3\text{Si})_2\text{S}$  with various chlorosilanes and with several organometallic chlorine-containing compounds has been reported [87]. Among the reactions studied was the reaction of the sulfide with  $\text{Ph}_3\text{SbCl}_2$  to yield  $\text{Ph}_3\text{SbS}$ . The antimony compound was identified by its mass spectrum and by elemental analysis.

It is known that  $\text{Me}_3\text{Sb}$  reacts with selenium to form the product  $\text{Me}_3\text{SbSe}_2$ , which quickly loses selenium to form  $\text{Me}_3\text{SbSe}$ . Kuhn and Schumann [88] attempted to stabilize the primary reaction product by coordination to a central metal atom. For this purpose they chose the cation  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{THF}]^+$ . The reaction involved heating  $\text{Me}_3\text{Sb}$  with selenium in toluene, and then adding, after cooling to  $40^\circ$ , a solution of  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{THF}][\text{BF}_4]$  in methylene chloride. The precipitated material which might be  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{Me}_3\text{SbS}_2)][\text{BF}_4]$  lost selenium to give the stable complex  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{Me}_3\text{SbSe})][\text{BF}_4]$ . The compound, after recrystallization from methylene chloride-ether mixture, was characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrometry, IR spectroscopy, and by elemental analysis.

There is conflicting data as to the type of compound formed when antimony(V) compounds of the type  $\text{R}_3\text{SbX}_2$  react with monobasic bidentate ligands. Some authors have reported compounds of the type  $\text{R}_3\text{SbL}_2$  but other authors have reported that only one X group can be replaced. Jha and Joshi [89] investigated the reaction of  $\text{R}_3\text{SbBr}_2$  ( $\text{R} = \text{Me}$  or  $\text{Ph}$ ) with a number of bidentate ligands (as their sodium salts) in methanol-benzene solution. In all cases only one ligand group L was attached to the antimony:

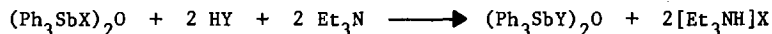


(where  $\text{R} = \text{Me}$  or  $\text{Ph}$  and  $\text{HL} =$  acetylacetone, 8-hydroxyquinoline, salicylaldehyde, *o*-hydroxyacetophenone, or 2-hydroxy-1-naphthaldehyde)

The new compounds were characterized by their IR and PMR spectra, elemental analysis, and molecular weight determinations. In some cases far-IR ( $500\text{--}100\text{ cm}^{-1}$ ) spectra were also obtained. For one compound  $\text{Ph}_3\text{Sb}(\text{OMe})\text{L}$  (where  $\text{HL} =$  acetylacetone), a  $^{13}\text{C}$  spectrum was also reported. All of the compounds were crystalline solids with sharp m.p.'s, and except for the two compounds  $\text{Ph}_3\text{Sb}(\text{OMe})\text{L}$  and  $\text{Me}_3\text{Sb}(\text{OMe})\text{L}$  (where  $\text{HL}$  was 8-hydroxyquinoline), all were white. On the basis of their IR spectra,

it was concluded that (except for the complex with 8-hydroxyquiniline) the ligands were bidentate with either two carbonyl oxygens or a carbonyl and a hydroxyl oxygen bonded to the Sb atom. With the 8-hydroxyquinoline complex, the nitrogen atom and the oxygen atom were bonded to the Sb atom. A sharp band at  $\sim 1070 \text{ cm}^{-1}$  in the IR spectrum was assigned to the Sb-OMe stretching mode and a band at  $\sim 400 \text{ cm}^{-1}$  was assigned to the Sb-O stretching mode. Since the configuration of the Sb atom was believed to be octahedral, three configurations were possible for each compound (except for the two compounds in which HL was acetylacetonone where only two configurations were possible), namely, one *fac*-configuration and two *mer*-configurations. On the basis of the PMR spectra, the authors concluded that the compounds possessed the *fac*-configuration (the OMe and one Ph group *trans*). This conclusion differed from the one reported by Jain and coworkers, who, on the basis of the PMR spectrum, suggested that the complex  $\text{Ph}_3\text{Sb}(\text{OMe})\text{L}$  (where HL was acetylacetonone) possessed a *mer*-configuration.

Pandey and Srivastava [90] have prepared a number of organoantimony(V) compounds of the type  $(\text{Ph}_3\text{SbY})_2\text{O}$ , where Y was a carboxylato, an imido, or an oximino group:



(where X was Cl or Br and HY was a carboxylic acid, an imide, or an oxime)

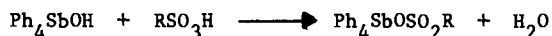
The carboxylic acids employed were trichloroacetic, crotonic, phenylacetic, and 2-phenylacrylic; the imides were succinimide, phthalimide, and 2-methylimidazoline; the oximes were those derived from acetone, acetophenone, cyclopentanone, and 2-pyridone. The new compounds were white crystalline solids, characterized by IR spectroscopy, PMR spectrometry, and elemental analyses. They were monomolecular as shown by cryoscopic measurements in benzene. Molar conductance values in acetonitrile solution ranged between  $5\text{--}8 \text{ ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$  for  $10^{-3}$  molar solutions. The authors suggested that the compounds contained trigonal-bipyramidal Sb atoms with two oxygen atoms (or an oxygen and nitrogen atom) in axial positions.

