Journal of Organometallic Chemistry, 404 (1991) 49–85
Elsevier Sequoia S.A., Lausanne
JOM 21438AS

ANTIMONY

ANNUAL SURVEY COVERING THE YEAR 1989

LEON D. FREEDMAN AND G.O. DOAK

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204 (U.S.A.)

Except for our Annual Survey covering the year 1987, no book or review article devoted exclusively to organoantimony chemistry was published in 1989. The use of organoantimony and organobismuth compounds in organic synthesis has been critically reviewed, however, in the fifth volume of the series *The Chemistry of the Metal-Carbon Bond* edited by Professor Frank R. Hartley [1]. Information about organoantimony chemistry has also been included in a review of organosilicon derivatives of phosphorus, arsenic, antimony, and bismuth [2] and in surveys of recent publications on the organometallic chemistry of the main-group elements [3], on the main-group elements of Groups IV and V [4], and on the organo derivatives of arsenic, antimony, and bismuth [5]. In addition, organoantimony compounds have been mentioned in reviews or annual surveys on the following subjects: 1,6-disubstituted triptycenes [6], the direct synthesis of organo derivatives of non-transition metals [7], a new approach to the preparation of gallium arsenide and related semiconductors [8], organometallic compounds in which the metals have uncommon valences [9], diffraction studies of organometallic compounds [10], and organometallic compounds containing metal-metal bonds [11]. The use of tertiary stibines in organometallic vapor-phase epitaxy (OMVPE) has been briefly discussed in a new book [12].

A new method for the preparation of phenylstibine and diphenylstibine has been reported [13]. The primary stibine was obtained by the hydrolysis or methanolysis of phenylbis(trimethylsilyl)stibine:

$$PhSb(SiMe_3)_2 + 2MeOH \xrightarrow[-50°C]{Et_2O} PhSbH_2 + 2Me_3SiOMe$$

Diphenylstibine was prepared in an analogous manner:

$$Ph_2SbSiMe_3 + MeOH \xrightarrow[25°C]{PhH} Ph_2SbH + Me_3SiOMe$$

The trimethylsilylstibines required for these syntheses were obtained by the following reactions:

$$PhSbCl_2 + 2Mg + 2Me_3SiCl \xrightarrow{THF} PhSb(SiMe_3)_2 + 2MgCl_2$$

$$Ph_2SbCl + Mg + Me_3SiCl \xrightarrow{THF} Ph_2SbSiMe_3 + MgCl_2$$

Previous review see J. Organomet. Chem., 380 (1990) 1–34

References p. 82

Diphenyl(trimethylsilyl)stibine underwent an exothermic reaction with sulfur both in benzene and in the absence of a solvent:

$$Ph_2SbSiMe_3 + \tfrac{1}{8}S_8 \longrightarrow Ph_2SbSSiMe_3$$

The compound thus obtained decomposed slowly on warming to yield triphenylstibine, antimony trisulfide, and bis(trimethylsilyl) sulfide. The interaction of phenylbis(trimethylsilyl)stibine and sulfur gave only a small amount of the expected insertion product:

$$PhSb(SiMe_3)_2 + \tfrac{1}{4}S_8 \longrightarrow PhSb(SSiMe_3)_2$$

The main substance obtained was diphenyl(trimethylsilylthio)stibine admixed with antimony trisulfide and bis(trimethylsilyl) sulfide.

Dimesitylstibine has been prepared by reducing trimesitylstibine with excess lithium and then protonating the resulting dimesitylstibide with trimethylammonium chloride [14]:

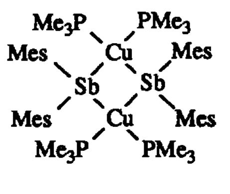
$$Mes_3Sb + 2Li \xrightarrow[25°C,\ 12\ h]{THF} Mes_2SbLi + MesLi$$

$$\xrightarrow{2[Me_3NH]Cl} Mes_2SbH + MesH + 2Me_3N + 2LiCl$$

(where Mes was mesityl)

The secondary stibine was surprisingly stable and showed no signs of oxidation after a period of weeks. The X-ray crystal structure (which was the first such type of information for a secondary stibine ever published) showed that the molecules possessed a C_2 axis, which bisected the C-Sb-C angle of 101.70(8)°. The presence of the Sb-H moiety was confirmed by the detection of a singlet at δ 4.90 in the PMR spectrum and a stretching vibration, $\nu_{Sb\text{-}H}$ = 1887.3 cm^{-1}, in the IR spectrum. When dimesitylstibine was lithiated with butyllithium and then added to a THF solution of copper(I) chloride and trimethylphosphine, a dimeric Cu(I) complex was formed:

$$Mes_2SbH + BuLi \xrightarrow[-78°C]{THF} Mes_2SbLi + BuH$$

$$2Mes_2SbLi + 2CuCl + 4Me_3P \xrightarrow[-78°C]{THF}$$  $$+ 2LiCl$$

The X-ray crystal structure of this complex showed that the geometry at the antimony and copper atoms was distorted tetrahedral. The Cu-Cu separation (3.95Å) was large enough to preclude any type of bonding interaction between these atoms. In the crystalline form, the complex was moderately stable in the absence of air but exhibited surface decomposition in the

presence of light. Solutions of the complex decomposed in a few hours at 25°C. The interaction of lithium dimesitylstibide and copper(I) chloride in the absence of trimethylphosphine resulted in the formation of elemental copper and a distibine:

$$2Mes_2SbLi + 2CuCl \longrightarrow Mes_2SbSbMes_2 + 2Cu + 2LiCl$$

The dehalogenation of alkyldibromostibines with magnesium in THF has been found to give yellow solutions that contained (according to ^1H and ^{13}C NMR studies) mainly five-membered rings together with much smaller amounts of four-membered rings [15]:

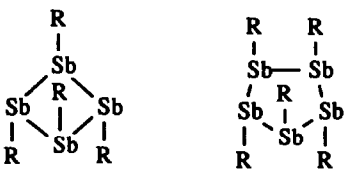
$$RSbBr_2 + Mg \longrightarrow {}^1/_n(RSb)_n + MgBr_2$$

(where R was Et, Pr, or Bu and *n* was 4 or 5)

The trimers $(RSb)_3$ could not be detected by PMR but were shown to be present by mass spectrometry. Evaporation of the yellow solutions to dryness gave (reversibly) black solids $(RSb)_x$, where *x* was much greater than 5:

$${}^1/_n(RSb)_n \rightleftharpoons {}^1/_x(RSb)_x$$

The alkyl groups in the cyclic compounds appeared to prefer *trans* configurations:



In solution the cyclic compounds were stable for several days and decomposed only slowly to antimony, tetraalkyldistibines, and trialkylstibines. The polymeric substances were significantly less reactive than the cyclic compounds in their interaction with bromine to form alkyldibromostibines and their oxidation with dry air to form compounds of the type $(RSbO)_x$. On being warmed to about 60°C in benzene, the polymeric substances were reconverted to the cyclic compounds $(RSb)_n$. The X-ray crystal structure of a 1:1 benzene adduct of tetramesityltetrastibetane was also determined. Like the tetraalkyltetrastibetanes discussed above, the substituents bonded to the antimony atoms occupied *trans* positions. The ring was sharply folded with Sb-Sb-Sb angles of 88.09°, 76.91°, 88.10°, and 76.92°. A benzene molecule was linked with good η^6-hapticity to one antimony atom of each $(MesSb)_4$ unit. The distance between the center of the benzene ring and the antimony atom was 3.81Å.

Compounds of the type $R_2SbMSbR_2$, where M was Se or Te, have been obtained by the following type of insertion reaction [16]:

$$R_2SbSbR_2 + M \longrightarrow R_2SbMSbR_2$$

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

The products were characterized by PMR, IR, Raman, and mass spectroscopy. A remarkable property of both methyl compounds was their thermochromism. Thus, the selenium compound was an orange liquid, which solidified to form red crystals. The tellurium compound was brown in the liquid state and blue-violet in the solid phase. Other compounds containing Sb-Se or Sb-Te bonds were prepared by the interaction of distibines and dichalcogenides at or below room temperature:

$$R_2SbSbR_2 + R'MMR' \longrightarrow 2R_2SbMR'$$

(where M was Se, R was Me or Et, and R′ was Me or Ph; or where M was Te, R was Me or Et, and R′ was Me or 4-MeC_6H_4)

All of the reactions appeared to go to completion and yielded substances that were stable enough to be distilled at reduced pressure. The two methyl tellurium compounds were thermochromic. Thus, the dimethylstibino derivative was a red liquid that became orange in the solid state, while the analogous diethylstibino compound exhibited a yellow liquid and an orange solid phase. When the stibino selenides were heated at elevated temperatures, scrambling of substituents was observed:

$$2R_2SbSeR' \rightleftharpoons R_3Sb + RSb(SeR')_2$$

After the trialkylstibines were removed from the equilibrium mixture by distillation, compounds of the type $RSb(SeR')_2$ could be isolated. In one case ($Me_2SbSeMe$), prolonged heating gave not only $MeSb(SeMe)_2$ but also $Sb(SeMe)_3$. Scrambling of substituents was less selective with the stibino tellurides. Mass spectrometry of the reaction mixtures revealed the presence of species of the types R_3Sb, R'_2Te, RR′Te, R′TeTeR′, and $RSb(TeR')_2$. Separation of these mixtures did not appear worthwhile. PMR spectroscopy of the various compounds prepared in this investigation showed an increase of deshielding in the sequence MeSb<MeTe<MeSe. The Sb-Se and Sb-Te valence vibrations of the methyl derivatives gave rise to intense and easily observed Raman signals. The EI mass spectra of all the chalcogenides exhibited molecular ions of high intensity. Fragmentation generally proceeded with complete cleavage of the organic substituents to give fragments of the type SbM, Sb_2M, or SbM_2.

Tetrakis(trimethylstannyl)distibine has been prepared by the following sequence of reactions [17]:

$$PhCH_2Cl + LiSb(SiMe_3)_2 \cdot 2THF \xrightarrow[-30°C]{PenH} PhCH_2Sb(SiMe_3)_2 + LiCl + 2THF$$

$$PhCH_2Sb(SiMe_3)_2 + 2Me_3SnCl \xrightarrow[r.t.]{DME} PhCH_2Sb(SnMe_3)_2 + 2Me_3SiCl$$

$$2PhCH_2Sb(SnMe_3)_2 \xrightarrow[DME,\ r.t.]{h\nu} (Me_3Sn)_2SbSb(SnMe_3)_2 + PhCH_2CH_2Ph$$

(where DME was 1,2-dimethoxyethane)

The distibine crystallized from the reaction mixture as dark red needles, which were sensitive to oxidation and hydrolysis. The NMR (^1H and ^{13}C), IR, and Raman spectra of this substance were recorded and analyzed. Recrystallization from benzene yielded a modification, which was studied by X-ray diffraction. The molecular parameters thus obtained were in agreement with the corresponding values of a different modification that had been described earlier by other investigators.

Electronic spectra of six distibines of the type R_2SbSbR_2 (where R was Me, Et, Ph, Me_3Si, Me_3Ge, or Me_3Sn) have been included in a paper mainly concerned with the synthesis, structure, and physical properties of tetrakis(trimethylgermyl)distibine [18]. Except for the pale yellow, nonthermochromic tetraphenyl compound, the distibines were red in the solid state but became yellow on melting or dissolution in organic solvents. The diffuse reflectance spectra of the five red solids showed continuous absorption from 250 to 600 nm with several broad maxima. The maxima of four of these thermochromic compounds in dilute solution were blue shifted by 200-300 nm; solution spectra of tetraethyldistibine were not recorded, but a blue shift was noted when the compound was melted. Only modest differences in the absorption maxima were observed on comparing the spectrum of tetraphenyldistibine in the solid state with its spectrum in solution. It was concluded that the spectra of the distibines were consistent with the visibly observed thermochromism of these substances.

Tris(pentafluorophenyl)stibine has been found to undergo facile redistribution reactions with antimony trichloride (in 2:1 and 1:2 molar ratios) in a dry oxygen-free atmosphere [19]:

$$2(C_6F_5)_3Sb + SbCl_3 \xrightarrow{60\text{-}70°C} 3(C_6F_5)_2SbCl$$

$$(C_6F_5)_3Sb + 2SbCl_3 \xrightarrow{60\text{-}70°C} 3C_6F_5SbCl_2$$

The redistribution reactions were complete in about 3 h. The products were viscous oils, which solidified on standing and could be recrystallized from dichloromethane to give the pure halostibines in yields of 70-75%. Oxidative chlorination at 0°C gave the corresponding antimony(V) chlorides in yields of 70%:

$$(C_6F_5)_2SbCl + Cl_2 \xrightarrow{CH_2Cl_2} (C_6F_5)_2SbCl_3$$

$$C_6F_5SbCl_2 + Cl_2 \xrightarrow{CH_2Cl_2} C_6F_5SbCl_4$$

The tetrachloride proved to be remarkably stable at room temperature and was unaffected by oxygen. Oxidative bromination of the halostibines at -178°C gave the expected mixed halides:

$$(C_6F_5)_2SbCl + Br_2 \xrightarrow{CH_2Cl_2} (C_6F_5)_2SbClBr_2$$

$$C_6F_5SbCl_2 + Br_2 \xrightarrow{CH_2Cl_2} C_6F_5SbCl_2Br_2$$

References p. 82

Both compounds were obtained in high yields (83-85%) and were stable at room temperature. All of the compounds prepared in this investigation exhibited characteristic IR absorptions attributed to the pentafluorophenyl groups. The stretching vibrations of the antimony-halogen bonds occurred at higher frequencies than in the corresponding phenyl derivatives. The spectra of all the chlorides showed a band between 320 and 340 cm^{-1}, which increased in intensity with increasing chlorine content. The bromides exhibited a strong band at 235 ± 5 cm^{-1}, which was assigned to Sb-Br stretching vibrations.

