ANTIMONY

ANNUAL SURVEY COVERING THE YEAR 1984 *

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Except for our Annual Survey covering the year 1982, no book or review devoted exclusively to organoantimony compounds appeared in 1984. A chapter on heterocyclic rings containing arsenic, antimony, or bismuth was included, however, in a new seven volume compendium on heterocyclic chemistry [1]. Organoantimony compounds were also described in two new volumes of the *Gmelin Handbook of Inorganic Chemistry*. One of these volumes was concerned with perfluoro compounds of the main-group elements [2]; the other dealt with coordination compounds of rhodium with ligands containing sulfur, selenium, tellurium, phosphorus, arsenic, antimony, or a metallic element [3]. In addition, information about organoantimony compounds was 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]. Organoantimony compounds were very briefly mentioned in review articles on the following subjects: double bonding between the heavier main-group elements [6, 7], the formation of semiconductors by the metalorganic chemical vapor deposition process [8], organometallic compounds containing metal-metal bonds [9], substitution reactions of metal carbonyls with Group V and Group VI ligands [10], diffraction studies of organometallic compounds [11], and the organometallic chemistry of the main group elements [12]. A number of references to organoantimony compounds were given in a recent book on the interaction of organometallic compounds and living organisms [13].

A planar stibinidene complex has been obtained in 30% yield by the following reaction [14]:

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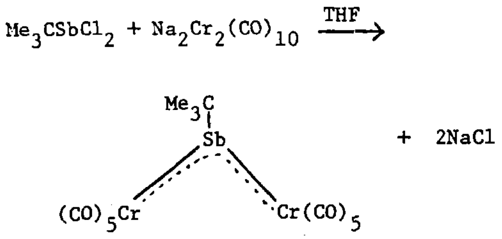
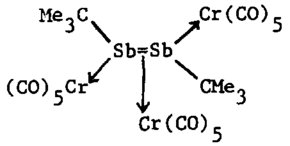
*Previous review see R.B. King and J.P. Oliver (Eds.), J.Organomet.Chem. Library, 17(1985)311-351.

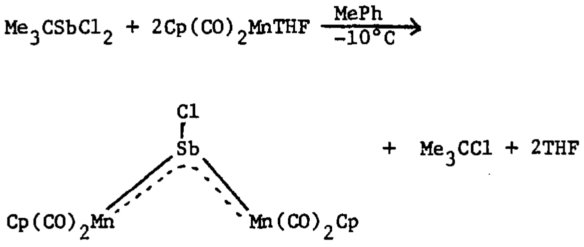


(where the dotted line in the above formula represents π-delocalization of the antimony lone pair electrons between the two chromium atoms)

In THF solution the complex existed as an orange adduct, $Me_3CSb[Cr(CO)_5]_2 \cdot THF$; when the THF was completely removed, the complex had an intense dark green color. A second complex, formulated as $[(CO)_5CrSb(CMe_3)Cl]_2$, was also isolated from the reaction mixture. When dichloromethane was used as the reaction medium, still another type of compound was formed. This was probably a distibene complex:

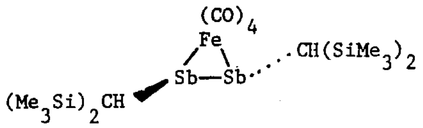


A stibinidene complex of manganese was prepared in 18% yield by the following reaction:

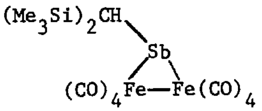


The formation of *tert*-butyl chloride in this reaction was suggested but not actually proven. The spectral (IR, UV, and PMR) properties of the stibinidene complexes of chromium and manganese were recorded and discussed.

A distibene complex of iron has been prepared in 20% yield by the interaction of bis(trimethylsilyl)methyldichlorostibine and the disodium salt $Na_2[Fe(CO)_4]$ in THF [15]. High resolution mass spectroscopy (HRMS) and X-ray crystallography were employed to show that the complex had the following structure:



The Sb—Sb bond length was 2.774 Å and indicated that the bond order was about 1.5. Treatment of the complex with nonacarbonyldiiron resulted in a 26% yield of the following "closed" bridging stibinidene complex:



The structure of this substance also was established with the aid of HRMS and X-ray crystallography. The existence of a "closed" structure was consistent with the observed pyramidality of the antimony atom (the sum of the bond angles was 287.1°); in the "open" form, the antimony geometry was expected to be trigonal planar. Although the Fe-Fe distance (2.801 Å) exceeded the usual single-bond range of 2.50 - 2.65 Å, it was concluded that the iron atoms were bonded to one another, albeit weakly. It was also noted that this substance (unlike comparable "open" complexes) acted as a Lewis base. Thus, it was readily protonated by reaction with the acid $HBF_4 \cdot OEt_2$ to form an unstable cation.

A phosphastibene has been included in a paper mainly devoted to diphosphenes, diarsenes, and phosphaarsenes [16]. The antimony compound was obtained by the base-promoted interaction of an arylphosphine and a dichlorostibine:

$$2,4,6\text{-}(Me_3C)_3C_6H_2PH_2 + (Me_3Si)_2CHSbCl_2 + 2DBU \xrightarrow{THF}$$

$$2,4,6\text{-}(Me_3C)_3C_6H_2P{=}SbCH(SiMe_3)_2 + 2DBU \cdot HCl$$

(where DBU was 1,5-diazabicyclo[5.4.0]undec-5-ene)

The dichlorostibine was prepared by treatment of antimony trichloride with a Grignard reagent at -40 to -50°C:

$$(Me_3Si)_2CHMgCl + SbCl_3 \xrightarrow{Et_2O} (Me_3Si)_2CHSbCl_2 + MgCl_2$$

The phosphastibene was not successfully purified because of its instability in solution but was characterized by ^{31}P NMR spectroscopy and high resolution mass spectroscopy. In solution the phosphastibene decomposed slowly to yield the symmetrical diphosphene ArP=PAr, where Ar was 2,4,6-$(Me_3C)_3C_6H_2$. The decomposition was monitored by ^{31}P NMR spectroscopy. It was suggested that the phosphastibene was a source of the free phosphinidine ArP which, in the absence of a suitable trap, dimerized to give the diphosphene. The nature of the double bond in the phosphastibene and in related compounds was discussed with the aid of the available X-ray diffraction and electronic spectral data. An extensive compilation of ^{31}P NMR spectroscopic information was also presented and analyzed.

A bis(diphenylstibino)zirconium compound has been prepared by the following sequence of reactions [17]:

$$Ph_3Sb + 2Li \xrightarrow{THF} Ph_2SbLi + PhLi$$

$$PhLi + Me_3CCl \longrightarrow PhH + Me_2C{=}CH_2 + LiCl$$

$$Cp_2ZrCl_2 + 2Ph_2SbLi \longrightarrow Cp_2Zr(SbPh_2)_2 + 2LiCl$$

The red microcrystalline product was sensitive to moist air and decomposed in a few minutes to a white solid. Hydrolysis in benzene yielded a mixture of diphenylstibinic acid and a zirconium compound formulated as $[Cp_2ZrO]_n$. Treatment with molecular iodine in THF resulted in the following reaction:

$$Cp_2Zr(SbPh_2)_2 + I_2 \xrightarrow{THF} Cp_2ZrI_2 + Ph_2SbSbPh_2$$

Reaction with mercuric chloride also gave tetraphenyldistibine:

$$Cp_2Zr(SbPh_2)_2 + HgCl_2 \xrightarrow{THF} Cp_2ZrCl_2 + Hg + Ph_2SbSbPh_2$$

Diphenylstibine may have been formed by reaction with two equivalents of phenol:

$$Cp_2Zr(SbPh_2)_2 + 2PhOH \xrightarrow{THF} Cp_2Zr(OPh)_2 + 2Ph_2SbH$$

This stibine was not actually isolated from the reaction mixture; instead, a dark brown insoluble solid was obtained that appeared to be a polymeric "antimonobenzene", $(PhSb)_n$. The PMR spectrum of the bis(diphenylstibino)zirconium compound in THF exhibited a single sharp resonance at δ6.31 for the cyclopentadienyl protons and multiplets at δ7.0-7.62 for the phenyl protons. Although no X-ray structural data were available for the compound, a tetrahedral arrangement around the zirconium atom was suggested.

