ADVANCES IN INORGANIC CHEMISTRY AND RADIOCHEMISTRY, VOL. 23

RECENT ADVANCES IN ORGANOTIN CHEMISTRY

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I. Introduction

The literature on organotin chemistry up to 1970 is summarized in the excellent monographs by Neumann (*1*) and Poller (*2*), and in the volumes edited by Sawyer (*3*). Since that date, periodic reviews of advances in the field, and accounts of some selected aspects have been published, but there has been no attempt to bring the general survey up to date.

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In this article, we have attempted to review the progress that has been made since 1970, and to give an account of the present status of the field, briefly sketching in the earlier background.

About 1000 papers are published annually on organotin chemistry, and we have been able to include only 5% of these. We have deliberately avoided treating in depth those aspects of the subject that have been thoroughly reviewed recently, and, in particular, we have avoided duplicating the excellent surveys of the use of organotin compounds in organic synthesis (*4*), of ^{119m}Sn Mössbauer spectroscopy (*5–9*), and of ^{119}Sn NMR spectroscopy (*10–12*) that are available.

The older literature on organotin chemistry is reviewed in references (*13*) to (*16*), and the periodical surveys are listed in references (*17*) to (*30*). Recent reviews of specific aspects of the subject are referred to at the appropriate place in the text, or are listed in references (*31*) to (*34*).

II. Preparation and Reactions of Organotin Compounds

A. The Sn–C Bond

The synthesis and properties of the tin–carbon bond were reviewed in reference (*35*). Three recent volumes of Gmelin, written by H. Schumann and I. Schumann, comprehensively cover the literature, up to the end of 1973, on tetraalkyltin compounds R_4Sn (*36*), R_3SnR' (*37*), and $R_2SnR'_2$, $R_2SnR'R''$, and $RR'SnR''R'''$ (*38*), and are invaluable sources of reference.

Four principal methods have been developed for forming a bond between tin and carbon.

(*i*) "Direct" synthesis from metallic tin, or by the analogous, oxidative addition-reactions of tin(II) compounds.

$$Sn^{\circ} \xrightarrow{RX} RSn^{IV}X \xrightarrow{RX} R_2Sn^{IV}X_2$$

(*ii*) From organic derivatives of more electropositive metals.

$$SnX_4 + 4\ RM \rightarrow R_4Sn + 4\ MX$$

(*iii*) From tin–lithium and tin–sodium compounds.

$$R_3SnM + R'X \rightarrow R_3SnR' + MX$$

(*iv*) By hydrostannation of an alkene or alkyne.

$$R_3SnH + R'_2C{=}CR'_2 \rightarrow R_3SnCR'_2CR'_2H$$

Advances since 1970 have been made in the improvement and exten-

sion of these established, general methods, rather than in the development of fundamentally new processes.

1. "Direct" Synthesis

The "direct" synthesis (*39*) has obvious attractions as an industrial process, but, in the absence of a catalyst, it proceeds readily only for allyl and benzyl halides, and much attention has been directed towards finding suitable promoters for the reactions.

One approach (*40*) has been to conduct the reaction in the presence of a more electropositive metal, often as an alloy. In the presence of magnesium, tin reacts with ethyl bromide to give tetraethyltin, and various additives promote the reaction, the sequence of effectiveness being carbitols $\sim I^- >$ tetrahydrofuran, tetrahydrothiophene > ether $\sim$ triethylamine $\sim Br^-$; the ions ClO_4^-, PF_6^-, BF_4^-, and BPh_4^- are without effect. It is suggested that this reflects the coordination of the additive (L) to the Grignard reagent that is first formed, making it more reactive towards metallic tin.

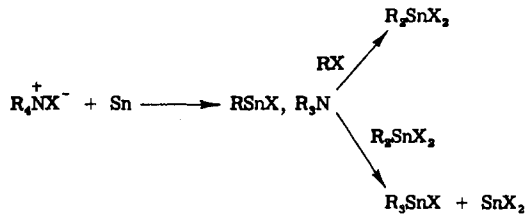
$$EtBr + Mg + 2\,L \rightarrow EtMgBrL_2 \rightleftharpoons Et^- {}^+MgBrL_2$$

$$4\,Et^- {}^+MgBrL_2 + Sn \rightarrow SnEt_4 + 2\,MgX_2 + 2\,Mg$$

For the reaction of butyl bromide with tin, to give Bu_3SnBr and Bu_2SnBr_2 (approximately equimolar), tetrabutylammonium iodide was found to be the best catalyst, and the mechanism was proposed (*41*) to be as follows.

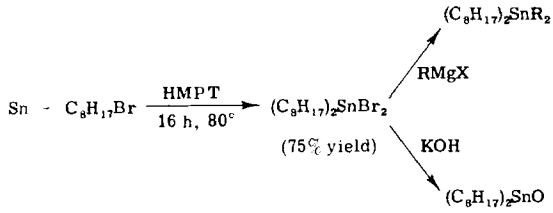
$$EtBr + Mg + 2\,L \rightarrow EtMgBrL_2 \rightleftharpoons Et^{-+}MgBrL_2$$

$$4\,Et^{-+}MgBrL_2 + Sn \rightarrow SnEt_4 + 2\,MgBr_2 + 2\,Mg$$



Metallic tin reacts with methyl halides and 2-halogenopropanoates at 135°, catalyzed by magnesium and butyl iodide in tetrahydrofuran, to give compounds $MeSnX_2CH_2CH_2CO_2R$, from which various other derivatives were prepared (*42*).

Cuprous iodide catalyzes the reaction of various alkyl chlorides, bromides, and iodides in hexamethylphosphoric triamide (HMPT), to give the complexed product R_2SnX_2, which can then be further alkylated with a Grignard reagent, or can be hydrolyzed to the oxide and converted into various other compounds, R_2SnY_2 (*43*). This promises to be a useful laboratory method, e.g.,



Monoalkyltin(IV) compounds can be prepared under suitable conditions from tin(II) compounds (*44–46*). Tin(II) bis(acetylacetonate) (acac) and related compounds react readily with a variety of alkyl bromides or iodides, to give the product $RSn(acac)_2X$, e.g.,

$$Sn^{II}(acac)_2 + CH_2I_2 \xrightarrow{24\ h} ICH_2Sn(acac)_2I\ (90\%)$$

The reaction is catalyzed by light, suggesting a homolytic mechanism.

$$R\cdot + SnX_2 \rightarrow RSn\dot{X}_2$$

$$RSn\dot{X}_2 + RY \rightarrow RSnX_2Y + R\cdot$$

Similarly, dicyclopentadienyltin(II) reacts with methyl iodide to give $Me(C_5H_5)_2SnI$, which is alkylated by more dicyclopentadienyltin, to give $MeSn(C_5H_5)_3$ (*45*).