Methyldichlorostibine has been prepared in 85% yield by the exchange reaction of equimolar amounts of dimethylchlorostibine and antimony trichloride [20]:

$$Me_2SbCl + SbCl_3 \xrightarrow{2\,h} 2MeSbCl_2$$

Several alkyldibromostibines have been obtained in an analogous manner:

$$R_2SbBr + SbBr_3 \longrightarrow 2RSbBr_2$$

(where R was Me, Et, Pr, or Bu)

Ethyldibromostibine was also synthesized by the following reaction sequence:

$$Et_2SbBr + Br_2 \xrightarrow{Et_2O} Et_2SbBr_3$$

$$Et_2SbBr_3 \longrightarrow EtSbBr_2 + EtBr$$

The elimination of ethyl bromide occurred at room temperature and led to a 90% yield of the dibromostibine. The interaction of triethylstibine and antimony tribromide resulted mainly in oxidation-reduction:

$$3Et_3Sb + 2SbBr_3 \longrightarrow 3Et_3SbBr_2 + 2Sb$$

All of the mass spectra of the dihalostibines prepared in this study exhibited molecular ions. The PMR spectra of these compounds were also investigated and were found to exhibit major solvent effects in $CDCl_3$ and C_6D_6.

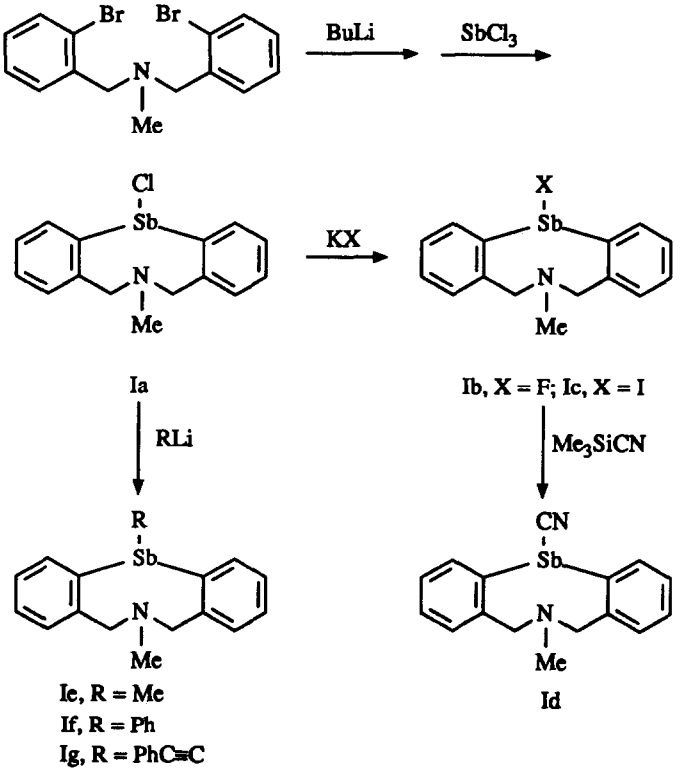
The interaction of a suspension of pulverized antimony in diethyl ether and a hexane solution of 5-bromopentamethyl-1,3-cyclopentadiene has been found to give a good yield of a dibromostibine [21]:

$$4Me_5C_5Br + 2Sb \xrightarrow[20°C]{3\,d} 2Me_5C_5SbBr_2 + (Me_5C_5)_2$$

The yellow powder thus obtained was too unstable to allow precise carbon and hydrogen analysis. The PMR spectrum exhibited a single singlet at δ 1.63, while the ^{13}C NMR spectrum

showed signals at δ 10.53 and 123.50. The intensity of the molecular ion in the mass spectrum was 7% of the most intense peak ($Me_5C_5^+$).

The heterocyclic chlorostibine Ia has been obtained in a 58% yield from bis(2-bromobenzyl)methylamine by a one-pot process [22]. Halogen exchange reactions with potassium fluoride or potassium iodide gave the expected fluorostibine Ib or iodostibine Ic. Treatment of the fluorostibine Ib with trimethylsilyl cyanide in dichloromethane afforded the corresponding cyanostibine Id. Reaction of the chlorostibine Ia with the appropriate organolithium reagents yielded the tertiary stibines Ie, If, and Ig. The interaction of the chlorostibine Ia and methyl iodide did not give the anticipated quarternary ammonium salt. Instead, the iodostibine Ic was produced in quantitative yield. This result was rationalized by assuming oxidative addition of methyl iodide to the antimony atom and subsequent reductive elimination of methyl chloride. It was concluded that this unexpected reaction pathway indicated the existence of transannular interaction between the antimony and nitrogen atoms. Examination of the PMR and ^{13}C NMR spectra of I revealed that there were linear relationships



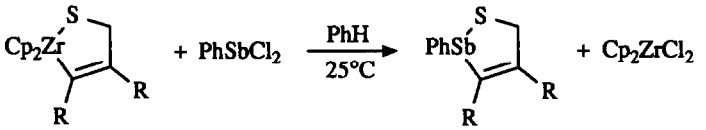
between the chemical shifts of the *N*-methyl groups and the Hammett σ_m constants of the substituents bonded to the antimony atoms:

for PMR $\delta_{Me} = 0.79\sigma_m + 2.46$ (for Ia, b, c, e, and f)
$\delta_{Me} = 0.30\sigma_m + 2.46$ (for Id, e, f, and g)

for ^{13}C NMR $\delta_{Me} = 5.87\sigma_m + 41.6$ (for Ia, b, c, e, and f)
$\delta_{Me} = 1.79\sigma_m + 41.5$ (for Id, e, f, and g)

According to the authors, the occurrence of these relationships was best explained by assuming that the nitrogen atoms were directly donating electron density to the antimony atoms.

The first examples of a new class of main-group metallacycles have been synthesized via transmetalation from zirconocene derivatives [23]:



(where R was H, Me, or Ph)

The yields were about 85%. All three of the compounds were air-stable solids and could be stored indefinitely in a dry atmosphere. Their NMR(^1H and ^{13}C) spectra were fully consistent with the proposed structures. The diastereotopic methylene protons appeared as a pair of well-resolved doublets in the room temperature PMR; no significant broadening occurred on warming to 90°C. Molecular weight determinations showed that the compounds were monomeric in benzene solution.

A number of compounds containing an Sb-N bond have been obtained by one of the following types of reactions [24]:

$$Ar_2SbCl + HL + Et_3N \xrightarrow{PhH} Ar_2SbL + Et_3N \cdot HCl$$

$$Ar_2SbCl + NaL \xrightarrow{PhH} Ar_2SbL + NaCl$$

(where Ar was Ph and HL was succinimide, phthalimide, isatin, 1,2,3-benzotriazole, 2-methylimidazole, 2-chloromethylbenzimidazole, benzothiazoline-2-thione, or carbazole; or where Ar was C_6F_5 and HL was succinimide or isatin)

All of the reactions were found to proceed under mild conditions and generally gave quantitative yields. The products were colorless solids with sharp melting points and normal molecular weights in freezing benzene, and they were unaffected by air, water, methanol, or carbon disulfide. Their molar conductances (10^{-3}M solutions in acetonitrile) ranged between 15 and 25 ohm^{-1} cm^2 mol^{-1}; these values indicated that ionic species were not present. The antimony-nitrogen bond in these substances was cleaved by bromine:

$$Ar_2SbNR_2 + Br_2 \xrightarrow[0°C]{CHCl_3} Ar_2SbBr + R_2NBr$$

(where R_2N was L)

The antimony-nitrogen bond was also cleaved by acetic acid, but the structures of the substances thus obtained were not elucidated. Phenyl isocyanate added to the antimony-nitrogen bond in the following manner:

$$Ar_2SbNR_2 + PhN{=}C{=}O \longrightarrow Ar_2SbN(Ph)\overset{\overset{O}{\|}}{C}NR_2$$

The IR and PMR spectra of the compounds prepared in this investigation were consistent with their proposed structures.

Dialkyldithiophosphate derivatives of antimony(III) have been prepared by one of three different reactions [25]:

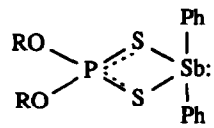
$$Ph_2SbCl + NaS_2P(OR)_2 \xrightarrow[reflux]{PhH} Ph_2SbS_2P(OR)_2 + NaCl$$

$$Ph_2SbO_2CMe + NaS_2P(OR)_2 \xrightarrow[reflux]{PhH} Ph_2SbS_2P(OR)_2 + MeCO_2Na$$

$$Ph_2SbO_2CMe + HS_2P(OR)_2 \xrightarrow[reflux]{PhMe} Ph_2SbS_2P(OR)_2 + MeCO_2H$$

(where R was Me, Et, Pr, Me_2CH, Bu, or Me_2CHCH_2)

All of the products were soluble in common organic solvents and were moisture sensitive. Osmometric molecular weights in chloroform solution showed that the substances were monomeric. They were also characterized by IR and NMR (^1H, ^{13}C, and ^{31}P) spectroscopy. The ^{13}C NMR results suggested that both phenyl groups were equivalent, while the ^{31}P NMR and IR data were consistent with the assumption that the dithiophosphate moieties were behaving as chelating ligands. It was concluded that the geometry around the antimony atom was trigonal-bipyramidal, with the axial positions being occupied by the phenyl groups and the equatorial positions by the two sulfur atoms of the ligand and by a lone pair of electrons:



The reaction of diphenylchlorostibine with the sodium salts of monothio-β-ketones (NaL) in a 1:1 molar ratio has been found to give high yields of compounds of the type Ph_2SbL [26]:

$$Ph_2SbCl + NaSC(Ph)CHC(O)R \xrightarrow{THF} Ph_2SbSC(Ph)CHC(O)R + NaCl$$

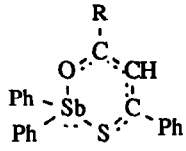
(where R was Ph, 4-MeC_6H_4, 4-FC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, or 4-$MeOC_6H_4$)

One of the substances was also obtained by the interaction of diphenylacetatostibine with the sodium salt of a monothio-β-ketone in a 1:1 molar ratio:

$$Ph_2SbO_2CMe + NaSC(Ph)CHC(O)R \xrightarrow{CHCl_3} Ph_2SbSC(Ph)CHC(O)R + NaO_2CMe$$

(where R was 4-MeC_6H_4)

All of these compounds were solids or viscous liquids. They were soluble in common organic solvents and were monomeric in chloroform solution at 45°C. They were moisture sensitive and decomposed on heating. Their IR spectra suggested that the ligands were chelating, and hence it was concluded that the antimony atom had a coordination number of four. The most plausible geometry appeared to be trigonal-bipyramidal with an oxygen atom and a lone pair of electrons occupying apical positions:



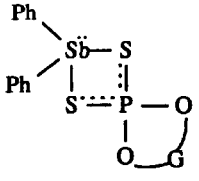
This type of structure was supported by the NMR(^1H and ^{13}C) spectra of these compounds.

Another series of organoantimony(III) compounds containing Sb-S bonds has been obtained by the following type of reaction [27]:

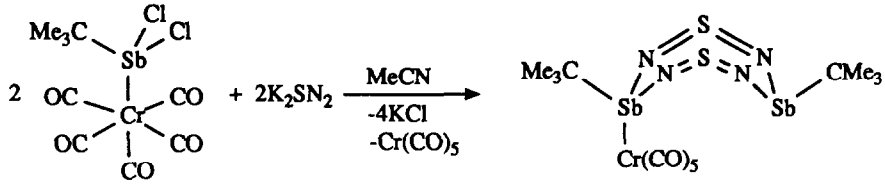
$$Ph_2SbCl + MS_2P\begin{<}O\\O\end{>}G \xrightarrow[\text{reflux}]{PhH} Ph_2SbS_2P\begin{<}O\\O\end{>}G + MCl$$

(where M was Na or NH_4 and G was CMe_2CMe_2, $CH_2CMe_2CH_2$, $CH_2CEt_2CH_2$, or CMe_2CH_2CHMe, where OGO was $(OPh)_2$)

The products were described as colorless or light yellow viscous liquids or semi-solids. Like the dialkyldithiophosphates and the monothio-β-ketone derivatives discussed above, they were moisture sensitive, soluble in organic solvents, and monomeric in chloroform. Spectral data again supported the conclusion that the antimony atom in these substances was four-coordinated. The following type of trigonal-bipyramidal structure was suggested:

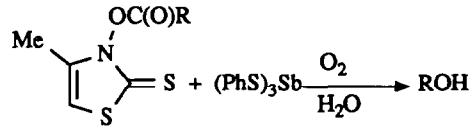


An eight-membered heterocyclic sulfur diimide derivative of antimony has been obtained as a chromium complex by means of the following reaction [28]:



The arsenic (but not the phosphorus) analog could be prepared in a similar manner. Attempted decarbonylation of the above antimony-containing heterocycle led to decomposition of the ring.

