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## ANTIMONY

ANNUAL SURVEY COVERING THE YEAR 1978

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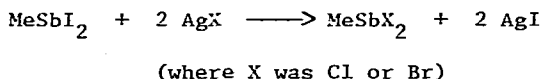
The preparation and reactions of organoantimony compounds have been thoroughly reviewed in a new volume of *Methoden der organischen Chemie (Houben-Weyl)* [1]. Levason and McAuliffe [2] have published an interesting account of their studies on the synthesis and complexation of tertiary stibines; and discussions of stibine complexes of the transition elements have also appeared in a recent book [3] and in a review article [4]. Heterocyclic derivatives of antimony have been mentioned in three reviews [5-7] published in 1978, while more general information about organoantimony chemistry has been included in an encyclopedia article on antimony compounds [8] and in two short surveys of recent work on organoarsenic, -antimony, and -bismuth compounds [9] and on the main-group elements of Group V [10].

A study has been made of the preparation of the primary alkylstibines  $RSbH_2$  (where R was Me, Et, or Bu) by the reduction of the corresponding alkyl-dichlorostibines with lithium aluminum hydride suspended in di-*n*-butyl ether [11]. It was also reported that methyl-, ethyl-, isopropyl-, and *n*-butylstibine could generally be obtained in satisfactory yields by the reduction of the alkyl-dihalostibine with sodium borohydride, but no details of this procedure were given. All of the alkylstibines proved to be thermally unstable, rapidly oxidizable, colorless liquids with strong alliaceous odors. Fortunately, these compounds were sufficiently volatile to be manipulated by standard vacuum-line techniques. The stability of the alkylstibines decreased with increasing alkyl chain length. Thus, a five mmol sample of ethylstibine completely decomposed at room temperature in one hour, while the decomposition of a 0.5 mmol sample of the *n*-butyl compound required

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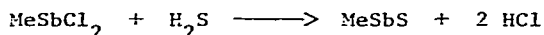
Antimony; Annual Survey covering the year 1977 see *J. Organometal. Chem.*, Vol. 163 (1978) p. 151-185.

only 15 minutes at 0°C. The decomposition products included hydrogen and non-volatile black solids analyzing for (RSb)<sub>x</sub>. The alkyl-dichlorostibines used for the preparation of the alkylstibines were obtained by the interaction of antimony trichloride and the corresponding tetraalkyllead compounds in refluxing benzene. Monoalkylation of the antimony occurred in high yield (> 80%), and no spectral evidence for any polyalkylation was found. Alkyldiiodostibines were obtained in about 20% yield via the reaction of alkylmagnesium iodides with antimony trichloride in ether. The trialkylstibines that were also formed in these reactions were removed by adding bromine to the reaction mixture and thus precipitating the tertiary stibines as trialkylantimony dibromides. Conversion of methyldiiodostibine to the corresponding bromine or chlorine compound was readily accomplished by metathesis:

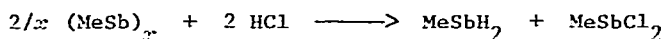


A considerable effort was made to prepare alkylstibonic acids, RSbO<sub>3</sub>H<sub>2</sub>, by the oxidation of alkyldihalostibines or by the interaction of an antimony(III) compound and an alkyl halide in an aqueous alkaline medium. No alkylstibonic acid, however, could be obtained in analytically acceptable form.

Methylstibine and disulfur dichloride have been found to react rapidly in benzene to produce methyldichlorostibine, hydrogen sulfide, and a lustrous, pale green solid, the analysis of which corresponded to (MeSb)<sub>x</sub> [12]. It was suggested that this solid was an analog of the ladder-structure polymer (MeAs)<sub>x</sub>. Like the arsenic compound, the solid was insoluble in all tested solvents, was indefinitely stable in air, and gave (on heating) a mass spectrum that corresponded to a pentameric composition. After standing for 500 days at 60°C, the solutions obtained by mixing methylstibine and disulfur dichloride exhibited a PMR singlet at δ = 0.835, which was tentatively attributed to thio-stibosobenzene formed by the following reaction:

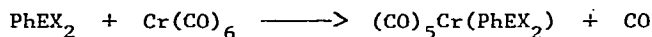


No evidence was obtained, however, for the presence of hydrogen chloride. It was suggested that this substance did form and was then consumed by reaction with the polymeric antimony compound:



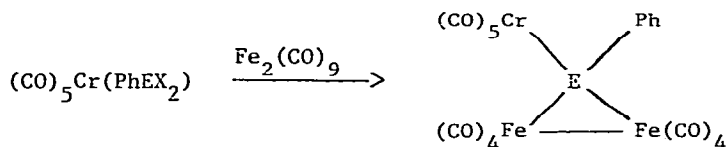
At the end of 500 days, the lustrous green solid had changed to a black solid believed to be a mixture of antimony, antimony trisulfide, and non-crystalline forms of  $(\text{MeSb})_x$ . A sharp PMR singlet at  $\delta = 1.70$  appeared in the reaction mixtures after about 30 days and was tentatively attributed to dimethyl sulfide formed from the methyl groups lost on C-Sb cleavage.

Phenyldichlorophosphine, phenyldichloroarsine, and phenyldiiodostibine have been converted to chromium carbonyl complexes by means of the following type of reaction [13]:



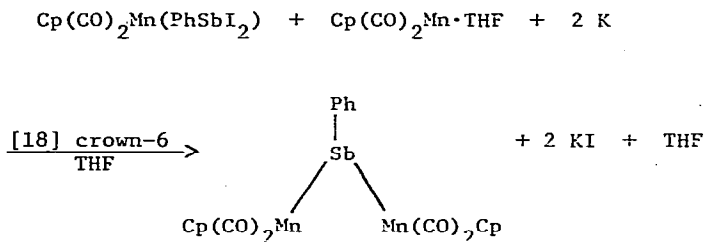
(where E was P or As, X was Cl; where E was Sb, X was I)

Treatment of these complexes with diiron enneacarbonyl yields cyclic derivatives:



Mass, IR, and NMR spectroscopy were used to help establish the structure of the three cyclic compounds; in addition, an X-ray crystallographic study of the phosphorus-containing compound clearly showed the presence of the three-membered ring.

The first compound containing a trigonal-planar antimony atom has been prepared by means of the following reaction [14]:

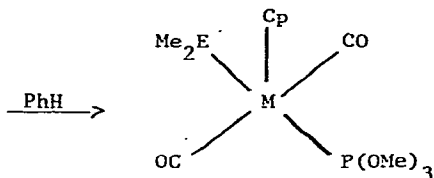
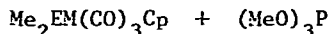


(where Cp was the cyclopentadienyl group)

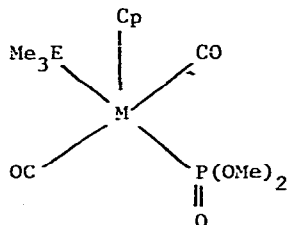
The trigonal-planar coordination of the antimony was confirmed by an X-ray structural analysis. Although the crystalline substance was relatively stable in air, its solutions in toluene, dichloromethane, or *n*-pentane were extremely air-sensitive. The mass spectrum of the substance was similar to that of its phosphorus and arsenic analogs.

It exhibited a molecular ion, which lost carbon monoxide to give  $\text{PhSb}(\text{MnCP})_2^+$ ; the smaller fragment  $\text{PhSbMnCP}^+$  was also observed. The IR spectrum showed a complex pattern of absorption bands that suggested the presence of rotamers.

Tricarbonyl complexes of the type  $\text{Me}_2\text{EM}(\text{CO})_3\text{Cp}$  (where E was As and M was Mo or W, and where E was Sb and M was W) have been found to undergo a substitution reaction at  $25^\circ\text{C}$  in which trimethyl phosphite replaces the carbonyl group *trans* to the  $\sigma$ -bonded  $\text{Me}_2\text{E}$  group [15]:

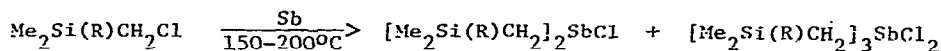


The resulting dicarbonyl complexes underwent a spontaneous isomerization in which a methyl group was transferred from the trimethyl phosphite ligand to the arsenic or antimony atom. This shift produced phosphonate complexes of the following type:



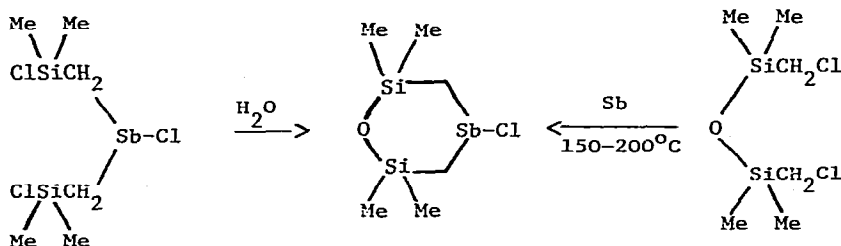
In a similar manner dimetallated antimony compounds of the type  $\text{MeSb}[\text{M}(\text{CO})_3\text{Cp}]_2$ , where M was Mo or W, were converted by double *trans*-carbonyl substitution into complexes which rapidly isomerized to yield substances containing both a trimethyl phosphite and a dimethyl phosphonate ligand.