A very useful route to monoalkyltin trihalides involves the reaction of stannous bromide with alkyl bromides in the presence of 5 mol % of a trialkylantimony compound (*47*). A typical example is shown in the following equation.

$$C_{18}H_{37}Br + SnBr_2 \xrightarrow[150°,\ 10\ h]{5\ mol\%\ Et_3Sb} C_{18}H_{37}SnBr_3\ (100\%)$$

2. *Formation from Organic Compounds of Other Metals*

The alkylation of tin tetrachloride with organolithium compounds, Grignard reagents, or organoaluminum compounds remains the most common route to tetraalkyltins, and thence, by the Kocheshkov disproportionation, to the various organotin halides.

$$SnCl_4 + 4\ RM \rightarrow R_4Sn + 4\ MCl$$

$$n\ R_4Sn + (4 - n)SnCl_4 \rightarrow 4\ R_nSnCl_{4-n}$$

These two methods, together with the Wurtz modification of co-reacting an alkyl halide and tin tetrachloride with metallic sodium, are used industrially (*34*).

Some typical recent examples are shown in the following equations.

$$Bu^t_2SnClF + Bu^tLi \longrightarrow Bu^t_3SnCl \qquad (48)$$

$$SnCl_4 + 4\,CH_2{=}CHMgBr \longrightarrow (CH_2{=}CH)_4Sn \quad (88\%) \qquad (49)$$

$$Me_2SnCl_2 + 2\,HC{\equiv}CMgBr \longrightarrow Me_2Sn(C{\equiv}CH)_2 \xrightarrow{BEt_3} Me_2Sn(Et)(BEt_2) \qquad (50)$$

$$Ph_2SnCl_2 + \text{(1,2-dilithiobiphenyl)} \longrightarrow \text{(Ph}_2\text{Sn-biphenyl)} \quad (23\%) \qquad (51)$$

$$Me_2SnCl_2 + \text{(2,2'-dilithiodiphenyl ether)} \longrightarrow \text{(Me}_2\text{Sn-diphenyl ether)} + \text{(bis(Me}_2\text{Sn)-diphenyl ether)} \qquad (52)$$

(31%) (4%)

By the same principle, starting from the appropriate, metal-substituted, organolithium compound, products containing both tin and another metal have been synthesized, e.g.,

$(Ph_3Sn)_nC[B(OMe)_2]_{4-n}$ (*53*)

$(Ph_3Sn)_nC(\text{B(O)(O)})_{4-n}$ (*54*)

$(Me_3Si)_2(Me_2Sn)_2(SnMe_2)_2$ (*55*)

By a similar process, stannylsilylthiomethanes have been prepared, and then converted by the Petersen reaction into stannylthiyl alkenes (*56*).

$$Me_3Si(RS)CH_2 \xrightarrow[(2)\ Me_3SnCl]{(1)\ BuLi} Me_3Sn(RS)C(H)SiMe_3 \longrightarrow Me_3Sn(RS)C(Li)SiMe_3 \xrightarrow{R'_2C=O} Me_3Sn(RS)C{=}CR'_2$$

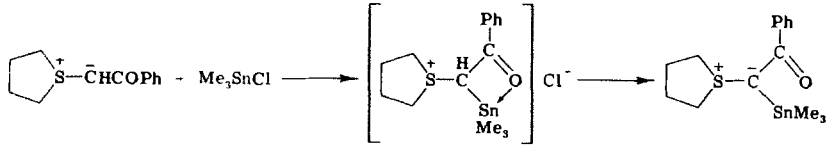
Seyferth prepared α-halogenoalkyl-lithium and -magnesium compounds by treating the appropriate *gem*-dihalides with butyllithium or with Grignard reagents at low temperature, and then used the products to prepare acyclic and cyclic α-halogenoalkyltin compounds (*57–60*). Typical examples are shown in the following equations.

$$Me_3SnNEt_2 + HCl_3 \rightarrow Me_3SnCl_3 \xrightarrow[-100°]{Pr^iMgCl} Me_3SnCl_2MgCl \xrightarrow{Me_3SnCl} (Me_3Sn)_2Cl_2$$

Iodomethylzinc iodide or bromomethylzinc bromide have likewise been used for preparing the compounds Me_3SnCH_2I, Me_3SnCH_2Br, $Me_2Sn(CH_2I)_2$, $Me_2Sn(CH_2Br)_2$, $Me_2PhSnCH_2I$, Ph_3SnCH_2I, and $Sn(CH_2I)_4$ (*61*). It is probable that the formation of tetraethyltin in 52% yield when diethyl sulfate is electrolyzed with a zinc cathode and a tin anode similarly involves an organozinc intermediate (*62*).

The availability of arylcopper(I) compounds has provided a useful, one-step route to triorganotin halides (*63*): the introduction of the final, aryl group is relatively slow, and the need to revert to the Kocheshkov disproportionation to remove the fourth organic group is avoided. By reaction between the appropriate arylcopper compounds and tin halides in ether or benzene at 0° or room temperature, such compounds as 2-$(Me_2NCH_2)C_6H_4SnPh_2Br$ and 2,6-$(MeO)_2C_6H_3SnMe_2Br$ can be prepared in high yield.

Ylids can also serve as the alkylating nucleophiles; an example is as follows (*64*).



The disproportionation reactions of organotin compounds may also be regarded as alkylations by organometallic compounds, as they involve transfer of an alkyl group from one tin atom to another. An ingenious application of this has been described in which α,ω-distannanes are caused to disproportionate into the corresponding tetraalkyltins and 1,1-dialkylstannacycloalkanes (*65*).

$$BrMg(CH_2)_nMgBr + 2\ R_3SnCl \rightarrow R_3Sn(CH_2)_nSnR_3 \xrightarrow{270-300°} R_4Sn + R_2Sn(CH_2)_n$$

The reaction is best suited to the preparation of the stannacyclopen-

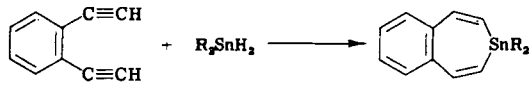
tanes (n = 4) and stannacyclohexanes (n = 5), which are formed in >85% yield. In contrast, the direct reaction between a di-Grignard or dilithium reagent and a dialkyltin dichloride gives the stannacycloalkane in only 10–30% yield, together with a substantial proportion of polymer. Attempts to make stannacyclobutanes by the disproportionation reaction were unsuccessful, although they may, apparently, be prepared by the direct reaction (*66*).