Esters (mixed anhydrides) of carboxylic acids and suitable thiohydroxamic acids have been found to react with tris(phenylthio)stibine at room temperature to give high yields of nor-alcohols [29]:



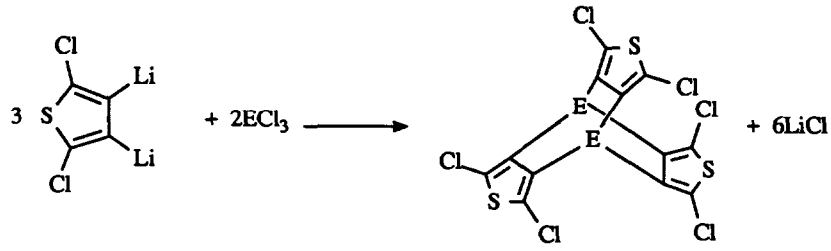
(where R was primary, secondary, or tertiary)

The decarboxylative hydroxylation reaction appeared to involve a radical chain mechanism in which a carbon-centered radical attacked the stibine and formed an oxygen-sensitive organoantimony compound:

$$R\bullet + (PhS)_3Sb \longrightarrow RSb(SPh)_2 + PhS\bullet$$

Spontaneous reaction of these intermediates with air and water presumably produced the nor-alcohols and antimony(III) oxide. In one experiment performed under strictly anaerobic conditions, it was found that the intermediate reacted with hydrochloric acid to yield mainly the hydrocarbon RH. Moreover, in a separate experiment, oxidation of the intermediate with nitrogen dioxide (instead of oxygen) gave the nitroalkane RNO_2 in modest yield. Further evidence for the proposed mechanism is discussed in the Annual Survey of Bismuth.

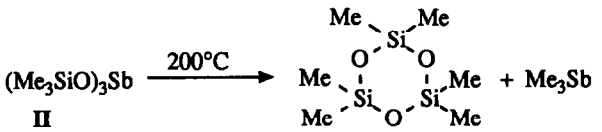
A number of new, air-stable heterocycles have been obtained by the following type of reaction [30]:



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

The molecular weights of these substances were confirmed by mass spectrometry, except for the di-tertiary bismuthine for which the molecular ion could not be detected. The dilithio compound required for these syntheses were prepared *in situ* by the interaction of butyllithium in hexane and either 2,5-dichloro-3,4-diiodothiophene or 2,5-dichloro-3,4-dibromothiophene in ether.

The decomposition of tris(trimethylsilyl)antimonite (II) at 200°C has been found to produce trimethylstibine and hexamethylcyclotrisiloxane [31]:



The interaction of II and antimony trichloride resulted in the following metathetical reaction:

$$\underset{\text{II}}{(Me_3SiO)_3Sb} + SbCl_3 \longrightarrow (Me_3SiO)_2SbCl + Me_3SiOSbCl_2$$

The mass spectrum of II was also studied.

A potentially bidentate ligand has been obtained by the following reaction sequence [32]:

$$2\text{-}Me_2SbC_6H_4Br + BuLi \xrightarrow[-63°C]{Et_2O} 2\text{-}Me_2SbC_6H_4Li + BuBr$$

$$2\text{-}Me_2SbC_6H_4Li + MeTeTeMe \longrightarrow 2\text{-}Me_2SbC_6H_4TeMe + LiTeMe$$

The air-sensitive liquid thus obtained was easily quaternized to a solid, mp 90-92°C:

$$2\text{-}MeTeC_6H_4SbMe_2 + MeI \xrightarrow{Me_2C=O} 2\text{-}MeTeC_6H_4SbMe_3I$$

The PMR spectrum of the tertiary stibine exhibited a singlet at δ 0.94 for the methyl groups bonded to antimony. On quaternization, the singlet shifted downfield to δ 1.88. The position of the MeTe PMR signal was almost the same in both compounds (δ 2.15 for the stibine; δ 2.1 for the methiodide). The stibine was further characterized by ^{13}C and ^{125}Te NMR spectroscopy and by mass spectrometry. The base peak in the mass spectrum corresponded to the $(M\text{-}Me)^+$ ion; the intensity of the molecular ion was 25%.

The kinetics of radical exchange (transmetallation) between phenyllithium and ^{14}C-labelled triphenylstibine or -bismuthine in various mixtures of pentane and diethyl ether has been studied at temperatures ranging from 248 to 307 K [33]:

$$(^{14}C_6H_5)_3E + 3PhLi \rightleftharpoons Ph_3E + 3^{14}C_6H_5Li$$

(where E was Sb or Bi)

The reaction was found to be second order overall, *i.e.* first order with respect to each reagent. The rate constant for triphenylstibine was two orders of magnitude higher than that for triphenylbismuthine. In the solvents having dielectric constant values (ϵ) greater than 2.8, the exchange rate constant for both compounds could be described in terms of the Kirkwood equation. As the value of ϵ increased, both the enthalpy and entropy of activation decreased and there was a direct linear relationship between the latter two parameters. The free energy of activation, however, remained practically constant for each system. It was concluded that the effect of the solvent on the reaction rate was primarily due to preferential non-specific solvation of the transition state.

In a paper devoted mainly to the conversion of organobismuth compounds to ketones or biaryls, the palladium-catalyzed decomposition of triphenylstibine has been reported to give a 93% yield of biphenyl [34]:

$$2Ph_3Sb \xrightarrow{Pd} 3Ph\text{-}Ph + 2Sb$$

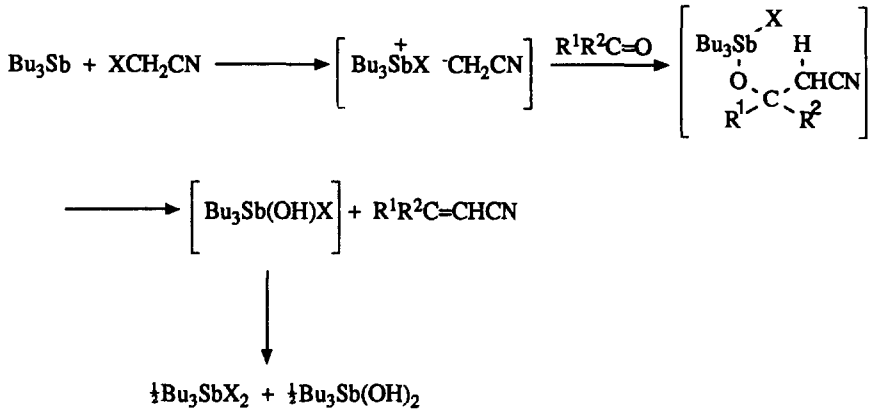
The reaction was carried out by adding 2 mmol of triethylamine to a solution of 1 mmol of palladium(II) acetate in hexamethylphosphoramide (HMPA), then adding 1 mmol of the stibine, and finally heating the mixture at 65°C for 10 min. A black powder precipitated, which was shown to contain metallic palladium. A high yield of biphenyl was also obtained when triphenylantimony dichloride was allowed to react under similar conditions except that only 0.05 mol of palladium(II) acetate per mol of organoantimony compound was used.

Professor Yao-Zeng Huang and his coworkers have continued to report interesting new uses of tertiary stibines in organic synthesis. In 1989 they published six papers on this subject. The first of these papers described the preparation of α,β-unsaturated nitriles in good yields by the interaction of chloroacetonitrile and an aldehyde in the presence of tributylstibine [35]:

$$RCH{=}O + ClCH_2CN + Bu_3Sb \xrightarrow[2\text{-}16\ h]{110\text{-}120°C} RCH{=}CHCN + \tfrac{1}{2}Bu_3SbCl_2 + \tfrac{1}{2}Bu_3Sb(OH)_2$$

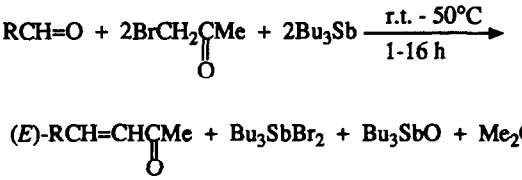
(where R was Pen, Oct, *trans*-HepCH=CH, 2-Fu, 2-Thi, Ph, 4-ClC_6H_4, or *trans*-PhCH=CH)

The ratio of *trans* to *cis* in the products was estimated by PMR and was found to vary from 55:45 to 75:25. Cyclopentanone and cyclohexanone were also converted to α,β-unsaturated nitriles, but the yields were only 33 and 50% , respectively. Acetophenone, however, did not react under the conditions employed. Heating was not required to effect the tributylstibine-mediated interaction of iodoacetonitrile and benzaldehyde; in fact, an exothermic reaction occurred at room temperature when the reagents were mixed. The following mechanism was proposed for the reactions described in this paper:



All of the α,β-unsaturated nitriles prepared in this investigation were characterized by IR, PMR, and mass spectrometry.

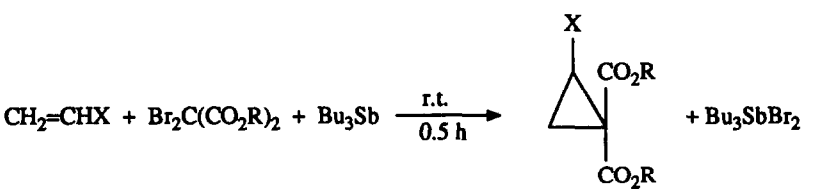
A second paper from Huang's laboratory was concerned with the use of tributylstibine to mediate the olefination of aldehydes with α-bromo ketones [36]:



(where R was Bu, Oct, *n*-$C_{11}H_{23}$, *trans*-MeCH=CH, *trans*-HepCH=CH, 2-Fu, 2-Thi, Ph, or *trans*-PhCH=CH)

The yields of α,β-unsaturated ketones ranged from 78-93%. The reactions were carried out without solvents or in aprotic solvents such as benzene, THF, dichloromethane, or acetonitrile. Triphenylstibine could also promote the interaction of bromoacetone and aldehydes, but higher temperatures were required and the yields were lower. Chloroacetone proved to be much less reactive than bromoacetone. α,β-Unsaturated ketones were also prepared from the following α-bromo ketones: bromoacetophenone, 3-bromo-2-butanone, and 1-bromo-3-methyl-2-butanone. The yields in most cases were very good.

The use of tributylstibine to promote the synthesis of certain 1,1,2-trisubstituted cyclopropanes in good yields was reported in a third paper [37]:



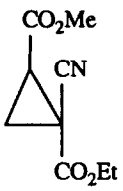
(where X was CH=O, C(O)Me, CN, or CO_2Et and R was Me or Et)

Replacement of the dialkyl dibromomalonate with ethyl dibromocyanoacetate gave similar results. Cyclic α,β-unsaturated ketones reacted with the dibromo compounds in the presence of tributylstibine to give good yields of the expected bicyclic derivatives. Some olefins (acrylamide, cinnamic ester, crotonic ester, β-ionone, *p*-chlorochalcone, styrene, maleic anhydride, diethyl maleate, and diethyl fumarate), however, did not give substituted cyclopropanes. When diethyl maleate or diethyl fumarate was used as the olefinic component, dimethyl dibromomalonate was found to undergo a coupling reaction:

$$2Br_2C(CO_2Me)_2 + 2Bu_3Sb \xrightarrow[4\ h]{60°C} (MeO_2C)_2C{=}C(CO_2Me)_2 + 2Bu_3SbBr_2$$

The reaction of ethyl dibromocyanoacetate with an acrylic ester gave not only the trisubstituted cyclopropane but also two reduction products:

$$CH_2{=}CHCO_2Me + Br_2C(CN)CO_2Et \xrightarrow{Bu_3Sb}$$



$$+ BrCH(CN)CO_2Et + NCCH_2CO_2Et$$

68% 6% 20%

Two isomeric cyclopropane derivatives obtained from the reaction of acrylonitrile with ethyl dibromocyanoacetate were shown to have *E* and *Z* configurations on the basis of PMR data; the *E* to *Z* ratio was 62:38 as determined by GLC analysis. The reaction of ethyl dibromophenylacetate with electron-deficient olefins in the presence of tributylstibine gave cyclopropanes only in low to moderate yields. The cause of the lower yields was shown to be competing side-reactions that formed two reduction products as well as the coupling product. The reaction of dimethyl dibromomalonate with the olefins was found to be promoted not only by tributylstibine but also by triethylstibine, triphenylstibine, tributylarsine, or tributylbismuthine. The two trialkylstibines gave the best yields of cyclopropane derivatives. When dimethyl dibromomalonate was refluxed in benzene with triphenylstibine in the absence of an olefin, triphenylantimony bromide hydroxide and dimethyl bromomalonate were formed almost quantitatively:

$$2Br_2C(CO_2Me)_2 + Ph_3Sb \xrightarrow[2\ h]{PhH} Ph_3Sb(OH)Br + CHBr(CO_2Me)_2$$

The formation of these products was explained by the following mechanism:

$$Ph_3Sb + Br_2C(CO_2Me)_2 \longrightarrow \left[Ph_3\overset{+}{S}bBr \;\; \overset{-}{B}rC(CO_2Me)_2 \right]$$

$$\xrightarrow{H_2O} Ph_3Sb(OH)Br + CHBr(CO_2Me)_2$$

Mechanisms were also proposed for the other reactions studied in this investigation.

