

ANTIMONY

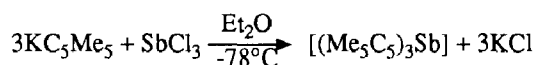
ANNUAL SURVEY COVERING THE YEAR 1988

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Except for our Annual Survey covering the year 1986, no book or review article devoted exclusively to organoantimony compounds was published in 1988. An interesting review of organically modified antimony(III) sulfides, however, appeared in 1987 [1] and was inadvertently omitted from our last Annual Survey. The preparation of several organoantimony compounds has been described in detail in a new volume of *Organometallic Syntheses* [2-6]. Information about organoantimony compounds has also been included in surveys of recent publications on organic derivatives of arsenic, antimony, and bismuth [7], on the main-group elements of Group V [8], and on the main-group elements of both Group IV and Group V [9]. Organoantimony compounds have been very briefly mentioned in review articles on the following subjects: energetics of organometallic species [10], reactions of compounds of the nonmetallic species [11], production of extrapure organometallic compounds for use in the epitaxial preparation of semiconducting materials [12], newer methods of arylation [13], organopalladium and organoplatinum compounds with pentahalophenyl ligands [14], the silicon group [15], diffraction studies of organometallic compounds [16], and Mössbauer spectroscopy [17].

The interaction of antimony trichloride and the potassium salt of pentamethylcyclopentadiene at -78°C has been found to give dimeric pentamethylcyclopentadiene and a 68% yield of an orange-red solid of empirical formula $\text{Me}_5\text{C}_5\text{Sb}$ [18]. The expected tertiary stibine was not isolated, but apparently it was formed and then underwent reductive elimination:

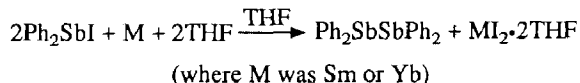


An X-ray diffraction study showed that the orange-red solid was a tetramer containing a non-planar Sb_4 ring with Sb-Sb bond lengths of 256.1 pm and with one η^1 - Me_5C_5 ring attached to each antimony atom. Cryoscopic measurements in benzene or cyclohexane, however, showed that the substance was monomeric (*i.e.* $\text{Me}_5\text{C}_5\text{Sb}$) in these solvents. These solutions, nevertheless, retained the distinctive color of the solid tetramer. The mass spectrum exhibited no $(\text{Me}_5\text{C}_5\text{Sb})_4$ or indeed any fragment containing both carbon and antimony; the highest observed mass corresponded to $\text{C}_{20}\text{H}_{30}^+$. Antimony was found only as $^{121}\text{Sb}^+$ and $^{123}\text{Sb}^+$. The PMR spectrum in C_6D_6 exhibited only a singlet at 1.96 ppm, *i.e.*, all the methyl groups were

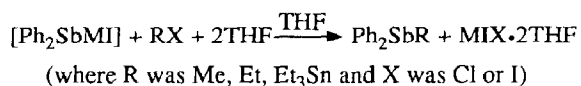
Previous review see *J. Organomet. Chem.*, 360(1989)263-296.

equivalent. The ^{13}C NMR spectrum in C_6D_6 showed a signal at 30.14 ppm (for the methyl groups) and at 120.56 ppm (for the ring carbon atoms). It was concluded, therefore, that in solution the compound existed as a pentahapto bonded species, *i.e.* $\eta^5\text{-Me}_5\text{C}_5\text{Sb}$. IR and UV data were also reported.

Tetraphenyldistibine has been prepared by the following type of reaction [19]:

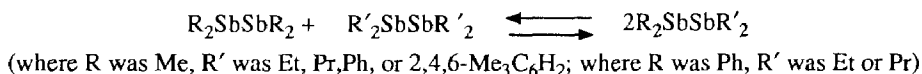


Apparently, an intermediate of the type Ph_2SbMI was formed in each of these reactions, and it could be trapped by the addition of an alkyl halide or a triethyltin halide:



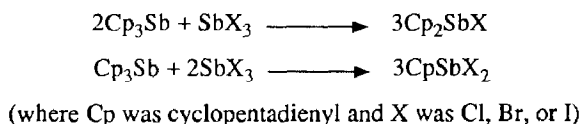
The yields of organoantimony compounds obtained in the trapping reactions ranged from 45-50%.

The interaction of two symmetrical tetraalkyldistibines with one another at 25°C has been shown to yield mixtures containing a mixed distibine in equilibrium with the parent distibines [20]:

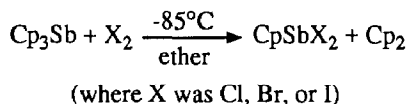


Mass and PMR spectroscopy were used to identify the products present in each equilibrium mixture and to determine their relative concentrations. The equilibrium constant for the interaction of tetramethyldistibine and tetramesityldistibine was 81; the other equilibrium constants ranged from 4 to 9. Attempts to isolate the mixed distibines by distillation or crystallization failed. It was therefore impossible to ascertain their colors or thermochromic behavior in the pure state.

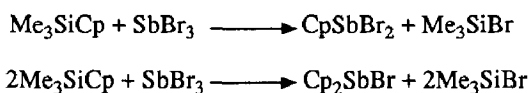
Dicyclopentadienylhalo- and cyclopentadienyldihalostibines have been prepared by the solid state interaction of tricyclopentadienylstibine and an antimony trihalide [21]:



In all cases the halo- and dihalostibines were light sensitive, moisture sensitive, yellow-to-orange oils or low melting solids and had short lifetimes even at low temperatures and in the absence of light. The dihalostibines could also be obtained by the interaction of the tertiary stibine and a halogen at low temperatures:

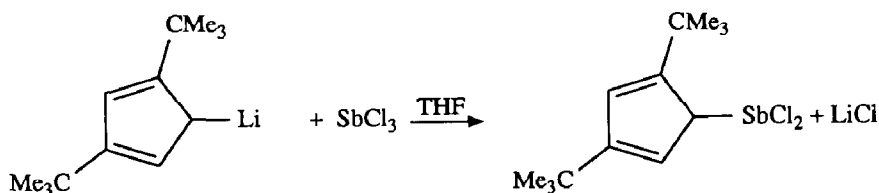


In addition, attempts were made to prepare the halo- and dihalostibines by the interaction of cyclopentadienylthallium (CpTl) and an antimony trihalide, but the organothallium compound was not reactive enough. Ligand exchange between an antimony trihalide and a Group IV derivative of the type Me_3MCp (where M was Si, Ge, Sn, or Pb) was successful only in the following cases:



The yields of bromo- and dibromostibines in the two reactions were described as being moderate. Attempts to synthesize tetracyclopentadienyldistibine by treatment of dicyclopentadienylhalostibines with activated magnesium in THF gave black, intractable tars. ^1H and ^{13}C NMR spectra of the halo- and dihalostibines indicated fluxionality of the cyclopentadienyl rings bonded to the antimony atoms. Singlets were observed for both nuclei and persisted in the temperature range from ambient to -80°C . Electron impact (EI) mass spectra were recorded for all of the compounds, but these highly moisture and oxygen sensitive substances were unable to survive the procedures required for field-desorption (FD) mass spectra scanning. With the exception of cyclopentadienyldibromostibine, the halo- and dihalostibines prepared in this investigation were included in a ^{121}Sb Mössbauer study of eighteen chemically and structurally related antimony(III) derivatives. The observed isomer shifts were interpreted by correlating electronegativity differences between antimony and the ligands bonded to it with their possible π -donating abilities.

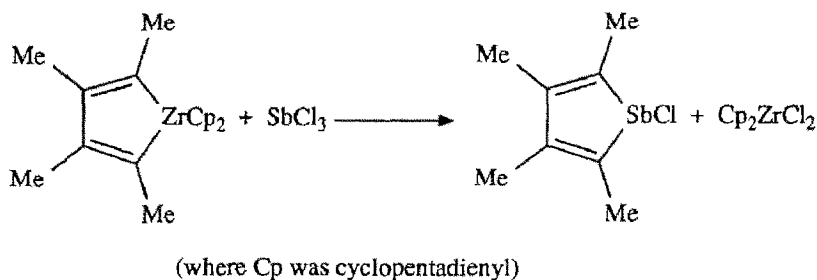
As part of an investigation of the fluxional behavior of σ -cyclopentadienyl compounds of the main-group elements, a di-*tert*-butylcyclopentadienyldichlorostibine has been obtained by the following reaction [22]:



The compound was obtained in 76% yield as a distillable, very air-sensitive liquid. It was

characterized by elemental analyses and spectroscopy (PMR, ^{13}C NMR, and mass). Variable temperature PMR studies were also performed. The results obtained suggested that the compound had a highly fluxional structure and that there was a rapid degenerate 1,2-shift of the SbCl_2 group.

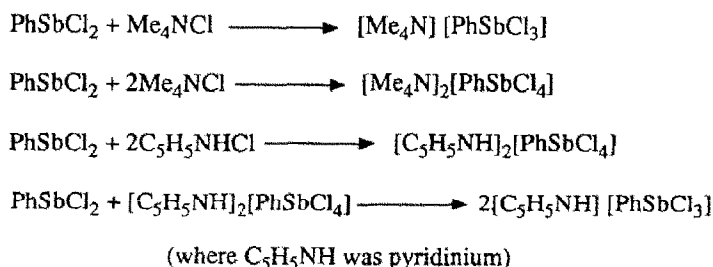
A number of main group heterocycles have been prepared by metallacycle transfer from zirconium [23]. For example, 1-chloro-2,3,4,5-tetramethylstibole has been obtained by the following reaction:

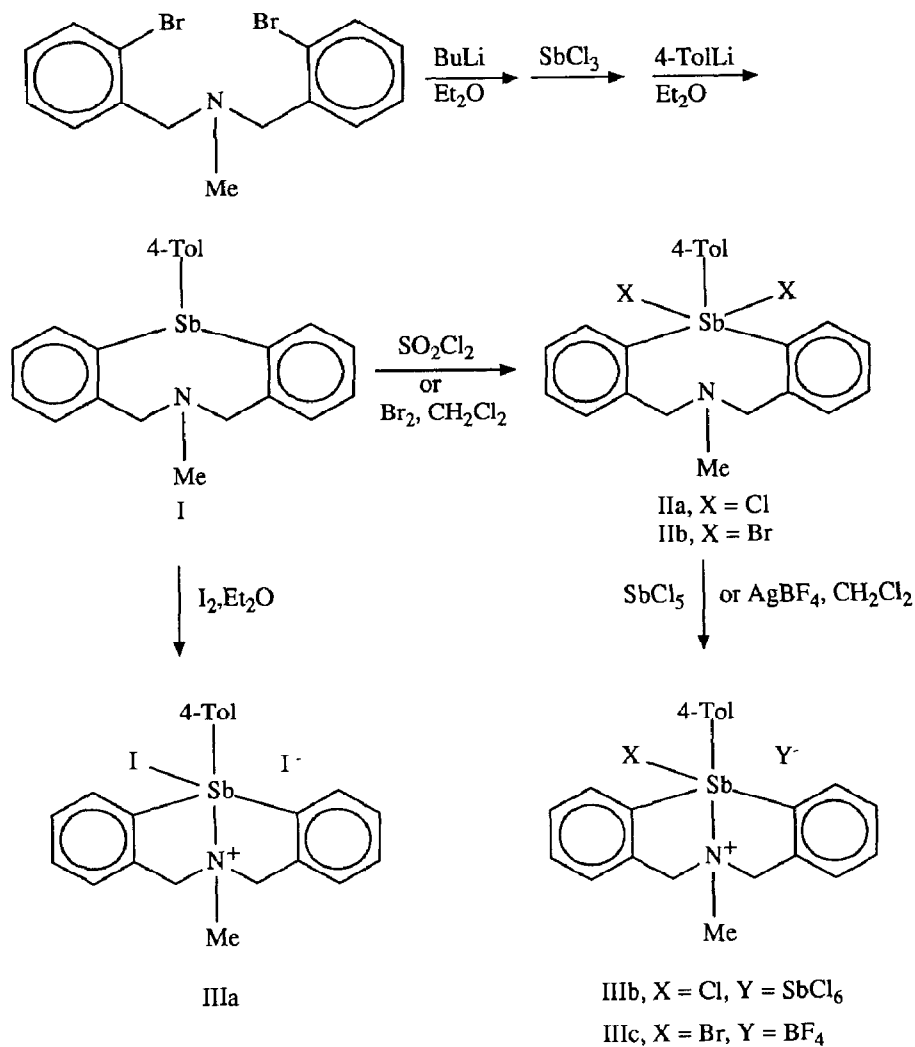


Addition of 1 equivalent of phenyllithium in 70:30 cyclohexane/ether to the chlorostibine gave a good yield of the expected 1-phenyl derivative, which was purified by high vacuum sublimation.