3. *Formation by Hydrostannation*

The hydrostannation reaction can proceed either by a free-radical mechanism, or, with polar-substituted alkenes or alkynes, by a polar mechanism, respectively resulting in anti-Markownikoff or Markownikoff orientation. Both types of reaction are particularly suitable for preparing functionally substituted, organotin compounds.

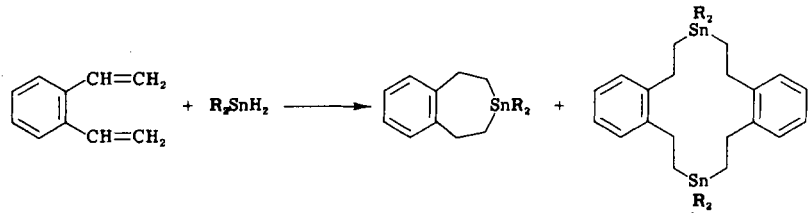
By the addition of organotin hydrides to norbornene and norbornadiene, and subsequent reactions of the products, a variety of norbornyl-, norbornenyl-, and nortricyclyl-tin compounds has been isolated, and identified (*67–69*).

1-Buten-3-ynes react by 1,4-addition to give allenic tin compounds; *o*-diethynylbenzene reacts to afford the benzostannepin (*70*),



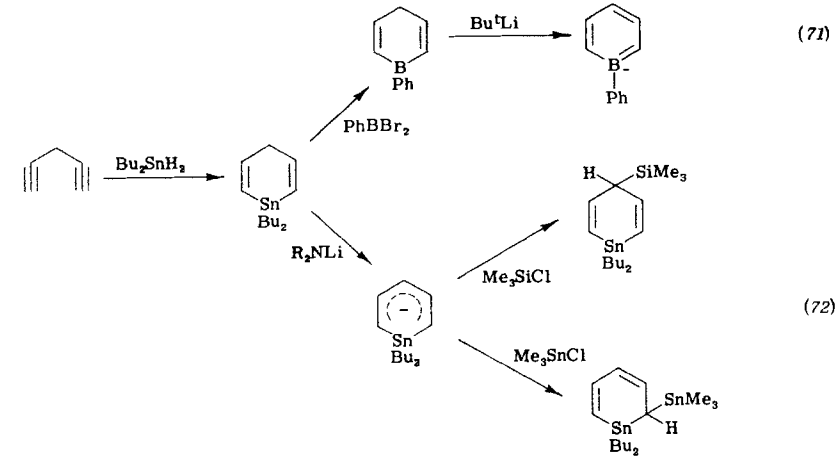
(R_2 = Me_2, Et_2, or EtPh)

and *o*-divinylbenzene gives the tetrahydro compound, together with the cyclic dimer.



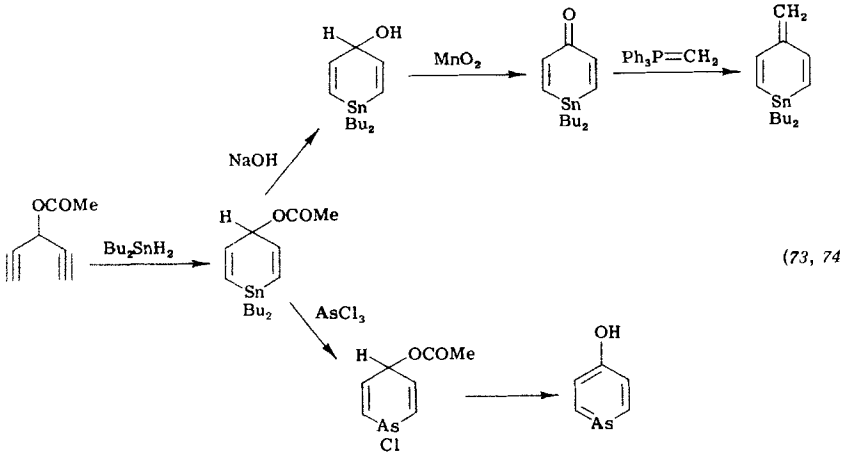
(R_2 = Et_2 or Ph_2) (R_2 = Ph_2)

The stanna-2,5-cyclohexadienes can be transformed into other metallocycloalkenes, as shown in the following equations.



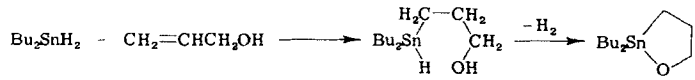
(71)

(72)



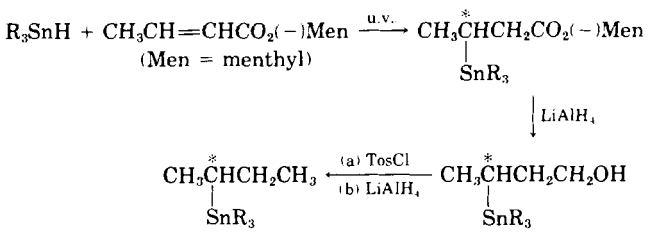
(73, 74)

Alkenes carrying C=N, OH, or $COCH_3$ substituents give the corresponding, functionally substituted, organotin compounds, and stannaoxacyclopentanes and stannaoxacyclopentenes have been prepared from dialkyltin dihydrides and allylic alcohols or propargylic acetates, e.g. (*75*),



Hydrostannation of chiral menthyl esters of substituted acrylic acids proceeds stereoselectively, providing a route to optically active alkyl-

tin compounds having an optical purity of 10–20% (*76*).



From the industrial point of view, the most important advance in hydrostannation is the reaction developed by the AKZO company for preparing organotin di- or trichlorides carrying a β-aldehyde, ketone, ester, or acid chloride group (*77, 78*). Hydrogen chloride is passed into an ethereal solution of the unsaturated compound in the presence of powdered tin or tin(II) chloride. The reactions apparently proceed through the chlorotin hydrides, and, with $SnCl_2$, the hydride dietherate, $HSnCl_3(OEt_2)_2$, may be preformed, and then caused to add to the unsaturated compound in a second step. Two examples are shown in the equations.

$$Sn + 2\ HCl + 2\ CH_2{=}CMeCO_2Me \rightarrow Cl_2Sn(CH_2CHMeCO_2Me)_2\ (85\%)$$

$$SnCl_2 + HCl + Me_2C{=}CHCOMe \rightarrow Cl_3SnCMe_2CH_2COMe\ (80\%)$$

The products are used as intermediates for PVC stabilizers. Further applications of the halogenotin hydrides can readily be envisaged.