A fourth paper from Huang's laboratory described the preparation of α,β-unsaturated esters and amides by the trialkylstibine-promoted reaction of derivatives of α-halo carboxylic acids with aldehydes or ketones [38]:

$$R^1R^2C{=}O + RCH(Br)COY + Bu_3Sb \xrightarrow[2.5 - 20\ h]{80 - 130°C}$$

$$R^1R^2C{=}C(R)COY + \tfrac{1}{2}Bu_3SbBr_2 + \tfrac{1}{2}Bu_3Sb(OH)_2$$

(where R^1 was Pr, *n*-$C_{11}H_{23}$, MeCH=CH, $Me_2C{=}CHCH_2CH_2C(Me){=}CH$, 2-Fu, Ph, or PhCH=CH, R^2 and R were H, and Y was OEt; where R^1 was Oct, PrCH=CH, 2-Fu, 2-Thi, or Ph, R^2 was H, R was Me, and Y was OEt; where R^1 was Ph, R^2 and R were H, and Y was OMe; where R^1 was Ph, R^2 was H, R was Et, and Y was OEt; where R^1 and R^2 were Me, R was H, and Y was OEt; where R^1R^2 were $(CH_2)_4$ or $(CH_2)_5$, R was H, and Y was OEt; where R^1 was Me_2CHCH_2, 2-Fu, or 4-ClC_6H_4, R^2 and R were H, and Y was NEt_2)

The yields obtained with the aldehydes were good or excellent, whereas the ketones gave only fair or poor yields. Ethyl chloroacetate reacted just as well as the bromo compound, but ethyl 2-chloropropanoate did not react even at 150°C. Triethylstibine was as effective as tributylstibine, while triphenylstibine, antimony trichloride, and tributylphosphine did not promote the olefination reaction. The reactions could be carried out without a solvent or in such aprotic solvents as THF, acetonitrile, hexane, or benzene. Ethyl bromoacetate and bromo-*N*,*N*-diethylacetamide were found to react with trialkylstibines to yield oily products, which were identified as quaternary antimony bromides from PMR, IR, and MS data. The bromides were converted by anion exchange to crystalline tetraphenylborates:

$$R_3Sb + BrCH_2COY \xrightarrow{r.t.} R_3\overset{+}{S}bCH_2COY\ Br^- \xrightarrow[EtOH]{NaBPh_4} R_3\overset{+}{S}bCH_2COY\ Ph_4B^-$$

(where R was Et or Bu, and Y was OEt or NEt_2)

Heating tributylcarbethoxyantimony bromide or tetraphenylborate with benzaldehyde gave a high yield of ethyl cinnamate:

$$PhCH{=}O + Bu_3\overset{+}{S}bCH_2CO_2Et\ X^- \xrightarrow[3\ h]{80 - 90°C} PhCH{=}CHCO_2Et$$

(where X was Br or Ph_4B)

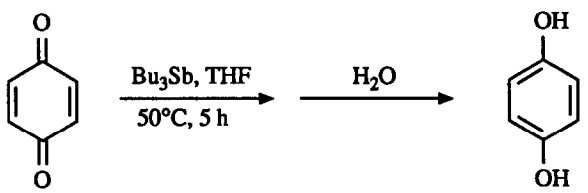
The authors concluded that a quaternary antimony halide was an intermediate in the trialkylstibine-mediated olefination reaction, and they proposed a mechanism.

The reduction of several types of organic compounds by trialkylstibines was reported in a fifth paper published by Huang and coworkers [39]. For example, a number of nitroarenes were converted to azoxy compounds in good yields by the following type of reaction:

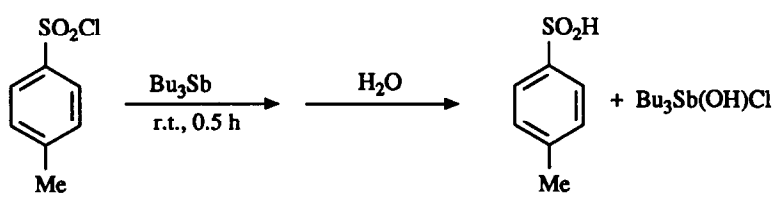
$$2ArNO_2 + 3R_3Sb \xrightarrow[r.t.]{THF} ArN{=}\overset{O}{\overset{\uparrow}{N}}Ar + 3R_3SbO$$

(where Ar was Ph, 2-ClC_6H_4, 4-ClC_6H_4, 3-BrC_6H_4, 4-BrC_6H_4, 4-IC_6H_4, or 2-Me-4-ClC_6H_3 and R was Et or Bu)

Other reduction products were not detected in these reactions. Surprisingly, the interaction of 1-bromo-2-nitrobenzene and a trialkylstibine did not proceed cleanly but gave an intractable mixture. The failure of 1-dimethylamino-4-nitrobenzene to react even in refluxing THF was attributed to the presence of an electron donating group. The reaction of electron-deficient nitroarenes such as 4-nitrophthalic anhydride and 4-nitrobenzoyl chloride with trialkylstibines resulted in polymerization of the substrates. Triphenylstibine proved to be inert towards nitrobenzene in refluxing THF. Treatment of quinone with tributylstibine in THF gave hydroquinone after protolysis:



The yield was 91%; the fate of the trialkylstibine was not mentioned. When 4-toluenesulfonyl chloride was mixed with tributylstibine, an exothermic reaction took place. 4-Toluenesulfinic acid was isolated from the reaction mixture in 98% yield after protolysis:



An exothermic reaction also occurred when α-bromophenylacetonitrile was mixed with tributylstibine. The product obtained in 91% yield showed that coupling had taken place:

$$2PhCH(Br)CN + Bu_3Sb \xrightarrow[10\ min]{r.t.} PhCH(CN)CH(CN)Ph + Bu_3SbBr_2$$

1,2-Dibromo-1-phenylethane was debrominated by tributylstibine at 100°C to give a 70% yield of styrene:

$$PhCH(Br)CH_2Br + Bu_3Sb \xrightarrow[4\ h]{100°C} PhCH{=}CH_2 + Bu_3SbBr_2$$

The debromination of 3,4-dibromobutanone was said to be more facile, while 1,2-dibromo-2-methylpropane did not react with tributylstibine even at 150°C.

The last organoantimony paper published by Huang's group in 1989 described the synthesis of alkyl aryl sulfones *via* the tributylstibine-assisted coupling of 4-toluenesulfonyl chloride with alkyl halides [40]:

$$4\text{-}MeC_6H_4SO_2Cl + RX + Bu_3Sb \xrightarrow[0.5\text{ - }12\ h]{r.t.\text{ - }50°C} 4\text{-}MeC_6H_4SO_2R + BuSb(X)Cl$$

(where RX was MeI, BuI, $CH_2{=}CHCH_2I$, $CH_2{=}CHCH_2Br$, $PhCH_2Br$, $PhCOCH_2Br$, MeO_2CCH_2Br, or (*E*)-$MeCH{=}CHCH_2Br$)

The yields of sulfones ranged from 51 - 90%. The alkyl bromides were less reactive than the iodides, while the chlorides were not effective at all. A mechanism for the coupling reaction was proposed by the authors.

The oxidative fluorination of tris(pentafluorophenyl)stibine with elemental fluorine in nitrogen (the F_2 to N_2 ratio was 1 to 20) has been found to give a 98% yield of the corresponding difluoride [41]:

$$(C_6F_5)_3Sb + F_2 \xrightarrow[-40°C]{CCl_3F} (C_6F_5)_3SbF_2$$

The colorless compound thus obtained was soluble in organic solvents, was air-stable, and possessed spectroscopic properties in agreement with those in the literature. An attempt to prepare the difluoride by the interaction of tris(pentafluorophenyl)antimony dichloride and cesium fluoride was unsuccessful but afforded the tris(pentafluorophenyl)trifluoroantimonate anion:

$$(C_6F_5)_3SbCl_2 + 3CsF \xrightarrow{MeOH} Cs[(C_6F_5)_3SbF_3] + 2CsCl$$

The same complex was formed in good yield by the following addition reaction:

$$(C_6F_5)_3SbF_2 + CsF \xrightarrow{MeOH} Cs[(C_6F_5)_3SbF_3]$$

The substance was a colorless solid, which was not sensitive to air or moisture. Its ^{19}F NMR spectrum supported the conclusion that the $(C_6F_5)_3SbF_3^-$ anion had the *mer* configuration. The adduct was also characterized by a molecular weight determination (which showed that the

substance was a 1:1 electrolyte in acetonitrile) and by Raman spectroscopy. A later paper from the same laboratory described the preparation of tris(pentafluorophenyl)antimony difluoride by the use of xenon difluoride [42]:

$$(C_6F_5)_3Sb + XeF_2 \xrightarrow[-30°C]{MeCN} (C_6F_5)_3SbF_2 + Xe$$

The colorless product was formed in quantitative yield and was spectroscopically identical to the antimony difluoride obtained by the use of elemental fluorine.

Salts of the type $[Ph_3EI][AsF_6]$ have been prepared in high yields by oxidizing triphenylphosphine, -arsine, -stibine, or -bismuthine with iodine and then adding silver hexafluoroarsenate to the reaction mixture [43]:

$$Ph_3E \xrightarrow[THF, -78°C]{I_2} \xrightarrow{AgAsF_6} [Ph_3EI]\,[AsF_6]$$

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

All of the salts were characterized by PMR, IR, and Raman spectroscopy. Direct evidence for the E-I bond was found in all four Raman spectra. For example, the Raman spectrum of the antimony compound exhibited a peak at 183.5 cm^{-1} that was assigned to $\nu_{Sb\text{-}I}$. The IR of all four salts had peaks that were assigned to $\nu_{As\text{-}F}$ and $\delta_{As\text{-}F}$. With the exception of the bismuth compound, the salts were stable for several days at room temperature in an inert atmosphere.

A study has been made of some of the electrochemical properties of complexes of iodine with triphenylamine, -phosphine, -arsine, or -stibine [44]. The maximum uptake of iodine by each of the triphenyl compounds was determined by placing both reactants in an evacuated tube with contact between them only in the gas phase. In this way, it was found that the maximum amount of I_2 absorbed per mol of triphenylstibine was 5.9 mol; the time required for equilibration was 25 days. Other compositions of triphenylstibine-iodine were prepared by thoroughly mixing and grinding weighed amounts of the two substances, sealing them in evacuated glass tubes, and keeping them at room temperature for 48 h. Up to an I_2/Ph_3Sb mol ratio of 1.5, only solid materials were observed. From an I_2/Ph_3Sb ratio of 1.5 to 3.5, a mixture of solid and liquid was present. Between 3.5 and the saturation value, the materials were liquid. Free energies of complex formation were determined from EMF data obtained from solid electrochemical cells with an AgI electrolyte. The cells were of the type $Pt|Ph_3Sb(I_2)_x|AgI|Ag|Pt$, where x was the mol ratio of I_2 to triphenylstibine. The free energy of formation of the complex at the maximum I_2/Ph_3Sb ratio was found to be 25 kJ/mol I_2. Electrical conductivities of the solid complexes of triphenylstibine and iodine were very low ($<10^{-5}$ ohm^{-1} cm^{-1}). The liquid complex had a higher conductivity and might have been expected to be an ionic conductor. The observation that a.c. and d.c. measurements on this complex yielded identical results indicated, however, that there was a significant electronic contribution to the conductivity.

3,5-Dinitrobenzoyl derivatives of antimony(V) have been prepared by the oxidative

addition of the benzoyl chloride to triarylstibines [45]:

$$Ar_3Sb + RCOCl \longrightarrow Ar_3Sb(COR)Cl$$

(where Ar was Ph or 4-MeC_6H_4 and R was 3,5-$(O_2N)_2C_6H_3$)

The reactions were carried out by refluxing equimolar quantities of the reactants in benzene or dichloromethane for 5 h. The benzoyl derivatives were pale yellow solids, which were soluble in benzene, chloroform, and dichloromethane, and were shown to be nonionic in solution. The molar conductances of 10^{-3}M solutions of these substances in acetonitrile were very low (4 - 7 ohm^{-1} mol^{-1} cm^2) and showed that there was little, if any, ionization. The relatively low melting points of the compounds were also consistent with non-ionic structures. The carbonyl stretching frequencies in the IR spectra were in the 1660 - 1670 cm^{-1} range. The antimony-acyl bond was found to be stable to methyl iodide and methyl alcohol. The triphenylantimony derivative also failed to react with cadmium perchlorate in refluxing dichloromethane. In contrast to 3,5-dinitrobenzoyl chloride, other acyl halides investigated (benzoyl chloride, acetyl chloride, and chloroacetyl chloride) did not form addition products with triphenylstibine.

The interaction of equimolar amounts of triphenylstibine and nitric acid in acetic anhydride at 0°C has been shown to yield triphenylantimony diacetate [46]:

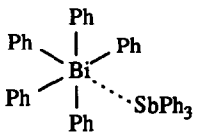
$$Ph_3Sb \xrightarrow[(MeCO)_2O]{HNO_3} Ph_3Sb(O_2CMe)_2$$

The product was characterized by PMR and mass spectroscopy. It was suggested that triphenylstibine was oxidized by the nitric acid to triphenylstibine oxide, which then reacted with the acetic anhydride to give the diacetate. Treatment of triphenylstibine oxide with acetic anhydride did in fact produce the diacetate; heating the latter compound *in vacuo* reconverted it to the oxide.

The interaction of pentaphenylbismuth and triphenylstibine in toluene has been found to give a 43% yield of pentaphenylantimony [47]:

$$Ph_5Bi + Ph_3Sb \xrightarrow{20°C} Ph_5Sb + Ph_3Bi$$

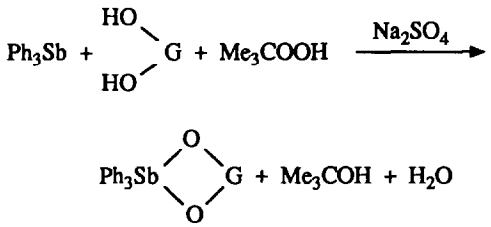
The intermediacy of the following hexacovalent intermediate was postulated:

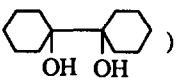


A much lower yield of a pentaarylantimony derivative was obtained when a tritolylstibine was allowed to react with pentaphenylbismuth. The bismuth reagent effected no observable phenylation of bulky tertiary stibines containing three naphthyl or cymantrenyl groups. Further

information about this work is discussed in the Annual Survey of Bismuth.

The reaction of triphenylstibine with vicinal diols in the presence of *tert*-butyl hydroperoxide has been employed to prepare seven heterocyclic derivatives of antimony [48]:



(where G was CH_2CH_2, CHMeCHMe, CMe_2CMe_2, CPh_2CPh_2, $CH_2CH(CH_2OH)$, or 1,2-C_6H_4, or where HOGOH was 

)

The yields ranged from 71 - 91%.