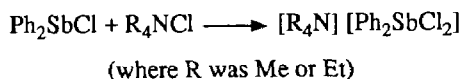
The azastibocine derivative I has been obtained in a 23% yield from bis(2-bromobenzyl)methylamine by a one-pot process [24]. Treatment of I with sulfuryl chloride or bromine in dichloromethane gave the expected pentacovalent antimony dihalides II. The dichloride IIa was converted by treatment with potassium fluoride in DMF to the corresponding pentacovalent difluoride. When I was allowed to react with iodine in diethyl ether, however, the ionic substance IIIa was obtained. Similar salts (IIIb and IIIc) were formed when the dichloride IIa reacted with antimony pentachloride or when the dibromide IIb reacted with silver tetrafluoroborate in dichloromethane. The ionic IIIb could be reconverted to the pentacovalent IIa by treatment with benzyltrimethylammonium chloride. PMR data were extensively used in this investigation to establish the structures of the various new compounds. It was also stated that analytical data were fully compatible with the assigned structures.

Phenyldichlorostibine has been found to react with tetramethylammonium or pyridinium chloride to give salts of both the phenyltrichloroantimonate and the phenyltetrachloroantimonate anion [25]:

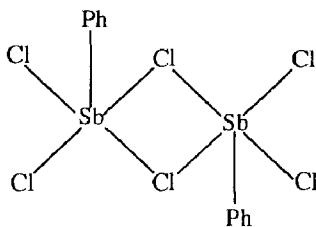




Under similar conditions diphenylchlorostibine yielded only the diphenyldichloroantimonate anion:

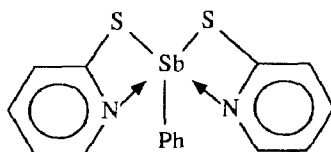


No anionic products, however, could be obtained from triphenylstibine. X-ray diffraction structures were obtained for the tetramethylammonium salts of both the phenyltrichloroantimonate and diphenyldichloroantimonate anions and for the pyridinium salt of the phenyltetrachloroantimonate anion. The phenyltrichloroantimonate anion proved to be a centrosymmetric dimer, with each antimony atom in square pyramidal coordination to an apical phenyl group and a basal system of four chlorine atoms:



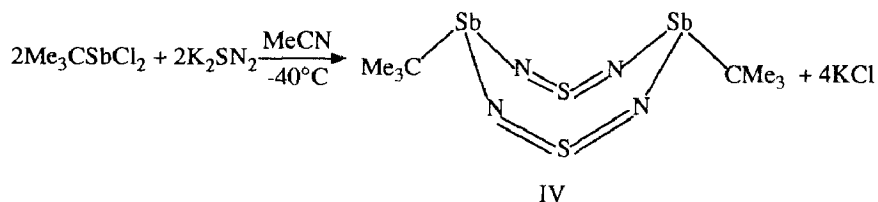
The Sb-Cl distances ranged from 2.423(3)Å to 3.121(4)Å, values clearly greater than the value of 2.32Å expected for a single bond. The other two anions were monomeric. The phenyltetrachloroantimonate anion also had a square pyramidal arrangement of chlorine atoms about the antimony and an apical phenyl group; the Sb-Cl distances ranged from 2.537(3)Å to 2.770(3)Å. The structure of the diphenyldichloroantimonate anion was described as pseudo trigonal-bipyramidal with the phenyl groups in equatorial positions and with axially placed chlorines. The mean Sb-Cl distance was 2.62Å. The various Sb-Cl distances observed in the three anions studied in this investigation were rationalized by assuming that chloride ion addition took place *trans* to the Sb-Cl bonds in the starting material and the negative charge was then delocalized via three-center bonding in the resulting Cl-Sb...Cl system.

Phenylbis(2-pyridinethiolato)stibine has been prepared by the interaction of phenyldichlorostibine and sodium 2-pyridinethiolate in ethanol at 343K [26]. An X-ray diffraction of this substance showed that each antimony atom was a member of two chelate rings:

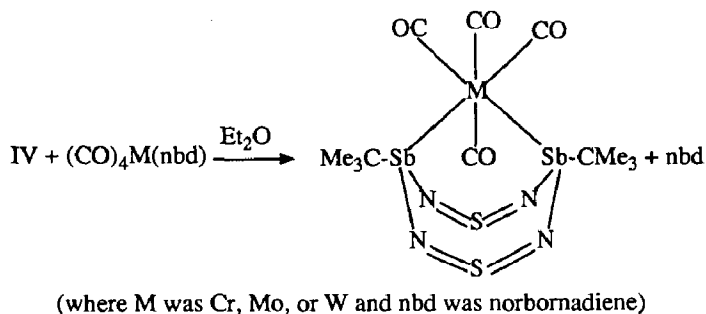


In the distorted tetragonal pyramidal (pseudo-octahedral) coordination about the antimony atom, the two sulfur and the two nitrogen atoms were in *cis*-positions, while the phenyl group occupied the apical position. The Sb-N distances were significantly longer than the sum of the covalent radii of antimony and nitrogen, whereas the Sb-C and Sb-S bond lengths agreed fairly well with the corresponding sums of the covalent radii. The intermolecular Sb...Sb distance of 4.145(1)Å was long enough to exclude Sb...Sb intermolecular interaction.

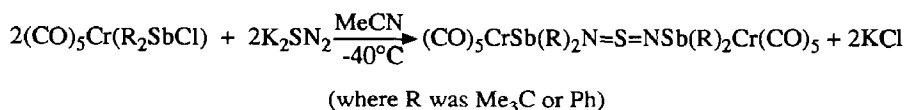
An eight-membered heterocyclic sulfur diimide derivative of antimony has been obtained in 43% yield by means of the following reaction [27]:



The orange solid thus obtained slowly decomposed at room temperature. When the pentacarbonylchromium complex $(\text{CO})_5\text{Cr}(\text{Me}_3\text{CSbCl}_2)$ was used in place of the *tert*-butyldichlorostibine, the above heterocycle with one of its antimony atoms coordinated to a $\text{Cr}(\text{CO})_5$ residue was formed. The heterocycle IV could be converted to stable chelate complexes in the following manner:

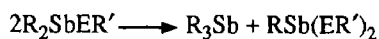


Interaction of the salt K_2SN_2 and the pentacarbonylchromium complex of di-*tert*-butyl- or diphenylchlorostibine yielded acyclic binuclear derivatives:



All of the sulfur diimide derivatives discussed in this paragraph were characterized by elemental analyses and by IR and NMR (^1H and ^{13}C) spectroscopy.

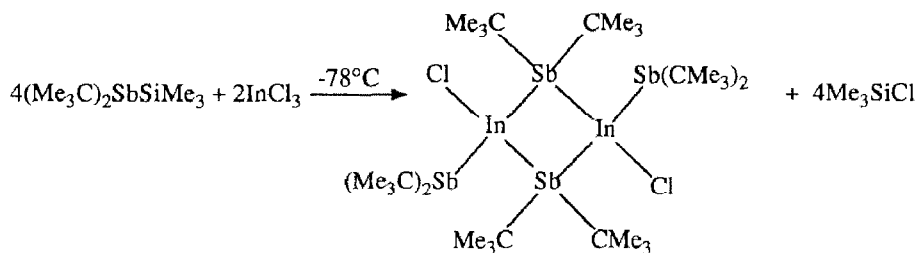
Seven compounds containing two Sb-S or Sb-Se bonds have been prepared by the following type of redistribution reaction [28]:



(where R and R' were Me, E was Se; where only R was Me, R' was Ph and E was S or Se; and where R was Et, R' was Me or Ph, and E was S or Se)

The syntheses were performed by heating the starting material at temperatures ranging from 80° to 145°C and in some cases at reduced pressure until all of the trialkylstibine had distilled from the reaction mixture. The seven new organoantimony compounds prepared in this investigation were characterized by PMR, Raman, and mass spectroscopy. All of them were described as having detestable odors.

The first dialkylstibino derivative of indium(III) has been obtained by the following reaction [29]:

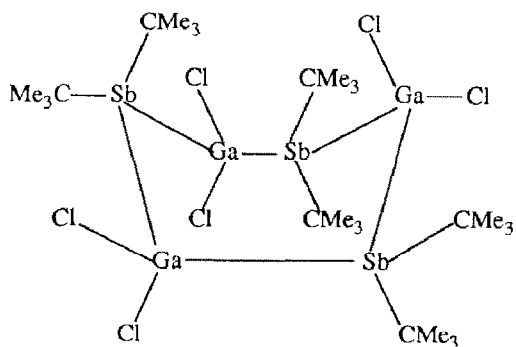


Even though a 3:1 mol ratio of di-*tert*-butyl(trimethylsilyl)stibine to indium chloride was employed, only disubstitution occurred. The dimeric nature of the new antimony-indium compound was established by X-ray crystallography. The average In-Sb bond length was 2.844(1)Å, a value that compares well with the sum of the covalent radii (2.84Å). The compound could not be characterized by EI-MS(70eV), because it decomposed to tetra-*tert*-butyldistibine in the inlet system. Molecular weight measurements in solution confirmed the dimeric nature of the compound. However, at ambient temperature only one type of *tert*-butyl resonance was observed in the ¹H and ¹³C NMR spectra. It was concluded that a rapid interchange of bridging and terminal di-*tert*-butylstibino groups occurred in solution.

The interaction of di-*tert*-butyl(trimethylsilyl)stibine and gallium chloride has been found to yield a trimer [30]:

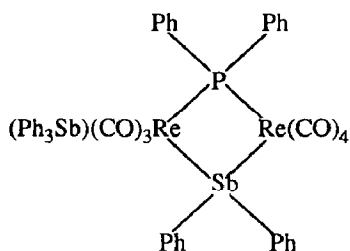


An X-ray diffraction study revealed a boat-type conformation with one antimony atom and one gallium atom 0.938Å and 0.620Å, respectively, above the central Ga₂Sb₂ plane of the molecule:



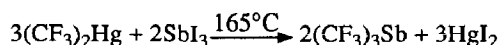
The average Ga-Sb bond length was 2.661(2)Å, about the same as the sum of the covalent radii (2.66Å) and similar to the bond distance in GaSb (2.649Å).