4. Formation from Sn–Li and Sn–Na Compounds

Synthetic and mechanistic aspects of the reactions of the alkali-metal derivatives of organotin compounds, R_3SnM ("organostannylanionoids") have been reviewed (*79, 80*). They may be prepared by reactions of the types shown in the following equations.

$$Me_4Sn \xrightarrow{Na\ in\ liq.\ NH_3} Me_3SnNa \qquad (81)$$

$$Me_6Sn_2 \xrightarrow[or\ Li\ in\ THF]{Na\ in\ tetraglyme} 2\ Me_3SnM \qquad (82)$$

$$Pr_3SnCl \xrightarrow[or\ Li\ in\ THF]{Na\ in\ liq.\ NH_3} Pr_3SnM \qquad (83)$$

$$RCl + SnCl_4 \xrightarrow{Na\ in\ C_6H_{12}} R_3SnNa \qquad (81)$$

$$Bu_3SnCl \xrightarrow{LiNPr^i_2} Bu_3SnLi \qquad (81a)$$

Primary and secondary alkyl halides react with the reagents R_3SnM largely by substitution, but *tert*-alkyl halides, if they can, undergo

elimination. The stereochemistry of the reaction is dependent on the structure of R and X, the solvent, and the nature of M, suggesting three possible mechanisms: SN2 at C, SN2 at X, and a radical-pair process (*84–86*).

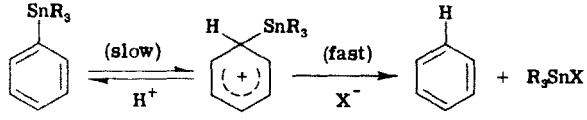
Recent examples of these reactions are the preparation of a series of norbornyl-, norbornenyl-, and norbornadienyl-tin compounds (*87*); 1-$AdSnMe_3$, $(1\text{-}Ad)_4Sn$; and 2-$AdSnMe_3$ (Ad = adamantyl) (*81, 83*); $Pr_3SnCH{=}CHCH{=}CH_2$ (*83*); and $(Me_3Sn)_4C$ (*82*).

By reaction with the appropropriate aryl halides can be prepared a variety of aryltin compounds that are not accessible from the reactions involving arylmagnesium halides and organotin halides (*88, 89*); there is evidence that an aryne intermediate may be involved (*90*). However, for some purposes, such as the addition to carbonyl compounds, oxiranes, and oxetanes, to give hydroxyalkyltin compounds, the Sn–Mg reagents may have advantages (see Section II,E) (*91–93*).

5. *Cleavage of the Sn–C Bond*

Heterolytic cleavage of the tin–carbon bond is reviewed in references (*94–96*). Cleavage by electrophiles (e.g., HgX_2 or halogen) is dominated by electrophilic attack at carbon, and cleavage by nucleophiles principally involves nucleophilic attack at tin. Much of the interest in these processes centers on the intermediate mechanisms that may exist between these extremes, in which electrophilic attack is accompanied by some nucleophilic assistance, and vice versa. Allylic, allenic, and propargylic compounds show a special reactivity by a special (SE2′ or SE2γ) mechanism.

The earlier work on acidolysis of the aryl–tin bond is reviewed in reference (*97*). Attachment of the proton to the aryl ring is rate-determining, and the Hammett ρ-factor for the reaction has been shown to be solvent-dependent (*98*).



Benzyl and heteroaryl (e.g., furanyl or thienyl) groups can be cleaved from the tin under basic conditions also, and nucleophilic attack on the tin is now assisted by attack of the solvent (e.g., water) on the organic group, through a transition state of the type HO---H---R---SnR_3OH (*99–101*).

Acidolysis of the alkyl–tin bond provides a useful route from tetraalkyltins to alkyltin carboxylates, and is discussed in Section II,C.

With functionally substituted, alkyltin compounds, the functional substituent may become involved in the cleavage process, resulting in an intramolecular reaction, e.g.,

$$Me_3SnCH_2CH_2CH_2OTs \xrightarrow{125^\circ} Me_3SnOTs + \text{cyclo-}C_3H_6\ (82\%) \quad (102)$$

$$Me_3SnCH_2CH_2CH\text{—}CH_2 \xrightarrow{BF_3} Me_3SnF + (CH_2\text{—}CHCH_2O)_3B \quad (103)$$

The mechanism of the cleavage of the alkyl–tin bond by mercuric halides and carboxylates has been thoroughly investigated, and the evidence is in favor of an open SE2 transition state (*104–110*).

The reactions of tetraorganotins with ICl, IBr, and ClCN have been investigated as synthetic routes to aryl cyanides (*111*) and alkyltin bromides and chlorides (*112, 113*).

The reaction of bromine with optically active *sec*-butyltin compounds Bu^sSnR_3, to give *sec*-butyl bromide, can give retention or inversion in the *sec*-butyl group, depending on the nature of the group R (*114*), and the inversion that is observed with *sec*-butyltrineopentyltin (*115*) appears to be the exception rather than the rule.

A lot of attention has also been paid to the reaction of organotin compounds with sulfur dioxide to give organotin sulfinates (*116–119*).

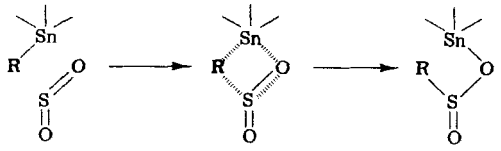
$$\text{—Sn—R} + SO_2 \longrightarrow \text{—Sn—OSR}\ (\text{O})$$

The topic has been reviewed (*120*).

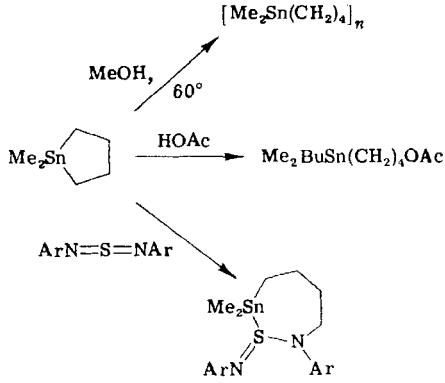
The reactivity of various groups (R) follows the sequence allyl, benzyl > aryl > alkyl, and usually proceeds readily to the stage of $R_2Sn(OSOR)_2$ (*121, 122*), but pentafluorophenyl- and trifluorovinyl-tin bonds are usually unreactive. The reactivity is enhanced by such ligands as bipyridyl (*123*).