Trimethylstibine has been included in a study of the influence of two different carrier gases (hydrogen and helium) on the temperature required for the onset of pyrolysis of twelve organometallic compounds [49]. As a general rule, the compounds began to pyrolyze at lower temperatures in hydrogen than in helium. For example, the onset temperature for trimethylstibine was 394°C in hydrogen and 436°C in helium. In the case of dimethyl ditelluride, however, pyrolysis in hydrogen began at a temperature 42° higher than pyrolysis in helium.

Tributylstibine has been used in the preparation of alumina-supported bimetallic catalysts of palladium alloyed with antimony [50]. The tertiary stibine was deposited on the palladium-on-alumina and subsequently reduced to metallic antimony in a hydrogen atmosphere at 573 or 773 K. The usefulness of these catalysts for the hydrogenation of isoprene was then explored.

A process known as molecular-beam epitaxy (MBE) has been employed for the preparation of thin semiconducting films of gallium antimonide [51]. Trimethylstibine used as the source of the antimony was found to decompose effectively at cracking temperatures higher than 800°C. The films thus obtained were said to have a mirror-like surface.

Triphenylstibine admixed with molybdenum(V) chloride, tungsten(VI) chloride, or niobium(V) chloride has been employed to catalyze the polymerization of 3-(hexyldimethylsilyl)-1-hexyne and 3-(dimethylphenylsilyl)-1-hexyne [52]. The best results were obtained when the stibine and molybdenum compound were used in a 1:1 ratio. Triphenylstibine has also been claimed to be a catalyst for the disproportionation of halosilanes of the type H_nSiX_{4-n}, where X was a halogen and n was 1, 2, or 3 [53], a beneficial component of photohardenable electrostatic masters, which could be employed for electrostatic proofing and similar purposes [54], and a cocatalyst for the preparation of aryl esters of carboxylic acids [55]. Other tertiary stibines were said to be useful as components of organometallic catalysts for reactions such as low-pressure hydroformylation [56].

A study has been reported of the UV absorption and magnetic circular dichroism of phosphabenzene, arsabenzene, and stibabenzene (the phosphorus, arsenic, and antimony analogs of pyridine) [57]. The lowest energy transition in each molecule was attributed to an $n\pi$ state. Three $\pi\pi^*$ transitions were also identified and were related to the L_b, L_a, and B_b states of the aromatic sextet. It was concluded from an analysis of orbital splittings that the effective π-orbital electronegativities of the phosphorus, arsenic, and antimony atoms in these compounds were higher than that of carbon. Thus, these heteroatoms appeared to be acting as π-electron acceptors while at the same time acting as σ-electron donors.

A critical analysis has been published of the closed- and open-shell configurations of heterocyclobutadienes of the following type [58]:

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

The definition of topological resonance energy (TRE) was modified, and new TRE values were calculated for both kinds of configuration. The quantum chemical parameters of these molecules and of their acylic counterparts were also evaluated.

Relationships have been developed that permitted the calculation of the steric effects of substituents bonded to sulfur, phosphorus, arsenic, or antimony [59]. The steric substituent constants, $R_S(Sb)$, of 25 atoms or groups bonded to antimony ranged from 0.24 for H to 2.18 for Et_2CH. The substituent constant for a given atom or group decreased as the size of the heteroatom increased. A strict linearity was observed between the steric effect of substituents on each of the four heteroatoms and the steric effect of the same substituents on carbon. Thus, for antimony the following equation was obeyed:

$$R_S(Sb) = 0.208 + 0.704R_S(C)$$

There have been numerous recent publications that mentioned the use of tertiary stibines as ligands in transition metal complexes. The metals coordinated to the antimony in these complexes included cobalt [60], copper [61], europium [62], iron [63-65], manganese [66,67], molybdenum [68-73], osmium [74], palladium [75], platinum [76,77], rhodium [78-82], ruthenium [79, 83-87], and tungsten [70, 71, 73]. The reaction of triphenylstibine with pentakis(2,6-dimethylphenylisocyanide)cobalt(II) perchlorate hemihydrate has also been studied [88].

Differential UV spectroscopy has been employed to study the 1:1 complexes of antimony tribromide with the following aromatic donors: benzene, toluene, *o*-xylene, *m*-xylene, 1,2,4-trimethylbenzene, durene, pentamethylbenzene, hexamethylbenzene, and hexaethylbenzene [89]. This procedure made it possible to identify the charge-transfer bands associated with complex formation. A linear relationship was observed between the position of the edge of the absorption band and the ionization potential of the organic ligand.

Workers in another laboratory have recorded the Raman spectra of the 2:1 complexes of antimony trichloride with benzene, benzene-d_6, toluene, *o*-xylene, *m*-xylene, *p*-xylene, mesitylene, and durene [90]. The observed complex-induced frequency shifts of vibrations belonging to the aromatic hydrocarbons were discussed in terms of the reduction of electronic charge on the ring framework and the greater amount of vibrational coupling upon complex formation. Vibrational coupling was observed between C=C stretching vibrations and internal modes of the methyl groups as well as between C-H stretching vibrations of the ring and the methyl groups. The postulated reduction of electronic charge was said to be directly related to the observed changes in the C-H stretching and out-of-plane vibrations of the ring as well as in the tangential C=C stretching vibrations.

A number of papers on the crystal and molecular structures of organoantimony(V) compounds from Sowerby's laboratory in England have been published. The present paper [91] deals with the crystal structure of the hydrate, $Ph_2SbCl_3 \cdot H_2O$, which can be readily obtained by crystallizing the anhydrous chloride from acetonitrile containing *ca.* 5% water. However, when Ph_2SbBr_3 was recrystallized from the same aqueous solvent, a 1:1 addition compound, $Ph_2SbBr_3 \cdot MeCN$, rather than the hydrate, was obtained. This addition compound was unstable, and rapidly lost MeCN at room temperature. The IR spectrum of the complex gave bands at 2270 and 2996 cm^{-1}, assigned to coordinated MeCN. The PMR spectrum of the complex in $CDCl_3$ gave peaks at δ 1.71 and 1.99, assigned to coordinated and free MeCN. A similar complex, $Ph_2SbCl_3 \cdot MeCN$ was obtained by recrystallizing the dimer $(Ph_2SbCl_3)_2$ from anhydrous MeCN. This too was unstable and rapidly lost MeCN at room temperature. The IR spectrum of this complex gave bands at 2276 and 2303 cm^{-1}, consistent with coordinated MeCN, and peaks at δ 1.57 and 2.00 in the PMR spectrum, consistent with coordinated and free MeCN. All attempts to prepare a hydrate of Ph_2SbBr_3 were unsuccessful. An X-ray diffraction study of $Ph_2SbCl_3 \cdot H_2O$ showed that the geometry around the Sb atom was somewhat distorted octahedral. The two phenyl groups were *trans* to each other. There were two independent Sb-Cl distances, 2.361 and 2.462 Å, with the chloride *trans* to the water atom having the shorter distance. There was intermolecular hydrogen bonding, O-H-Cl, involving both hydrogen atoms of the water molecule. The authors suggested that the considerable stability of the hydrate (requiring heating to 100°C *in vacuo* to remove the water molecule) could be attributed to this hydrogen bonding. The X-ray structure determination of $Ph_2SbBr_3 \cdot MeCN$ revealed that the geometry around the Sb atom was also essentially octahedral with an Sb-N bond. The Sb-Br bond *trans* to the MeCN was somewhat shorter (2.519 Å) than the independent Sb-Br distances (2.605 Å), and the Sb-N distance (2.53 Å) was long and presumable weak. There was some distortion of the octahedral geometry in that the Br-Sb-N angle was 82.8°, leading to a Br-Sb-Br angle of 93.5°.

The crystal structures of the complexes $SbCl_5 \cdot DPSO$ and $Ph_2SbCl_3 \cdot DPSO$ (where DPSO was diphenylsulfoxide) have been determined [92]. The Sb-Cl bond lengths were somewhat longer in the latter complex.

The interesting organoantimony(V) compound, $[Bu_4N]_2[Ph_2SbO(MoO_4)]_2$, has been prepared by Liu and coworkers [93]. It was obtained by adding diiodotriphenylantimony in dichloromethane to an excess of tetrabutylammonium molybdate in methanol-dichloromethane.

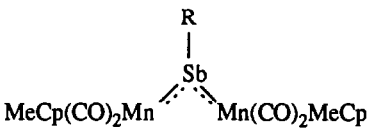
The addition of diethyl ether then produced microcrystals which were removed by filtration and dissolved in acetonitrile. The addition of benzene gave colorless crystals of the organoantimony(V) molybdate. The crystal and molecular structure of the compound was determined by X-ray diffraction. The compound was centrosymmetric and contained a planar 8-membered ring formed from two octahedral Ph_2SbO_4 groups and two tetrahedral MoO_4 groups, by sharing 4 oxygen atoms alternately. The two organoantimony octahedra were joined together by edge sharing, and the benzene rings protruded out of the 8-membered ring.

In a second paper from the same laboratory, the preparation of a different product, $[Bu_4N]_2[Ph_3Sb(MoO_4)_2]\cdot 3H_2O$, was described [94]. This was obtained by adding diiodotriphenylantimony in dichloromethane to two molar equivalents of tetrabutylammonium molybdate in methanol solution. Addition of diethyl ether to the resulting solution precipitated the product which was recrystallized from acetonitrile-ether. It was characterized by elemental analyses, IR, UV, and PMR spectroscopy.

In two papers devoted to the formation of metal-element double bonds by chlorosilane elimination, Schubert and coworkers [66, 67] reported that the reaction of Ph_3SbBr_2 or Ph_3AsCl_2 and the manganese complex $[MeCp(CO)_2MnSiMePh_2]^-$ (where Cp was cyclopentadienyl) occurred instantaneously to give compounds containing manganese-antimony or manganese-arsenic bonds:

$$[MeCp(CO)_2MnSiMePh_2]^- + Ph_3SbBr_2 \longrightarrow MeCp(CO)_2MnSbPh_3 + Ph_2MeSiBr + Br^-$$

Dihalostibines reacted to form dinuclear stibinidene-bridged complexes of the following type [66]:



The crystal and molecular structure of μ-oxo-bis[bromotriphenylantimony(V)] has been determined by Ouchi and Sato [95] by means of X-ray diffraction. The compound was prepared by treating dibromotriphenylantimony in benzene solution with triethylamine and traces of water. The resulting compound, $(Ph_3SbBr)_2O$, was recrystallized from acetonitrile. There were 8 molecules in the unit cell. There were,however, two crystallographic independent molecules, both of which contained trigonal-bipyramidal antimony atoms with the phenyl groups in equatorial positions and the bromine atoms in axial positions. The two antimony atoms were linked by an oxygen atom axial to the two antimony atoms. The two independent molecules differed principally in the Sb-O-Sb angle, which was 170.2° in one molecule and 176.8° in the other molecule. The Sb-Br bond distances were longer than the sum of the covalent radii while the Sb-O distances were considerably shorter.

Previous X-ray diffraction studies of the compounds $Ph_3Sb(O_2CMe)_2$ and $Ph_3Sb(O_2CPh)_2$ have shown that the (C=)O-Sb distances were considerably less than the sum of the covalent radii and indicated weak bond formation between the carbonyl oxygens and the

antimony atom. Domagala and coworkers [96] have now investigated a number of compounds of the type $R_3Sb(O_2CR')_2$, where R was Me, cyclohexyl, Ph, 4-$MeOC_6H_4$, 4-FC_6H_4, and 2,4,6-$Me_3C_6H_2$, and where R′ was a heterocylic ring (2-furyl, 2-thienyl, 2-pyrryl, and 2-(*N*-methyl)pyrryl), in the expectation that these compounds might possess structures which approached pentagonal bipyramidal, *i.e.* the antimony might have a coordination number of seven. A total of 27 new organoantimony(V) compounds were prepared. Two different synthetic methods were employed. In one method compounds of the type R_3SbO or $R_3Sb(OH)_2$ were treated with the requisite carboxylic acid in a 1:2 molar ratio in chloroform solution. In the second method dibromotricyclohexylantimony was treated with silver oxide and two molar equivalents of the requisite carboxylic acid in aqueous acetone. The new compounds were characterized by elemental analyses, IR spectra, and, with a few compounds, Raman spectra and molecular weight determinations. Ten new organobismuth(V) compounds, described in the organobismuth section in this Journal, were also prepared. For all of these compounds the IR bands νC=O and νC-O (in cm^{-1}), both in the solid state and in solution ($CHCl_3$ or CS_2), were tabulated. In addition the differences, νC=O - νC-O, in the solid state ($\Delta\nu_F$) and in solution ($\Delta\nu_L$) were calculated. Finally the differences, $\Delta\nu_L$ - $\Delta\nu_F$ were listed. With the exception of the tricyclohexyl and trimesityl compounds, the νC=O bands were displaced towards lower wave numbers in the compounds in the solid state as compared with those in solution. By contrast the νC-O bands were shifted to higher wave numbers in the solid state. Again, except for the tricyclohexyl and trimesityl compounds, the νC=O - νC-O differences were smaller in the solid state than in solution (*i.e.* νC=O - νC-O was positive). The authors interpreted these results as indicating that the carbonyl oxygens reacted weakly with the antimony atom to give it a formal coordination number of seven. With the bulky cyclohexyl and trimesityl compounds, however, the $\Delta\nu_L$- $\Delta\nu_F$ values were negative. This result suggested that there was no interaction between the carbonyl oxygens and the antimony atom in these compounds.