A diamagnetic rhenium compound that contained both a bridging Ph₂Sb group and a coordinated molecule of triphenylstibine has been prepared by the interaction of [Re₂(CO)₈(μ-H)(μ-PPh₂)] and triphenylstibine in xylene at 463-473 K in a glass bomb tube [31]. X-ray diffraction showed that each molecule of the rhenium compound had C₁ point-group symmetry and a nearly planar four-membered ring:



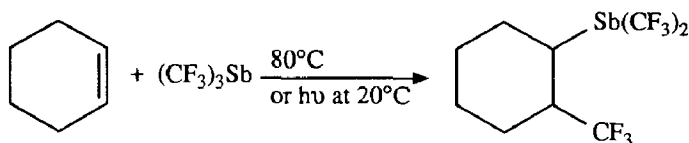
The mean value of the Re(μ -Sb) bond length was 2.740(1)Å, while the terminal Re-Sb bond length was 2.671(1)Å.

An investigation of the reactions between bis(trifluoromethyl)mercury and several halides of elements of main groups V and VI has included the following synthesis [32]:



The yield of tris(trifluoromethyl)stibine was 63%; traces (*ca.* 2%) of bis(trifluoromethyl)-iodostibine were also recovered from the reaction mixture. The tertiary stibine was characterized by mass and NMR (^{13}C and ^{19}F) spectroscopy.

The addition of tris(trifluoromethyl)stibine to cyclohexene has been found to give a mixture of *cis* and *trans* forms of a disubstituted cyclohexane [33]:

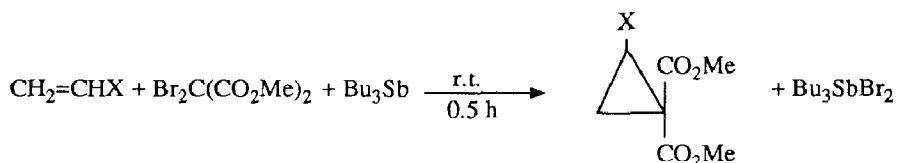


Excellent yields were obtained when the reactants were irradiated for 3h or heated at 80°C for 18h. Irradiation of the product for 100h caused cleavage of the C-Sb bond and formation of trifluoromethylcyclohexane, perfluoropropylcyclohexane, and various unidentified by-products. The disubstituted cyclohexanes were very stable thermally and survived unchanged after long heating at 150°C for 48h. They were characterized by ^{19}F NMR and mass spectroscopy. Treatment with chlorine in nitrogen at -20°C or bromine in trichloromethane at -78°C gave quantitative yields of the corresponding antimony dihalides. These substances, which were also mixtures of *cis* and *trans* isomers, were not isolated but were identified by ^{19}F NMR.

A study has been reported of displacement and electron-transfer reactions between 2-chloro-1,3,2-benzodioxastiboles and a variety of bases [34]. The interaction of 2-chloro-5-*tert*-butyl-1,3,2-benzodioxastibole and phenylmagnesium bromide in THF was included in this study. After acid hydrolysis, the products of this reaction included triphenylstibine (in unspecified yield) as well as *tert*-butyl alcohol, catechol, 4-*tert*-butylcatechol, phenol, biphenyl, and 1-phenylethanol. A detailed mechanism for the reaction was proposed.

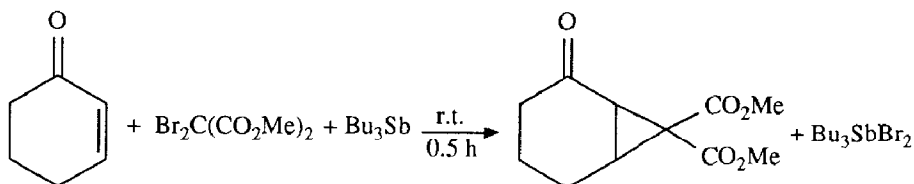
Technology for the production of extrapure triethylstibine has been described in an obscure Russian journal [35], but details of this study were not published in *Chemical Abstracts*.

Four papers on the use of tertiary stibines in organic synthesis have been reported in 1988 from the laboratory of Professor Yao-Zeng Huang. The first of these papers described the preparation of cyclopropane derivatives in good yields by the interaction of dimethyl dibromomalonate and an electron-deficient olefin in the presence of tributylstibine [36]:

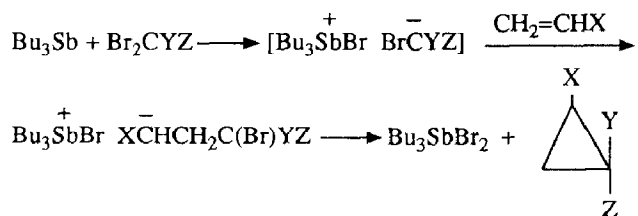


(where X was CH=O, C(O)Me, CN, or CO₂Et)

Replacement of the dimethyl dibromomalonate with diethyl dibromomalonate or ethyl dibromocynoacetate gave similar results. Olefins such as ethyl cinnamate, ethyl crotonate, β-ionone, *p*-chlorochalcone, or styrene did not give cyclopropane derivatives, while methyl 2-methylacrylate polymerized under the conditions of the above reactions. With 2-cyclohexenone, however, the reaction took place smoothly:



The following mechanism was suggested for these reactions (where Y and Z were electron-withdrawing groups):

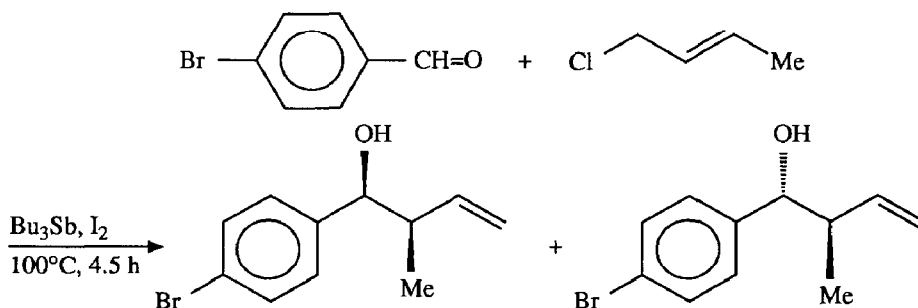


A second paper from Huang's laboratory described what was termed a "Barbier-type" reaction between allyl halides and aldehydes in the presence of a trialkylstibine [37]:

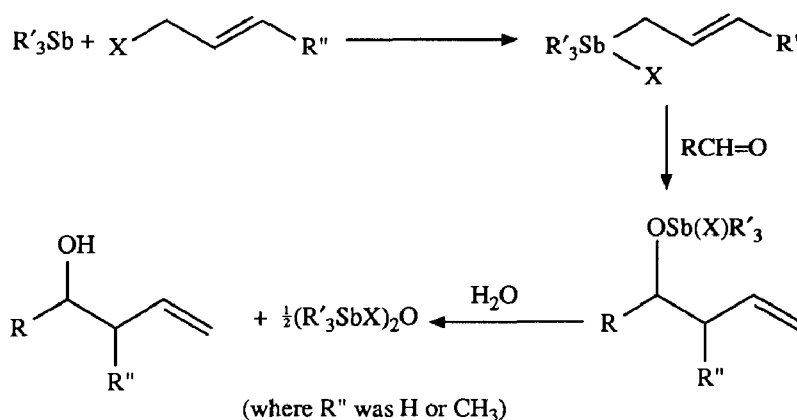


(where R was Oct, *trans*-HepCH=CH, PhCH=CH, 2-Fu, Ph, 4-ClC₆H₄, or 4-BrC₆H₄, X was Cl, Br, or I, and R' was Et or Bu)

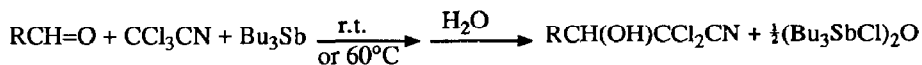
The yields ranged from 60 to 96%. Crotyl chloride reacted with 4-bromobenzaldehyde in the presence of tributylstibine, but a catalytic amount of iodine was necessary:



The ratio of *erythro* to *threo* form was 3:1. The isomer that would have resulted from the addition of the aldehyde to the CH_2 group of the crotyl chloride was not detected. Ketones such as cyclohexanone or acetophenone did not react with allyl halides under the conditions used in these experiments. The following mechanism was suggested for the "Barbier-type" reaction:

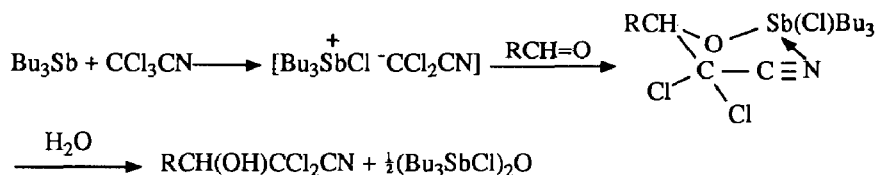


The use of tributylstibine to mediate the synthesis of α,α -dichloro- β -hydroxy nitriles was reported in a third paper [38]:



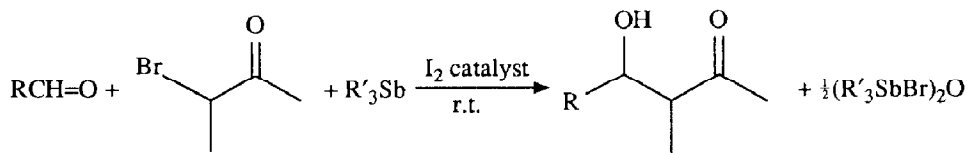
(where R was Bu, Oct, *trans*-MeCH=CH, *trans*-HepCH=CH, 2-Fu, Ph, 4-MeC₆H₄, 4-O₂NC₆H₄, or *trans*-PhCH=CH)

Ketones and imines did not react under the conditions employed with aldehydes. The following mechanism was proposed for the above type of reaction:



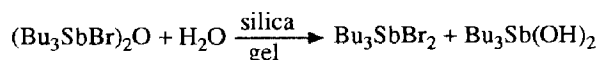
The isolated yields obtained in these reactions ranged from 70 to 99%.