Mixtures of chlorostibines and tertiary antimony dichlorides have been obtained by the interaction of chloromethylsilanes and antimony in the presence of a quaternary ammonium or phosphonium iodide [16]:



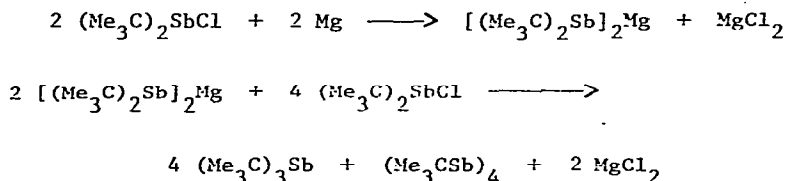
(where R was Me or Cl)

Hydrolysis of the chlorostibine in which R was Cl yielded a heterocyclic chlorostibine that could also be prepared by the direct reaction of antimony and a disiloxane:



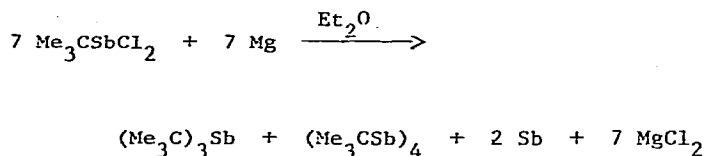
The structures of all the organoantimony compounds were established by elemental analysis and by PMR and mass spectroscopy.

The interaction of di-*tert*-butylchlorostibine and magnesium in tetrahydrofuran has been found to give a 38% yield of tri-*tert*-butylstibine and a 42.1% yield of tetra-*tert*-butylcyclotetrastibine,  $(\text{Me}_3\text{CSb})_4$  [17]. The formation of these products was explained by the following reaction sequence:



The tertiary stibine was isolated in pure form by distillation from the reaction mixture, while the cyclic compound was sublimed as a yellow crystalline substance from the residue remaining in the reaction flask. The PMR spectrum of the latter compound consisted of a singlet at  $\delta = 336$  Hz with respect to benzene as an internal standard. Its mass spectrum exhibited a molecular ion and peaks corresponding to  $(\text{Me}_3\text{C})_3\text{Sb}_4^+$ ,  $(\text{Me}_3\text{C})_2\text{Sb}_4\text{H}^+$ ,  $\text{Me}_3\text{CSb}_4^+$ ,  $\text{Sb}_4\text{H}^+$ ,  $\text{Sb}_4^+$ ,  $\text{Sb}_3^+$ , and  $\text{Me}_3\text{C}^+$ .

A mixture of tri-*tert*-butylstibine and tetra-*tert*-butylcyclotetrastibine has also been obtained by the interaction of *tert*-butyldichlorostibine and magnesium [18]. The following stoichiometry was suggested:

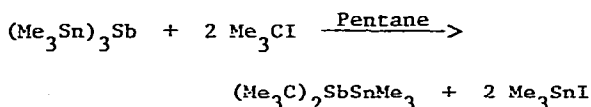


The dichlorostibine used in this reaction was prepared by the addition of *tert*-butylmagnesium chloride to antimony trichloride at  $-40^{\circ}\text{C}$ :



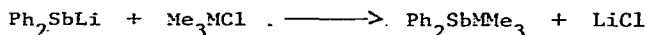
This compound was obtained in 32% yield as a colorless, crystalline, air-sensitive substance which melted at  $30^{\circ}\text{C}$  and could be purified by sublimation or distillation. It was studied by IR and PMR spectroscopy.

The reaction of tris(trimethylstannyl)stibine with *excess tert*-butyl iodide at room temperature has been found to result in the cleavage of two Sn-Sb bonds [19]:

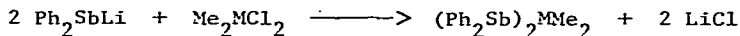


The antimony compound thus obtained was isolated by vacuum distillation as a colorless, spontaneously inflammable liquid. Strangely enough, the interaction of *equimolar* amounts of tris(trimethylstannyl)stibine and *tert*-butyl iodide yielded tetrakis(trimethylstannyl)distibine,  $(\text{Me}_3\text{Sn})_4\text{Sb}_2$ . The stoichiometry and mechanism of this unusual reaction were not established. The distibine was a red, air-sensitive solid, which was moderately soluble in hydrocarbon solvents and melted with decomposition at  $93^{\circ}\text{C}$ . IR, PMR, and mass spectroscopy were used to characterize both of the antimony compounds prepared in this investigation.

Lithium diphenylstibide, obtained via the cleavage of triphenylstibine with lithium in tetrahydrofuran, has been used to prepare seven organoantimony compounds by means of the following reactions [20]:



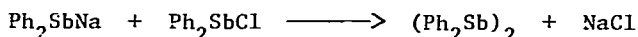
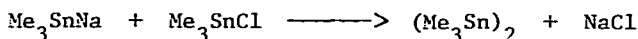
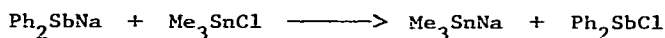
(where M was Si, Ge, or Sn)



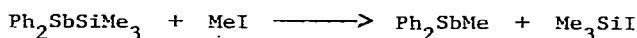
(where M was C, Si, Ge, or Sn)

All seven compounds in solution were stable for only a few minutes at room temperature and, accordingly, had to be handled quickly at low temperature. Nonetheless, they were characterized not only by elemental analysis but also by IR, PMR, and mass spectroscopy. Surprisingly, the

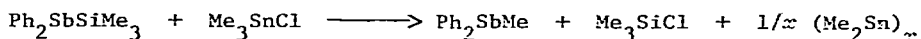
interaction of chlorotrimethylstannane and sodium diphenylstibide (prepared from triphenylstibine and sodium in liquid ammonia) gave very little of the expected diphenyl(trimethylstannyl)stibine but yielded mainly hexamethyldistannane and tetraphenyldistibine. Formation of these substances was tentatively explained by the following sequence of reactions:



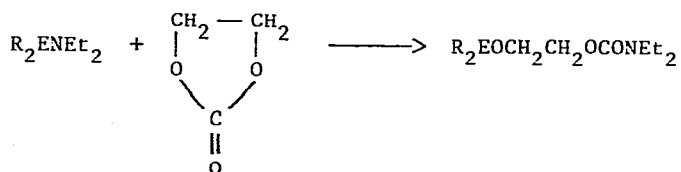
Two reactions of diphenyl(trimethylsilyl)stibine were also briefly studied. The interaction of this stibine and methyl iodide proceeded at room temperature in the following manner:



Diphenyl(trimethylsilyl)stibine did not react with chlorotrimethylstannane at room temperature but at 60°C gave diphenylmethylstibine and probably chlorotrimethylsilane. The polystannane expected on the basis of the following equation, however, could not be isolated:



A study has been made of the reaction of ethylene carbonate with *N,N*-diethylaminodialkylarsines and -stibines [21]:

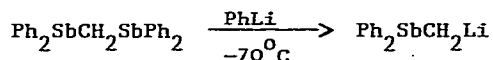


(where E was As or Sb)

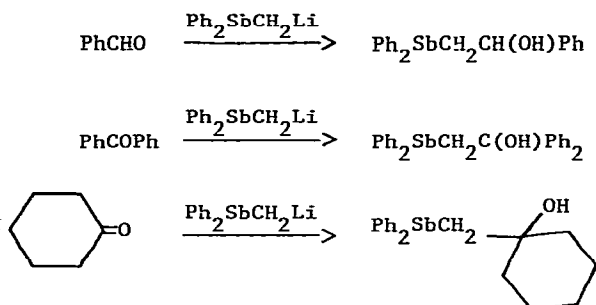
The rate of reaction of the aminoarsines (where R was C<sub>1</sub>-C<sub>4</sub> alkyl, PhCH<sub>2</sub>, or cyclohexyl) varied with R in the following order: secondary > primary > Me. Taft plots for the two types of aminoarsines (*i.e.* those with primary or secondary R groups) gave positive ρ<sup>\*</sup> values. These results were believed to be consistent with a four-center mechanism.

No substituent effect was observed in the case of the aminostibines, and it was concluded that the hyperconjugation effect of the substituent on the electron density of the Group V element decreased with an increase in the atomic size of that element.