In the compounds other than those where R was cyclohexyl or mesityl, the $\Delta\nu_L$- $\Delta\nu_F$ values were found to vary with the nature of R. Thus, where R was Me the values varied from 9-24 cm^{-1}, but were from 27-49 cm^{-1} where R was 4-$MeOC_6H_4$, from 30-62 cm^{-1} where R was Ph, and from 50-65 cm^{-1} where R was 4-FC_6H_4. The authors attributed these results to the inductive effect of the R group on the Lewis acidity of the antimony atom.

In addition to the IR (and some Raman) spectral results, an X-ray diffraction study of the compound $Ph_3Sb(O_2CR')_2$, where R′ was 2-thienyl, was carried out. The molecule could be considered as a greatly distorted trigonal bipyramid with the acyloxy groups in axial positions. The (C=)O-Sb distances (274.4 and 294.9 pm) were considerably shorter than the sum of the covalent radii (360 pm). One C-Sb-C angle was increased to 145.9°, while the other C-Sb-C angles decreased to 104.4° and 109.5°. The structure of the molecule thus tended towards a distorted pentagonal bipyramid, with four oxygen atoms and a carbon atom place equatorially and two carbon atoms place axially.

Nomura and coworkers [97] have previously reported that organoantimony(V) compounds $Ph_3Sb(O_2CR)_2$ reacted with amines to produce amides and triphenylstibine oxide:

$$Ph_3Sb(O_2CR)_2 + 2R'NH_2 \longrightarrow 2RCONHR' + Ph_3SbO + H_2O$$

References p. 82

Further work showed that triphenylstibine oxide would serve as a catalyst for the production of amides:

$$RCO_2H + R'NH_2 \xrightarrow{Ph_3SbO} RCONHR' + H_2O$$

The same research group [98] has now reported on the use of triphenylstibine oxide, both as a reactant and as a catalyst, for the formation of dipeptides. Triphenylstibine oxide was treated with the stoichiometric amount of an *N*-protected amino acid in acetone solution to produce the bis(acyloxy)triphenylantimony compounds $Ph_3Sb(O_2CR)_2$. The *N*-protected amino acids used were derived from glycine, phenylalanine, and leucine, and the *N*-protecting group was benzyloxycarbonyl. With phenylalanine, the compound with a benzoyl-protected amino group was also prepared. Yield data, mps, and some ^{13}C NMR and IR data for the four compounds were listed. The three compounds with a benzyloxycarbonyl-protected amino group were then treated with an amino compound in a solvent to form the amide and triphenylstibine oxide. Several different solvents were used, chloroform, triethylamine or a mixture of the two. The amines used were hexylamine and the ethyl esters of glycine and leucine. A yield of 93% amide was obtained from hexylamine (in 20 fold excess and no solvent) and benzyloxycarbonyl *N*-protected glycine. With the ethyl esters of glycine and leucine, ethyl esters of the dipeptides glycylglycine, glycylleucine, and phenylalanineleucine, with the benzyloxycarbonyl-protected amino groups still intact, were obtained. The glycylleucine dipeptide compound was obtained in 95% yield when the solvent was chloroform-triethylamine. Since triphenylstibine oxide and carboxylic acids react to form bis(acyloxy)triphenylantimony compounds, the use of triphenylstibine oxide as an amidation catalyst was investigated. The reaction of glycine ethyl ester and benzyloxycarbonyl *N*-protected glycine reacted to produce a 100% yield of the dipeptide derivative when catalyzed by 25 mol % of triphenylstibine oxide. The solvent was chloroform-DBU. The same ester and benzyloxycarbonyl *N*-protected phenylalanine gave a 51% yield of the dipeptide derivative. Five mol % of triphenylstibine oxide was used, and the solvent was chloroform-triethylamine.

The method described in the previous paper for the synthesis of dipeptides has been further improved by Nomura and coworkers [99]. They had previously found that triphenylstibine oxide was an excellent catalyst for converting thiocarboxylic acids into amides. This amidation reaction was then extended to amino acids by warming an *N*-protected amino acid with an amino acid ester in the presence of catalytic amounts of triphenylstibine oxide and phosphorous pentasulfide. In all but one reaction the *N*-protecting group was benzyloxycarbonyl and the ethyl esters of either glycine or leucine were used as the amine for the amidation reaction. The condensation reactions were carried out at 35 or 40°C over periods that ranged from 2 to 7 h. In a typical reaction 5 mmol of *N*-protected amino acid was stirred with 0.54 mmol of triphenylstibine oxide and 1 mmol of phosphorous pentasulfide at 50°C for 0.5-1 h in benzene solution. After cooling to room temperature, the amino acid ester and triethylamine (5.0 mmol of each) were added dropwise, and the product purified by extraction and recrystallization. Thus, from *N*-protected alanine and glycine ethyl ester, *N*-protected alanylglycine ethyl ester was prepared in 90% yield, and glycylglycine ethyl ester was obtained

in 83% yield. Only traces of the latter compound were obtained in the absence of triphenylstibine oxide or phosphorous pentasulfide. A total of seven different dipeptide ethyl esters were prepared by this procedure in yields ranging from 51-99%. It was also found that acetic acid was converted to thioacetic acid by stirring at 35°C in benzene solution with triphenylstibine oxide and phosphorous pentasulfide. The yield was quantitative. No reaction occurred between acetic acid and phosphorous pentasulfide in the absence of triphenylstibine oxide.

A comparison of hydrogen bonds and coordination bonds in a number of isostructural systems has been published [100]. Compounds of the type ArXH were compared with the compounds $ArXER_n$, where Ar was C_6H_4Y(Y = COR, NO_2, C_5H_4N, *etc.*), X was O, S, or N, and E was Hg, Sn, Pb, or Sb. The extent of the interaction of these substances with nitrogen, phosphorous, and oxygen bases was determined from IR and UV spectral data. It was concluded that, in spite of the great size and polarizability of ER_n groups, there was a great similarity between hydrogen bonds and coordination bonds. The antimony compounds included in this study were $4\text{-}O_2NC_6H_4SSbPh_4$ and $4\text{-}O_2NC_6H_4OSbPh_4$.

Equilibrium constants have been determined for the complexation of compounds of the type $4\text{-}O_2NC_6H_4OY$ and $4\text{-}O_2NC_6H_4SY$ (where Y was an organometallic group which included Ph_4Sb) and bases such as pyridine, triethylamine, and triphenylphosphine in benzene solution [101]. Differences between coordination with amines and the phosphine were consistent with hard and soft acid-base (HSAB) theory.

Aubagnac and coworkers [102] have studied the molecular structures of onium salts in which the cations were Ph_4P^+, Ph_4As^+, and Ph_4Sb^+, and the anion was Ph_4B^-. Also included in the study were the compounds $NaBPh_4$, Ph_4PBr, Ph_4AsCl, and Ph_4SbBr. The authors were interested in discovering the effect of increasing the ionic radius of the anion and/or cation on the structure of salts in which both the anion and cation were monovalent. The compound [Ph_4Sb] [Ph_4B] had not been previously reported. It was prepared from Ph_4BNa and Ph_4SbBr, and was characterized by elemental analyses and IR spectroscopy. Elemental analyses and IR spectra were also given for [Ph_4B] [Ph_4As] and [Ph_4B] [Ph_4P]. The compounds were studied in the solid state (X-ray diffraction), in solution (^{11}B, ^{13}C, ^{31}P, and ^{75}As NMR), and in the gas phase (positive ion fast atom bombardment mass spectrometry). Although the crystal structures of the Ph_4P^+, Ph_4As^+, Ph_4Sb^+, and Ph_4B^- ions (where the corresponding counterions were small) are well known from a number of previous studies, and no anomalies have been reported, the present authors were unable to obtain satisfactory crystal structures for the phosphonium, arsonium, or stibonium tetraphenylborates (apparently due to the disordered character of the crystals). The NMR results were normal. The main difference between the simple ions, Na^+, Br^-, and Cl^-, and the onium tetraphenylborates was an effect on the *para* carbon atom in the ^{13}C NMR spectra. Thus, δC_4 = 131.3 for Ph_4SbBr and δC_4 = 132.4 for [Ph_4Sb] [Ph_4B]. The positive ion fast atom bombardment mass spectra of the four compounds $NaPh_4B$, Ph_4PBr, Ph_4AsCl, and Ph_4SbBr were recorded and the results discussed. However, the three onium tetraphenylborates did not give significant results. No ions of the cationic or anionic parts were recorded in the positive or negative modes. Two possible explanations were offered for these results: (a) when the counterion size was similar to that of the ion, cleavage of the crystal lattice

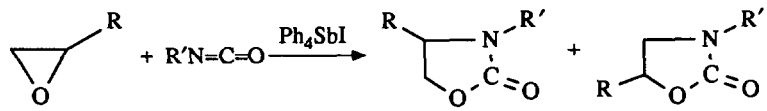
became very difficult or (b) when the difference in electronegativity between the ion and counterion was small, the compounds had a low polar character.

An X-ray diffraction study of the peroxide $Ph_4SbOOCMe_3$ revealed that the antimony atom possessed a trigonal-bipyramidal configuration [103].

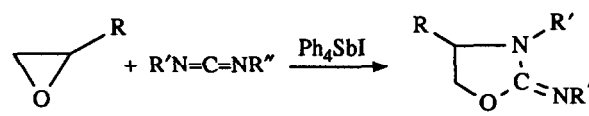
Previous reports from Sowerby's laboratory have shown that there was considerable interaction between a carbonyl oxygen and the antimony atom in triphenylantimony diacetate, but that there was only weak interaction involving the carbonyl oxygen and antimony in tetraphenylantimony formate. IR evidence, however, has suggested that tetraphenylantimony acetate probably contained a bidentate acetate group. Bone and Sowerby [104] have now determined the crystal structure of tetraphenylantimony acetate. The geometry of the antimony atom was that of a greatly distorted trigonal bipyramid, with one phenyl group and an oxygen in axial positions. The O-Sb-C_{axial} angle was 169.8°. There was a strong interaction between the carbonyl oxygen and the antimony atom. This O-Sb distance, 2.858 Å, was considerably shorter than the Sb-O (carbonyl) distance in triphenylantimony diacetate.

Tetraphenylantimony acetate formed a 1:1 crystalline adduct with acetic acid. An eight-membered heterocyclic ring structure has been suggested by previous workers for this compound. Bone and Sowerby have now determined the crystal structure of this adduct. The antimony was essentially a trigonal bipyramid but the Sb-O (carbonyl) distance, 3.307 Å, was considerably longer than in tetraphenylantimony acetate. The acetic acid molecule was hydrogen bonded to the acetate carbonyl oxygen, and was orientated away from the Ph_4Sb unit.

Previous papers from Matsuda's laboratory have reported on the unique catalytic activity of tetraphenylantimony iodide in condensation reactions for the production of heterocyclic ring systems. A new paper [105] from the same laboratory dealt with the use of tetraphenylantimony iodide for the condensation of oxiranes with isocyanates to produce mixtures of 3,4- and 3,5-disubstituted oxazolidine-2-ones (both α- and β-cleavage of the oxirane ring):

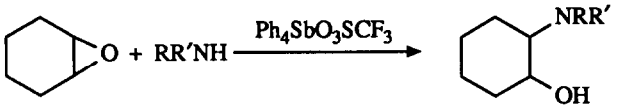


It was also found that tetraphenylantimony iodide catalyzed the reaction of oxiranes with carbodiimides to yield only 3,4-disubstituted oxazolidine-2-imines:

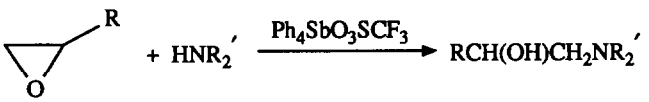


The authors stated that this was the first example of the cycloaddition of heterocumulenes via the selective α-cleavage of oxirane rings. The oxazolidine-2-imines were readily hydrolyzed under acid conditions to producce oxazolidine-2-ones, and under alkaline conditions to produce β-aminoalcohols.

A second paper [106] from Matsuda's laboratory described the use of tetraphenylantimony trifluoromethanesulfonate as a catalyst for the condensation of oxiranes with primary and secondary amines to produce β-amino alcohols. This catalyst proved to be more efficient for the condensation than tetraphenylantimony iodide. Thus, cyclohexene oxide reacted with a number of amines to produce 2-aminocyclohexanols:



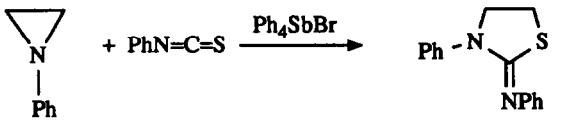
Both primary amines (aniline and benzylamine) and secondary amines (diethylamine, piperidine, and pyrrolidine) were used in the above reaction. Only *trans*-amino alcohols were obtained. Although tetraphenylantimony iodide was only slightly less effective as a catalyst than the trifluoromethyl compound, no reaction occurred when tetraphenylantimony chloride was used. Nor did the reaction proceed in the absence of a catalyst. In addition to cyclohexene oxide, the condensation of amines with mono-substituted oxiranes catalysed by tetraphenylantimony trifluoromethanesulfonate was studied:



(where R was Me, Ph, OMe, OAc, or OCOC(Me) = CH_2)

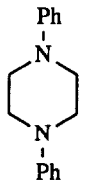
With one exception, the reaction was completely regiospecific in that the only product was that obtained by β-cleavage of the oxirane ring. However, when R was Ph and R′ was Et, a mixture of 2-diethylamino-1-phenylethanol (65%) and 2-diethylamino-2-phenylethanol (35%) was obtained. All of the above reactions were carried out in dichloromethane. In the case of cyclohexene oxide and diethylamine, when methanol was used as the solvent, no reaction occurred. The authors speculated on the mechanism of the reaction involving the catalytic activity of the stibonium compound in the condensation of amines with oxiranes to produce amino alcohols.