Allyl- and vinyl-tin compounds react with retention in the structure of the organic group (*124*), and a kinetic study of the reaction of aryl

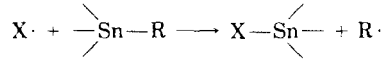
and benzyl compounds suggested that the reaction is best represented as proceeding through an SEi transition state (*125–127*).



Angle-strain in the small-ring stannacycloalkanes confers on them an anomalously high reactivity. This is most obvious in the stannacyclopentanes which, for example, undergo ionic polymerization in polar solvents such as methanol, react readily with acetic acid (*128*), and react additively with diarylsulfurdiimides (*129*).



Cleavage of the tin–carbon bond can also be achieved by bimolecular, homolytic substitution (SH2) at the tin center (*130–132*).



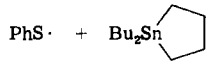
The alternative of an SH2 process at the α-carbon center has not yet been identified. Examples of the unimolecular thermolysis or photolysis of the tin–carbon bond are known (see Section II,G), but have not yet been investigated extensively.

Whereas bromine radicals (*133*) and succinimidyl radicals (*134*) react by the SH2 mechanism at the tin center in tetraalkyltins, but not in alkyltin halides, alkoxyl radicals (*135*) and ketone triplets (*136*) react with alkyltin halides, but not tetraalkyltins; this may reflect the conflicting, electronic demands of the radical reagents which, as electrophilic species, should be more reactive towards tetraalkyltins than alkyltin halides, but which would also tend to make use of a 5*d* orbital

on tin to establish a 5-coordinate transition state or intermediate, and these orbitals are more accessible in the alkyltin halides. There is some inconclusive evidence that at least some of these reactions do involve a transient Sn(V) radical intermediate (*132, 137*).

The relative reactivities of alkyltin compounds towards *tert*-butoxyl radicals, ketone triplets, and succinimidyl radicals are dominated by the steric effect of the alkyl ligands ($R^p > R^s$), but that towards bromine atoms follows the reverse sequence ($R^p < R^s$).

The stannacyclopentanes are again particularly reactive (*138*). Alkoxyl radicals will now react at the tin center in the fully alkylated compounds, with opening of the ring, and benzoyloxyl and alkylthiyl radicals will also induce ring cleavage. For example, 1,1-dibutylstannacyclopentane reacts homolytically with benzenethiol to give tributyl(phenylthio)tin.



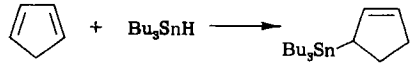
$$Bu_2(PhS)SnCH_2CH_2CH_2CH_2\cdot + PhSH \longrightarrow Bu_3SnSPh + PhS\cdot$$

6. *Allylic and Related Tin Compounds*

The allylic, allenic, propargylic, 2,4-dienylic, cyclopentadienylic, and related tin compounds present special, structural features and show special reactivity by both heterolytic and homolytic mechanisms.

Allyltin compounds can be prepared by simple modifications of the usual reaction involving allyl Grignard reagents (*139*), by the 1,4-addition of trialkyltin hydrides to 1,3-dienes (*140, 141*), or by the reaction of an aldehyde or ketone with the appropriate, tin-carrying, Wittig reagents (*142*).

$$CH_2{=}CHCH_2MgCl + SnCl_4 \longrightarrow (CH_2{=}CHCH_2)_4Sn \xrightarrow{SnX_4} (CH_2{=}CHCH_2)_nSnX_{4-n}$$



$$CH_2{=}\overset{+}{C}HPPh_3 + Me_3SnLi \longrightarrow Me_3SnCH_2CH{=}PPh_3 \xrightarrow{R_2C=O} Me_3SnCH_2CH{=}CR_2$$

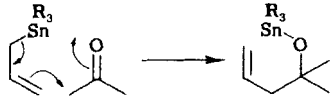
The allyltin halides can then be obtained by a disproportionation reaction between tetraallyltin and tin tetrachloride or tetrabromide, a reaction that is exothermic (*143, 144*).

Allyltin compounds can also be formed by elimination from the tin derivatives of allyldialkylcarbinols (*145*).

$$Bu_3SnOCR_2CH_2CH{=}CH_2 \rightleftharpoons Bu_3SnCH_2CH{=}CH_2 + O{=}CR_2$$

Photoelectron spectroscopy shows that the carbon–tin bond prefers that orientation in which it lies parallel to the $p\pi$ orbitals of the double bond, to permit carbon–metal hyperconjugation (*146*).

Cleavage of the Sn–C bond is dominated by electrophilic or homolytic attack at the γ-carbon of the allylic group, leading to allylic rearrangement, and these reactions [e.g., acidolysis (*147–149*)] usually occur more readily than with the corresponding alkyltin compounds. The reaction with thiocyanogen is considered to be an S$_E$2γ process, but that with iodine in a polar medium may be accompanied by an S$_E$2 component (*150, 151*). Complete allylic rearrangement is involved in the addition to carbonyl compounds (*152–154*) and, presumably, also in the carbonyl elimination (*145*).



The S$_H$2γ mechanism is most clearly shown by the exchange of $R_3Sn\cdot$ (*155, 156*), and by the reaction with alkyl halides (*157, 158*).

$$R'CH_2{=}CH{-}CH_2SnR_3 \rightarrow R'CH_2CH{=}CH_2 + \cdot SnR_3$$

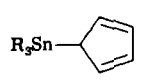
$$R_3Sn\cdot + XR' \rightarrow R_3SnX + R'\cdot$$

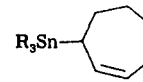
The equilibrium between propargyl- and allenyl-tin compounds is not spontaneous, but it occurs in the presence of Lewis acids or coordinating solvents, and an ion-pair mechanism has been proposed (*159*). Substitution by iodine, or addition to chloral, occurs with propargyl/allenyl rearrangement (*160, 161*), analogous to the allylic rearrangement already mentioned.

$$Sn{-}\overset{1}{C}{-}\overset{2}{C}{\equiv}\overset{3}{C} \xrightarrow{Cl_3CCHO} Cl_3CCH(OSn){-}\overset{3}{C}{=}\overset{2}{C}{=}\overset{1}{C}$$

$$\overset{1}{C}{=}\overset{2}{C}{=}\overset{3}{C}{-}Sn \xrightarrow{Cl_3CCHO} Cl_3CCH(OSn){-}\overset{1}{C}{-}\overset{2}{C}{\equiv}\overset{3}{C}$$

Compounds in which the R_3Sn group is attached to a 2,4-dienyl group, such as cyclopentadiene, cycloheptadiene, cycloheptatriene, and cyclononatetraene, whose formulas are shown, are fluxional.