β -Hydroxy ketones have also been synthesized in a reaction mediated by trialkylstibines [39]:

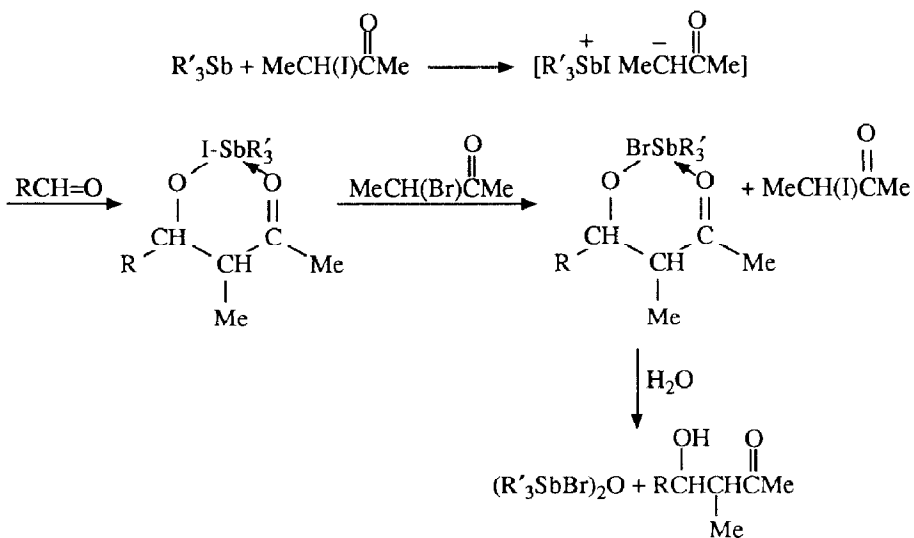


(where R was Me_2CHCH_2 , Oct, $\text{MeCH}=\text{CH}$, $\text{PhCH}=\text{CH}$, Fe, 2-Pyr, 3-Pyr, Ph, 4-ClC₆H₄, 4-BrC₆H₄, or 6-methylcyclohexa-1,3-dienyl and R' was Et or Bu)

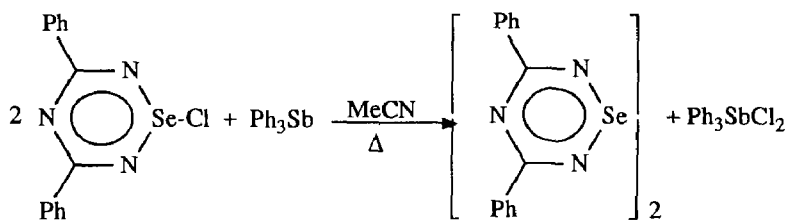
The yields ranged from 60 to 98%; the ratio of *erythro* to *threo* form was determined in each case. When 4-nitrobenzaldehyde was employed, 3-iodo-2-butanone was used instead of the bromo compound; the time required was only 1.5h rather than the 16-50h needed in the other cases. The oxybis(tributylantimony) dibromide isolated in those reactions employing tributylstibine could be converted by treatment with silica gel to a mixture of tributylantimony dibromide and tributylantimony dihydroxide:



The mechanism suggested for the formation of the β -hydroxy ketones involved the partial conversion of the bromo ketone to the corresponding iodo compound, which then reacted in the following manner:

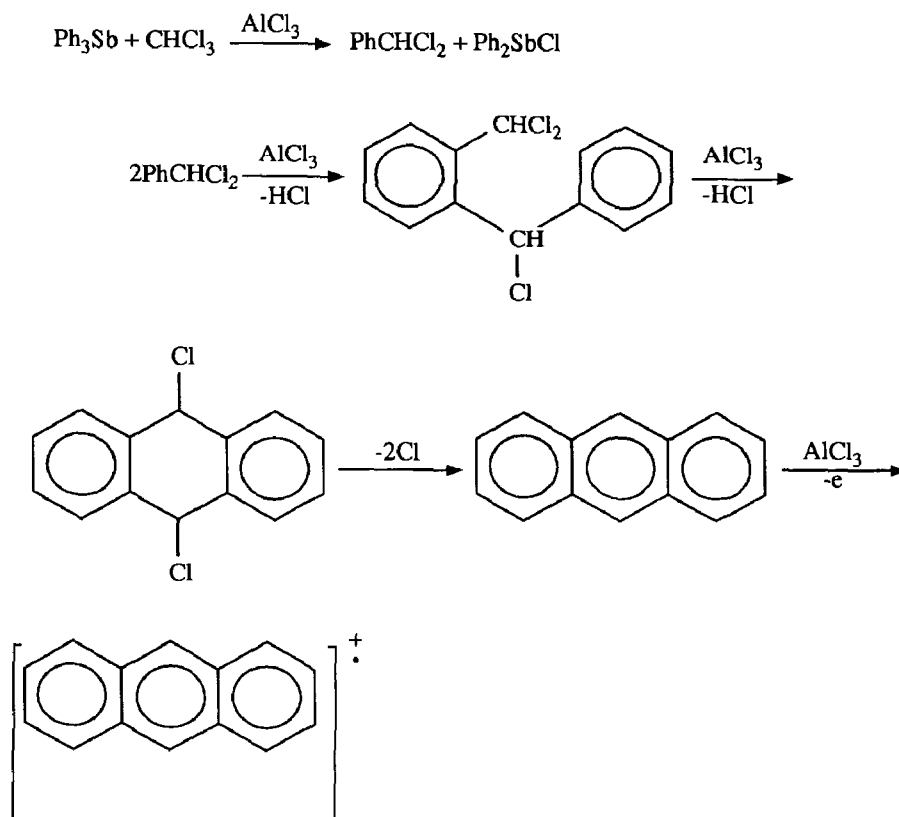


Triphenylstibine has been used as a reducing agent in the following reaction [40]:

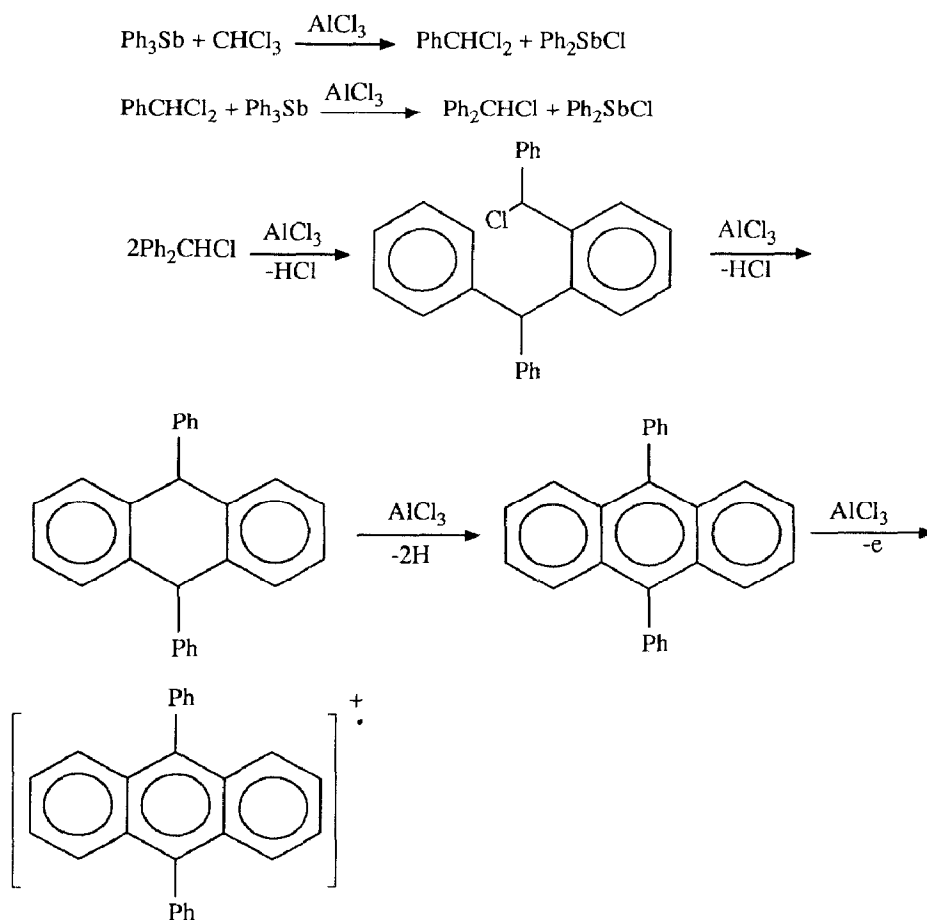


The triphenylantimony dichloride that was presumably formed in this reaction was apparently not identified. The molecular structure of the red dimeric product was determined by single-crystal X-ray diffraction and was found to consist of a cofacial arrangement of two heterocyclic rings linked by a long (2.792Å) Se...Se contact.

EPR studies have demonstrated the generation of polycyclic aromatic cation radicals during the Friedel-Crafts reaction of triphenylstibine with various haloalkanes [41]. For example, the reaction of 0.001M triphenylstibine in chloroform in the presence of excess aluminum chloride led to the formation of the anthracene cation radical. The following series of reactions was suggested:

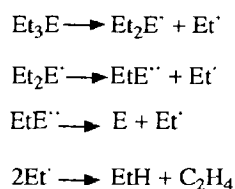


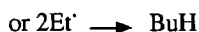
When the concentration of triphenylstibine was 0.1M, however, a different sequence of reactions appeared to occur:



Other polycyclic radical ions were formed by the aluminum chloride catalyzed reaction of triphenylstibine with 1,1,2,2-tetrachloroethane, 1,1,2,2-tetrabromoethane, or 1,1-dichloroethane. The importance of the concentration of the triphenylstibine was emphasized. The possibility of preparing new deuterated radical cations by the methods employed in this investigation was also mentioned.

A kinetic study of the thermal decomposition of triethylarsine, -stibine, and -bismuthine in the gas phase has been reported [42]. The temperature range used for the stibine was 305°-340°C. Analysis of the decomposition products of the stibine showed that their yields remained practically constant in this temperature range. The stibine gave a high yield of ethane (65%), an appreciable quantity of butane (16%), and rather small amounts of butylenes, propene, ethylene, propane, and methane. The following free-radical mechanism was suggested:





(where E was As, Sb, or Bi)

The rates of decomposition for the three compounds obeyed first order kinetics up to a conversion of 60-70%. In all cases the decompositions were accompanied by the formation of metallic films on the reactor walls. The thermal stability of the three compounds decreased in the order $\text{Et}_3\text{As} > \text{Et}_3\text{Sb} > \text{Et}_3\text{Bi}$. For the stibine the temperature dependence of the rate constant could be described by the following equation:

$$\ln k = (31.1 \pm 1.7) - (45,300 \pm 2000)/RT$$

The pyrolytic decomposition of tris(trifluoromethyl)stibine in the gas phase has been monitored by ultraviolet photoelectron spectroscopy [43]. The temperatures employed ranged from $< 530 \text{ K}$ to $> 1100 \text{ K}$. The expected trifluoromethyl radical was not observed, but at least three other gaseous species were detected. Two of these were unambiguously shown to be CF_2 and C_2F_4 . The third species could not be identified; trifluoromethyldifluorostibine and CF_3Sb were suggested as possible structures.

Trimethylstibine has been included in a study of the onset of pyrolysis of six common organometallic compounds [44]. The method employed in this study involved monitoring the formation of (unidentified) solid decomposition products. Hydrogen was used as the carrier gas. The pyrolysis onset temperature for the stibine was found to be $412.0 \pm 2.0^\circ\text{C}$.

A process known as organometallic vapor phase epitaxy (OMVPE) has been employed for the preparation of thin semiconducting films of alloys of the type $\text{GaP}_{1-x}\text{Sb}_x$ and $\text{InP}_{1-x}\text{Sb}_x$ (where x ranged from 0 to 1.0) [45]. The gallium alloys were grown at temperatures ranging from 530 to 600°C , the indium alloys from 460 to 600°C . Trimethylstibine was used as the source of the antimony.

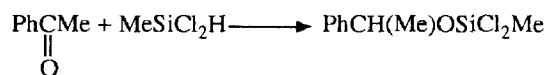
Films of indium antimonide, InSb , have been deposited on gallium arsenide, GaAs , substrates at room temperature by excimer laser photolysis at 193 or 248 nm of a mixture of trimethylindium and trimethylstibine in a hydrogen carrier medium [46]. *In situ* UV absorption spectroscopy was used to monitor and control the partial pressures of the organometallic reactants during the deposition. The films obtained in this investigation were compared to thermally grown indium antimonide by optical microscopy and X-ray analysis.