The use of organoantimony halides as catalysts for the cycloaddition of heterocumulenes to strained ring compounds by regioselective ring opening was then extended to the reaction of heterocumulenes (isothiocyanates, carbon disulfide, and carbon dioxide) with substituted aziridines [107]. The products of the reaction were 1,3-thiazolidines when the heterocumulene was phenylisothiocyanate:



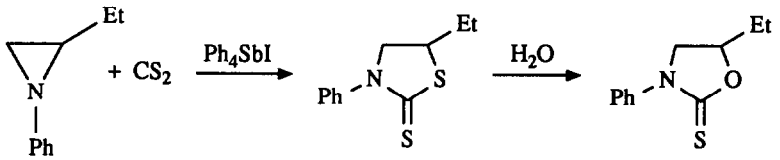
III

The reaction was carried out at 80-100°C with 0.1 molar equivalent of the antimony compound as catalyst. If tributyltin iodide was used as the catalyst, a mixture of III (57%) and the piperizine compound IV (23%) was obtained.

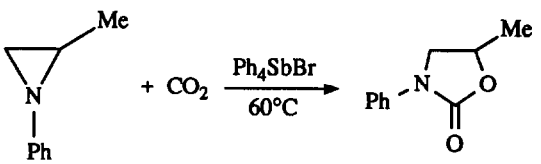


IV

Other aziridines used in this reaction were 1-phenyl-2-methyl-, 1-phenyl-2-ethyl-, and 1-butyl-2-ethylaziridine. The catalysts used were tetraphenylantimony bromide and iodide and dibromo- and dichlorotriphenylantimony. When the heterocumulene was carbon disulfide, the main product in the crude reaction mixture was a thiazolidinethione, but after work up only an oxazolidinethione was obtained:



With carbon dioxide a 1,3-oxazolidine-2-one was obtained:



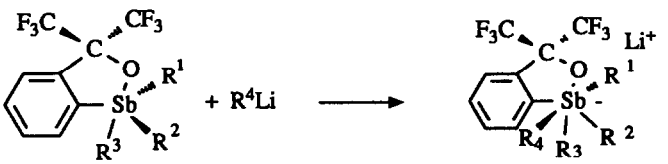
The reactions with both CS_2 and CO_2 were carried out in autoclaves.

The catalytic activity of tetraphenylantimony iodide was also extended to the condensation of heterocumulenes (carbon dioxide, phenylisocyanate, and diphenylcarbodiimide) with oxetanes [108]. Thus, oxetane and carbon dioxide were heated in an autoclave in the presence of 0.05 molar equivalent of tetraphenylantimony iodide to yield 1,3-dioxan-2-one in 96% yield. Oxetane was also found to react with a number of isocyanates at room temperature in a solvent (THF or benzene) to yield 1,3-oxazin-2-ones. A total of ten different alkyl or arylisocyanates were used, and the yields varied from 40 to 100%, with the largest yield obtained from methylisocyanate and the lowest yield from 2-chloroethylisocyanate. Three different carbodiimides (diphenyl, dimethyl, and methylphenyl) were found to react with oxetane to yield 1,3-oxaxin-3-imines in 99, 95, and 92% yields, respectively. The reactions were carried out by stirring the oxetane (10 mmol), the isocyanate or carbodiimide (5 mmol) with 0.5 mmol of tetraphenylantimony iodide in the appropriate solvent for periods that varied

from 2 to 65 h. The products were purified by column chromatography followed by distillation or recrystallization.

In addition to oxetane itself, several substituted oxetanes (2-Me, 3-Me, 3,3-di-Me, or 2-Ph) were condensed with carbon dioxide, or with methyl- or phenylisocyanate to yield substituted 1,3-dioxan-2-ones or 1,3-oxazin-2-ones, respectively. With isocyanates and 2-substituted oxetanes, two isomeric oxazines (4- or 6-substituted) were possible. With 2-methyloxetane and phenylisocyanate, only the 6-methyl derivative was obtained (*i.e.* ring fission occurred only at the unsubstituted site). With 2-phenyloxetane, however, and either methyl- or phenylisocyanate, mixtures of the 4- and 6-isomers were obtained, with the 4- isomer being predominant in both cases.

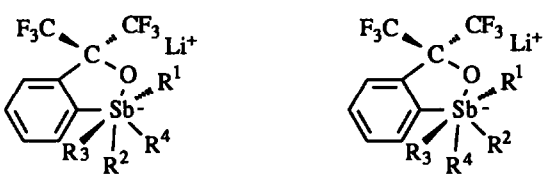
In two preliminary papers [109, 110] Akiba and coworkers have described the preparation of the benzoxastibole V and its conversion to an ate complex VI with methyllithium:



V VI

(where R^1, R^2, and R^3 were 4-tolyl and R^4 was Me)

This reaction was carried out at -78°C and the product was assigned structure VI on the basis of its ^{19}F NMR spectrum (two quartets). When the reaction mixture was warmed to -20°C, a new singlet appeared in the ^{19}F spectrum to which structure VII was assigned. Finally, at ~0°C a third singlet appeared to which structure VIII was assigned.

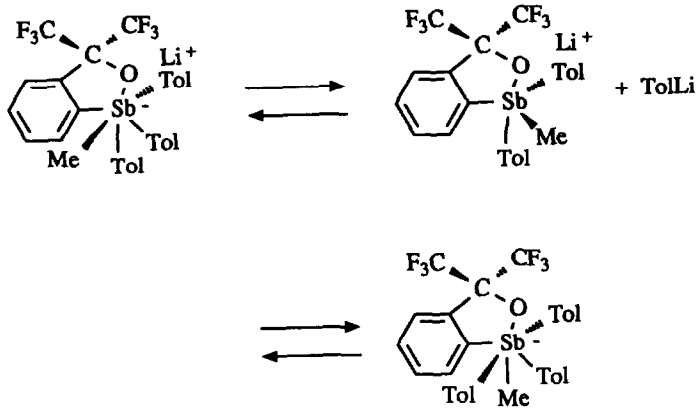


VII VIII

At equilibrium the ratio of VI:VII:VIII was found to be 61:23:16. Several suggestions were considered for the mechanism of the equilibration, but no definite conclusions were established. A new paper [111] from Akiba's laboratory has greatly expanded the earlier work. A total of eleven benzoxastiboles of type V (where R^1, R^2 and R^3 were groups such as Me, Ph, or various substituted phenyl groups) were synthesized. From these benzoxastiboles, eight different "ate" complexes of type VI (VII and VIII) were prepared. For compound VI ($R^1 = R^2 = R^3$ = 4-tolyl, R^4 = Me), the NMR evidence clearly established the assigned structure, but there was no chemical evidence for the assignments for VII and VIII, and in the new paper the assignments

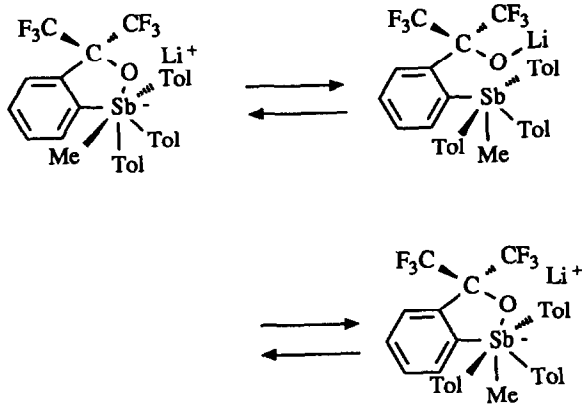
from the earlier papers (given above) were reversed, *i.e.* VI:VIII:VII = 63:23:16 at equilibrium. The same equilibrium mixture was established when compound V (R^1 = Me, R^2 = R^3 = 4-tolyl) was converted to an "ate" compound by treatment with 4-tolyllithium. In order to study the electronic effect of substituents on the equilibrium, VI ⇄ VII ⇄ VIII, compound VI (R^1 = R^2 = R^3 = 4-tolyl, R^4 = 4-$CF_3C_6H_4$), was prepared from V (where R^1 = R^2 = R^3 = 4-tolyl) and 4-$CF_3C_6H_4Li$. The product when the reaction was carried out at -78°C, possessed structure VI (R^4 = 4-$CF_3C_6H_4$) exclusively (as shown by high-field ^{19}F NMR, 470 MHz), and isomerization to structures VIII and VII proceeded very slowly even at 25°C. After 66 h the ratio VI:VIII:VII was 74:6:20. When compound V (R^3 = 4-$CF_3C_6H_4$, R^1 = R^2 = 4-tolyl) was treated with 4-tolyllithium at -78°C, compounds VIII, VII, and VI (R^4 = 4-$CF_3C_6H_4$, R^1 = R^2 = R^3 = 4-tolyl) were obtained in a ratio of 70:13:17, and the ratio became 11:38:51 after 32 h. It was concluded that the thermodynamic stability falls in the order VI > VII > VIII, *i.e.*, the isomer that bears the electronegative $CF_3C_6H_4$ group *anti* to the oxygen as the least stable isomer. In support for these conclusions, *ab initio* calculations were carried out on three model species, H_5SbF^-, H_5SbOH^-, and $H_4SbF_2^-$. The results were in conformance with the previous conclusion that the compound with the $CF_3C_6H_4$ group *anti* to the oxygen would be the least stable. The authors also studied various compounds of type VI where R^1 = R^2 = R^3 = 4-$CF_3C_6H_4$, and R^4 was phenyl or a substituted phenyl group (4-$MeOC_6H_4$, 4-MeC_6H_4, Ph, or 4-$CF_3C_6H_4$). It was found that the three singlets of the ^{19}F NMR spectra for R^1, R^2, and R^3 groups were shifted to higher fields as the electronegativity of the substituent on R^4 increased. From this result it was concluded that the apical oxygen atom was electron-withdrawing.

The authors next attempted to determine the mechanism for the isomerization VI ⇄ VIII ⇄ VII. It was first noted that the rate of isomerization VI ⇄ VIII at -20°C (R^1 = R^2 = R^3 = 4-tolyl, R^4 = Me) was independent of the amount of added methyllithium (more or less than one equivalent). This result ruled out attack of methyllithium at antimony in structure V to form a heptacoordinate intermediate, or an intermolecular equilibrium between V and VI. It was also found that an equilibrium mixture of VI and VIII at -20°C, when quenched with an excess of ethanol, led to a mixture of two compounds, V (R^1 = R^2 = R^3 = 4-tolyl, and R^1 = Me, R^2 = R^3 = 4-tolyl). The rate of quenching with ethanol was only one-tenth as fast as the equilibrium VI ⇄ VIII. This result was evidence against an intermolecular dissociative mechanism for the isomerization, since the 4-tolyllithium (or methyllithium) formed in the dissociation should react much faster with the ethanol than with V:



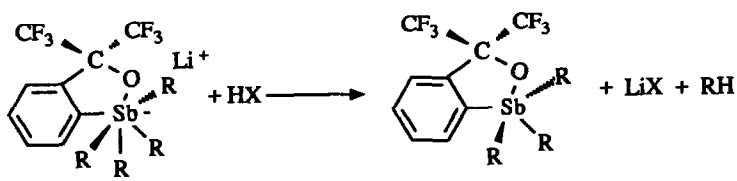
(where Tol was 4-MeC_6H_4)

It was also found that the isomerization did not occur in the presence of hexamethylphosphoric triamide and was greatly retarded in the presence of 12-crown-4. This result strongly suggested that the lithium ion played an important role in the isomerization and was in agreement with the following *dissociative mechanism:*



The participation of the lithium ion in the isomerization was also evidence for a non-dissociative mechanism for the isomerization VI ⇄ VIII ⇄ VII.

When a mixture of isomers of types VI, VII, and VIII was treated with water or a protic acid, an exocyclic Sb-C bond was cleaved to regenerate a benzoxastibole:



If the four R groups were not the same a mixture of RH compounds was obtained. The authors carried out a number of studies on this protonolysis reaction, using a variety of protic acids in addition to water. A mechanism for the protolysis was suggested.