The photolysis of metal-substituted arsines and stibines of the type $Cp(CO)_3MER_2$ (where M was Mo or W, E was As or Sb, and R was Me, Me_2CH, or Me_3C) has been studied by matrix isolation experiments at 12K [18]. IR spectroscopic evidence was presented that indicated that photolysis in methane matrices produced the double bonded complexes $Cp(CO)_2M{=}ER_2$ via 16-electron species of the type $Cp(CO)_2MER_2$. In dinitrogen matrices, the 16-electron species in which M was Mo and R was Me reacted to give complexes of the type $Cp(CO)_2(N_2)MoEMe_2$.

The reduction of bis(trimethylsilyl)methyldichlorostibine with magnesium in THF has been shown to give a mixture of a tristibirane and a tetrastibetane [19]:

$$(Me_3Si)_2CHSbCl_2 + Mg \longrightarrow 1/n[(Me_3Si)_2CHSb]_n + MgCl_2$$

(where n was 3 or 4)

The total yield of the cyclic compounds was 88%. The mixture was obtained as a reddish brown, air-sensitive oil, which was very soluble in *n*-pentane, benzene, and chloroform. Attempted separation of the components by distillation led to decomposition. The greater volatility of the tristibirane, however, made it possible to obtain the mass spectrum of each compound. Conspicuous in both spectra were the high intensities of the molecular ions and the $[M-(Me_3Si)_2CH]^{+\cdot}$ fragments. The PMR spectrum of the mixture indicated that the ratio of tristibirane to tetrastibetane was about 3:2. It also suggested that the former compound had a *cis, trans* configuration while the tetrastibetane had an all-*trans* configuration in which all of the substituents on the ring were equivalent.

The first compounds of the type $R_2SbMSbR_2$, where M was Se or Te, have been obtained in high yields by the interaction of a distibine with an excess of selenium or tellurium in benzene at ambient temperature or in refluxing carbon disulfide [20]:

$$R_2SbSbR_2 + 1/nM_n \longrightarrow R_2SbMSbR_2$$

(where M was Se and R was Me, Et, or Ph; or where M was Te and R was Me or Et)

All five compounds were soluble in common organic solvents. Dilute solutions of the alkyl derivatives were yellow, while similar solutions of the phenyl derivative were colorless. On exposure to the air, the alkyl derivatives decomposed rapidly and produced an unpleasant odor; the phenyl derivative was less sensitive towards oxygen. When stored in sealed tubes at 25°C, the five compounds appeared to be stable for weeks. A remarkable property of both methyl compounds was their thermochromism. The selenium compound, which was an orange-red liquid at room temperature, solidified at 5°C to form red crystals, which became yellow below -20°C. The tellurium compound was brown in the liquid state but became blue-violet in the solid phase below its melting point of 8°C. It was suggested that both methyl compounds were associated in the solid phase, whereas the bulkier substituents in the other three compounds prevented the close approach of the heavy atoms. The composition and structure of the five compounds were established by elemental analysis and by PMR, vibrational, and mass spectroscopy. The PMR spectra of both methyl derivatives showed one sharp singlet for each compound; the chemical shifts of the selenium and tellurium compounds were $\delta 1.30$ppm and $\delta 1.46$ppm, respectively. Another compound containing a tellurium-antimony bond was obtained in quantitative yield by the interaction of tetraethyldistibine and di-*p*-tolyl ditelluride at 25°C:

$$Et_2SbSbEt_2 + p\text{-}MeC_6H_4TeTeC_6H_4Me\text{-}p \longrightarrow 2\ p\text{-}MeC_6H_4TeSbEt_2$$

The substance was an orange, air-sensitive liquid that was very soluble in non-polar solvents. Its mass spectrum exhibited an intense molecular ion; the base peak corresponded to the loss of an ethyl group from the molecular ion.

Tetraphenyldiphosphine and tetraphenyldiarsine have been found to undergo the following exchange reaction [21]:

$$Ph_2PPPh_2 + Ph_2AsAsPh_2 \longrightarrow 2\ Ph_2PAsPh_2$$

Equilibrium was reached in a few hours in several organic solvents, and the average value of the equilibrium constant at 30°C was about 0.3. In contrast, there was little or no reaction between tetraphenyldiphosphine and tetraphenyldistibine in either chloroform or THF even after 10 days at 30°C. Absence of exchange was confirmed by noting that the diphenylstibide ion and diphenylchlorophosphine reacted predominantly to give symmetrical products:

$$2\ Ph_2Sb^- + 2\ Ph_2PCl \xrightarrow{THF} Ph_2SbSbPh_2 + Ph_2PPPh_2 + 2\ Cl^-$$

The diphenylstibide ion was obtained by the reduction of tetraphenyldistibine with sodium:

$$Ph_2SbSbPh_2 + 2\ Na \xrightarrow{THF} 2\ Na^+ + 2\ Ph_2Sb^-$$

The mass spectrum of an equimolar mixture of the diphosphine and the distibine did exhibit a peak attributed to Ph_4PSb^+ and thus suggested the possibility of exchange in the gas phase.

Dirhenium(I) complexes of tetraphenyldistibine have been prepared by the following reactions carried out in toluene at room temperature [22]:

$$[Re_2Br_2(CO)_6(THF)_2] + Ph_2SbSbPh_2 \longrightarrow [Re_2Br_2(CO)_6(Ph_2SbSbPh_2)] + 2THF$$

$$[Re_2I_2(CO)_8] + Ph_2SbSbPh_2 \longrightarrow [Re_2I_2(CO)_6(Ph_2SbSbPh_2)] + 2CO$$

The crystal and molecular structure of the bromo compound was solved by X-ray diffraction methods. The molecule consisted of two pseudo-octahedral rhenium(I) centers joined by bromine and tetraphenyldistibine bridges. The average Sb-Sb distance was 2.826Å. Chemical evidence and mass spectral data were employed to investigate the stability of the two antimony-containing complexes. It was concluded that these complexes were less stable than the analogous arsenic complexes, which were in turn less stable than the phosphorus complexes. An attempt to prepare an analogous tetraphenyldibismuthine complex resulted in decomposition, presumably to triphenylbismuthine and elemental bismuth.

Octacarbonyldicobalt and tetraphenyldistibine have been found to react in benzene at room temperature to form a presumably oligomeric $SbPh_2$ complex [23]:

$$[Co_2(CO)_8] + Ph_2SbSbPh_2 \longrightarrow 2CO + 2/n[\{Co(\mu\text{-}SbPh_2)(CO)_3\}_n]$$

Cryoscopic measurements in benzene gave an apparent molecular weight corresponding to a value of *n* between 2 and 2.3 (depending on the concentration of the complex). Treatment of the complex with triphenylphosphine in benzene at room temperature gave a monomeric complex with a terminal $SbPh_2$ group:

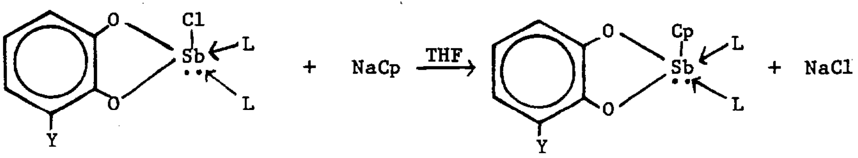
$$1/n[\{Co(\mu\text{-}SbPh_2)(CO)_3\}_n] + Ph_3P \longrightarrow [Co(SbPh_2)(CO)_3(PPh_3)]$$

It was concluded from IR and other evidence that the cobalt atom exhibited trigonal-bipyramidal geometry and that the three carbonyl groups occupied the equatorial positions.