The compound  $\mu$ -oxo-bis(2-hydroxyethanesulfonato)triphenylantimony(V),  $(\text{Ph}_3\text{SbOS}(\text{O}_2)\text{CH}_2\text{CH}_2\text{OH})_2\text{O}$ , was obtained from isethionic acid  $(\text{HOS}(\text{O}_2)\text{CH}_2\text{CH}_2\text{OH})$  and  $\text{Ph}_3\text{SbO}$  [91]. The compound crystallized from an acetone solution of the two components after standing for one day. The structure of the compound was determined by X-ray diffraction. The unit cells contained two centrosymmetrical molecules with a linear Sb-O-Sb bridge as the central part. Each Sb atoms formed a slightly distorted trigonal bipyramid with the three phenyl groups in equatorial positions and two oxygen atoms in apical positions. The  $\text{O}_1\text{-Sb-O}_2$  angle (where  $\text{O}_1$  was the central oxygen



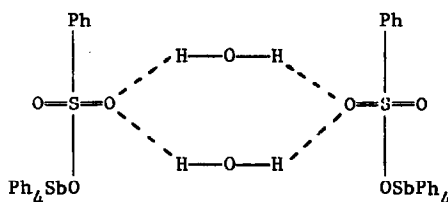
atom and  $O_2$  was the oxygen atom of the sulfonate group) was  $175.2^\circ$ . The  $Sb-O_2$  bond length was  $2.276\text{\AA}$ ; it was concluded that this bond possessed considerable ionic character.

A number of tetraphenylantimony alkyl- and arylsulfonates have been prepared by Rütner and coworkers [92]. Their synthesis involved the reaction between  $Ph_4SbOH$  and the appropriate sulfonic acid in methanol solution:



(where  $R = Me, CF_3, CH_2CH_2OH, Ph, 4-MeC_6H_4,$  or  $2,4-(NO_2)_2C_6H_3$ )

One of these compounds ( $R = Ph$ ) contained a mole of water of crystallization; the other compounds were anhydrous. They were characterized by IR spectroscopy, PMR spectrometry, elemental analysis, and molecular weight determinations (by osmometry in  $CHCl_3$  solution). The crystal structure of one of the compounds,  $Ph_4SbOSO_2Ph \cdot H_2O$ , was determined by X-ray diffraction. The configuration of the Sb atom was that of a distorted trigonal bipyramid (distorted towards a tetrahedral structure). The crystal was quasi-dimeric, with two molecules connected by hydrogen bonds forming an 8-membered ring (VI):



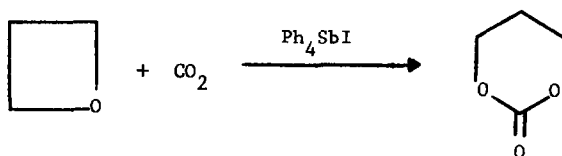
VI

The water of crystallization was readily removed by warming, or by dissolution in  $CHCl_3$  to form a separate water phase. The  $Sb-O$  distance was intermediate between the  $Sb-O$  distance in  $Ph_4SbOH$  (where the Sb was five covalent) and the  $Sb-O$  distance in a compound of the type  $Me_4SbO_2CR$  ( $R = 2-HO, 4-EtOC_6H_3$ ), where the Sb was tetrahedral. This bond distance, together with the fact that the configuration of the Sb atom was distorted towards a tetrahedral configuration, suggested that that  $Sb-O$  bond possessed a rather strong ionic character. This conclusion was strengthened by a comparison of the  $Sb-C$  (axial) and  $Sb-C$  (equatorial) bond distances, which were considerably shorter in  $Ph_4SbOSO_2Ph \cdot H_2O$  than in  $Ph_4SbOH$ , but longer than in the compound  $Me_4SbO_2CR$ . Finally, the ionic character of the  $Sb-O$

bond was supported by the IR data where the S-O asymmetric stretch (Sb-O-S) was shifted to longer wave lengths compared to the positions of the other two S-O bonds. This shift was considered to be due to a higher bond order for this bond associated with the more ionic character of the Sb-O bond.

It is known that a small number of compounds show NQR frequencies  $\nu$  or quadrupole coupling constants  $e^2qQ/h$  with positive temperature coefficients  $\alpha = (1/\nu)(\delta\nu/\delta T)_p$  in certain temperature ranges. This phenomenon, called anomalous temperature dependence, is in contradiction to the original Bayer theory. A number of possibilities involving various intra- and intermolecular interactions have been suggested to explain the anomalous temperature effect. Burkert and Klobasa [93] have prepared three organometallic compounds,  $[\text{Ph}_4\text{E}][\text{IO}_4]$ , where E was P, As, or Sb, to study the effect. All three compounds were prepared from the corresponding hydroxides  $\text{Ph}_4\text{EOH}$  by reaction with periodic acid. They were recrystallized from ethanol and were characterized by elemental analysis. All three compounds showed temperature dependence of the  $^{127}\text{I}$  quadrupole coupling constants  $e^2qQ/h$  in the  $^{127}\text{I}$  powder spectra as a function of temperature. The authors suggested that dynamic effects within the lattice made the main contribution to the anomalous temperature coefficients.

Tetraphenylantimony iodide was found to be a very effective catalyst for the formation of trimethylene carbonate from oxetane and  $\text{CO}_2$  [94]:



The yield (100°C for 4 h) was 96%. Other catalysts,  $\text{Ph}_4\text{PI}$ ,  $\text{Bu}_4\text{NI}$ ,  $\text{Ph}_3\text{SbI}_2$ ,  $\text{Ph}_3\text{SbO}$ , or  $\text{Ph}_3\text{Sb}$ , were totally ineffective while  $\text{Ph}_4\text{SbBr}$  gave only a 2% yield of trimethylene carbonate.

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