(162,163)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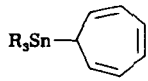
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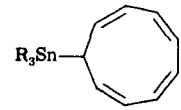

(166)

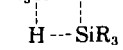
The chemistry of cyclopentadienyltin compounds is reviewed in references (*167*) and (*168*). The ready disproportionation of $(C_5H_5)_4Sn$ with $SnCl_4$ (*169*), and the sensitivity of the cyclopentadienyl–tin bond to acidolysis and to photolysis (*170*) suggests that these compounds may find application in synthesis.

B. The Sn–H Bond

A comprehensive review of the literature on the organotin hydrides up to the end of 1974 is available in a recent volume of Gmelin (*170a*).

The hydrides are usually prepared by reducing an organotin chloride, alkoxide, or oxide with lithium aluminum hydride or with poly(methylsiloxane), $[MeSiHO]_n$.

The reduction of tributyltin methoxide with optically active methylphenyl-1-naphthylsilane involves retention of configuration at the silicon atom and follows second-order kinetics (*171*). The reaction between tributyltin methoxide and ring-substituted dimethylphenylsilanes shows a Hammett ρ-value of $+0.903$, and that between dimethylphenylsilane and ring-substituted tributyltin phenoxides shows a ρ-value of -1.319; this is compatible with the reactions proceeding through a 4-centered (SNi-Si) transition state (*172, 173*).



The mixed halide-hydrides Ph_2SnHCl and Ph_2SnHBr have been prepared from the reaction of diphenyltin dihydride with the appropriate diphenyltin dihalides (*174*).

The tin hydrides find important applications as reducing agents. Many of their reactions (particularly the reduction of alkyl halides and the hydrostannation of simple alkenes and alkynes) are known to proceed through $R_3Sn\cdot$ intermediates, and this aspect of their chemistry is referred to in Section II,G.

The synthetic applications have been reviewed (*175*). General developments have included the generation of the tin hydride *in situ*

from sodium borohydride and a catalytic amount of trialkyltin chloride (*176, 177*). Small proportions of dialkyltin dihalides or dialkoxides have been shown to catalyze the hydrostannation of aldehydes and ketones by dialkyltin dihydrides, probably through the formation of intermediates R_2SnXH; under these conditions, many aldehydes and ketones can be reduced (*178*) to alcohols at 30°.

Promising experiments have also been made at immobilizing the tin hydride on a polymer, but, as yet, regeneration of the hydride has been incomplete (*179*).

Trimethyltin hydride has been shown to add to trimethylvinyltin, and triethyltin hydride to triethylvinyltin, to give both the 1,1- and the 1,2-distannylethanes, whereas triphenyltin hydride reacts with triphenylvinyltin to give only the 1,2-adduct (*180*).

$$R_3SnH + R_3SnCH{=}CH_2 \rightarrow (R_3Sn)_2CHCH_3 + R_3SnCH_2CH_2SnR_3$$

C. The Sn–O, Sn–N, and Sn–S Bonds

Organotin chlorides, R_nSnCl_{4-n}, are usually obtained from the Kocheshkov disproportionation between tetraalkyltins and tin tetrachloride, and other organotin derivatives, R_nSnX_{4-n}, are then prepared by substitution reactions of the chlorides. The chemistry of the chlorides is reviewed in reference (*181*).

For preparing the acetates, thallous acetate has been used as the reagent as an alternative to sodium acetate (*182*). Alternatively, the carboxylates can be prepared directly by acidolysis of the tetraalkyltins (*183*).

$$R_4Sn + n\ R'CO_2H \rightarrow R_{4-n}Sn(OCOR')_n + n\ RH$$

Successive groups are replaced with increasing difficulty. Vinyl groups are replaced more readily than saturated alkyl groups, and, with trifluoroacetic acid, two vinyl groups are displaced exothermically at room temperature, and a third after several hours of heating (*184*). With trifluoromethanesulfonic acid, all four vinyl groups are displaced at −78°, to give a compound that was shown by Mössbauer spectroscopy to contain both Sn(II) and Sn(IV), and that was assigned the formula $Sn^{II}[Sn^{IV}(SO_3CF_3)_6]$. Trivinyltin carboxylates have also been prepared from the reaction between tetravinyltin and mercury(I) carboxylates, which may be generated electrochemically *in situ* (*185*).

Tetraallyltin is more reactive than tetravinyltin, but, with methanol as the solvent, acidolysis can be restricted to the stage of the formation of the triallyltin or diallyltin carboxylates (*186*).

Trimethyltin chloride reacts with carboxylic acids at 100° to give the corresponding chloride carboxylates $Me_2Sn(Cl)OCOR$ (*187, 188*), and diethyltin dihydride, triethyltin hydride, hexaethylditin, and bis(triethyltin) oxide have been shown to react with lead tetraacetate to give diethyltin diacetate or triethyltin acetate, as appropriate (*189*).

The organotin alkoxides R_3SnOR' and $R_2Sn(OR')_2$ can be prepared by treating the appropriate organotin chlorides with sodium alkoxides, and this procedure has been extended to the preparation of the monoalkyltin trialkoxides, $RSn(OR')_3$ (*190*), which serve as useful reagents for the synthesis of other monoalkyltin derivatives. Alternatively, the trialkoxides can be prepared by alcoholysis of the tris(amino) compounds $RSn(NR'_2)_3$ (*191*).

The trialkyltin alkoxides can often be prepared more conveniently by azeotropic dehydration of the appropriate bis(trialkyltin) oxide and alcohols, or by heating together the bis(trialkyltin) oxide and dialkyl carbonate (*192*). The latter reaction involves formation, and then decarboxylation, of the alkyl trialkyltin carbonate, e.g.,

$$(Bu_3Sn)_2O + (MeO)_2CO \rightarrow Bu_3SnOMe + Bu_3SnOCO_2Me \rightarrow 2\ Bu_3SnOMe + CO_2.$$

There is a growing interest in the tin enolates that can be prepared by treating enol acetates with trialkyltin methoxides, e.g. (*193*),

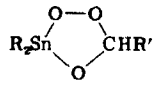
$$Bu_3SnOMe + CH_2{=}CHOCOCH_3 \rightarrow Bu_3SnOCH{=}CH_2 + MeOCOCH_3.$$

The products are in metallotropic equilibrium between the *O*-bonded (enol) and *C*-bonded (keto) isomers, and the topic has been reviewed (*194*).