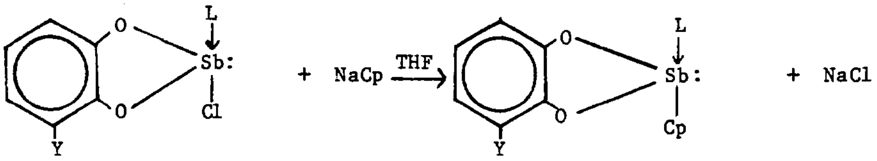
Two investigations of the structure of tetramethyldistibine were described in 1984. In one of these studies [24] the substance was subjected to single-crystal X-ray analysis at -21° and -139°C, and it was concluded that the molecules adopted an antiperiplanar conformation in which all of the antimony atoms were aligned in a collinear chain. The intermolecular Sb···Sb separations were very short (3.709Å at -21°C and 3.678 Å at -139°C); they were, in fact, only about 25% longer than the intramolecular bond lengths (2.830Å at -21°C and 2.838Å at -139°C). The authors did not elucidate the significance of the changes in the distances observed when the temperature was lowered from -21°C to -139°C.

In a second study [25] in another laboratory, the crystal was cooled to -160°C before being characterized by X-ray diffraction. The bond distances and the bond angles observed were quite similar to those reported in the paper reviewed above. Other properties of tetramethyldistibine showed, however, that this compound exhibited a different molecular structure in the liquid phase and in solution. Thus, the Raman spectrum of the solid showed an intense band at 179 cm^{-1} (assigned to the *trans* Sb-Sb stretch), while the liquid had two Sb-Sb bands (at 175 and 143 cm^{-1}), indicating the presence of a second (probably gauche) conformer. The ^{13}C NMR spectrum of tetramethyldistibine in C_4D_8O solution had a resonance at δ -10.6, while in the solid it was δ -6.4. In benzene the compound showed a dipole moment of 0.95 ± 0.04 D. Since the symmetrical *trans* conformation (observed in the solid state) would have had no dipole moment, a significant fraction of the tetramethyldistibine molecules in solution must have adopted another conformation. It was also concluded that the antimony atoms of distibines used primarily *p* orbitals for bonding, since the bond angles about antimony were close to 90°. The antimony $5p_z$ orbitals were, presumably, aligned along the chain of antimony atoms in the solid state, and the Sb···Sb linkages probably involved partial bonding via *p* orbitals.

Cyclopentadienyl derivatives of antimony(III) have been obtained by the following types of reactions [26]:



(where Y was H or OH and L was formamide, dimethylformamide, or urea)



(where Y was H or OH and L was $Me_2S{=}O$)

The ligands L in the above equations behaved as O-donors. The cyclopentadienyl derivatives were colored solids; their colors ranged from orange to brown. They were soluble in THF but were insoluble in benzene or chloroform. On heating they decomposed without melting. They were hydrolyzed by hot dilute acids, alkalies, or water. They were further characterized by elemental analyses, IR, and electronic spectra. It was suggested that the cyclopentadienyl ring was σ-bonded to antimony in the amide complexes, whereas the Cp-Sb bond had some π-character in the dimethylsulfoxide complexes.

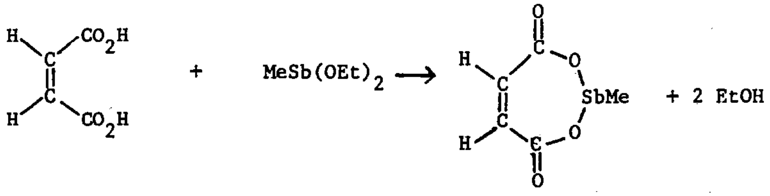
Dicyclopentadienyl derivatives of antimony(III) have also been described [27]. They were prepared by the following type of reaction:

$$ArOSbCl_2 + 2\ NaCp \xrightarrow{THF} Cp_2SbOAr + 2\ NaCl$$

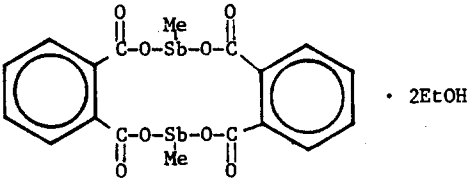
(where Ar was Ph, *o*-MeC_6H_4, *m*-MeC_6H_4, *p*-MeC_6H_4, *o*-$O_2NC_6H_4$, *p*-$O_2NC_6H_4$, *o*-HOC_6H_4, *m*-HOC_6H_4, *p*-HOC_6H_4, 2,3-$(HO)_2C_6H_3$, 3,5-$(HO)_2C_6H_3$, α-naphthyl, or β-naphthyl)

The compounds thus prepared were solids that ranged in color from orange-red to dark brown. They all decomposed below 100°C, but they were stable in a dry atmosphere at ambient temperatures. Molecular weight determinations showed that these substances were monomeric. Elemental analyses and IR spectra were also reported.

The interaction of equimolar quantities of methyldiethoxystibine and maleic acid in absolute ethanol at - 78°C has been found to yield a seven-membered heterocycle [28]:



Under similar conditions the stibine and phthalic acid gave a fourteen-membered ring:



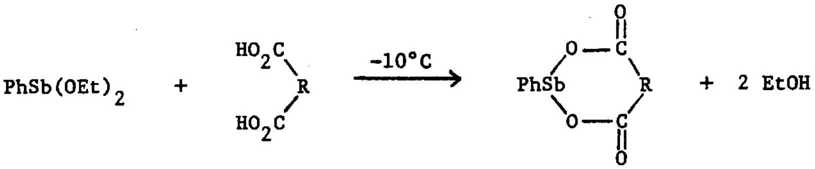
The above compound crystallized as a diethanolate and was subjected to an X-ray diffraction study. The molecular structure of this substance was rather complicated. Each antimony atom was hexacoordinate; it was bonded not only to the methyl group and the two oxygen atoms indicated in the formula but was also chelated to a carbonyl oxygen atom and was coordinated to an ethanol oxygen atom and to an oxygen atom of a second heterocyclic ring. When the reaction of methyldiethoxystibine with maleic or phthalic acid was carried out at room temperature, polymeric compounds were obtained. These substances had the same analytical composition as those prepared at -78°C.

In a second paper from the same laboratory, the reaction of phenyldiethoxystibine with carboxylic acids in absolute ethanol was described [29]. Two moles of acid per mole of stibine were used in the following reactions:

$$\mathrm{PhSb(OEt)_2 + 2\ RCO_2H \xrightarrow{0°C} PhSb(O_2CR)_2 + 2\ EtOH}$$

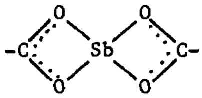
(where R was Me_3C, CF_3, or Ph)

The reaction of phenyldiethoxystibine with an equimolar quantity of maleic or phthalic acid yielded a heterocyclic compound:



(where R was CH=CH or 1,2-C_6H_4

Both of these substances crystallized with a molecule of ethanol coordinated to the antimony atom. It was suggested that the heterocyclic rings might consist of fourteen members like the phthalic acid derivative described in the paragraph above. The IR spectra of all five compounds indicated the presence of the following type of chelated structure:



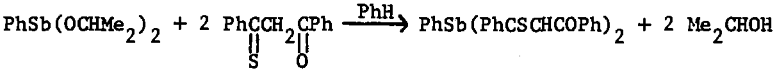
The yields ranged from 66-94%.