A variation of OMVPE called the interdiffused multilayer process (IMP) has been used to improve the compositional uniformity of epitaxial layers of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ (where x was less than one) [47]. In some experiments trimethylstibine was used for extrinsic doping of the layers, all of which were grown at a temperature of 410°C . The electrical properties of both doped and undoped layers were then compared.

Irradiation of trimethylstibine with a 5300\AA YAG laser beam has been employed in the chemical vapor deposition of diamond-like carbon films [48]. The temperature of the substrate during the formation of the films was 800°C . The films had a Vickers hardness of 8000 .

A combination of spin trapping, HPLC, and ESR has been used to study intermediates formed during the photolysis of triphenylstibine [49]. Each spin adduct detected was separated by HPLC and then rapidly identified by its ESR spectrum.

Trivalent antimony compounds have been employed as catalysts or cocatalysts in a number of polymerization reactions. Thus, these substances have been said to be useful for promoting the polymerization of fluorine-containing phenylacetylenes [50,51] and 1-chloro-1-alkynes [52], the copolymerization of cyclic imines and cyclic carbonates [53], and the copolymerization of carbon monoxide and olefins [54]. Electrical conductive polymers containing 1,3,4-thiadiazole-2,5-diyl groups with stibole-diyl groups on one or both sides have been found to have numerous uses [55]. The dehydrochlorination rate of PVC prepared with the aid of free radical sources has been found to be depressed when triphenylstibine was present during the polymerization reaction [56]. Triphenylstibine has also been found to be useful for increasing the resistance of zeolite-containing cracking catalysts to poisoning by metals [57]. In addition, it has been used as a cocatalyst in the hydrosilylation of acetophenone catalyzed by the platinum complex *cis*-PtCl₂(PhCH=CH₂)₂ [58]:



The HeI photoelectron spectra of the four compounds of the type Ph₂ESiMe, where E was N, P, As, or Sb, have been reported and have been assigned with the aid of the spectra of related simpler molecules [59]. The substitution of a trimethylsilyl group for a hydrogen atom in compounds of the type Ph₂EH resulted in a significant reduction of the lone pair ionization energy of the fifth group atom except where E was N. It was suggested that the introduction of the trimethylsilyl group into diphenylamine was accompanied by a structural change (perhaps an increase in non-planarity around the nitrogen atom).

Several tertiary stibines (Me₃Sb, Et₃Sb, Pr₃Sb, Bu₃Sb, and Ph₃Sb) have been included in a study of the relationships between the gas-phase heats of formation of metal alkyls and the Pauling electronegativities of the metals [60]. Linear or near-linear relationships were observed between these electronegativities and the average difference in heat of formation on homologous substitution (*i.e.*, Me for H, Et for Me, *etc.*). The relationships could also be theoretically derived from Pauling's definition of electronegativity. For alkyl substitutions in which an ethyl group was replaced by a propyl (or higher) group, no electronegativity dependence was observed. This result suggested that the influence of the metal extended only to its next nearest neighbors. Deviations from the proposed correlations were ascribed to experimental inaccuracies.

Non-empirical molecular orbital calculations have been employed to elucidate trends in the structure and reactivity of Group V alkyls, alkylidenes, and alkylidynes [61]. Included in this study were methylstibine, stibaethene (CH₂=SbH), and stibaethyne (CH≡Sb). The predicted carbon-antimony distances in the three substances were 2.19Å, 2.01Å, and 1.88Å, respectively. Not surprisingly, it was suggested that phosphorus-carbon, arsenic-carbon, and antimony-carbon multiply bonded compounds would undergo analogous chemical reactions. The chemical reactivity of these species was expected to increase in the order Sb > As > P. It was also noted that compounds containing antimony-carbon multiple bonds have not yet been reported in the literature.

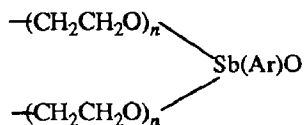
Stibabenzene (the antimony analog of pyridine) and stibole (the antimony analog of pyrrole) have been included in a study that employed *ab initio* molecular orbital theory to characterize a series of potentially aromatic metal-substituted benzene and cyclopentadiene analogs [62]. The structures of these metallocycles were predicted with the aid of the 3-21G* basis set and SCF wave functions. As a measure of the delocalization stabilization, energy and enthalpy changes for the appropriate bond separation and "superhomodesmic" reactions were calculated (with the aid of 3-21G* Hartree-Fock energies) for these compounds and for some smaller acyclic structures. It was concluded that stibabenzene was 72-79% as aromatic as pyridine but that stibole exhibited no delocalization stabilization.

A study has been reported of hyperconjugation in forty phenyl derivatives of mercury and of some of the main-group elements belonging to Groups III, IV, and V [63]. Triphenylstibine was the only antimony compound included in the study. It was shown that hyperconjugation increased with an increase in chemical bond polarization (which was assumed to be proportional to the bond refraction, R_D). The following linear relationship was observed between the $\sigma_p^+ - \sigma_p$ value of the group bonded to the phenyl ring and the sum of the refractions of the bonds involved in the hyperconjugation:

$$\sigma_p^+ - \sigma_p = -(0.0235 \pm 0.0019) \Sigma R_D + (0.198 \pm 0.036)$$

In addition to a paper [31] already discussed, there have been a number of other 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 [64], gold [65], iridium [66, 67], iron [68-70], molybdenum [64, 71-77], nickel [78], osmium [69, 79] palladium [80], platinum [81], rhodium [82, 83], ruthenium [69, 84-87], and tungsten [64, 74-76].

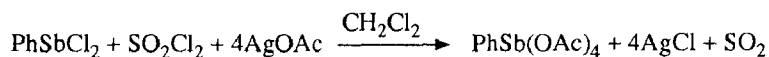
Anhydrides of arylstibonic acids $(\text{ArSbO}_2)_n$, where Ar was Ph, 4-MeC₆H₄, or 4-ClC₆H₄, have been found to be very effective catalysts for the polymerization of oxiranes [88]. The antimony compounds were prepared by heating the corresponding arylstibonic acids *in vacuo* at 100°C. The oxiranes employed were ethylene oxide, propylene oxide, 1,2-butylene oxide, and epichlorohydrin. The anhydrides dissolved in the oxiranes to give clear solutions. This was followed by an induction period before polymerization occurred. The induction period was shortest when $(4\text{-ClC}_6\text{H}_4\text{SbO}_2)_n$ was used as the catalyst and longest with $(4\text{-MeC}_6\text{H}_4\text{SbO}_2)_n$. It was suggested that the anhydrides reacted with the oxiranes to form polymeric alkoxides of the type:



A degradation method has been used to prepare a number of polytungstates of arylstibonic acids, as well as polytungstates and polymolybdates of aryl and alkyl arsonic acids [89]. The crystal types and cell dimensions of the compounds were determined. The following antimony compounds were prepared: $2\text{gu}_2\text{O} \cdot [5(4\text{-O}_2\text{NC}_6\text{H}_4\text{SbO}_2) \cdot 5\text{WO}_3]$.

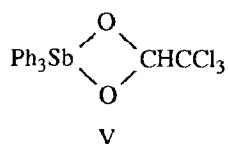
$\text{gu}_2\text{O}[3(\text{PhSbO}_2)\cdot 3\text{WO}_3]$, $4\text{gu}_2\text{O}\cdot [9(4\text{-MeC}_6\text{H}_4\text{SbO}_2)\cdot 12\text{WO}_3]$, and $3.5\text{gu}_2\text{O}\cdot [9(4\text{-ClC}_6\text{H}_4\text{SbO}_2)\cdot 12\text{WO}_3]$ (where gu was the guanadinium cation).

The reaction between dichlorophenylstibine and sulfuryl chloride followed by treatment with silver acetate gave tetraacetatophenylantimony [90]:



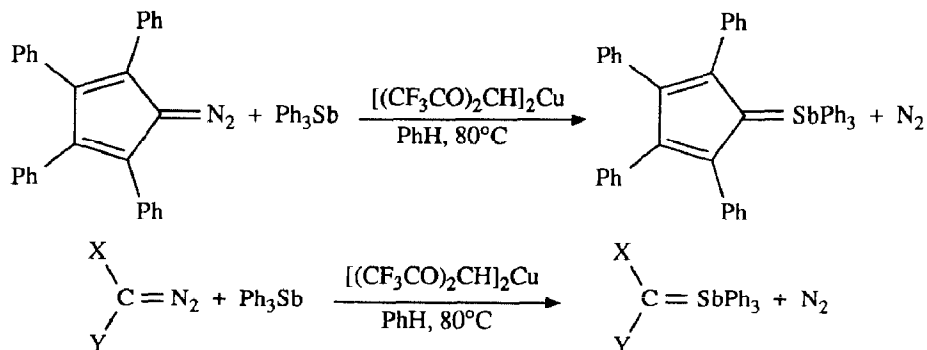
The compound, after recrystallization, was obtained as colorless crystals, mp 117°C. It was extremely susceptible to moisture. The compound was characterized by elemental analysis, IR and PMR spectra. In the IR spectrum the C=O asymmetric and symmetric stretching vibrations occurred at 1717 and 1365 cm^{-1} , respectively, but the spectrum did not rule out acetate groups acting as bidentate ligands. The molecular structure of the compound was determined by X-ray diffraction. The Sb atom was found to be hexacoordinate with three monodentate acetate groups and one symmetrically bonded bidentate acetate group. Two of the monodentate acetate groups occupied axial positions, and the Sb atoms, the bidentate acetate group, and one monodentate acetate group formed a plane, so that the Sb atom was essentially octahedral.

The synthesis of 2,2-dihydro-2,2,2-triphenyl-4-(trichloromethyl)-1,3,2-dioxastibetane (V) by the condensation of chloral hydrate with triphenylantimony dichloride has been previously reported by Ouchi and coworkers [91]:

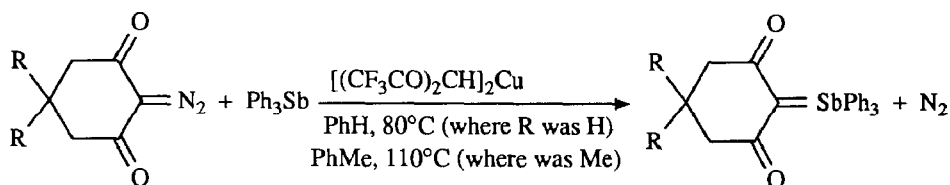


Ouchi [92] has now reported an X-ray diffraction study of this interesting compound. The molecular structure was that of a deformed square pyramid with one phenyl group in the apical position. The 4-membered ring was essentially planar. Bond lengths and bond angles were reported.

Bis(hexafluoroacetylacetonato)copper(II) has been found to be an efficient homogeneous catalyst for the conversion of certain diazo compounds to stibonium ylides [93]:

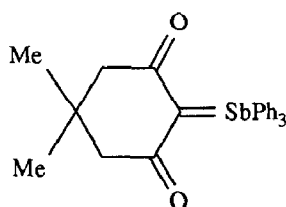


[where X and Y were PhSO_2 , $4\text{-MeC}_6\text{H}_4\text{SO}_2$, or MeC(O) ;
or where X was MeC(O) and Y was PhC(O)]



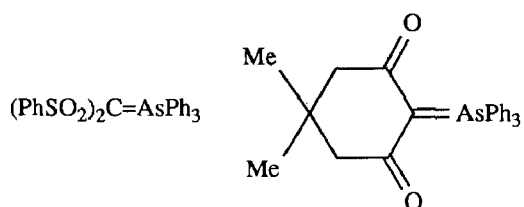
The mechanism of the above reactions apparently involved the thermal decomposition of the diazo compound to a carbene, which was then trapped by the triphenylstibine. The catalyst was thought to serve as a template in which the reactants were coordinated at *cis* sites in a six-coordinate intermediate. The yields of stibonium ylides ranged from 32 to 78%.