Many organotin derivatives of functionally substituted alcohols have been prepared, partly for their structural interest, and partly for their use as reaction intermediates. In particular, alkylstannatranes, $RSn(OCH_2CH_2)_3N$ (*195–202*) and the halogenoalkoxytin compounds $R_3SnO(CH_2)_nX$ (n = 2–5) (*203–206*) have attracted much attention. A variety of dialkyltin and trialkyltin derivatives of carbohydrates has also been prepared, in order to modify the reactivity of specific hydroxyl groups (*207–211b*). For example, azeotropic dehydration of a mixture of D-glucose and bis(tributyltin) oxide effects stannylation of the 1-, 4-, and 6-hydroxyl groups.

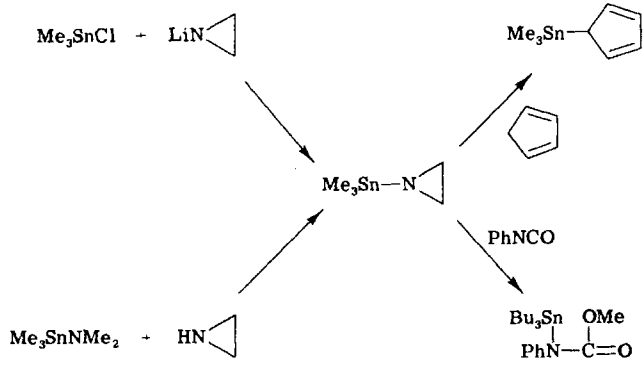
The lower trialkyltin hydroxides and oxides, which are usually readily interconverted, have been characterized by IR and Mössbauer spectroscopy (*212*). The dimer of di-*n*-butyltin oxide $(Bu_2SnO)_2$ has been reported to be formed as a crystalline solid when dibutyltin dichloride is hydrolyzed with ammonium hydroxide (*213*).

Trialkyltin methoxides react with anhydrous hydrogen peroxide in ether to give the rather unstable bis(trialkyltin) peroxides, $R_3SnOOSnR_3$ (*214*). Under the same conditions, dialkyltin dimethoxides give polymeric peroxides, $(R_2SnOO)_n$, but, if an aldehyde is present, monomeric peroxides of the following structure are obtained (*215*).



The chemistry of the peroxides of the Group IV metals has been reviewed (*216*).

The aminotin compounds are less readily prepared, and are more reactive both in substitution and addition processes, than the alkoxides. The established routes to, and reactions of, these compounds are exemplified by recent work on the aziridine derivatives (*217*).



The aminotin compounds can also be prepared from the reaction between aminosilanes and alkoxytin compounds, and this reaction has been extended to the preparation of the first sulfinylaminotin compounds (*218*).

$$Bu_3SnOMe + Me_3SiNMe_2 \rightarrow Bu_3SnNMe_2 + Me_3SiOMe$$

$$Bu_3SnOMe + Me_3SiNSO \rightarrow Bu_3SnNSO + Me_3SiOMe$$

The aminotin compounds react with aldehydes by addition and elimination, to give enamines (*219*), but some ketones, by acidolysis, give tin enolates, e.g. (*220*),

$$CH_3COCHMe_2 + Bu_3SnNEt_2 \longrightarrow \underset{80\%}{Bu_3SnCH_2COCHMe_2} + \underset{20\%}{CH_2{=}C(CHMe_2)(OSnBu_3)}$$

N,N-Dialkylamides are much less reactive than ketones or esters, and acidolysis gives the *C*-bonded product (*221*).

$$Bu_3SnNEt_2 + CH_3CONR_2 \rightarrow Bu_3SnCH_2CONR_2 + HNEt_2$$

Organotin enamines can be prepared by treating organotin halides with the lithium or magnesium derivatives of enamines, and also by treating distannazanes with tin enolates (*222, 223*).

$$Sn{-}N{-}Sn + C{=}C{-}O{-}Sn \longrightarrow C{=}C{-}\underset{\displaystyle Sn}{N} + C{-}\underset{\displaystyle Sn}{C}{=}N + Sn{-}O{-}Sn$$

Like the tin enolates, the tin enamines are metallotropic.

Cyanamide can be stannylated under various conditions to give bis(stannyl)carbodiimides (*224–227*), and bis(stannyl)sulfurdiimides have been prepared from the reaction between S_4N_4 and trimethyldimethylaminotin (*228*).

$$2\ R_3SnX + H_2NC{\equiv}N \rightarrow R_3SnN{=}C{=}NSnR_3$$

$$Me_3SnNMe_2 + N_4S_4 \rightarrow Me_3SnN{=}S{=}NSnMe_3$$

The organotin thiolates are more readily prepared, and are less reactive, than either the alkoxy or the amino compounds, and the alkynylthiyltin compounds $Me_3SnSC{\equiv}CPh$, $Me_3SiC{\equiv}CSSnMe_3$, and $Me_3CC{\equiv}CSSnBu_3$ have recently been prepared by extension of the established, general methods (*229*).

Dithiastannacyclopentanes and dithiastannacyclohexanes have been obtained by treating diphenyltin dichloride with the appropriate lead dithiolates (*230*), e.g.,

$$Ph_2SnCl_2 + Pb(SCH_2CH_2S) \longrightarrow Ph_2Sn\begin{cases}S\\ \\S\end{cases}$$

Sodium dicyanoethylenedithiolate reacts with trimethyl- or triphenyl-tin chloride to give anionic trialkylstannadithiacyclopentenes, but dialkyltin dichlorides undergo dealkylation (*231*).