The reaction of phenyldichlorostibine with the sodium salts of monothio-β-diketones (NaL) in a 1:2 molar ratio has been found to give quantitative yields of derivatives of the type $PhSbL_2$ [30]:

$$PhSbCl_2 + 2\ Na(RCSCHCOR') \xrightarrow{CHCl_3} PhSb(RCSCHCOR')_2 + 2\ NaCl$$

(where R was Me and R' was p-MeC_6H_4; or where R was Ph and R' was Ph, p-MeC_6H_4, p-FC_6H_4, p-ClC_6H_4, or p-BrC_6H_4)

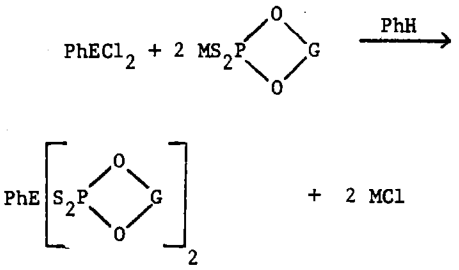
One of these compounds was also obtained by the interaction of phenyldiisopropoxystibine with a monothio-β-diketone in a 1:2 molar ratio:



$$PhSb(OCHMe_2)_2 + 2\ Ph\underset{\overset{\|}{S}}{C}CH_2\underset{\overset{\|}{O}}{C}Ph \xrightarrow{PhH} PhSb(PhCSCHCOPh)_2 + 2\ Me_2CHOH$$

All of these substances were non-volatile, colored solids, which were soluble in common organic solvents and were monomeric in refluxing benzene solution. Their IR spectra suggested that the ligands were chelating, and hence it was concluded that the antimony atom had a coordination number of five. The most plausible geometry appeared to be square-pyramidal with the phenyl group occupying the apical position. Since the antimony lone pair was presumably stereochemically active, the geometry could also be considered pseudooctahedral. The possible existence of *cis* and *trans* geometrical isomers of these compounds was noted, and some PMR results supporting this hypothesis were mentioned.

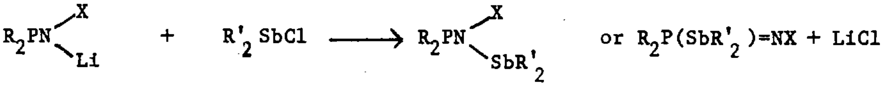
Cyclic dithiophosphates of arsenic and antimony have been obtained by the following type of reaction [31]:



(where E was As or Sb, M was H or NH_4, and G was $CH_2CMe_2CH_2$, CMe_2CMe_2, CMe_2CH_2CHMe, or CHMeCHMe)

All of these compounds were soluble in common organic solvents and were monomeric in refluxing benzene; they were non-volatile even under reduced pressure. The monomeric nature of these substances and structural evidence deduced from IR, PMR, and ^{31}P NMR spectroscopy indicated that the dithiophosphate ligands were bidentate and that the arsenic and antimony atoms were pentacoordinate. It was also suggested that the geometry around these atoms was square-pyramidal with a phenyl group occupying the apical position. The mass spectra of two representative compounds at about 200°C exhibited no detectable molecular ion peaks, and pyrolytic decomposition may have occurred.

Two types of structures (I and II) have been observed for compounds prepared by the following type of reaction [32]:

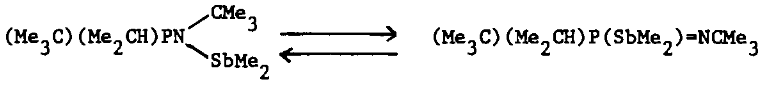


$$R_2PN\begin{matrix}X\\Li\end{matrix} + R'_2SbCl \longrightarrow R_2PN\begin{matrix}X\\SbR'_2\end{matrix} \quad \text{or} \quad R_2P(SbR'_2)=NX + LiCl$$

I II

(where R was Et, Me_2CH, or Me_3C, R' was Me or Me_3C, and X was an alkyl or aryl group or $SiMe_3$)

When R and X were *tert*-butyl, a single isomer of type II was formed. Decreasing the steric hindrance of X by replacing it with a *sec*-alkyl group led to an isomer of type I in which the phosphorus atom is three-coordinate. A similar change in one R group made the stabilities of the isomers of both types comparable, and it became possible to observe the following equilibrium by means of ^{31}P NMR:



$$(Me_3C)(Me_2CH)PN\begin{matrix}CMe_3\\SbMe_2\end{matrix} \rightleftarrows (Me_3C)(Me_2CH)P(SbMe_2)=NCMe_3$$

This type of dynamic equilibrium was termed "stibinotropy". When X was trimethylsilyl, however, the product was of type II even when the steric hindrance in the molecule was very low. Stibinotropy was again observed when X was a phenyl group and R was *tert*-butyl. The introduction of a trifluoromethyl group into the aromatic nucleus shifted the equilibrium completely to the side of the type II isomer; a decrease in steric hindrance by changing R to isopropyl returned the equilibrium to a spectrally observable magnitude. Increasing the temperature increased the proportion of type II isomers present in all cases.

In a paper on sulfur diimide derivatives of phosphorus, arsenic, antimony, and bismuth, the following reaction was described [33]:

$$(Me_3C)_2SbCl \; + \; K_2SN_2 \xrightarrow[-40^\circ C]{MeCN} (Me_3C)_2SbN{=}S{=}NSb(CMe_3)_2 \; + 2\,KCl$$

The organoantimony compound thus obtained was an intensely colored, crystalline substance and was thermochromic; on cooling a reversible lightening of the color was observed. The substance was less stable than the corresponding arsenic compound but more stable than the bismuth compound, which decomposed under ambient conditions. All of the sulfur diimides were studied by IR, PMR, and mass spectroscopy.

Triphenylphosphonium bis(diphenylstibino)methylide has been prepared in over 95% yield by the interaction of diphenylchlorostibine and triphenylphosphonium methylide in toluene at 70°C [34]:

$$3\,Ph_3P{=}CH_2 + 2\,Ph_2SbCl \longrightarrow Ph_3P{=}C(SbPh_2)_2 + 2\,Ph_3\overset{+}{P}Me\,Cl^-$$

The following sequence of steps leading to this result was suggested:

$$Ph_3P{=}CH_2 + Ph_2SbCl \longrightarrow Ph_3\overset{+}{P}CH_2SbPh_2\;Cl^-$$

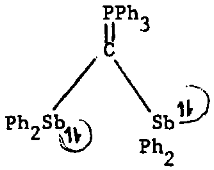
$$Ph_3\overset{+}{P}CH_2SbPh_2\;Cl^- \; + \; Ph_3P{=}CH_2 \longrightarrow Ph_3P{=}CHSbPh_2 \; + \; Ph_3\overset{+}{P}Me\;Cl^-$$

$$Ph_3P{=}CHSbPh_2 + Ph_2SbCl \longrightarrow Ph_3\overset{+}{P}CH(SbPh_2)_2\;Cl^-$$

$$Ph_3\overset{+}{P}CH(SbPh_2)_2\;Cl^- \; + \; Ph_3P{=}CH_2 \longrightarrow Ph_3P{=}C(SbPh_2)_2 \; + \; Ph_3\overset{+}{P}Me\;Cl^-$$