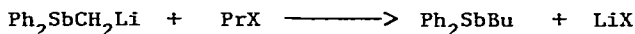
Diphenylstibinomethylithium has been prepared by the interaction of methylenebis(diphenylstibine) and phenyllithium in tetrahydrofuran [22]:



Reaction of this substance with aldehydes or ketones gave modest yields of the expected alcohols [23]:

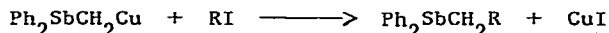
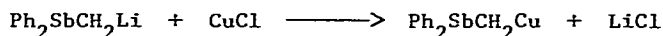


Diphenylstibinomethylithium also coupled with alkyl halides, but the yields were very low:



(where X was Br or I)

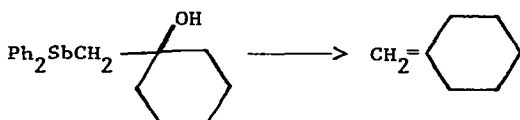
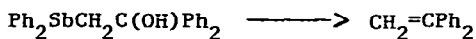
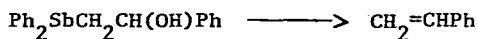
Much better yields of coupling products were obtained by first converting the diphenylstibinomethylithium to an organocopper compound and then allowing the latter substance to react with the alkyl halide:



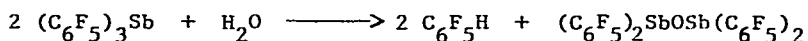
(where R was Pr, Hex, or Oct)

Heating the alcohols mentioned above or treating them at room temperature with two equivalents of perchloric acid in methanol resulted in the formation of olefins [24]:

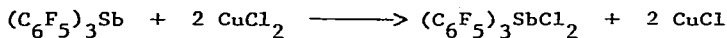
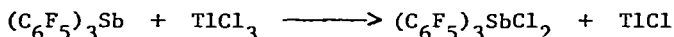




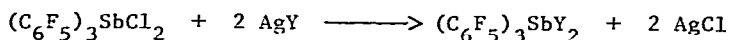
A study of the chemical behavior of tris(pentafluorophenyl)stibine has been reported [25]. Addition of water to a petroleum ether solution of the stibine caused cleavage of one of the C-Sb bonds and formation of a bis(diarylantimony) oxide:



Oxidative chlorination of the stibine was accomplished not only by chlorine but also by thallium(III) chloride or copper(II) chloride:

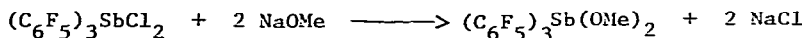


Bromine similarly converted the stibine to a dibromide, but it was necessary to cool the reaction mixture. Above room temperature the dibromide decomposed slowly to regenerate the free halogen. No reaction between the stibine and iodine was observed. Treatment of tris(pentafluorophenyl)antimony dichloride with silver nitrate or silver perchlorate resulted in the following metathetical reactions:



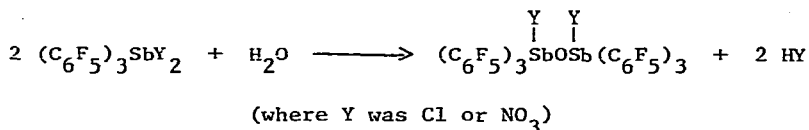
(where Y was  $\text{NO}_3$  or  $\text{ClO}_4$ )

Although the dichloride was unaffected by methanol or ethanol, it reacted with sodium methoxide to yield a dialkoxide:

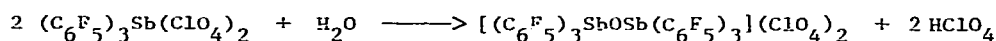


When sodium salts of the bidentate ligands acetylacetonate or oxine were used, the hexacoordinate complexes  $(\text{C}_6\text{F}_5)_3\text{SbCl}(\text{Acac})$  and

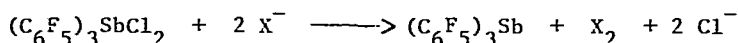
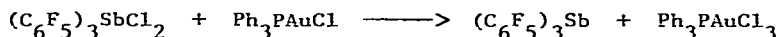
$(C_6F_5)_3SbCl(Ox)$  were obtained (where HACac was acetylacetonate and Ox was the 8-quinolinolate group). Addition of water to solutions of tris(pentafluorophenyl)antimony dichloride or dinitrate resulted in the formation of pentavalent oxybis(triarylantimony) derivatives:



When the diperchlorate was used, hydrolysis gave a binuclear cationic compound containing tetracoordinate antimony:



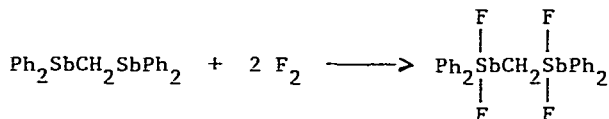
Tris(pentafluorophenyl)antimony dichloride proved to be an oxidizing agent. Thus, it converted gold(I) to gold(III), and bromide or iodide ion to the free halogen:



(where X was Br or I)

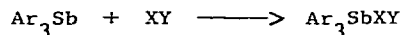
Attempts to isolate transition metal complexes of tri(pentafluorophenyl)-stibine were unsuccessful. Thus, it did not react with anhydrous nickel(II) halides in ethanol or with Ni(I) formed by the sodium borohydride reduction of an ethanol solution of nickel(II) chloride. Similarly, mixing the stibine and silver perchlorate in benzene gave only unchanged starting material.

Fluorine diluted with argon has been shown to be a useful reagent for the oxidative fluorination of tertiary arsines, stibines, and bismuthines [26]. The reactions were carried out in trichlorofluoromethane at low temperatures, and the yields of fluorinated products were very good. Thus, triphenylstibine and methyldiphenylstibine were converted to the corresponding difluorides in yields of 88% and 74%, respectively, while methylenebis(diphenylstibine) gave a tetrafluoride in 91% yield:



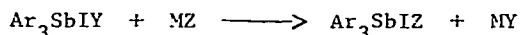
The compounds synthesized were studied by  $^{19}\text{F}$  and  $^{13}\text{C}$  NMR spectroscopy.

The oxidation of triarylstibines by iodine halides, cyanogen halides, or thiocyanogen has been found to give good yields of addition products [27]:



(where Ar was Ph or 4-MeC<sub>6</sub>H<sub>4</sub> and XY was ICl, IBr, ICN, BrCN, or (SCN)<sub>2</sub>)

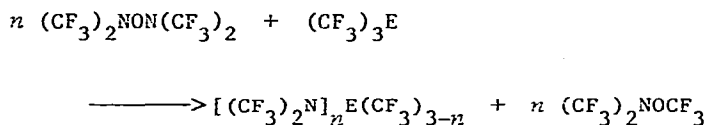
The mixed dihalides obtained in this manner underwent metathetical reactions in which the chloride or bromide was selectively replaced:



(where Y was Cl or Br and MZ was KNCO, AgNCO, or KNCS)

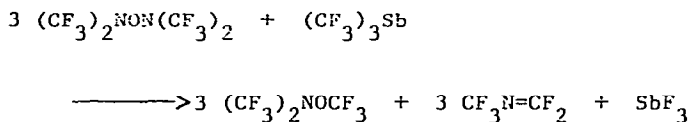
The IR spectra of the antimony compounds containing a pseudohalide group suggested that the nitrogen was directly bonded to the metal in these substances.

Compounds containing P-N or As-N bonds have been prepared by means of the following type of reaction [28]:



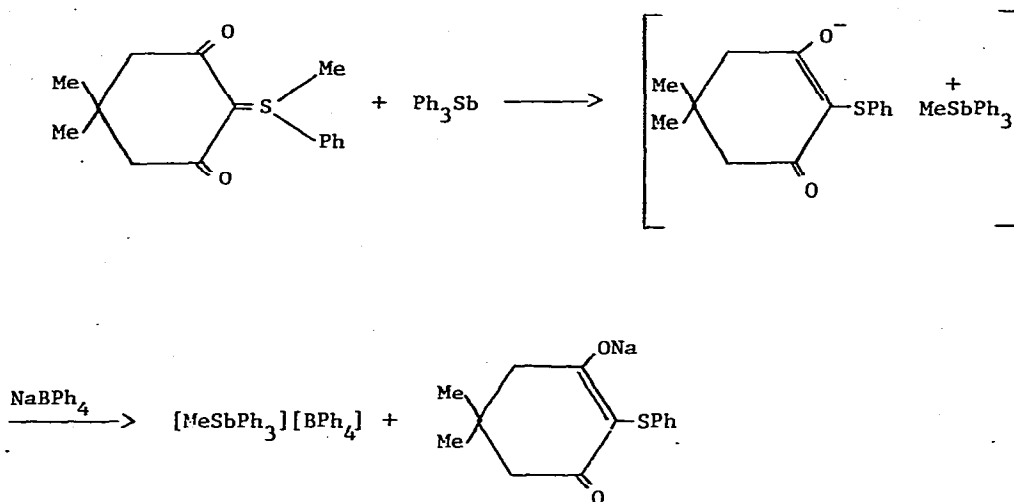
(where E was P,  $n$  was 1, 2, or 3; where E was As,  $n$  was 1 or 2)

In contrast to these results, the reaction with tris(trifluoromethyl)-stibine yielded no compounds containing Sb-N bonds:

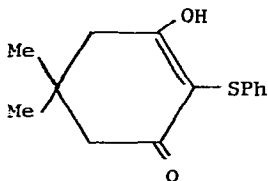


Two possible mechanisms for the above reaction were suggested.

Heating triphenylstibine and a carbonyl-stabilized sulfonium ylid in the presence of sodium tetraphenylborate has been found to result in removal of a methyl group from the sulfur atom [29]. The following reaction pathway was suggested:



The postulated stibonium tetraphenylborate was not isolated in pure form, but acidification of the reaction mixture did give a small yield of 2-phenylthiodimedone:



Trimethylstibine and triethylstibine have been included in a study of the thermal decomposition of alkyl derivatives of indium or antimony at 250–500°C [30]. In every case the reaction yielded the free metal and various gaseous products. It was concluded that the decompositions occurred via free-radical mechanisms.

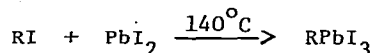
Schemes for purifying trialkylstibines have been described in an article on design principles for efficient systems useful for the complete purification of chlorides, hydrides, and alkyl derivatives of a number of main-group elements [31].