The chemical and spectral properties and the dipole moments of the stibonium ylides whose syntheses have been described in two recent papers [93,94] have now been reported in considerable detail [95]. In addition, the crystal structure of ylide VI has been determined by X-ray diffraction.



VI

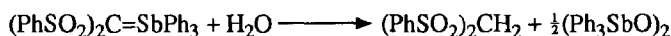
In order to compare the properties and structures of stibonium ylides with those of the corresponding arsonium ylides, crystal structure studies were carried out on the two arsonium ylides VII and VIII.



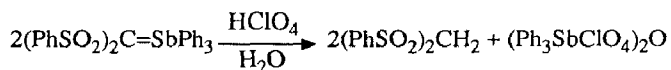
VII

VIII

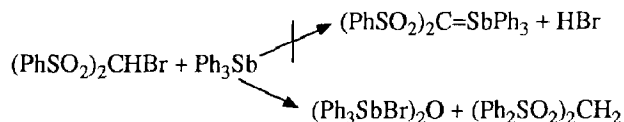
The stibonium ylides were all solids, stable in a dry atmosphere but readily hydrolysed in protic solvents by traces of moisture, *e.g.*:



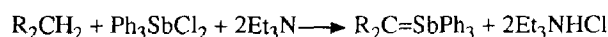
A number of attempts were made to prepare crystalline salts of these ylides (perchlorates or bromides) but invariably only hydrolysis products were obtained, *e.g.*:



Similar oxybis(triphenylantimony) derivatives were obtained in attempts to prepare stibonium ylides by the following type of reaction:



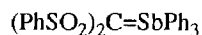
In the above reaction $(\text{Ph}_3\text{SbBr})_2\text{O}$ was obtained in 75% yield. In yet another attempt to prepare stibonium ylides, triphenylantimony dichloride was treated with the appropriate methylene compound in the presence of triethylamine:



When R_2CH_2 was acetylacetone, the desired ylide, contaminated with $(\text{Ph}_3\text{SbCl})_2\text{O}$, was obtained in 53% yield. The mixture could not be separated. The ylide obtained from benzoylacetone (yield 27%) was similarly contaminated with $(\text{Ph}_3\text{SbCl})_2\text{O}$. An ylide, apparently uncontaminated with the oxybis compound, was obtained from cyclohexane-1,3-dione, but in only 4% yield. No ylide was obtained from dimedone, dimethyl malonate, or bis(phenylsulfonyl)methane, but only the oxybis compound $(\text{Ph}_3\text{SbCl})_2\text{O}$.

An attempt was made to carry out the Wittig reaction with the stibonium ylides containing sulfonyl or carbonyl substituents, using highly reactive 2,4-dinitrobenzaldehyde as the substrate. In no case did a reaction proceed. An attempt to react $(4\text{-MeC}_6\text{H}_4\text{SO}_2)_2\text{C}=\text{SbPh}_3$ with nitrosobenzene was also unsuccessful. These results were not unanticipated since all of these ylides contained deactivating substituents, and arsonium ylides with similar structures were known to be unreactive towards electrophiles.

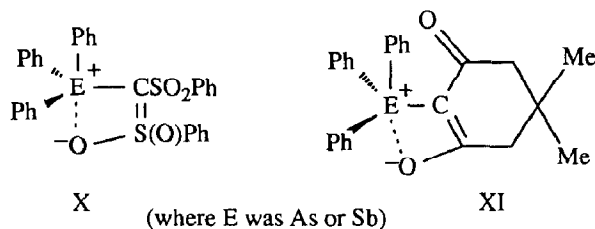
A comparison was made between the two stibonium ylides VI and IX and the two arsonium ylides VII and VIII (the structure of all of these had been determined by X-ray diffraction).



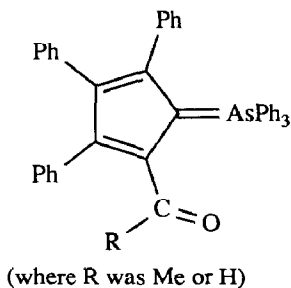
IX

The $\text{As}=\text{C}$ distances were considerably shorter than the $\text{As}-\text{C}(\text{phenyl})$ distances in both arsonium ylides. The $\text{Sb}=\text{C}$ distances were also shorter than the $\text{Sb}-\text{C}(\text{phenyl})$ distances and fell between the values for an $\text{Sb}-\text{C}$ single and double bond. They were, however, closer to the values for a double bond than was the case for the arsonium ylides. This result suggested that the $\text{As}=\text{C}$ bond possessed more single bond character (and hence more dipolar character) than the $\text{Sb}=\text{C}$ bond. In most of the ylides considered in the present paper, there was one $\text{As}-\text{O}$ or $\text{Sb}-\text{O}$ bond distance considerably shorter than the sum of the Van der Waals radii. This

indicated that the following canonical forms X and XI made considerable contributions to the structures of the molecules:

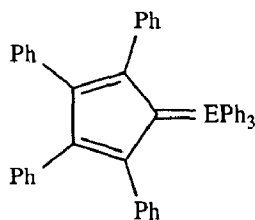


These structures (which resembled the transition state for Wittig-type reactions) were more important for the stibonium ylides than for the arsonium analogs (as judged by the X-ray diffraction results) due to the greater intrinsic polarity of the stibonium ylides. The importance of these canonical forms was strengthened by the IR spectral results. Thus, in the spectrum of the ylide $(\text{MeCO})(\text{PhCH}_2\text{SO}_2)\text{C}=\text{SbPh}_3$, no normal carbonyl stretching absorption was found. Similarly, no normal carbonyl frequencies were found for the following two arsonium ylides:



These results were consistent with strong intramolecular interactions between the carbonyl oxygen and the Sb or As atom. In general, the IR stretching frequencies become lower in going from phosphonium ylides to stibonium ylides, a result consistent with an increase in polarity of ylides in descending the periodic table.

Electronic spectral studies carried out in methanol solution on stibonium ylides sufficiently soluble in this solvent contained a broad band between 240-325 nm which was associated with intramolecular charge transfer. The electronic spectra of the arsonium and stibonium ylides were remarkably similar, a fact which suggested similar electronic structures for both types of ylides. The exception to this generalization was found for the two ylides XIIa and XIIb, where the λ_{max} difference between the two compounds was quite large.



XII

(a, E was As; b, E was Sb)

This result was consistent with the belief that the dipolar forms X and XI were of great importance for these ylide compounds. The PMR spectra of the stibonium ylides containing carbonyl or sulfonyl substituents and their arsonium analogs were also quite similar. In no case was there evidence for more than one geometric isomer at room temperature. The ^{13}C spectra of the ylide carbon atoms of three stibonium ylides compared with the ^{13}C spectra of the ylide carbon atoms of the three corresponding arsonium ylides suggested that the carbon atoms of the stibonium ylides carried less negative charge than those of the arsonium ylides. This result was also consistent with the previously discussed greater importance of the canonical forms X and XI for the stibonium ylides. Finally, dipole moments for two of the stibonium ylides and their two arsonium analogs were determined. There was surprisingly little difference between the values found for the antimony and the arsenic compounds. In addition to the ylides a dipole moment of $D \leq 0.7$ was found for triphenylstibine oxide $(\text{Ph}_3\text{SbO})_2$. This result was consistent with the centrosymmetric structure recently found for this compound by several investigators.

Triphenylantimony dibromide, in the presence of two equivalents of base, has proved to be an effective reagent for the oxidation of α -keto alcohols to diketones [96]. A number of α -keto alcohols $\text{RCHOHCOR}'$ (where R and R' were Ph, 4-MeC₆H₄, 2-furyl, or 2-thienyl; where R was Ph, R' was 2-furyl or Me) as well as two esters, $\text{PhCHOHCO}_2\text{Et}$ and $\text{MeCHOHCO}_2\text{Et}$, were oxidized in large yields. The base used was either triethylamine or DBU and the solvent was CDCl_3 or CH_2Cl_2 . A mechanism involving base-catalyzed ligand exchange of apical bromine to give either a hypervalent antimony compound or a stibonium bromide followed by elimination of Ph_3Sb was suggested. An even more effective reagent than Ph_3SbBr_2 was bis(2-pyridyloxy)tri-4-tolylantimony, formed by treating Ph_3SbBr_2 with 2-pyridone and triethylamine. With this reagent no base was used in the oxidation, the yields were large (58-97%), and the reaction time was greatly reduced. Finally, a catalyzed debromination and oxidation cycle was devised using Ph_3Sb , a base, and ethyl 2,3-dibromo-3-phenylpropionate as a bromine donor.

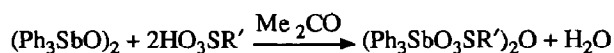
The formation of donor-acceptor complexes between Bu_3B and compounds of the type $\text{R}_3\text{MOOCMe}_3$ (where M was Si, Ge or Sn) or $\text{R}_4\text{SbOOCMe}_3$ (where R was Me or Ph) was indicated by negative values for the entropy of mixing [97]. The Si and Ge peroxides formed only weak complexes with Bu_3B , whereas the Sn and Sb complexes reacted to give free radicals.

Huber and coworkers [98] had previously reported that the oxidation of trimesitylstibine with hydrogen peroxide in acetone solution gave the corresponding dihydroxide rather than the expected stibine oxide. The crystal structure of this dihydroxide, determined by X-ray diffraction, has now been reported in a paper from the same laboratory [99]. The molecular structure of the compound is that of a trigonal bipyramid with the two hydroxyl groups in axial positions. The O-Sb-O angle is 176.7° , and the C-Sb-C angles differ only slightly from 120° . The Sb-O distances corresponded to those of other compounds containing covalent Sb-O bonds (e.g. Ph_4SbOH), and the intermolecular distances exceed the sum of the Van der Waal's distances. In the IR spectrum of the compound there was no band between 3000 and 3500 cm^{-1} ; this result excluded the presence of hydrogen bonded hydroxyl groups. A band at 3650 cm^{-1} was assigned to the OH stretching frequency.

In addition to this study on the structure of trimesitylstibine dihydroxide, the authors prepared a number of triarylstibine oxides $(Ar_3SbO)_2$ (where Ar was 2-MeOC₆H₄, 4-FC₆H₄, 4-ClC₆H₄, and 2,5-Me₂C₆H₃) as well as the oxide derived from 5-phenyldibenzostibole. All of these compounds were obtained by the oxidation of the corresponding stibine by 35% H₂O₂ in acetone solution. Molecular weight data on these compounds were of considerable interest. In benzene solution the 4-chloro and the 2,5-dimethyl compounds gave values in excellent agreement with those calculated for dimers. In chloroform, however, both the 4-chloro and the 2-methoxy compounds gave values somewhat lower than those for the dimer, while the 2,5-dimethyl compound gave a value (486) only slightly above that for the monomer (453). The authors assigned bands in the IR spectra of these compounds in the region 629-670 cm⁻¹ to $\nu_{as}(Sb_2O_2)$, and a band at 180 cm⁻¹ to $\delta(Sb_2O_2)$.