The bis(diphenylstibino)methylide was a light yellow solid, mp 165°C, and was surprisingly insensitive to air and moisture. It was only sparingly soluble in inert organic solvents, but a ^{31}P NMR signal could be obtained in hot THF (δ 28.23, relative to H_3PO_4). A peak at 975 cm^{-1} in the IR spectrum was assigned to the P=C stretching frequency. An

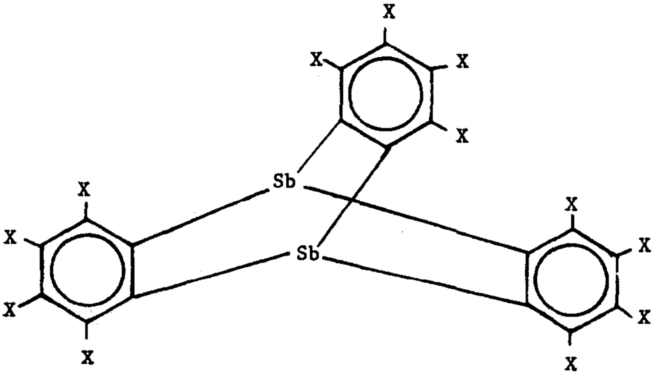
X-ray crystallographic study showed that the ylidic carbon atom deviated by only 0.12Å from the plane of the heavy elements (P, Sb, Sb). The sum of the valence angles at the ylidic carbon atom was 358.9°. The Sb-C-Sb angle was 116.9°; one of the P-C-Sb angles was 130.5° while the other was 111.5°. The large difference between the latter two angles was attributed to an opposite orientation of the two $SbPh_2$ groups relative to the P=C bond:



The lone pairs of electrons at the antimony atoms were oriented in the plane of the three heavy atoms. The conformational orientation of the groups and lone pairs linked to the antimony atoms was considered the most interesting feature of the molecular geometry and was discussed in terms of lone pair repulsion and of electrostatic and steric forces.

Arsenic, antimony, and bismuth compounds have been obtained by the interaction of inorganic derivatives of the three elements with L-cysteine in water [35]. Indentifiable substances, however, could not be isolated by allowing this amino acid to react with the organoantimony compounds PhSbO or $[Me_4N][PhSbCl_3]$. The products obtained under various conditions gave IR spectra that suggested that the L-cysteine had reacted through the deprotonated sulfur atom.

In continuation of earlier work from Massey's laboratory, the following antimony analogs of triptycene have been studied [36]:



(where X was F or Cl)

Both compounds were prepared by heating a mixture of the 1,2-diiodotetrahalobenzene and antimony powder in a sealed tube at 250°C. The yield of fluoro compound was about 60%; the yield of chloro compound was only about 5%. The fluoro compound formed hemi-solvates with hexane, cyclohexane, benzene, and toluene; the much less soluble chloro compound formed hemi-solvates with dimethylformamide, diethylformamide, pyridine, and nitrobenzene. The fluoro compound did not react with iodine in refluxing chloroform; chlorine in carbon tetrachloride, however, caused oxidation and produced a precipitate of $(C_6F_4)_3Sb_2Cl_4$ within a few minutes at room temperature. On boiling with a large excess of water, this tetrachloride was hydrolyzed to give a water-insoluble solid which analyzed for the dioxide $(C_6F_4)_3Sb_2O_2$. Thermal decomposition before volatilization made it impossible to obtain the molecular weight of the dioxide by mass spectrometry. Apparently, the same dioxide could be obtained by prolonged hydrogen peroxide oxidation of the original di-tertiary stibine $(C_6F_4)_3Sb_2$ or by hydrolysis of the ill-defined solid produced when bromine was allowed to attack the stibine in carbon tetrachloride. A dinitrate $(C_6F_4)_3Sb_2(OH)_2(NO_3)_2$ was obtained by dissolving the stibine in hot, concentrated nitric acid, diluting the mixture with water, and then allowing the solution to stand for two days. After four recrystallizations from water the dinitrate was converted to the tetrahydroxo compound $(C_6F_4)_3Sb_2(OH)_4$; the IR spectrum of this substance was almost the same as that of the dioxide. The mass spectra of both di-tertiary stibines exhibited relatively intense molecular ions, but the base peak in both cases was the $C_6X_4Sb^+$ ion. The ^{13}C NMR spectrum of the fluoro compound dissolved in acetone-d_6 was of second order but clearly showed the expected three groups of peaks corresponding to the three types of carbon present in the molecule.

The preparation of diphenylpyridylphosphines, -arsines, and -stibines has been accomplished by the following type of reaction sequence carried out in liquid ammonia [37]:

$$Ph_3E \xrightarrow[2)\ NH_4Cl]{1)\ Na} Ph_2ENa$$

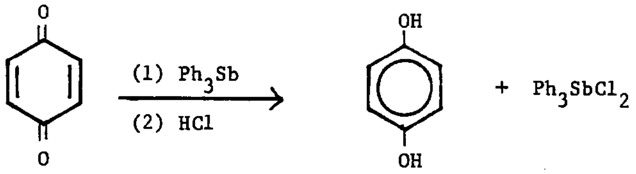
$$Ph_2ENa + ArCl \longrightarrow Ph_2EAr + NaCl$$

(where E was P, As, or Sb and Ar was 2- or 4-pyridyl)

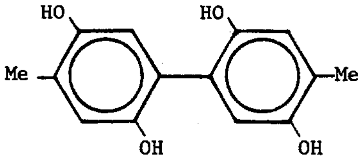
The products solidified after vacuum distillation and were then recrystalized from heptane and alcohol. Their structures were confirmed by PMR spectroscopy.

Triarylphosphines, -arsines, - and -stibines have been synthesized from elemental phosphorus, arsenic, or antimony by a "one-pot" reaction under conditions favoring an $S_{RN}1$ mechanism [38]. The element was first treated with sodium or potassium in liquid ammonia to form a species that behaved like E^{-3}, where E was P, As, or Sb. To this solution was added *tert*-butyl alcohol in order to neutralize any amide ion that might also have formed. An aryl halide was then added, and the reaction mixture was irradiated with lamps having a maximum emission at 350nm. This procedure gave a 40% yield of triphenylstibine when sodium was used and a 45% yield when potassium was used.

A study has been reported of the reaction of triphenylstibine with the following quinones: 1,4-benzoquinone, *p*-toluquinone, 2,5-diphenyl-1,4-benzoquinone, 2,5-di-*tert*-butyl-1,4-benzoquinone, and 1,4-naphthoquinone [39]. When 1,4-benzoquinone and the stibine were allowed to react in refluxing ether and the reaction mixture was then treated with hydrochloric acid, the main products were hydroquinone (92%) and triphenylantimony dichloride (94%):