The photoinitiated polymerization of various vinyl monomers has been shown to be promoted by triphenylstibine, trimethylantimony dibromide, triphenylantimony dichloride, or pentaphenylantimony [32]. Solutions of each of these organoantimony compounds in methacrylic acid or methyl methacrylate exhibited a characteristic new peak in the 288–293 nm region of the ultraviolet spectrum. This peak was tentatively attributed to some

kind of interaction between the carbonyl oxygen and the antimony atom. The relative effectiveness of the organoantimony compounds as promoters of the polymerization reactions varied with the particular monomer employed. It was concluded that the mechanism by which the antimony compounds promoted these polymerizations was not identical for all four substances.

A study has been reported of the poisoning effect of triphenylamine, -phosphine, -arsine, -stibine, and -bismuthine on the hydrogenation of isoprene with palladium on carbon [33]. The magnitude of the effect increased in the order  $\text{Ph}_3\text{N} \ll \text{Ph}_3\text{P} < \text{Ph}_3\text{As} < \text{Ph}_3\text{Sb} < \text{Ph}_3\text{Bi}$ . It was concluded that these poisons not only had a blocking effect on the active site of the catalyst but in some cases also changed the nature of the active site. When the poisoned catalysts were recovered from the reaction mixtures and reused after adequate washing, they showed almost the same reactivity as the nonpoisoned catalyst.

Trimethylstibine has been found to be an effective catalyst for the preparation of alkyllead triiodides by the following type of reaction [34]:



(where R was Et, Pr,  $\text{Me}_2\text{CH}$ , Bu, or  $\text{Me}_3\text{C}$ )

No mechanism for this reaction was suggested, but it was noted that trialkylstibines were good catalysts for the analogous reaction between a tin(II) halide and an alkyl halide.

Electronic emission spectroscopy has been used in an investigation of the complexes formed between oxygen and various organic derivatives of Group IV and Group V elements [35]. Included in this study were triphenylamine, -phosphine, -arsine, -stibine, and -bismuthine. All of these compounds were found to form reversible complexes with oxygen in *n*-hexane at 77 K. Maximum complexing occurred with the amine, while the complex-forming ability of the other four compounds increased with the atomic number of the heteroatom. It was concluded that the  $\pi$ -donor properties of the compounds were predominant in determining the nature of the complexing.

X-ray diffraction has been employed to determine the crystal and molecular structure of diphenyl(2,6-dimethylphenylthio)stibine,  $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{SSbPh}_2$  [36]. The C-Sb bond lengths (2.14 and 2.15 Å) and the valence angles at the antimony atom ( $97.3^\circ$ ,  $93.4^\circ$ , and  $94.1^\circ$ ) were in close agreement with comparable values previously reported for oxybis-(diphenylantimony),  $(\text{Ph}_2\text{Sb})_2\text{O}$ . The dihedral angle between the plane of the thiophenol ring and the plane defined by the Sb-S-C linkage was  $73.2^\circ$ ,

an arrangement that placed the antimony atom at a distance of only 3.73 Å from one of the methyl groups. Calculation of the orientation of this methyl group by the atom-atom potential method led to the conclusion that the van der Waals radius of antimony was 1.8-1.9 Å.

The microwave spectra of normal and  $\beta,\beta$ -dideutero  $^{121}\text{Sb}$ -stibabenzene and  $^{123}\text{Sb}$ -stibabenzene have been determined in the 26.5-40.0 GHz region, and the data thus obtained have been employed to deduce structural information about these substances [37]. The results strongly supported a planar  $C_{2v}$  structure in which the C-Sb bond was shorter than expected for a single bond and the C-C bond lengths were close to those in benzene and its derivatives. The C-Sb-C angle was  $93^\circ$ , the smallest intervalency angle observed so far for the Group V heterobenzene series; the other bond angles within the stibabenzene ring were all greater than  $120^\circ$ . Nuclear quadrupole coupling constants for the two antimony isotopes were also calculated from the spectral data and were then used to estimate relative Sb  $5p$  populations along the three principal inertial axes. It was concluded that the antimony atom in stibabenzene was a  $\sigma$  donor, but it was not clear whether the heteroatom was a  $\pi$  donor or  $\pi$  acceptor overall.

Studies have been reported of the gas-phase IR and liquid-phase Raman spectra of (trifluoromethyl)dimethylstibine [38], bis(trifluoromethyl)methylstibine [39], and their arsenic and phosphorus analogs. The assignment of the observed absorption bands in the spectra of the (trifluoromethyl)dimethyl derivatives was based on  $C_s$  local symmetry and was aided by a normal coordinate analysis. The absorption bands in the bis(trifluoromethyl)methyl derivatives were assigned by analogy to the results previously reported for compounds of the types  $\text{Me}_3\text{E}$  (where E was P, As, or Sb) and  $\text{Me}_2\text{AsX}$  (where X was Cl or Br) as well as by a normal coordinate analysis.

A detailed analysis has been made of the IR and Raman spectra of triethylarsine and triethylstibine in both the liquid and solid states [40]. The observed complexity of the spectra in the region containing the C-As and C-Sb stretching bands was apparently due to rotational "isomerism" resulting from restricted rotation about the carbon-heteroatom bonds. It was concluded that crystalline triethylarsine contained only one conformer and that in this conformer the arrangement of the methyl groups relative to the unshared pair of electrons was either *trans, trans, trans* or *gauche, gauche, gauche*. Liquid triethylarsine consisted principally of this same conformer plus a second conformer. Two conformers were present in both liquid and solid triethylstibine, but no definite conclusions regarding their structure were reached.

The spin-lattice relaxation times ( $T_1$ ) have been determined for the carbon atoms in triphenylphosphine, -arsine, and -stibine [41]. All of

the ortho, meta, and para carbons were found to relax exclusively by the dipole-dipole mechanism. The  $\alpha$  carbons (*i.e.* those linked directly to the heteroatom) in the phosphine and arsine relaxed predominantly by the dipole-dipole mechanism below about 40°C, but the spin-rotation mechanism was most important above this temperature. The  $\alpha$  carbons in the stibine showed non-exponential decay, since the carbons bound to  $^{121}\text{Sb}$  relaxed by the scalar-coupling mechanism at all temperatures while the carbons bound to  $^{123}\text{Sb}$  relaxed by the dipole-dipole mechanism at low temperatures and spin-rotation at higher temperatures. The  $^{121}\text{Sb}$ - $^{13}\text{C}$  coupling constant was calculated to be 450 Hz.

Triethylstibine has been included in an investigation of a semi-empirical quantitative theory on retention volume in gas chromatography [42]. The other compounds employed in this study were ethyl derivatives of group III, IV, V, VI, and VII. For each group, the observed retention volumes were plotted as a function of the normal boiling points of the substances.

Structural information about a variety of heterotriptycenes have been calculated with the aid of a simplified force field model [43]. The calculated values were in excellent agreement with the available X-ray data. Included in this study were heterotriptycenes in which the bridgehead atoms were P and Sb, C and Sb, N and Sb, or Sb and Sb.

The effect of complex formation on the  $^{19}\text{F}$  NMR spectrum of the ligand has been studied in metal carbonyls of the types  $\text{LCr}(\text{CO})_5$ ,  $\text{LMo}(\text{CO})_5$ ,  $\text{LW}(\text{CO})_5$ ,  $\text{LMn}(\text{CO})_4\text{Br}$ , and  $\text{LFe}(\text{CO})_4$ , where L was the meta or para isomer of tris(fluorophenyl)phosphine, -arsine, or stibine [44]. It was concluded among other things that there was a significant amount of  $d_{\pi} - d_{\pi}$  interaction between the phosphorus, arsenic, or antimony ligand and the metal carbonyl moiety.

In addition to two papers [15,44] already discussed, there have been numerous 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 [45], cobalt [46], iron [47-49], manganese [50,51], molybdenum [52-55], nickel [56,57], palladium [56,58,59], platinum [56,58-60], rhenium [50], rhodium [61-63], ruthenium [64,65], silver [66], tungsten [52,53,55], and vanadium [67]. Tetramethyldistibine and tetraethyldistibine have been found to react with photochemically generated solutions of pentacarbonyl(tetrahydrofuran)-chromium and -tungsten to yield binuclear complexes of the type  $(\text{CO})_5\text{MSbR}_2\text{SbR}_2\text{M}(\text{CO})_5$ , where M was Cr or W and R was Me or Et [45]. The carbonyl complexes thus prepared were characterized by IR, PMR, and mass spectra.

Molecules of the type  $\text{R}_n\text{SbCl}_{4-n}\text{Acac}$ , where HACac was acetylacetone

and R was alkyl or aryl, have been the subject of a number of chemical investigations in recent years. Such molecules as  $\text{RSbCl}_3\text{Acac}$  can exist in two different forms based on octahedral geometry for the Sb atom. In one form two chlorine atoms are *trans*, in the other form a chlorine and the R group are *trans*. Molecules of the type  $\text{R}_2\text{SbCl}_2\text{Acac}$  can obviously exist in three forms, namely, two chlorine atoms *trans*, two R groups *trans*, or one R groups *trans* to one chlorine atom. Spectroscopic studies of compounds of these two types have not clearly distinguished between the various structures. Accordingly, Kanehisa and coworkers [68] have determined the crystal structures of the three compounds  $\text{MeSbCl}_3\text{Acac}$ ,  $\text{Me}_2\text{SbBr}_2\text{Acac}$ , and  $\text{Ph}_2\text{SbCl}_2\text{Acac}$  by means of X-ray diffraction. The bromide  $\text{Me}_2\text{SbBr}_2\text{Acac}$  was used rather than that chloride since the latter was unstable in the solid state.  $\text{Ph}_2\text{SbCl}_2\text{Acac}$  gave two types of crystals (when recrystallized from benzene) with melting points of  $184.5^\circ\text{C}$  and  $192^\circ\text{C}$ . The crystal structure of the lower melting form had been previously determined by other workers. This earlier work was confirmed by the present authors.