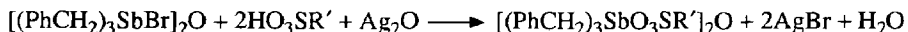
Huber and coworkers [98] had also shown that trimesitylantimony dihydroxide reacted with sulfonic acids to give rise to compounds of the type Mes₃SbO·HO₃SR (where Mes was 2,4,6-Me₃C₆H₂), in which the Sb-O bond possessed considerable double bond character. The structure of these compounds was quite different from the structures of compounds obtained from triarylstibine oxides and sulfonic acids. The same authors [100] have now investigated the reaction of trimesitylantimony dihydroxide and carboxylic acids. The resulting compounds were all of the type Mes₃Sb(OH)O₂CR (where R was H, Me, CHCl₂, CH₂F, CF₃, or 1-adamantyl). Two of the compounds (where R was H or CH₂F) contained a molecule of water of crystallization. All of the compounds were monomolecular in chloroform solution. They were characterized by elemental analyses, IR, and PMR spectroscopy. In addition, an X-ray diffraction study of the adamantyl compound was reported. The molecular structure of this compound was that of a slightly distorted trigonal bipyramid with the three mesityl groups in equatorial positions. The O-Sb-O angle was 175.5°, and the Sb-OH distance was 202.6 pm, quite typical of covalent Sb-O bond distances. There was, therefore, no evidence of intermolecular hydrogen bonding. The IR spectrum was also consistent with this finding. There was essentially no evidence that the carbonyl oxygen of the carboxyl group interacted with the Sb atom. Although the adamantyl compound did not show evidence of intermolecular hydrogen bonding, the IR spectra of the other carboxylates indicated the presence of hydrogen bonds. It was concluded that the bulky adamantyl group prevented the formation of hydrogen bonds.

In yet another paper from Huber's laboratory [101], the preparation of seventeen new μ -oxobis(triorganoantimony) sulfonates of the type $(R_3SbO_3SR')_2O$ (where R was Ph or benzyl and R' was Me, CH₂CH₂OH, Ph, 4-MeC₆H₄, or 2,4-(O₂N)₂C₆H₃; and where R was Me and R' was CF₃, 4-MeC₆H₄, Ph, Me, and CH₂CH₂OH) was described. Three new compounds of the type $(Me_3SbO_3SR')_2O \cdot 2H_2O$ (where R' was CF₃, 4-MeC₆H₄, and Ph) were also obtained. A number of synthetic procedures were used in the preparation of these compounds. In one method $(Ph_3SbO)_2$ was treated with the requisite sulfonic acid in acetone solution at room temperature:

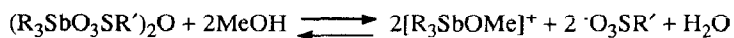


Where R' was 2,4-(O₂N)₂C₆H₃, it was necessary to carry out the reaction in boiling benzene and

to remove the water by azeotropic distillation. The method used for preparing all of the benzyl compounds depended upon the following reaction:



The methyl compounds ($\text{Me}_3\text{SbO}_3\text{SR}'$)₂O·2H₂O were prepared from the sulfonic acid and $\text{Me}_3\text{Sb}(\text{OH})_2$ in ether ($\text{R}' = \text{CF}_3$) or acetone ($\text{R}' = 4\text{-MeC}_6\text{H}_4$ or Ph) solution. When they were treated for 24h at 110°C, the corresponding anhydrous sulfonates were obtained. The anhydrous compound ($\text{Me}_3\text{SbO}_3\text{SMe}$)₂O was obtained from $\text{Me}_3\text{Sb}(\text{OH})_2$ and MeSO_3H in methanol solution by removing the solvent *in vacuo*, and recrystallizing the residue from methanol-ether. The compound ($\text{Me}_3\text{SbO}_3\text{SCH}_2\text{CH}_2\text{OH}$)₂O, also prepared from $\text{Me}_3\text{Sb}(\text{OH})_2$ and the corresponding sulfonic acid, was obtained only as an oil. All of the new compounds were characterized by elemental analyses and IR spectrometry. Molecular weight determinations, carried out on the ($\text{Ph}_3\text{SbO}_3\text{SR}'$)₂O compounds in methanol solution, gave values between one-third and one-fourth of the values expected for the monomers. Conductivity measurements in methanol and chloroform solution on two compounds [$(\text{Me}_3\text{SbO}_3\text{SPh})_2\text{O}$ and $(\text{Ph}_3\text{SbO}_3\text{SPh})_2\text{O}$] showed that these were 1:2 electrolytes in methanol. The molecular weight results were thus explained by the following solvolytic reactions:



On the basis of the IR spectra of all of the non-hydrated sulfonate compounds, it was concluded that these contained a pentacoordinate antimony atom with a unidentate $\text{O}_3\text{SR}'$ ligand in one apical position and the μ -oxygen atom in the other apical position. A correlation between $\nu_{\text{as}}\text{Sb-O-Sb}$ absorption bands and the Sb-O-Sb bond angles in six compounds in which the crystal structure had been determined, was established. On the basis of this correlation it was believed that the Sb-O-Sb bond angles in $\{[2,4\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3]_3\text{SbO}_3\text{S}\}_2\text{O}$ and $\{[2,4,6\text{-(O}_2\text{N)}_3\text{C}_6\text{H}_2]_3\text{SbO}_3\text{S}\}_2\text{O}$ were linear, whereas the same angle in the other sulfonate compounds was bent.

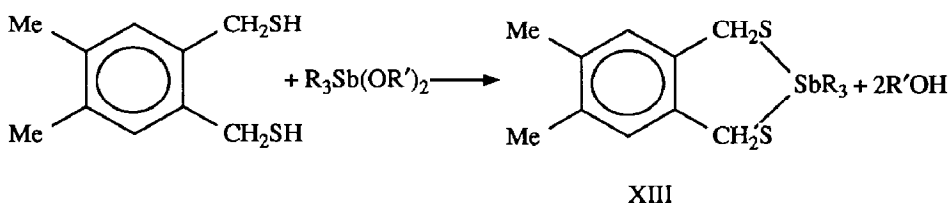
The structures of the three hydrated compounds ($\text{Me}_3\text{SbO}_3\text{SR}'$)₂O·2H₂O were quite different from those of the anhydrous compounds, as revealed by an X-ray diffraction study of the compounds ($\text{Me}_3\text{SbO}_3\text{SPh}$)₂O·2H₂O. This compound was ionic, consisting of $2[\text{PhSO}_3]^-$ and $[(\text{Me}_3\text{SbOH}_2)_2\text{O}]^{2+}$ ions. Each antimony atom was a distorted trigonal bipyramid with a water molecule and the μ -oxygen atom in apical positions. The Sb-O-Sb angle was 153.2°, and the $\mu\text{-O-Sb-O(H}_2\text{O)}$ angles were 171.7° and 171.0°. The mean $\mu\text{-O-Sb-C}$ angle was 98.3°. The Sb-O(H₂O) distance was considerably longer than a normal Sb-O covalent bond and indicated that the water molecules were only lightly bonded (in conformity with the ease of dehydration by heating). The hydrogens of the water molecules formed hydrogen bonds with the oxygen atoms of the sulfonate anions. The Sb-O (anion) distances were only slightly shorter than the sum of the Van der Waal's distances, indicating essentially no coordination of these oxygen atoms to the antimony atoms. The IR spectra of all three hydrated compounds were similar and indicated that all three compounds possessed similar structures.

The reaction between triphenyl- or trimethylantimony dibromides and the sodium salts of four potentially bidentate ligands (ethyl acetoacetate, salicylaldehyde, 2-hydroxyacetophenone, and 2-hydroxy-1-naphthaldehyde) resulted in the displacement of only one bromine, even when three molar equivalents of the sodium salts were used [102]. The resulting complexes were white crystalline compounds, sensitive to moisture, but otherwise stable at ambient temperatures. They were characterized by elemental analyses, PMR and IR spectroscopy. Molecular weight determinations showed that the compounds were monomolecular in benzene. It was concluded, based on the IR spectral results, that all of the ligands were bidentate and thus the antimony atom possessed octahedral geometry.

In a theoretical article [103] devoted to linear or non-linear E-X-E fragments in species of the type R_3EXER_3 , where R was an organic group, E was a main group element, and X was O, N, or C, a number of antimony compounds of the type $R_3(Y)SbOSb(Y)R_3$, where Y represented a wide range of nucleophilic anions, were discussed. It was concluded that a linear SbOSb would be favored in those compounds where a terminal ligand Y was tightly bound, with a short Sb-Y distance.

The crystal and molecular structure of 1,1-dichloro-1,1-dihydro-1-methylstibolane has been determined by X-ray diffraction [104]. Although the geometry of the Sb atom was pseudo trigonal-bipyramidal with the 5-membered ring spanning two equatorial positions, this geometry was greatly distorted towards octahedral by the approach of a Cl atom of a neighboring molecule. This Cl atom bisected the C-Sb-C angle between the Me group and one of the ring C atoms attached to the antimony. This Cl atom, three C atoms, and the Sb atom were in a plane, with two other Cl atoms in axial positions. The two Sb-Cl distances were 2.519 and 2.485Å, with the longer distance involved in the short intermolecular contact. The Sb-Cl intermolecular distance was 3.613Å compared to the sum of the Van der Waals radii of 4.01Å. The endocyclic C-Sb-C angle was 90.4° and the 5-membered ring had a twisted conformation. The authors noted that in this compound the ligand preference rule for trigonal bipyramidal molecules (the most electronegative groups occupy axial positions) would seem to take preference over the tendency for the 5-membered ring to be attached to one equatorial and one axial position. Ring strain was relieved by distortion towards octahedral geometry.

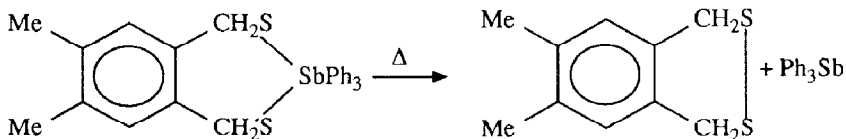
Arbuzov and coworkers [105] have prepared the seven-membered ring compound 1,3,5,5-tetrahydro-3,3,3,7,8-pentamethyl-2,4,3-benzodithiastibepin (XIII, R = Me) and the triphenyl compound (XIII, R = Ph) by means of the following type of reaction:



(where R was Me or Ph and R' was Me or Et)

The same products were obtained from the dimercaptan and R_3SbCl_2 in the presence of Et_3N , but the yields were lower. The stibepin XIII (R = Ph) was a stable crystalline compound but the

trimethyl compound was unstable and decomposed on standing in the air. IR and PMR spectra for both compounds were reported. No broadening of the methylene proton NMR signals was effected by lowering the temperature of solutions of either compound to -124°C . The thermal decomposition of the dithiastibepin ($\text{R} = \text{Ph}$), either by melting or in a boiling benzene solution, gave 1,4-dihydro-6,7-dimethyl-2,3-benzodithiin:

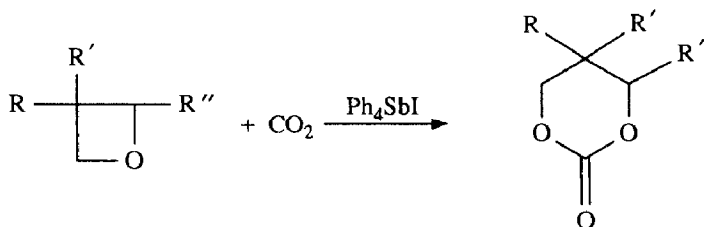


The same disulfide and Me_3Sb were obtained from the trimethyl compound at room temperature.