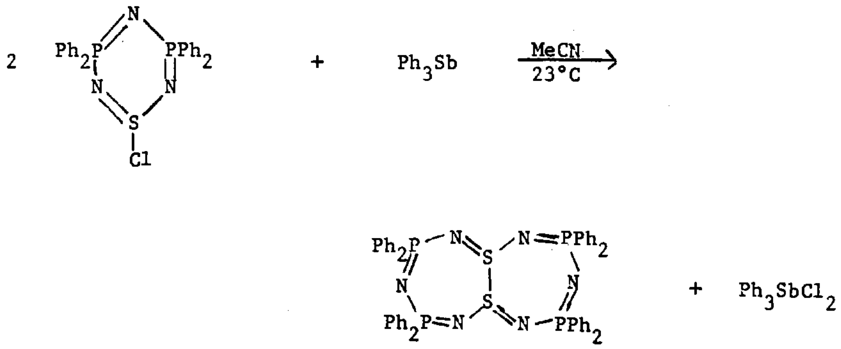


About 8% of 2-phenylhydroquinone was also isolated. Under identical conditions 1,4-naphthoquinone produced 89% of th corresponding hydroquinone and 11% of the 2-phenyl derivative; the triphenylstibine was converted to triphenylstibine oxide and diphenylstibinic acid. When the reaction between 1,4-benzoquinone and triphenylstibine was carried out in refluxing benzene, the main product isolated was 2-phenylhydroquinone; hydroquinone and triphenylantimony dichloride were also detected. 1,4-Naphthoquinone and the stibine, however, gave about the same results in both solvents. 2,5-Diphenyl-1,4-benzoquinone in refluxing benzene yielded only 6% triphenyl-1,4-benzoquinone; most of the quinone used in this reaction was recovered unchanged. 2,5-Di-*tert*-butyl-1,4-benzoquinone reacted with triphenylstibine in refluxing benzene only in the presence of catalytic quantities of benzoyl peroxide; under these conditions 23% of 2,5-di-*tert*-butyl-3-phenyl-1,4-benzoquinone was produced. The behavior of *p*-toluquinone in refluxing benzene was distinctly different from that of the other quinones studied in this investigation. In addition to *p*-toluquinol (2-methyl-1,4-benzenediol) and diphenylstibinic acid, the following biphenyl derivative was identified:



The reactivity of 2,5-diphenyl-1,4-benzoquinone increased when the reaction was carried out in refluxing xylene. Under these conditions, a 60% yield of triphenyl-1,4-benzoquinone was obtained; in addition, a 13% yield of biphenyl was produced by the decomposition of the triphenylstibine. 2,5-Di-*tert*-butyl-1,4-benzoquinone, however, proved to be inert even when treated with triphenylstibine in refluxing xylene. Formation of the various reaction products identified in this study was explained by mechanisms that involved free radicals.

The preparation of a twelve-membered inorganic heterocycle with a transannular sulfur-sulfur bond has been accomplished by means of the following reaction [40, 41]:



The heterocycle was obtained in about 40% yield as a bright yellow precipitate; triphenylantimony dichloride was isolated from the filtrate. The structure of the heterocycle was established by means of elemental analyses, ^{31}P, Raman, and mass spectroscopy, and X-ray crystallography.

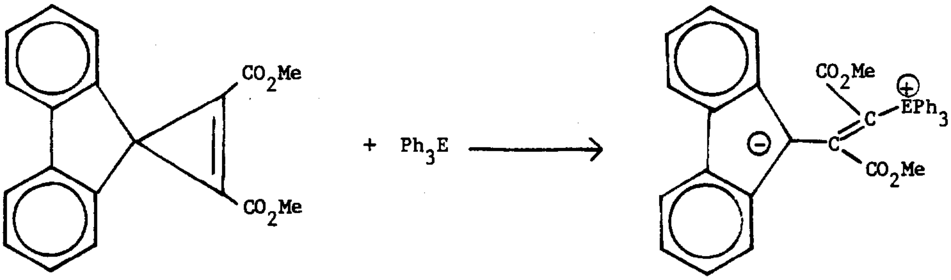
Treatment of the nickel(II) iodo-complex $[Ni(Me_2SbCH_2CH_2CH_2SbMe_2)I_2]$ with molecular iodine has been found to cause instant decomposition of the complex and formation of the tetraiodide $Me_2Sb(I_2)CH_2CH_2CH_2Sb$-$(I_2)Me_2$ [42]. The latter compound was identified by PMR spectroscopy.

The nickel complex used in this study was prepared by the interaction of nickel(II) iodide and 1,3-bis(dimethylstibino)propane:

$$NiI_2 + Me_2SbCH_2CH_2CH_2SbMe_2 \xrightarrow{BuOH} [Ni(Me_2SbCH_2CH_2CH_2SbMe_2)I_2]$$

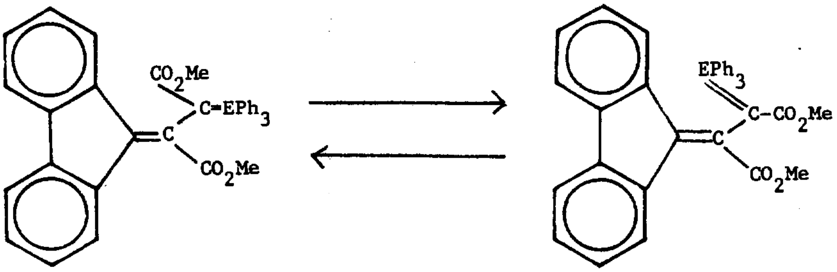
Electrochemical oxidation of triphenylstibine at a platinum anode has been used for preparation of quarternary stibonium salts of the type $[Ph_3SbR]X$ (where R was thienyl and X was ClO_4 or BF_4; or where R was tolyl and X was ClO_4) [43]. A large excess of thiophene or toluene was present during the oxidation, which was carried out in acetonitrile under an argon atmosphere. The supporting electrolyte was sodium perchlorate or tetraethylammonium tetrafluoroborate, and the base employed was trisodium phosphate. According to the coulometric data obtained, the electrolysis required about two electrons per molecule of triphenylstibine. The yields of stibonium salts ranged from 42-51%.

Ylids have been obtained by the following type of reaction [44]:



(where E was P, As, or Sb)

The PMR spectrum of each ylid in toluene-d_8 at about 25°C showed four MeO signals instead of the expected two. This result was attributed to the existence of a mobile equilibrium involving *s-trans* and *s-cis* conformations:



A study has been reported of the palladium-catalyzed cleavage of triphenylphosphine or triphenylstibine in an atmosphere of carbon dioxide or a mixture of carbon monoxide, nitric oxide, and nitrogen [45]. When either the phosphine or the stibine was heated with a palladium(II) salt at 180-200°C in an atmosphere of carbon dioxide, benzoic acid was the major product; the yields were 15-40% based on palladium. The stibine gave higher yields than did the phosphine; this result was attributed to the relative weakness of the Ph-Sb bond. When the cleavage reactions were carried out under a pressure of carbon monoxide, nitric oxide, and nitrogen, much higher (up to six times) amounts of benzoic acid were obtained. In a typical reaction, triphenylstibine (20 mmol) and palladium(II) chloride (10 mmol) were dissolved in toluene and heated at 200°C in an atmosphere of carbon monoxide, nitric oxide, and nitrogen (in a ratio of 1:1:3) at 2300 psig for three hours; about 50 mmol of benzoic acid were produced together with some benzophenone and anthraquinone. A mechanism was proposed that accounted for these products. The mechanism suggested the intermediacy of various species containing C-Pd bonds.

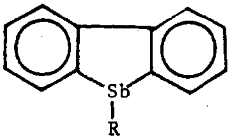
In a paper devoted mainly to the palladium-catalyzed exchange of aryl groups between different triarylphosphines at 100°C, a somewhat similar reaction between triphenylstibine and a triarylphosphine was also described [46]. For example, it was noted that the interaction of triphenylstibine and tri-*p*-tolylphosphine in the presence of palladium(II) acetate resulted in the formation of mixed phenyl *p*-tolyl phosphines; the major product of this reaction, however, was biphenyl. It was concluded that the cleavage of the Ph-Sb bonds occured at a much faster rate than the cleavage of the *p*-tolyl-P bonds of tri-*p*-tolylphosphine. The possible involvement of free radicals in these reactions was also discussed.