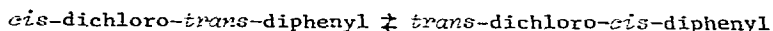
The X-ray diffraction study showed that the compound  $\text{MeSbCl}_3\text{Acac}$  possessed a structure in which the methyl, one chlorine, and the Acac ring were all in the basal plane of the octahedron with two chlorines in *trans* position. In both  $\text{Me}_2\text{SbBr}_2\text{Acac}$  and  $\text{Ph}_2\text{SbCl}_2\text{Acac}$ , the two alkyl or aryl groups were in *trans* position. All three compounds possessed slightly distorted octahedral geometry. A comparison of the crystal structure of the low-melting and the high-melting forms of  $\text{Ph}_2\text{SbCl}_2\text{Acac}$  showed that the former had looser packing and a smaller number of short inter-atomic contacts, which the authors suggested could possibly contribute to the difference in melting points. From the X-ray data it was determined that in the higher melting form one phenyl ring was approximately perpendicular ( $89^\circ$ ) to the bisector of the Cl-Sb-Cl angle whereas the other phenyl ring was approximately parallel. The dihedral angle between the two rings was  $92^\circ$ . However, in the lower melting form the phenyl rings made angles of about  $65^\circ$  or  $77^\circ$  to the Cl-Sb-Cl bisector, and the dihedral angle between the two rings was  $38^\circ$ . These differences in the conformations of the phenyl rings were the main structural differences between the two forms.

Meinema and Noltes [69] have reported the synthesis of a series of hexavalent heterocyclic antimony compounds of the type  $\text{R}_2\text{SbCl}_2\text{X}$ , where  $\text{R}_2$  was  $(\text{CH}_2)_4$ ,  $(\text{CH}_2)_5$ ,  $o,o'$ - $\text{C}_6\text{H}_4\text{C}_6\text{H}_4$ , or  $o,o'$ - $\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4$ , and HX was acetylacetonate (HAcac) or dipivaloylmethane (HDpm). The compounds were easily prepared by the reaction of the corresponding trichloro compound  $\text{R}_2\text{SbCl}_3$  with either HAcac or HDpm. They were characterized by elemental analyses and PMR spectra; molecular weight data and melting points were



also reported. Three structures for the octahedral hexavalent antimony compounds were considered. The first of these, where the heterocyclic C-Sb-C ring was *trans*, was excluded by the constraints of the five or six-membered ring. The asymmetric structure where all of the ligands were *cis* was excluded by the PMR data so that the remaining structure, where both rings were *cis* and the two chlorines *trans*, was considered to be correct. Dipole moment studies were in agreement with this structure. The availability of these new compounds in which the heterocyclic ring was forced into a *cis* position allowed a study of the influence of stereochemistry on the strength of the metal-ligand interactions in this type of  $d^{10}$  metal complex.

It has been known from previous work that dichloro- $\beta$ -diketonatodiphenylantimony compounds ( $\text{Ph}_2\text{SbCl}_2\text{X}$ , where X is a bridging diketone) exist in solution in two isomeric forms, namely, a *cis*-dichloro-*trans*-diphenyl and a *trans*-dichloro-*cis*-diphenyl form. By means of PMR it has been demonstrated that the *cis*-dichloro-*trans*-diphenyl isomer  $\text{Ph}_2\text{SbCl}_2\text{X}$  (where X = Acac) undergoes fast ligand exchange with HDpm, whereas the *trans*-dichloro-*cis*-diphenyl isomer either does not exchange or does so at a very slow rate. There is also a slow isomerization:



The authors made use of their new compounds, in which the heterocyclic ring is *cis* and the two chlorines *trans*, to study ligand exchange. In accordance with previous results with the diphenyl compounds, it was found that compounds of the type  $(\text{CH}_2)_n\text{SbCl}_2\text{X}$ , where  $n = 4$  or  $5$  and X = Acac or Dpm, underwent only very slow exchange reactions with the other diketone, *i.e.* HDpm or HACac. By contrast the authors found that  $\text{R}_2\text{SbCl}_2\text{X}$  (where R = Me or Et and again X = Acac or Dpm and in which the Me or Et groups were known to be in *trans*-position) underwent instantaneous ligand interchange with the free  $\beta$ -diketones.

The authors also reported that both the PMR chemical shift data and IR spectroscopic data point to the occurrence of a stronger antimony- $\beta$ -diketone interaction in the *trans*-dichloro- $\beta$ -diketonato-*cis*-diorganoantimony compounds than in the *cis*-dichloro- $\beta$ -diketonato-*trans*-diorganoantimony compounds. This conclusion was discussed in considerable detail in terms of the hybridization of the antimony valence orbitals.

The mechanism for  $\beta$ -diketone ligand exchange was considered to involve metal-oxygen bond cleavage as the rate-controlling step. The observation that the  $\beta$ -diketone was more strongly bonded in the *trans*-dichloro-*cis*-diorganoantimony compounds than in the *cis*-dichloro-*trans*-diorganoantimony compounds was in accord with these results.

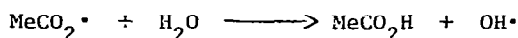
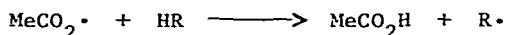
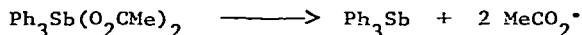
Ebina, Ouchi, and coworkers [70] have reported on the crystal structure of the complex formed by the reaction between a tri-*p*-tolylantimony(V) dihalide and the hydrated  $\beta$ -diketone  $\text{PhCOCH}_2\text{C}(\text{OH})_2\text{CF}_3$ . The molecule crystallized with one-half a mole of solvent (1,2-dichloroethane) when crystallized from dichloroethane and petroleum ether. The antimony compound was monomeric, and coordination around the antimony was that of a distorted octahedron. The three O atoms of the  $\beta$ -diketone hydrate and the three C atoms of the *p*-tolyl groups were bonded to the Sb atom in facial positions. Two of the oxygen atoms, those from the *gem*-diol, thus form an unusual four-membered chelate ring. The O-Sb-O angle in this ring was found to be  $66.3^\circ$ . The Sb-O distance for the third oxygen (from the keto group) was found to be unusually long (2.568 Å), a fact which suggested that the carbonyl oxygen possessed only weak coordinating ability. The three C-Sb distances for the three *p*-tolyl groups were equivalent to within experimental error. Owing to repulsions between the bulky *p*-tolyl groups, the three C-Sb-C angles were slightly greater than  $100^\circ$ .

In continuation of previous work on fluorinated  $\beta$ -diketones coordinated to triarylantimony(V), Ebina and coworkers [71] have reported on the crystal structure of the compound  $\mu$ -oxo-bis[tris(*p*-chlorophenyl)-(1,1,1-trifluoro-2,4-pentanedionato-*O,O'*)antimony(V)]-chloroform(1/2). The complex consisted of two tris(*p*-chlorophenyl)-(1,1,1-trifluoro-2,4-pentanedionato)antimony(V) units joined by an oxygen bridge. The Sb-O-Sb linkage was linear, and the authors believed that this was the first example of a linear Sb-O-Sb linkage. The geometry around each Sb atom was that of a distorted octahedron. The bridging oxygen and one of the oxygens of the  $\beta$ -diketone were in *trans*-position. The  $\beta$ -diketone was coordinated to the Sb in an enolate form. The  $\beta$ -diketone skeleton was slightly twisted from a planar form. Bond lengths, bond angles, and estimated standard deviations were reported.

An interesting series of compounds has been prepared by the reaction of triarylantimony dibromides with *gem*-diols [72]. The compounds were of the type  $\text{Ar}_3\text{Sb}(\text{O})\text{OCRR}'$ , where Ar was Ph, *p*- $\text{MeC}_6\text{H}_4$ , or *p*- $\text{ClC}_6\text{H}_4$  and where  $\text{R} = \text{R}' = \text{CF}_3$ ,  $\text{R} = \text{CF}_3$ ,  $\text{R}' = \text{H}$ , and  $\text{R} = \text{CCl}_3$ ,  $\text{R}' = \text{H}$ . The products were all monomolecular in benzene and were soluble in organic solvents but insoluble in water. They were stable at room temperature. From spectral data (IR and PMR) the authors concluded that the compounds existed as trigonal bipyramids with the two oxygen atoms bridging equatorial-axial positions. The absence of two types of aryl signals in the PMR spectra was attributed to Berry pseudorotation.

A thermogravimetric and differential thermal analysis study of a number of organoantimony(V) compounds of the type  $\text{R}_3\text{SbL}_2$ , where R = Ph or Me and L = Br, Cl, F,  $\text{MeCO}_2$ ,  $\text{PhO}$ , *p*- $\text{MeC}_6\text{H}_4\text{O}$ , *p*- $\text{MeC}_6\text{H}_4\text{CO}_2$ , or  $\text{CCl}_3\text{CH}(\text{O})\text{O}$ ,

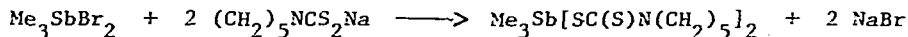
has been reported by Ouchi and coworkers [73]. Products of thermal decomposition were studied by PMR and IR. It was concluded that triphenylantimony diacetate decomposed into  $\text{Ph}_3\text{Sb}$  and  $\text{MeCO}_2\text{H}$  by a radical-type mechanism as follows:



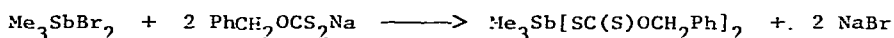
(where HR = starting compound)

The thermogravimetric and differential thermal analysis curves for the other compounds were similar to those of the diacetate, a fact which suggested that all of the compounds decomposed by a similar mechanism.