REFERENCES

1 L.D. Freedman and G.O. Doak, *Chem. Met.-Carbon Bond*, **5** (1989) 397.
2 D.A. Armitage, *Chem. Org. Silicon Compd.*, **2** (1989) 1363.
3 P.D. Lickiss, *Annu. Rep. Prog. Chem., Sect. B*, **85** (1989) 241.
4 P.G. Harrison, *Annu. Rep. Prog. Chem., Sect. A*, **85** (1989) 69.
5 J.L. Wardell, *Organomet. Chem.*, **17** (1989) 130.
6 A.G. Massey, *Adv. Inorg. Chem.*, **33** (1989) 1.
7 A.G. Massey and R.E. Humphries, *Aldrichimica Acta*, **22** (1989) 31.
8 A.H. Cowley and R.A. Jones, *Angew. Chem., Int. Ed. Engl.*, **28** (1989) 1208.
9 K. Akiba, *Gendai Kagaku*, **219** (1989) 16; *Chem. Abstr.*, **111** (1989) 213935f.
10 D.R. Russell, *Organomet. Chem.*, **17** (1989) 406.
11 M.J. Went, *Organomet. Chem.*, **17** (1989) 145.
12 G.B. Stringfellow, *Organometallic Vapor-Phase Epitaxy*, Academic Press, San Diego, CA, 1989, pp. 183-184, 327-333.
13 M. Ates, H.J. Breunig, and S. Gülec, *Phosphorus, Sulfur Silicon Relat. Elem.*, **44** (1989) 129.
14 A.H. Cowley, R.A. Jones, C.M. Nunn, and D.L. Westmoreland, *Angew. Chem., Int. Ed. Engl.*, **28** (1989) 1018.
15 M. Ates, H.J. Breunig, S. Gülec, W. Offermann, K. Häberle, and M. Dräger, *Chem. Ber.*, **122** (1989) 473.
16 H.J. Breunig, *Phosphorus Sulfur*, **38** (1988) 97.
17 G. Becker, M. Meiser, O. Mundt, and J. Weidlein, *Z. Anorg. Allg. Chem.*, **569** (1989) 62.
18 S. Roller, M. Dräger, H.J. Breunig, M. Ates, and S. Gülec, *J. Organomet. Chem.*, **378** (1989) 327.
19 P. Raj, A.K. Aggarwal, and A.K. Saxena, *J. Fluorine Chem.*, **42** (1989) 163.
20 M. Ates, H.J. Breunig, and S. Gülec, *J. Organomet. Chem.*, **364** (1989) 67.
21 P. Jutzi and K.-H. Schwartzen, *Chem. Ber.*, **122** (1989) 287.
22 K. Ohkata, S. Takemoto, M. Ohnishi, and K. Akiba, *Tetrahedron Lett.*, **30** (1989) 4841.
23 S.L. Buchwald, R.A. Fisher, and W.M. Davis, *Organometallics*, **8** (1989) 2082.
24 P. Raj, A.K. Aggarwal, and N. Misra, *Polyhedron*, **8** (1989) 581.
25 R. Karra, Y.P. Singh, and A.K. Rai, *Phosphorus, Sulfur Silicon Relat. Elem.*, **45** (1989) 145.
26 R. Gupta, Y.P. Singh, and A.K. Rai, *Main Group Met. Chem.*, **12** (1989) 117.
27 S.K. Pandey, G. Srivastava, and R.C. Mehrotra, *J. Indian Chem. Soc.*, **66** (1989) 558.

28 M. Herberhold, K. Schamel, A. Gieren, and T. Hübner, *Phosphorus, Sulfur Silicon Relat. Elem.*, **41** (1989) 355.

29 D.H.R. Barton, D. Bridon, and S.Z. Zard, *Tetrahedron*, **45** (1989) 2615.

30 A.-R. Al-Soudani and A.G. Massey, *Appl. Organomet. Chem.*, **2** (1988) 553.

31 M.G. Voronkov, S.V. Basenko, V. Yu. Vitkovskii, S.M. Nozdrya and R.G. Mirskov, *Metalloorg. Khim.*, **2** (1989) 310: *Chem. Abstr.*, **112** (1990) 118988n.

32 T. Kemmitt and W. Levason, *Organometallics*, **8** (1989) 1303.

33 A.V. Severin and A.P. Batalov, *Radiokhimiya*, **30** (1988) 537.

34 D.H.R. Barton, N. Ozbalik, and M. Ramesh, *Tetrahedron*, **44** (1988) 5661.

35 Y.-Z. Huang, Y. Shen, and C. Chen, *Synth. Commun.*, **19** (1989) 83.

36 Y.-Z. Huang, C. Chen, and Y. Shen, *Synth. Commun.*, **19** (1989) 501.

37 C. Chen, Y. Liao, and Y.-Z. Huang, *Tetrahedron*, **45** (1989) 3011.

38 Y.-Z. Huang, C. Chen, and Y. Shen, *J. Organomet. Chem.*, **366** 1989) 87.

39 Y.-Z. Huang, C. Chen. F. Zhu, and Y. Liao, *J. Organomet. Chem.*, **378** (1989) 147.

40 C. Chen, F. Zhu, and Y.-Z. Huang, *J. Chem. Res., Synop.*, (1989) 381.

41 R. Kasemann and D. Naumann, *J. Fluorine Chem.*, **41** (1988) 321.

42 W. Tyrra and D. Naumann, *Can. J. Chem.*, **67** (1989) 1949.

43 I. Tornieporth-Oetting and Th. Klapötke, *J. Organomet. Chem.*, **379** (1989) 251.

44 S. Aronson and Y.R. Zhang, *Solid State Ionics*, **36** (1989) 81.

45 A. Asthana and R.C. Srivastava, *J. Organomet. Chem.*, **366** (1989) 281.

46 E. Maccarone, A. Passerini, R. Passerini, and G. Tassone, *Gazz. Chim. Ital.*, **119** (1989) 545.

47 V.V. Sharutin, *Zh. Obshch. Khim.*, **58** (1988) 2305.

48 V.A. Dodonov, S.N. Zaburdyaeva, and N.N. Nevkina, *Metalloorg. Khim.*, **2** (1989) 1296; *Chem. Abstr.*, **113** (1990) 6478k.

49 D.A. Jackson, Jr., *J. Cryst. Growth*, **94** (1989) 459.

50 H.R. Aduriz, P. Bodnariuk, B. Coq, and F. Figueras, *J. Catal.*, **119** (1989) 97.

51 H. Ito and T. Ishibashi, *Jpn. J. Appl. Phys., Part 1*, **27** (1988) 1554.

52 T. Masuda, K. Tsuchihara, K. Ohmameuda, and T. Higashimura, *Macromolecules*, **22** (1989) 1036.

53 S. Shimozaki and Y. Yoshimura, Jpn. Kokai Tokkyo Koho JP 01 122, 915 [89 122, 915]; *Chem. Abstr.*, **111** (1989) 216737d.

54 G.B. Blanchet-Fincher and C.R. Fincher, Jr., Eur. Pat. Appl. EP 315, 116; *Chem. Abstr.*, **111** (1989) 144075m.

55 Y. Nakajima and F. Matsunaga, Jpn. Kokai Tokkyo Koho JP 01 290, 652 [89 290, 652]; *Chem. Abstr.*, **112** (1990) 178332d.

56 J.L. Stavinoha, G.W. Phillips, T.A. Puckette, and T.J. Devon, Eur. Pat. Appl. EP 326, 286; *Chem. Abstr.*, **112** (1990) 98823z.

57 J. Waluk, H.-P. Klein, A.J. Ashe III, and J. Michl, *Organometallics*, **8** (1989) 2804.

58 R.K. Mishra and B.K. Mishra, *Chem. Phys. Lett.*, **151** (1988) 44.

59 V.I. Galkin, R.D. Sayakhov, R.A. Cherkasov, and A.N. Pudovik, *Dokl. Akad. Nauk SSSR*, **299** (1988) 884.

60 S. Nèmeth, L.I. Simándi, G. Argay, and A. Kálmán, *Inorg. Chem. Acta*, **166** (1989) 31.

61 E. Makanova and G. Ondrejovic, *Polyhedron*, **8** (1989) 2469.

62 G.F. Payne, O.L. Keller, J. Halperin, and W.C. Wolsey, *J. Chem. Soc., Chem. Commun.*, (1989) 50.

63 N.Y.M. Iha, H.E. Toma, and J. Farias de Lima, *Polyhedron*, **7** (1988) 1687.

64 G. Bellachioma, G. Cardaci, E. Colomer, R.J.P. Corriu, and A. Vioux, *Inorg. Chem.*, **28** (1989) 519.

65 M. Wieber and H. Höhl, *Z. Naturforsch., B: Chem. Sci.*, **44** (1989) 1149.

66 U. Kirchgässner and U. Schubert, *Chem. Ber.*, **122** (1989) 1481.

67 U. Schubert, U. Kirchgässner, J. Grönen, and H. Piana, *Polyhedron*, **8** (1989) 1589.

68 D. Schnurpfeil, U. Dittmar, K. Kramer, and R. Megdiche, *Z. Phys. Chem. (Leipzig)*, **269** (1988) 794.

69 R.T.C. Brownlee, B.P. Shehan, and A.G. Wedd, *Aust. J. Chem.*, **41** (1988) 1457.

70 P.K. Baker, S.G. Fraser, and T.M. Matthews, *Inorg. Chim. Acta*, **150** (1988) 217.

71 P.K. Baker and S.G. Fraser, *Transition Met. Chem.*, **13** (1988) 284.

72 P.K. Baker and A. Bury, *Polyhedron*, **8** (1989) 917.

73 P.K. Baker, M. Bamber, and G.W. Rogers, *J. Organomet. Chem.*, **367** (1989) 101.

74 M. Castiglioni, R. Giordano, and E. Sappa, *J. Organomet. Chem.*, **342** (1988) 97.

75 K.R. Nagasundara, N.M.N. Gowda, and G.K.N. Reddy, *Indian J. Chem., Sect. A*, **28A** (1989) 1001.

76 I.V. Gavrilova, M.I. Gel'fman, and N.V. Ivannikova, *Koord. Khim.*, **15** (1989) 679; *Chem. Abstr.*, **111** (1989) 145705d.

77 H.-A. Brune, R. Klotzbücher, and G. Schmidtberg, *J. Organomet. Chem.*, **371** (1989) 113.

78 R.J.H. Clark and A.J. Hempleman, *Inorg. Chem.*, **28** (1989) 92.

79 D.S. Pandey and U.C. Agarwala, *Inorg. Chim. Acta*, **159** (1989) 197.

80 M.M.T. Khan, B.T. Khan, and P.J. Reddy, *J. Mol. Catal.*, **54** (1989) 171.

81 K.-S. Shin, R.J.H. Clark, and J.I. Zink, *J. Am. Chem. Soc.*, **111** (1989) 4244.

82 S.P. Best, P. Chandley, R.J.H. Clark, S. McCarthy, M.B. Hursthouse, and P.A. Bates, *J. Chem. Soc., Dalton Trans.*, (1989) 581.

83 A. Mishra and U.C. Agarwala, *J. Chem. Soc., Dalton Trans.*, (1988) 2897.

84 L. Chen and A.J. Poë, *Inorg. Chem.*, **28** (1989) 3641.

85 V. Chauhan and S.K. Dikshit, *Synth. React. Inorg. Met.-Org. Chem.*, **19** (1989) 571.

86 M. Gupta, J. Seth, and U.C. Agarwala, *Synth. React. Inorg. Met.-Org. Chem.*, **19** (1989) 583.

87 M. Gupta, J. Seth, and U.C. Agarwala, *Bull. Chem. Soc. Jpn.*, **62** (1989) 3397.

88 C.A.L. Becker and J.C. Cooper, *Inorg. Chim. Acta*, **158** (1989) 141.

89 I.V. Makarov, V.V. Denisov, and G.V. Verevkin, *Zh. Neorg. Khim.*, **34** (1989) 1476.

90 H. Bettermann and H.-H. Perkampus, *Spectrochim. Acta, Part A*, **45A** (1989) 735.

91 T.T. Bamgboye, M.J. Begley, and D.B. Sowerby, *J. Organomet. Chem.*, **362** (1989) 77.

92 E.G. Zaitseva, S.V. Medvedev, and L.A. Aslanov, *Metalloorg. Khim.*, **1** (1988) 1360; *Chem. Abstracts*, **112** (1990) 36021e.

93 B. Liu, Y. Ku, M. Wang, B. Wang and P. Zheng, *J. Chem. Soc., Chem. Commun.*, (1989) 651.

94 B. Liu, A. Feng, and Y. Gu, *Huaxue Xuebao*, **47** (1989) 683.

95 A. Ouchi and S. Sato, *Bull Chem. Soc. Jpn.*, **61** (1988) 1806.

96 M. Domagala, F. Huber, and H. Preut, *Z. Anorg. Allg. Chem.*, **574** (1989) 130.

97 R. Nomura, T. Wada, Y. Yamada, and H. Matsuda, *Chem. Lett.*, (1986) 1901.

98 R. Nomura, Y. Yamada, and H. Matsuda, *Appl. Organomet. Chem.*, **2** (1988) 557.

99 R. Nomura, Y. Yamada, and H. Matsuda, *Appl. Organomet. Chem.*, **3** (1989) 355.

100 L.M. Epstein, E.S. Shubina, and D.N. Kravtsov, *J. Mol. Struct.*, **177** (1988) 327.

101 L.M. Epshtein, E.S. Shubina, L.D. Ashkinadze, and D.N. Kravtsov, *Metalloorg Khim.*, **1** (1988) 211; *Chem. Abstr.*, **111** (1989) 23610y.

102 J.-L Aubagnac, F.H. Cano, R. Claramunt, J. Elguero, R. Faure, C. Foces-Foces, and P. Raj, *Bull. Soc. Chim. Fr.*, (1988) 905.

103 V.E. Shklover, Yu.T. Struchkov, V.A. Dodonov, T.I. Zinov'eva, and V.L. Antonovskii, *Metallorg. Khim.*, **1** (1988) 1140; *Chem. Abstr.*, **112** (1990) 21063u.

104 S.P. Bone and D.B. Sowerby, *Phosphorus, Sulfur Silicon Relat. Elem.*, **45** (1989) 23.

105 M. Fujiwara, A. Baba, and H. Matsuda, *J. Heterocycl. Chem.* **25** (1988) 1351.

106 M. Fujiwara, M. Imada, A. Baba, and H. Matsuda, *Tetrahedron Lett.*, **30** (1989) 739.

107 R. Nomura, T. Nakano, Y. Nishio, S. Ogawa, A. Ninagawa, and H. Matsuda, *Chem. Ber.*, **122** (1989) 2407.

108 M. Fujiwara, A. Baba, and H. Matsuda, *J. Heterocycl. Chem.*, **26** (1989) 1659.

109 K. Akiba, H. Fujikawa, Y. Sunaguchi, and Y. Yamamoto, *J. Am. Chem. Soc.*, **109** 1987) 1245.

110 K. Akiba, H. Fujikawa, Y. Sunaguchi, and Y. Yamamoto, *Stud. Org. Chem. (Amsterdam)*, **31** (1987) 135.

111 Y. Yamamoto, H. Fujikawa, H. Fujishima, and K. Akiba, *J. Am. Chem. Soc.*, **111** (1989) 2276.