A study has been reported of the kinetics of the thermal decomposition of triethylstibine in the gas phase at temperatures of 305-340°C [47]. Analysis of the decomposition products showed that their yields scarcely changed in this temperature range. There was a high yield of ethane (65.6%) and small amounts of butane, isobutylene, propene, ethylene, propane, and methane. The following free-radical mechanism was suggested:

$$\begin{aligned}
&\mathrm{Et_3Sb} \longrightarrow \mathrm{Et_2Sb\cdot} + \mathrm{Et\cdot}\\
&\mathrm{Et_2Sb\cdot} \longrightarrow \mathrm{EtSb} + \mathrm{Et\cdot}\\
&\mathrm{EtSb} \longrightarrow \mathrm{Sb} + \mathrm{Et\cdot}\\
&\mathrm{2Et\cdot} \longrightarrow \mathrm{C_2H_6} + \mathrm{C_2H_4}\\
\text{or }&\mathrm{2Et\cdot} \longrightarrow \mathrm{C_4H_{10}}
\end{aligned}$$

The rate of the decomposition was a first order reaction up to a conversion of 80-90%. The reaction was accompanied by the formation of metallic antimony on the walls of the reactor. The temperature dependence of the rate constant was described by the equation $\ln k = (31.1 \pm 1.7) - (45{,}300 \pm 2000)/RT$.

X-ray diffraction has been employed for the determination of the structures of 5-chloro-5*H*-dibenzostibole and 5-phenyl-5*H*-dibenzostibole [48]:



(where R was Cl or Ph)

The tricyclic system in both compounds was almost coplanar; the deviation from coplanarity was somewhat greater in the phenyl derivative. The angle between the phenyl group and the central ring was 88.3°.

High performance liquid chromatography (HPLC) has been investigated for the separation and determination of various organometallic compounds [49]. Included in this study were several derivatives of phosphorus, antimony, and bismuth. In the series triphenylphosphine, -stibine, and -bismuthine, there was a significant increase in retention time in going from the phosphine to the stibine to the bismuthine. Pentaphenylphosphorus and -antimony were retained less strongly than the corresponding trivalent compounds. Antimony and bismuth derivatives of ferrocene and cyclopentadienylmanganesetricarbonyl (cymantrene) were also subjected to HPLC. The retention times of the ferrocenyl and cymantrenyl compounds decreased in going from the antimony to the bismuth derivatives. The cymantrenyl compounds were retained about twice as strongly as the corresponding ferrocenyl compounds.

Triphenylstibine has been included in an investigation of the solubility and solvolytic behavior of various Lewis acids and bases in fused bromoacetic acid at 60°C [50]. The solubility of the antimony compound was 4.32g per 100g of solvent. The solution was described as colorless, but no further information about the interaction of triphenylstibine and bromoacetic acid was given.

Organometallic substances of various types have been studied in order to nominate compounds to the National Cancer Institute as candidates for carcinogen bioassay [51]. Both triphenylstibine and triphenylantimony dichloride were included in the preliminary list of 1,815 compounds.

The dichloride was believed to have no commercial importance and was not further considered. The U.S. production of triphenylstibine, however, was more than 2.3 million grams in 1980, and it was one of five compounds recommended for biological testing.

Trimethylstibine has been employed as the antimony source for the production of thin alloy films by a process known as organometallic vapor-phase epitaxy [52]. Triphenylstibine has proved useful as an ingredient of certain light-sensitive substances [53, 54], as an additive to semi-metallic materials with high abrasion resistance [55], and in the manufacture of several types of polymers [56-60].

In addition to a paper [42] already discussed, 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 copper [61], gold [62-64], iridium [65-67], iron [68, 69], manganese [70], molybdenum [71-73], nickel [74-77], osmium [78], palladium [79], platinum [80, 81], rhenium [82], rhodium [67, 83, 84], ruthenium [85, 86], tungsten [73, 87], and vanadium [88, 89].

Sowerby and coworkers [90] have prepared the compound $Ph_2Sb(OAc)_3$ from Ph_2SbCl_3 and AgOAc in toluene. Although analyses and the IR spectrum of the compound were acceptable, it was hydrolytically unstable and single crystals were not obtained. When recrystallized from acetic anhydride an oxygen-bridged species, $[Ph_2Sb(OAc)_2]_2O$, was obtained. An X-ray diffraction study of this compound revealed that each antimony atom possessed a coordination number of seven due to the presence of two (asymmetrically) chelating acetate groups attached to each antimony atom. When $Ph_2Sb(OAc)_3$ was recrystallized from dichloromethane with no precautions to exclude hydrolysis, a complex basic acetate, $[Ph_8Sb_4O_6(HOAc)_3]\cdot CH_2Cl_2$, was obtained. An X-ray diffraction study of this compound showed the presence of an Sb_4O_6 cage with acetate bridges between two pairs of antimony atoms. In addition there were two Sb_2O_2 rings, in which one of the oxygen atoms in each ring was a hydroxy group which was hydrogen-bonded to an oxygen in the neighboring Sb_2O_2 ring. Each antimony atom possessed octahedral geometry.

Kolondra and coworkers [91] have previously reported on the vibrational spectra (Raman and IR) of the compound $Me_2SbCH_2SbMe_2$ and of the two dihalogen derivatives $Me_2Sb(X_2)CH_2Sb(X_2)Me_2$, where X was Cl or Br. The IR and Raman data of the unhalogenated compound were consistent with the existence of two rotamers of C_s and C_{2v} symmetry, whereas the spectra of the halogenated compounds, both as powders and in solution, showed no evidence of more than one form. The crystal structure of the dichloride was also determined. The same authors have now reported [92] that the Raman spectra of the dibromide, taken on a single crystal of the compound, was different from the spectrum of the same compound as a powder or in solution. Thus, the Sb-C-Sb symmetric and asymmetric stretching vibrations were split in the single crystal but not in the powder or in solution. Accordingly, they determined the crystal structure of the dibromide. They found that the unit cell contained 2x2 symmetry-independent molecules which differed in the angle of twisting around the Sb-C-Sb bond. In both molecules, both antimony atoms were trigonal bipyramids with both bromines in axial positions. However, in one molecule the plane passing through C-Sb_1-C (where each C was a methyl carbon) was inclined at an angle of 66.6° to the C-Sb_2-C plane, whereas in the other molecule this angle was 72.8°. By contrast in the compound $Me_2Sb(Cl_2)CH_2Sb(Cl_2)Me_2$ the angle of twisting around the Sb-C-Sb bond gave only a single value, 52.6°.

The molecular and crystal structure of dibromotris(cymantrenyl)-antimony has been reported in the Russian chemical literature [93]. The geometry of the antimony atom was that of a trigonal bipyramid with two axial bromine atoms. Bond geometries were described.

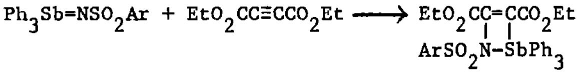
A series of compounds of the type Ar_3SbXL, where Ar was C_6Cl_5 or C_6F_5, X was Cl, Br, or OMe, and L was an acetylacetonato or oxinato group (oxine = 8-hydroxyquinoline), has been prepared by Espinosa and coworkers [94]. The compounds where X = Cl or Br were obtained from Ar_3SbCl_2 or Ar_3SbBr_2 and either sodium acetylacetonate or sodium oxinate:

$$Ar_3SbX_2 + NaL \xrightarrow{C_6H_6} Ar_3SbXL + NaX$$

The compounds $Ar_3Sb(OMe)L$ were prepared by treating the compounds $Ar_3Sb(OMe)_2$ with either acetylacetone or oxine. The solvent for this reaction was methanol. The compounds were characterized by elemental analyses, IR and UV spectroscopy, and molar conductance. On the basis of the IR data it was concluded that the antimony atom in the compounds $Ar_3Sb(OMe)_2$ possessed a trigonal bipyramidal structure. In the remaining compounds the antimony atom was octahedral, with the acetylacetonato or oxinato group acting as a bidentate ligand.