Ouchi and coworkers [74] have reported on the synthesis of compounds of the type  $\text{Me}_3\text{SbL}_2$ , where HL was either a secondary amine-*N*-carbodithioic acid or an *O*-alkyl dithiocarbonic acid. The compounds were obtained by the reaction of  $\text{Me}_3\text{SbBr}_2$  and the sodium salt of the desired thio acid. For example  $\text{Me}_3\text{SbBr}_2$  was allowed to react with 2 molecular equivalents of sodium pyrrolidine-*N*-carbodithioate as follows:



In a similar type of reaction  $\text{Me}_3\text{SbBr}_2$  reacted with sodium *O*-benzyl dithiocarbonate:



The authors were unable to prepare similar compounds from  $\text{Ph}_3\text{SbBr}_2$  and the thio compounds. It was necessary to use exactly two equivalents of the thio compound for one equivalent of  $\text{Me}_3\text{SbBr}_2$ . Any excess of the thio compound above two equivalents led to reduction of the antimony with loss of an R groups and production of compounds of the type  $\text{R}_2\text{SbL}$ . Reduction of antimony by excess thio compound was also found with triarylantimony dibromides or dichlorides. Two compounds of the type  $\text{Me}_3\text{Sb}[\text{SC}(\text{S})\text{N}(\text{CH}_2)_n]_2$ , where  $n = 4$  or  $5$  (i.e.,  $\text{HN}(\text{CH}_2)_n =$  pyrrolidine or piperidine), and four compounds of the type  $\text{Me}_3\text{Sb}[\text{SC}(\text{S})\text{OR}]_2$ , where  $\text{R} = \text{Pr}$ ,  $\text{Me}_2\text{CH}$ ,  $\text{Me}_2\text{CHCH}_2$ , and  $\text{PhCH}_2$ , were reported. They were characterized by elemental analysis, PMR and IR spectroscopy.

Very little information as to the structure of the Sb(V) compounds prepared could be deduced from the IR spectra. In the PMR spectra the methyl protons of the methyl groups attached the antimony occurred as sharp

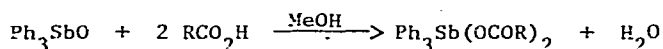
singlets with no indication of any broadening as low as  $-60^{\circ}\text{C}$ . From these results the authors concluded that the compounds probably occurred as trigonal bipyramids with three equatorial methyl groups and two axial unidentate dithiocarboxy ligands. There was, of course, the possibility of Berry pseudorotation occurring at a rate too rapid to be detected by PMR.

In an attempt to prepare  $\text{Ph}_3\text{Sb}(\text{SR})_2$ , where  $\text{R} = \text{Pr}$  or  $\text{Bu}$ , Chatterjee [75] allowed  $\text{Ph}_3\text{SbCl}_2$  to react with  $\text{RSH}$  under anhydrous conditions in the presence of  $\text{NH}_3$ . Not unexpectedly,  $\text{Ph}_3\text{Sb}$  was obtained.

The preparation of trimethylantimony(V) bis(*N,N*-dimethyldithiocarbamate),  $\text{Me}_3\text{Sb}(\text{S}_2\text{CNMe}_2)_2$ , from  $\text{Me}_3\text{Sb}$  and  $\text{Me}_2\text{NC}(\text{S})\text{S}_2\text{C}(\text{S})\text{NMe}_2$  (tetramethylthiuram disulfide) has been described by Cras and Willems [76]. An X-ray diffraction study of the crystalline product revealed that it was a slightly distorted trigonal bipyramid. Both  $^{121}\text{Sb}$  Mössbauer and PMR spectra for the compound were reported.

A number of organoantimony compounds have been prepared by Gopinathan and Gopinathan [77] by the reaction between such antimony compounds as  $\text{SbCl}_3$ ,  $\text{SbCl}_5$ , or  $\text{Ph}_3\text{SbBr}_2$  and a variety of chelating oxygen and nitrogen compounds such as 8-hydroxyquinoline, salicylaldehyde, *N*-benzoyl-*N*-phenylhydroxylamine, dehydroacetic acid, or acetoacetanilide. The compounds obtained from  $\text{Ph}_3\text{SbBr}_2$  were all of the type  $\text{Ph}_3\text{SbL}_2$ , where L was the chelating ligand. All of the compounds were non-electrolytes in nitrobenzene, and those compounds which were soluble in benzene gave ebullioscopic molecular weights which indicated that the compounds were monomeric. IR, PMR, and UV spectroscopic data were given for only a few of the compounds, and these data were used in interpreting the strength of the chelation for several of the compounds reported.

A series of triphenylantimony dicarboxylates of the type  $\text{Ph}_3\text{Sb}(\text{OCOR})_2$  (where  $\text{R} = \text{H}$ ,  $\text{Me}$ ,  $\text{ClCH}_2$ ,  $\text{Cl}_3\text{C}$ ,  $\text{MeCH}_2$ ,  $\text{CH}_2 = \text{CH}$ ,  $\text{CH}_2 = \text{C}(\text{Me})$ ,  $\text{Ph}$ , *o*- $\text{ClC}_6\text{H}_4$ , or *p*- $\text{H}_2\text{NC}_6\text{H}_4$ ) were prepared by the following reaction [78]:



The PMR spectra as well as elemental analyses (Sb only) were reported for all of the compounds.

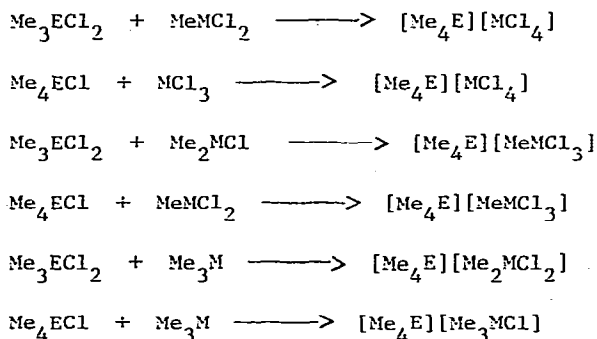
By means of X-ray diffraction Starikova and coworkers [79] have determined the structure of the peroxy compound  $[\text{Me}_3\text{COOSbPh}_3]_2\text{O}$ . The coordination polyhedron of the antimony was a somewhat distorted trigonal bipyramid with the three phenyl groups in equatorial positions. Values for the Sb-C and Sb-O distances were given.

The molecules  $\text{Me}_3\text{SbX}_2$ , where  $\text{X} = \text{F}$ ,  $\text{Cl}$ ,  $\text{Br}$ , or  $\text{I}$ , have been studied by IR and Raman spectra by a number of authors, and force constants have

been determined. In a theoretical paper by Namasivayam and Viswanathan [80] the method of Redington and Aljibury [81] has been used for calculating angle parameters and other molecular constants from experimentally determined vibrational fundamentals. Force constants, mean amplitudes of vibration, bond charge and path length parameters, and rotation distortion constants for all four  $\text{Me}_3\text{SbX}_2$  molecules have been calculated.

In an earlier paper Bowen and Long reported on the Mössbauer spectra of organoantimony(V) compounds of the type  $\text{Ph}_{5-n}\text{SbCl}_n$ , where  $n = 1-4$ . The present paper by these same authors [82] reports on the Mössbauer spectra of several arylstibonic acids  $\text{RSbO}_3\text{H}_2$ , one diarylstibinic acid  $\text{R}_2\text{SbO}_2\text{H}$ , and  $\text{Ph}_3\text{SbO}$ . The stibonic acids and the stibinic acid were amorphous, polymeric materials, but  $\text{Ph}_3\text{SbO}$  showed signs of crystallinity. For comparison, the Mössbauer spectrum of  $\text{Ph}_4\text{SbOH}$ , which is known to be a trigonal bipyramid with an apical OH group from X-ray diffraction studies, was also included. The Mössbauer spectra of  $\text{Ph}_3\text{SbO}$  closely resembled that of  $\text{Ph}_4\text{SbOH}$ , and the authors concluded that the oxide was a trigonal bipyramid with bridging Sb-O-Sb bonds in apical positions. There was a linear increase of  $\delta$ , the isomer shift, with increasing number of aryl groups in the series  $\text{Ph}_4\text{SbOH}$ ,  $\text{Ph}_3\text{SbO}$ ,  $\text{R}_2\text{SbO}_2\text{H}$ , and  $\text{RSbO}_3\text{H}_2$ . By the use of an additive model to obtain orbital populations along the Sb-ligand bonds for various assumed geometries (octahedral and trigonal-bipyramidal), it was concluded that the stibinic and stibonic acids were also probably trigonal-bipyramidal molecules with bridging Sb-O-Sb bonds in apical positions.