The aminolysis of thioacetic and thiolobenzoic acids by Et_2NH , Ph_2NII , or PhNH_2 was greatly aided by the use of catalytic amounts of triphenylstibine oxide [106].

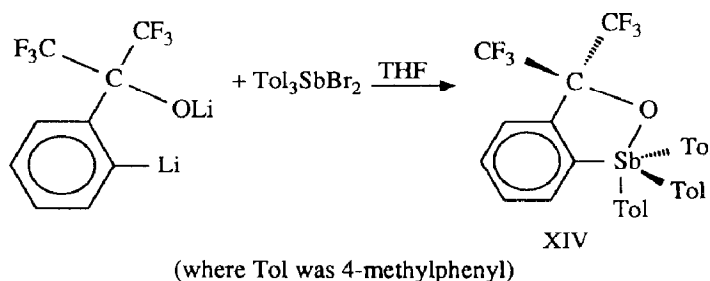
The use of triphenylantimony dichloride as a flame retardant for certain types of epoxy resins has been described in some detail [107].

In continuation of work from Matsuda's laboratory on the use of organoantimony compounds as catalysts for condensation reactions, it was found that tetraphenylantimony iodide (as well as diphenyltin diiodide) was an effective catalyst for the condensation of oxetanes with CO_2 to give dioxanones [108]:

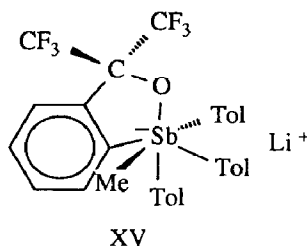


In another paper from the same laboratory Ph_4SbI was found to be a unique catalyst for the cycloaddition of oxiranes or oxetanes with diphenyl- or phenylethylketene to yield γ - or δ -lactones [109].

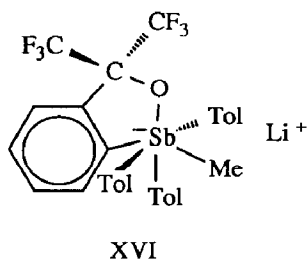
Akiba and coworkers [110] have prepared 1,1,1,3-tetrahydro-1,1,1-tri-4-tolyl-2,1-benzoxastibole (XIV) in the following manner:



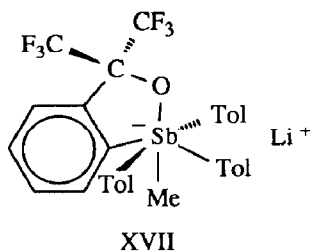
When treated with one equivalent of methyllithium at -78°C , XIV gave an ate complex to which structure XV was assigned.



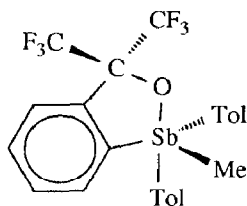
The structure assigned to XV was based on an ^{19}F NMR spectrum which consisted of two quartets ($\delta = -74.2$ and -74.9 from CFCl_3 ; $J_{\text{F,F}} = 9\text{Hz}$ at -50°C). No other isomer was detected at -50°C during 5h. When the solution was heated to -20°C , a new singlet appeared in the ^{19}F spectrum within 1.5h ($\delta = -73.8$ at -50°C ; -74.0 at 35°C). Structure XVI was assigned to this isomer:



Finally, when heated to 35°C , another singlet appeared at about 0°C ($\delta = -74.0$ at -50°C , -73.8 at 35°C). Structure XVII was assigned to this isomer:



Although there was no evidence for the assignment of these structures to XVI and XVII, it was assumed that structure XVI, with a tolyl group *trans* to the oxygen, would be the preferred structure. At equilibrium the ratio of XV:XVI:XVII was 61:23:16. The authors then prepared another benzoxastibole (XVIII) which reacted with 4-tolylithium at -40°C to give a mixture of XV, XVI and XVII in a ratio of 86:9:5.

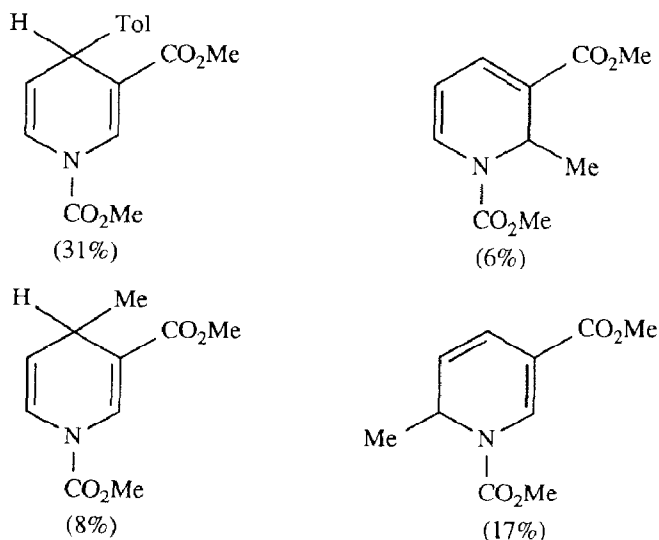


XVIII

After standing at 20°C the equilibrium mixture had the same ratio of isomers (61:23:16) as previously found.

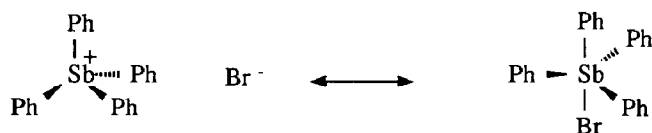
The authors then investigated the mechanism of the equilibrium $XV \rightleftharpoons XVI \rightleftharpoons XVII$. If the mechanism involved an intermolecular dissociative equilibrium, it might be possible to detect $TolLi$ or $MeLi$ by ^{13}C NMR spectroscopy. Neither compound could be found in the equilibrium mixture. The authors then quenched the mixture with a 10 and a 100 molar excess of ethanol at -20°C to give a mixture of XIV and XVIII in a ratio of 5:95. The rate of this quenching reaction was determined and a second order rate constant of $1.8 \pm 0.1 \times 10^{-5} \text{ mol}^{-1} \text{ s}^{-1}$ was calculated. This rate was only about 1/10 as fast as the rate of the equilibration $XV \rightleftharpoons XVI$, also determined at -20°C. (A first order rate constant of $1.9 \pm 0.1 \times 10^4 \text{ s}^{-1}$ was calculated). This result excluded the possibility of an intermolecular dissociation as playing the major role in the reaction mechanism. The mechanism of equilibration was not determined.

In addition to quenching the equilibrium mixture with ethanol, quenching with other protic acids (H_2O , 2,6- $Me_2C_6H_3OH$, $PhOH$, and $MeCO_2H$) was carried out. In every case a mixture of XIV and XVIII was found, with the ratio XVIII:XIV increasing as the pK_a of the protic acid decreased. The authors also carried out a preliminary investigation of the reaction of electrophiles with the equilibrium mixture (XV, XVI, XVII). Thus, 1,3-dicarbomethoxy-pyridinium chloride gave the following products:



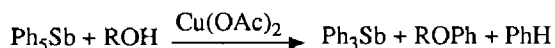
4-Tollyllithium and the same pyridinium chloride gave methyl nicotinate and 3-(4-toluoyl)pyridine. Another electrophile studied was 4-methoxybenzoyl chloride. This gave 4-methyl-4'-methoxybenzophenone; 4-tollyllithium and the same benzoyl chloride gave 4-methoxy-4',4''-dimethyltriphenylcarbinol. Thus, the actual reacting species was the ate-complex mixture rather than 4-tollyllithium (or methylolithium).

Since nearly all antimony compounds of stoichiometry Ph_4SbX whose structures have been determined contain 5-coordinate antimony, Ferguson and coworkers [111] examined the structures of three organoantimony(V) compounds, Ph_4SbBr , $\text{Ph}_4\text{SbClO}_4$, and Ph_4SbBF_4 , in a search for a tetrahedral Ph_4Sb^+ cation. An X-ray diffraction study of Ph_4SbBr revealed that the Sb atom was essentially trigonal bipyramidal. Although the Sb-C distances were essentially normal, the Sb-Br distance was considerably longer than in such compounds as SbBr_3 , $\text{Ph}_2\text{SbBrCl}_2$ and Ph_2SbBr_3 , and the $\text{C}_{\text{eq}}\text{-Sb-C}_{\text{ap}}$ angle was 95.8° rather than the expected 90° . These results, together with conductance data in acetonitrile solution, suggested that the structure of Ph_4SbBr was best represented as a hybrid between two canonical forms:



An attempt to determine the molecular structure of Ph_4SbBF_4 was consistent with total scrambling of the Sb and B atoms and gave no clear location for the phenyl carbon atoms. Tetraphenylstibonium perchlorate, however, was found to contain independent Ph_4Sb^+ cations and ClO_4^- anions. The salt was isomorphous with Ph_4EClO_4 (where E was As or Bi) and with $\text{Ph}_4\text{As}^+ \text{I}^-$. The Sb-C distance was 2.095\AA , considerably shorter than the Sb-C distance in organoantimony(V) compounds containing 5-coordinate antimony atoms, but longer than the $\text{Sb}=\text{C}$ distance found for two antimony ylides.

The thermal decomposition of pentaphenylantimony is known to occur at $160\text{-}200^\circ\text{C}$ to give quantitative yields of Ph_3Sb and biphenyl. Dodonov and coworkers [112] have now found that Ph_5Sb decomposed in toluene at room temperature in the presence of $\text{Cu}(\text{OAc})_2$. In addition to Ph_3Sb , formed in quantitative yield, both biphenyl and benzene were produced. Neither increasing the temperature nor increasing the amount of catalyst to one molar equivalent affected the course of the reaction. The reaction of Ph_5Sb with alcohols was also found to be quite different when $\text{Cu}(\text{OAc})_2$ was added. Whereas, in the absence of the catalyst, alkoxytetraphenylantimony compounds were formed which subsequently decomposed to yield Ph_3Sb , benzene, and the aldehyde corresponding to the alcohol used, in the presence of $\text{Cu}(\text{OAc})_2$, alkyl phenyl ethers were produced:



The yield of ether was dependent on the amount of catalyst used and the presence (or absence) of oxygen. Thus, BuOPh was formed in 92% yield when 2 molar equivalents of $\text{Cu}(\text{OAc})_2$ were used and the reaction was run in air at 80°C .

The cleavage of the C-As and C-Sb bond in pentaphenylarsenic and pentaphenylantimony by halogens and interhalogens (ICl and IBr) has been reported by Raizada and Nigam [113]. Thus, pentaphenylantimony with one molar equivalent of I₂ in MeCN solution, gave Ph₄SbI. With two molar equivalents, Ph₃SbI₂ was obtained, but with bromine only Ph₃SbBr₂ was found regardless of the molar ratio of bromine used. Iodine monochloride gave only Ph₃SbCl₂, but with IBr, either Ph₄SbBr or Ph₃SbBr₂ could be obtained by using one or two molar equivalents of IBr, respectively.

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