Mössbauer spectra for InSb, three inorganic Sb compounds, and one organic Sb compound Me_3SbCl_2, as a function of temperature, have been determined by Hedges and Bowen [95]. In the case of Me_3SbCl_2, the temperature range was 11-100 K. Within the limits of experimental error, the Debye model gave a reasonable approximation for the temperature dependence of the Mössbauer recoil-free fraction for the compounds investigated. In the case of Me_3SbCl_2, due to the large quadrupole splitting, it was necessary to use the complete transmission integral to account properly for the thickness effects. The temperature variation of the effective thickness gave a Debye temperature of $\Theta_D = 81$ K, assuming the effective vibrating mass was the Sb atom and $\Theta_D = 61$ K assuming it was the molecule as a whole. Raman data were of no help in determining the effective mass.

Kuplennik and coworkers [96] have found that compounds of the type $Ph_3Sb{=}NSO_2Ar$, where Ar = Ph or *p*-MeC_6H_4, reacted with diethyl acetylenedicarboxylate to form cyclic antimony compounds:



$$\mathrm{Ph_3Sb{=}NSO_2Ar + EtO_2CC{\equiv}CCO_2Et \longrightarrow \begin{array}{c} EtO_2C\,C{=}C\,CO_2Et \\ |\quad\;\; | \\ ArSO_2N{-}SbPh_3 \end{array}}$$

The structure of these compounds was determined by PMR, ^{15}N NMR, and IR spectroscopy, as well as by elemental analysis and molecular weight determinations. The cyclic compound, where Ar = Ph, was found to react with gaseous HCl in dichloroethane to give dichlorotriphenylantimony and the compound $PhSO_2NH(EtO_2C)C{=}CHCO_2Et$.

A number of pentacoordinate compounds of Sb(V) of the general type Ar_4SbL (where Ar was phenyl or *p*-tolyl and where L was a anionic group bonded to the antimony through either nitrogen or oxygen) have been prepared by Raj and coworkers [97]. The ligand LH included imides such as succinimide or phthalimide, heterocyclic amines, amides such as *N*-bromobenzamide, substituted benzoic acids, and oximes. A total of twenty-five such compounds were listed. They were characterized by elemental analyses, PMR and IR spectra. Molar conductivity data in acetonitrile, methanol, and nitrobenzene showed that the compounds were non-ionic in these solvents.

Three different synthetic methods were used for their preparation:

$$\mathrm{Ar_4SbBr + NaL \longrightarrow Ar_4SbL + NaBr}$$

$$\mathrm{Ar_4SbOMe + HL \longrightarrow Ar_4SbL + MeOH}$$

$$\mathrm{Ph_4SbBr + HL + Et_3N \longrightarrow Ph_4SbL + Et_3NHBr}$$

On the basis of their non-conductance in polar solvents and their PMR and IR spectra, it was concluded that all of these compounds contained a trigonal-bipyramidal antimony atom. The Sb-N and Sb-O bonds in all of these compounds were cleaved by Br_2 or $TeCl_4$ with the formation of Ar_4SbBr or Ar_4SbCl, respectively. Several of the compounds were tested for antimicrobial, insecticidal and anti-cholinisterase activities.

A number of compounds of the type R_3SbL, where R was methyl or phenyl and H_2L was a dibasic tetradentate Schiff base containing the ONNO donor system, have been prepared [98]. The Schiff bases were derived from (a) ethylenediamine and either salicylaldehyde or *o*-hydroxyacetophenone, (b) *o*-phenylenediamine and salicylaldehyde, or (c) 2-hydroxy-1-naphthaldehyde and *o*-phenylenediamine. The synthesis involved either of two different reactions:

$$R_3SbBr_2 + Na_2L \longrightarrow R_3SbL + 2NaBr$$

$$R_3Sb(OMe)_2 + H_2L \longrightarrow R_3SbL + 2MeOH$$

The solvent in these reactions was benzene. The resulting compounds were yellow to orange solids. Molecular weight determinations showed them to be monomeric in benzene. Both IR and PMR spectra for the compounds were given. In the IR spectra the C-O stretching frequencies occurred at higher frequencies than in the free ligands because of Sb-O bond formation. In the PMR spectra the peak for the CH=N proton showed an upfield shift which suggested that the azomethine nitrogens were also coordinated to the antimony atoms. In the case of compounds of type Me_3SbL, two different methyl signals in a ratio of 2:1 were seen which indicated that two of the methyl groups were in a different environment from the third. On the basis of these spectral results, the authors concluded that the antimony atom had a pentagonal bipyramidal structure employing an sp^3d^3 hybridization state.

Shabana and coworkers [99] have reported that 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide (Lawesson Reagent) was an effective reagent for the sulfuration of phosphous, arsenic, and antimony compounds . The only reaction describing sulfuration of an antimony compound was the conversion of triphenylstibine oxide to triphenylstibine sulfide in 40% yield by means of the Lawesson reagent.

Mohan and Durai [100] have applied the general quadratic valence force field to the four dihalotrimethylantimony compounds Me_3SbX_2 (X = F, Cl, Br, or I) by using molecular kinetic constants and Wilson's F-G matrix method. Other molecular characteristic constants, such as compliance constants, Coriolis coupling constants, vibrational mean amplitudes, and rotation distortion constants, were also calculated. It was shown that the calculated kinetic constants led to acceptable values for the molecular constants.

The interfacial polymerization of Ph_3SbCl_2 with diamines in the presence of NaOH, Et_3N, and phase-transfer agents such as onium salts and crown ethers has been studied [101]. The use of the phase-transfer agents gave increased yields and enabled the preparation of some polymers which could not otherwise be prepared.

A number of compounds with the general formula R_4SbY, where R was Me or Ph and Y was a bidentate ligand such as the anion of 8-hydroxyquinoline, anthranilic acid, or acetylacetone, have been reported by Schmidbaur and coworkers [102]. The crystal structure of the compound Me_4SbY, where Y was the 8-hydroxyquinoline anion, was determined. The antimony atom was a distorted octahedron. The ^{127}Sb Mössbauer spectra of these six compounds were also determined. The Mössbauer spectra of the compounds where Y was the 8-hydroxyquinoline or acetylacetone anion were best interpreted as involving octahedral antimony, but where Y was the anthranilate anion, the antimony appeared to be pentacoordinate. Four stibonium compounds $Me_4Sb{\cdot}H(OCOCCl_3)_2$, $Me_4Sb{\cdot}H(OCOPh)_2$, $Me_4Sb{\cdot}C_6H_4(CO_2)_2H$-*o*, and $Me_4Sb{\cdot}C_6H_3(OH)(CO_2)OEt$ were also prepared. The last compound above was derived from 4-ethoxysalicylic acid. The Mössbauer spectra of these four compounds were in agreement with a structure involving a tetramethylstibonium cation, with probably only weak interactions of the anions with the stibonium cations.

The tetraphenylantimony halides Ph_4SbX (X = Br or Cl) acted as catalysts for the hydration of ethylene oxide in the presence of CO_2 or ethylene carbonate [103]. With a slight excess of water the predominant product was ethylene glycol, but when the ratio of water to ethylene oxide was one or less, the product was diethylene glycol.

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