A number of tetramethyl arsonium and stibonium salts of methylgallium and -indium anions were prepared by Widler and coworkers [83]. The compounds were prepared by the following types of reaction:



(where E = As or Sb and M = Ga or In)

Elemental analyses were given for all of the compounds prepared. The IR, Raman, and PMR spectra were used to deduce the structure of the

gallium-and indium-containing anions. X-ray diffraction studies on two arsonium salts were also reported.

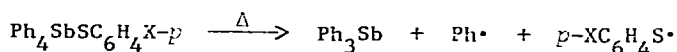
An X-ray diffraction study of the crystalline compound  $\text{Me}_4\text{SbOP(S)Me}_2$  has been reported by Schwarz and Hausen [84]. The antimony atom occurred as a distorted trigonal bipyramid, while the phosphorus atom was a distorted tetrahedron. Three of the methyl groups attached to the antimony were equatorial, and the equatorial-axial C-Sb-C angle was  $102.4^\circ$ . Bond lengths and other bond angles were also reported.

Although it is known that  $\text{Me}_4\text{SbF}$  is monomeric in solution and possesses five-coordinate antimony, it has also been shown that the Sb-F stretching mode in the IR spectrum is lowered from  $385\text{ cm}^{-1}$  to  $308\text{ cm}^{-1}$  when the spectrum was determined in the solid state as compared with the spectrum in solution or in the molten state. Accordingly, Schwarz and Guder [85] determined the structure of  $\text{Me}_4\text{SbF}$  in the solid state by X-ray diffraction. The compound consisted of polymeric chains with bridging fluorine atoms; the antimony atoms were six coordinate. In these chains the Sb-F-Sb angle was  $153.1^\circ$  and the F-Sb-F angle was  $99.8^\circ$ . Other angles as well as interatomic distances were given. In addition to  $\text{Me}_4\text{SbF}$ , the authors have also determined the structure of  $\text{Me}_3\text{SbF}_2$ . Here the antimony was a trigonal bipyramid with the three methyl groups in equatorial positions. The F-Sb-F angle was  $178.3^\circ$ , and the three C-Sb-C angles differed only slightly from  $120^\circ$ .

Previously reported studies on dimethylantimony trichloride have shown that it exists in two different forms. One form is ionic and has the structure  $[\text{Me}_4\text{Sb}][\text{SbCl}_6]$ ; the other form is covalent and in solution contains pentacoordinate antimony. In the solid state, however, the covalent form appears to be dimeric; each antimony atom is hexacoordinate and there are Sb-Cl-Sb bridges. This conclusion was based on Mössbauer and other spectral studies. Schwarz and Guder [86] have now reported on an X-ray diffraction study of the covalent and the ionic forms of dimethylantimony trichloride. The covalent form in the solid state did indeed consist of a dimer with a four-membered ring of alternating Sb and Cl atoms. The two Me groups were *trans* with a C-Sb-C angle of  $165.4^\circ$ . The Cl-Sb-Cl angle for the two non-bridging chlorine atoms was  $94.5^\circ$ , and the Sb-Cl-Sb angle in the four-membered ring was  $100.7^\circ$ - $100.8^\circ$ . The ionic form contained both tetrahedral and octahedral antimony atoms. The tetrahedron and octahedron were only slightly distorted from ideal geometry. Bond lengths and bond angles for both forms of the compound were reported.

Hausen and coworkers [87] have reported on the X-ray crystal structure of the compound  $[\text{Me}_4\text{Sb}][\text{GaCl}_4]$ . Both the Sb and the Ga atoms were tetrahedral with only slight deviations from ideal geometry.

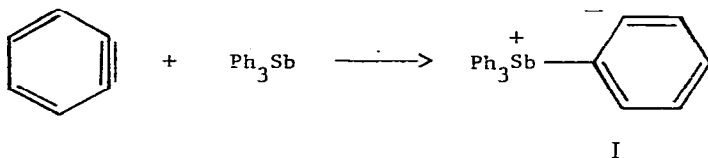
Wardell and Grant [88] have reported on the thermal decomposition of compounds of the type  $\text{Ph}_4\text{SbSC}_6\text{H}_4\text{X-p}$ , where  $\text{X} = \text{OMe}, \text{Me}, \text{or Br}$ . Decomposition of the compound  $\text{Ph}_4\text{SbSC}_6\text{H}_4\text{OMe-p}$  was studied in solution in the cavity of an ESR spectrometer and in the presence of the spin-trapping agent  $t\text{-BuN=O}$ . The detection of the nitroxide  $t\text{-Bu(Ph)NO}\cdot$  was taken as an indication of the formation of phenyl radicals during the decomposition. In all cases, decomposition of the compounds  $\text{Ph}_4\text{SbSC}_6\text{H}_4\text{X-p}$  proceeded more readily than decomposition of  $\text{Ph}_4\text{SbOPh}$ . The decomposition products included  $\text{PhH}, \text{Ph-Ph}, \text{Ph}_3\text{Sb}, p\text{-XC}_6\text{H}_4\text{SPh}$ , and  $(p\text{-XC}_6\text{H}_4\text{S})_2$ . The authors suggested that, unlike the decomposition of  $\text{Ar}_4\text{SbOH}$  compounds to  $\text{Ar}_3\text{SbO}$  and  $\text{ArH}$ , the decomposition of the mercaptides does not involve a radical chain mechanism but rather the reaction:



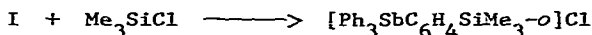
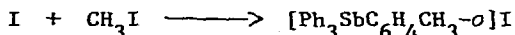
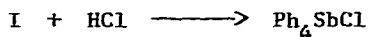
In a paper devoted to anionic complexes of tellurium of the type  $[\text{R}_4\text{E}]_2[\text{C}_4\text{H}_8\text{TeX}_2\text{X}'_2]$ , where  $\text{X}$  was a halogen,  $\text{X}'$  was a halogen,  $\text{NCO}, \text{NCS}$ , or  $\text{N}_3$ ,  $\text{C}_4\text{H}_8\text{Te}$  was telluracyclopentane, and  $\text{E}$  was  $\text{N}, \text{P}, \text{As}, \text{or Sb}$ , the compound  $[\text{Ph}_4\text{Sb}]_2[\text{C}_4\text{H}_8\text{TeI}_2\text{Cl}_2]$  was described [89].

IR and Raman spectroscopy has been used to study the electron-donating properties of organometallic groups in compounds of the type  $p\text{-O}_2\text{NC}_6\text{H}_4\text{SY}$  (where  $\text{Y}$  was  $\text{HgPh}, \text{SnPh}_3, \text{PbPh}_3, \text{SbPh}_2$ , or  $\text{SbPh}_4$ ) [90] and of the type  $p\text{-O}_2\text{NC}_6\text{H}_4\text{OY}$  (where  $\text{Y}$  was  $\text{HgPh}, \text{SnPh}_3, \text{PbPh}_3$ , or  $\text{SbPh}_4$ ) [91].

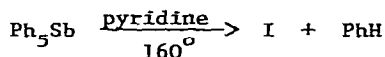
In a paper devoted largely to the decomposition of pentaphenylbismuth (see Bismuth section) in organic solvents, Razuvaev and co-workers [92] have reported on the compound formed from benzyne (from the decomposition of  $\text{Ph}_3\text{Bi}$ ) and triphenylstibine. They isolated an organic antimony compound which was believed to be the dipolar ion I formed in the following manner:



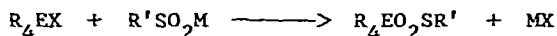
This substance dissolved in polar solvents and decomposed without melting above  $250^\circ\text{C}$ . It reacted with various compounds according to the following equations:



The dipolar ion was also formed from pentaphenylantimony by decomposition in pyridine at 160°:



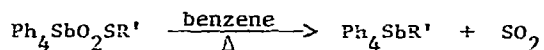
The syntheses of a large number of sulfinato complexes derived from the reaction of sodium or silver sulfinates with ammonium, phosphonium, arsonium, or stibonium halides have been described by Lorenz and Thekumparampil [93]. The preparation involved the following metathetical reactions:



(where E = N, P, As, or Sb, M = Na or Ag, R = Me or Ph, R' = Me, Ph, or *p*-MeC<sub>6</sub>H<sub>4</sub>, and X = Cl, Br, or I)

The resulting compounds varied greatly in their properties from the purely ionic ammonium compounds to the pentacoordinate antimony compounds. The organoantimony compounds prepared were Me<sub>4</sub>SbO<sub>2</sub>SR and Ph<sub>4</sub>SbO<sub>2</sub>SR, where R = Me, Ph, or *p*-MeC<sub>6</sub>H<sub>4</sub>. The mass spectra of the compounds were reported. The IR spectra were also given, and assignments of bands were made. It was concluded that all of the antimony compounds existed as trigonal bipyramids with an axial R'SO<sub>2</sub> group. However, even at low temperatures (-60°C), the Me<sub>4</sub>SbO<sub>2</sub>SMe showed only one methyl signal for the four methyl groups attached to the antimony.

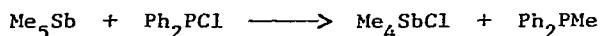
All of the compounds R<sub>4</sub>EO<sub>2</sub>SMe, where R = Me or Ph and E = N, P, As, or Sb, were oxidized in methanol solution in a stream of air to the corresponding sulfonates, R<sub>4</sub>EO<sub>3</sub>SMe. All of the sulfinato compounds, when heated in benzene or toluene, decomposed with the evolution of SO<sub>2</sub>, but only in the case of the antimony compounds Ph<sub>4</sub>SbO<sub>2</sub>SR', where R' = Me, Ph, or *p*-MeC<sub>6</sub>H<sub>4</sub>, was it possible to identify the products:



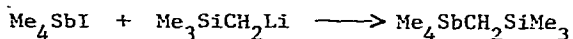
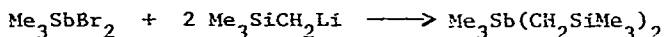
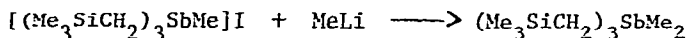
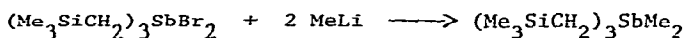
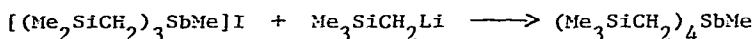
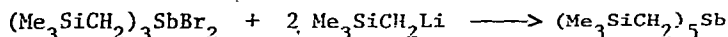
Pentamethylantimony has been found to react with diphenylphosphinic



acid and both phenyl- and methylphosphonic acids to form the compounds  $\text{Me}_4\text{SbOP(O)Ph}_2$ ,  $\text{Me}_4\text{SbOP(O)(OH)Ph}$ , and  $\text{Me}_4\text{SbOP(O)(OH)Me}$ , respectively [94]. The two compounds derived from methyl- and phenylphosphonic acids were found to be associated in chloroform solution with the value of  $x = 2.1-2.5$  for the compounds  $[\text{Me}_4\text{SbOP(O)(OH)R}]_x$  ( $R = \text{Me}$  or  $\text{Ph}$ ). NMR spectra ( $^1\text{H}$  and  $^{31}\text{P}$ ) were reported for the compounds. A single methyl peak was found for the methyl groups attached to Sb for each of the compounds. The reaction of  $\text{Me}_5\text{Sb}$  and  $\text{Ph}_2\text{PCl}$  proceeded according to the equation:

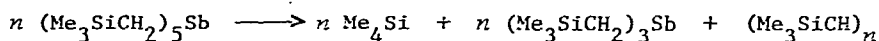
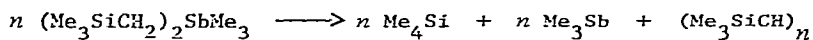


Schmidbaur and Hasslberger [95] have reported the synthesis of all five antimony compounds of the type  $\text{Me}_n\text{Sb}(\text{CH}_2\text{SiMe}_3)_{5-n}$ , where  $n = 0, 1, 2, 3$  or  $4$ . They were prepared from the appropriate antimony bromide either by methylation or trimethylsilylmethylation as follows:



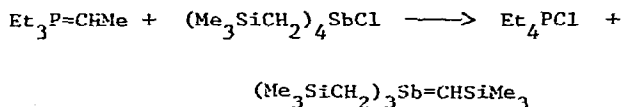
The compounds were not always obtained in pure form. Thus,  $\text{Me}_3\text{SiCH}_2\text{SbMe}_4$  was always contaminated with some  $(\text{Me}_3\text{SiCH}_2)_2\text{SbMe}_3$  and  $\text{Me}_5\text{Sb}$  because of disproportionation of the tetramethyl compound.

Thermal decomposition of two of the compounds above  $150^\circ$  proceeded as follows:

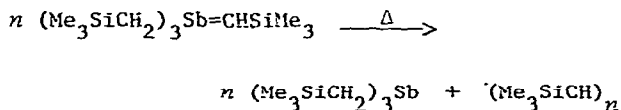


It was believed that both of these thermal decompositions involved the intermediate formation of ylids, namely  $\text{Me}_3\text{Sb}=\text{CHSiMe}$  in the first reaction and  $(\text{Me}_3\text{SiCH}_2)_3\text{Sb}=\text{CHSiMe}_3$  in the second reaction.

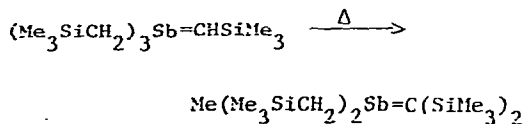
The compound  $(\text{Me}_3\text{SiCH}_2)_5\text{Sb}$  reacted with  $\text{HCl}$  to give  $\text{Me}_4\text{Si}$  and  $(\text{Me}_3\text{SiCH}_2)_4\text{SbCl}$ . The latter compound was soluble in benzene, pentane, or ether and appeared to be monomeric by a cryoscopic molecular weight determination. This chloride reacted with  $\text{Et}_3\text{P}=\text{CHMe}$  by dehydrohalogenation to give an antimony ylid:



The ylid was easily decomposed but was stable at low temperatures. Distillation gave decomposition as follows:

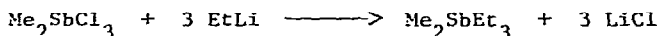
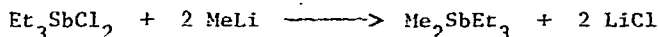


However, under carefully controlled conditions it was possible to isolate an isomerization product of the ylid:

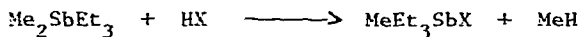


The reaction of  $\text{Me}_3\text{Sb}$  and  $\text{Me}_3\text{SiCH}_2\text{I}$  gave the stibonium salt  $[\text{Me}_3\text{SbCH}_2\text{SiMe}_3]\text{I}$ , but this did not react with  $\text{Et}_3\text{P}=\text{CHMe}$  to give an identifiable product.

The pentaalkylantimony compound  $\text{Me}_2\text{SbEt}_3$  has been prepared by Tempel and coworkers [96] by two similar methods:

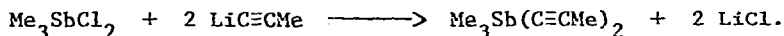


Acids, alcohols, and other compounds with available protons reacted with the pentaalkylantimony to give methane and the tetraalkylantimony compound:



(where  $\text{HX}$  was  $\text{MeOH}$ ,  $\text{CD}_3\text{OH}$ ,  $\text{EtOH}$ ,  $\text{MeNH}_2$ ,  $\text{MeCO}_2\text{H}$ ,  $\text{CD}_3\text{CO}_2\text{H}$ ,  $\text{Me}_2\text{PO}_2\text{H}$ ,  $\text{HCl}$ , or  $\text{F}_2\text{PO}_2\text{H}$ )

The PMR spectra of all of these compounds were tabulated. Another pentaalkyl compound was prepared as follows:

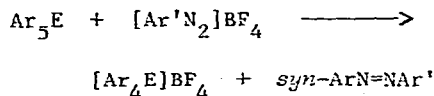


The IR and Raman spectra of both  $\text{Me}_2\text{SbEt}_3$  and  $\text{Me}_3\text{Sb}(\text{C}\equiv\text{CMe})_2$  were given, and assignments of the various bands were made. An X-ray diffraction study of  $\text{Me}_3\text{Sb}(\text{C}\equiv\text{CMe})_2$  was also carried out, and the compound was shown to be a trigonal bipyramid with equatorial methyl groups.

In addition to the above pentaalkylantimony compounds the antimony gallates  $[\text{MeEt}_3\text{Sb}][\text{Me}_2\text{GaCl}_2]$ ,  $[\text{Me}_2\text{SbEt}_2][\text{EtGaCl}_3]$ ,  $[\text{Me}_3\text{EtSb}][\text{Et}_2\text{GaCl}_2]$ , and  $[\text{Me}_3\text{EtSb}][\text{GaCl}_4]$  were prepared and characterized.

The PMR, Raman, and IR data were used to suggest structures for the various compounds under investigation. It was concluded that the alkoxides  $\text{MeEt}_3\text{SbOMe}$ ,  $\text{MeEt}_3\text{SbOCD}_3$ , and  $\text{MeEt}_3\text{SbOEt}$ , as well as the compound  $\text{MeEt}_3\text{SbONHMe}$ , were trigonal-bipyramidal structures, but that the compounds  $\text{MeEt}_3\text{SbOC}(\text{O})\text{Me}$ ,  $\text{MeEt}_3\text{SbC}(\text{O})\text{CD}_3$ , and  $\text{MeEt}_3\text{SbOP}(\text{O})\text{Me}_2$  contained six-covalent antimony. Two of the compounds, however, namely,  $[\text{MeEt}_3\text{Sb}]\text{Cl}$  and  $[\text{MeEt}_3\text{Sb}]\text{O}_2\text{PF}_2$ , were believed to be salts.

Nesmeyanov and coworkers [97] have shown that  $\text{Ph}_5\text{P}$ ,  $\text{Ph}_5\text{As}$ , and  $\text{Ar}_5\text{Sb}$  will react with diazonium tetrafluoroborates with the formation of an onium tetrafluoroborate and a *syn*-azo compound:



With antimony the pentaaryl compounds used were  $\text{Ph}_5\text{Sb}$  and  $(p\text{-MeC}_6\text{H}_4)_5\text{Sb}$ , and the diazonium salts were  $[\text{Ar}'\text{N}_2]\text{BF}_4$  (where  $\text{Ar}' = \text{Ph}$ ,  $p\text{-MeC}_6\text{H}_4$ , or  $p\text{-O}_2\text{NC}_6\text{H}_4$ ). The authors postulated that the driving force for the reaction involved the ease of elimination of an  $\text{Ar}_4\text{E}^+$ , *i.e.*, the phosphonium, arsonium, and stibonium cations were good leaving groups.

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