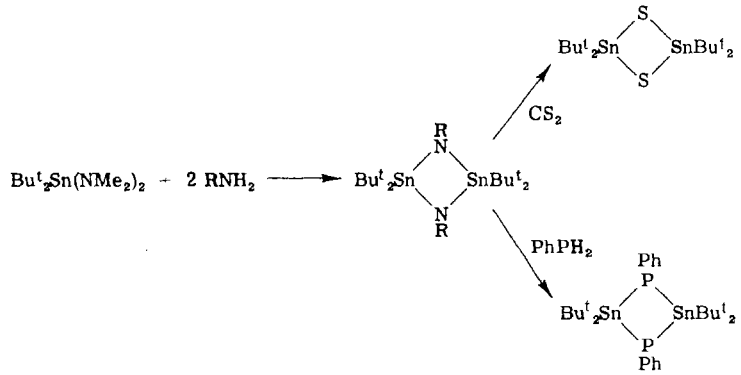
Dialkyltin compounds R_2SnXY, where X and Y are dissimilar ligands, are readily accessible, often merely by disproportionation between the compounds R_2SnX_2 and R_2SnY_2. Typical examples of such compounds that have been characterized are as follows: $Me_2SnClBr$, Et_2SnBrI, Bu_2SnClI (*232*) $MeSnFCl_2$ (*233*), $MeSnCl(SO_3F)_2$ (*234*), $Me_2SnCl(OMe)$ (*235*), $Me_2SnCl(NMe_2)$ (*236*), $Me_2SnCl(P^tBu_2)$ (*237, 238*), $Me_2SnCl(OCOR)$ (*239–241*), $BuSnCl(O^iPr)_2$, $BuSn(O^iPr)(OCOCH_3)_2$ (*242*), $Bu_2Sn(OPh)OCOPh$ (*243*), $Bu_2Sn(OEt)(OCH_2CH_2NH_2)$ (*244*), and $^tBu_2SnCl(OH)$ (*245*).

By a similar disproportionation involving stannoxanes, $(R_2SnO)_n$, stannathianes, $(R_2SnS)_n$, and stannazanes, $(R_2SnNR)_n$, or by a controlled solvolysis reaction, oligomeric, functionally substituted stannoxanes, stannathianes, and stannazanes, can be prepared. The most familiar of these are the tetraalkydistannoxanes, $XR_2SnOSnR_2X$.

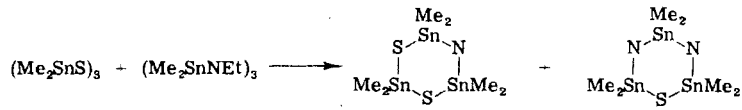
In recent years, the stannoxanes $N_3Me_2SnOSnMe_2OMe$, $N_3SnR_2OSnR_2OSnR_2N_3$, $N_3SnR_2OSnR_2OSnR_2OSnR_2N_3$ (*246*), $R_3SnOSnR'_2X$ (e.g., $Me_3SnOSnBu_2Cl$), $ClBu_2Sn(OSnBu_2)_nCl$ (n = 2–12), and $BuSn[(OSnBu_2)_nCl]_3$ (n = 1–4) (*247*), the stannathianes $ClMe_2SnSSnMe_2Cl$, $FBu_2SnSSnBu_2F$, $Cl_2PhSn(SSnBu_2)_nCl$ (n = 1 and 2), and $Cl_2BuSn(SSnBu_2)_2Cl$ (*248*), and the stannazanes $ClMe_2SnNEtSnMe_2Cl$ and $Cl_2MeSnNEtSnMe_2Cl$ (*249*) have been characterized.

A number of mixed metalloxanes, R'_nMOSnR_rX (M = Hg, Tl, Si, Ge, or Pb), have similarly been synthesized from the stannoxanes $(R_2SnO)_n$ and the metal compounds R'_nMX (*250*), and the borostannoxanes $B(OSnR_3)_3$ and $(RO)_2BOSnR_2OSnR_2OB(OR)_2$ have also been characterized (*251, 252*).

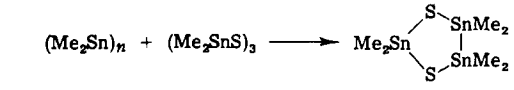
Whereas most dialkylbis(dialkylamino)tin compounds react with primary amines to give cyclotristannazanes di-*tert*-butylbis(dimethylamino)tin reacts to give a cyclodistannazane, from which the cyclodistannathiane and cyclodistannaphosphazane can be prepared (*253*).



NMR spectroscopy shows that, in solution, $(Me_2SnS)_3$ and $(Me_2SnNEt)_3$ are in equilibrium with the corresponding cyclotristannaazadithiane and cyclotristannadiazathiane (*254*).



In a rather different type of process, oligomeric dimethyltin and tris(dimethyltin sulfide) react together to give the dithiatristannacyclopentane (*255*).



D. Compounds Having Sn–Sn Bonds

Tin–tin bonds are usually best prepared by reducing an Sn–O or Sn–N bonded compound with a tin hydride. For example, trimethyl(diethylamino)tin is reduced by alkyltin trihydrides to give decaorganotetratins (*256*).

$$3\ Me_3SnNEt_2 + RSnH_3 \rightarrow RSn(SnMe_3)_3 + 3\ Et_2NH$$

(R = e.g., Me, Pe, or Ph)

In a modification of this method, the Sn–O bonded compound can be generated *in situ* by partial acidolysis of a tin hydride, and, from the reaction between diphenyltin dihydride and carboxylic acids, a number of 1,2-bis(acyloxy)-1,1,2,2-tetraphenylditins, $(RCO_2)Ph_2SnSnPh_2(O_2CR)$ (e.g., R = CH_3, CF_3, Ph_3Si, or Ph_3Ge), have been prepared (*257, 258*).

The simple hexaalkylditins, $R_3SnSnR'_3$, do not disproportionate on heating, but, in oxolane (tetrahydrofuran) or acetonitrile in the presence of a base such as a Grignard reagent, or in the more strongly basic solvent hexamethylphosphoric triamide (HMPT), disproportionation readily occurs at room temperature, and, in HMPT, addition occurs to such alkynes as phenylacetylene and diphenylbutadiyne. The disproportionation is considered to proceed by nucleophilic attack upon tin (*259, 260*), e.g.,

$$BrMgMe + R_3SnSnR'_3 \rightarrow MeSnR_3 + BrMgSnR'_3$$

$$BrMgSnR'_3 + R'_3SnSnR_3 \rightarrow R'_3SnSnR'_3 + BrMgSnR_3, \text{ etc.}$$

A similar mechanism probably applies to the reaction of the reagents $LiMMe_4$ (M = B, Al, Ga, or Tl), (*261*), e.g.,

$$Li^+\ Me_3\bar{T}l{-}Me + Me_3Sn{-}SnMe_3 \rightarrow Me_4Sn + Li^+\ Me_3\bar{T}lSnMe_3$$

The tin–tin bond is also cleaved by alkylmercuric halides, triethyl-

tin halides, trimethyllead chloride, and, catalytically, dicobalt octacarbonyl (*266*).

$$RHgX + Me_3SnSnMe_3 \rightarrow Me_3SnX + RHgSnMe_3 \rightarrow RSnMe_3 + Hg^{\circ} \text{ (262, 263)}$$

$$R_3SnX + Me_3SnSnMe_3 \rightarrow Me_3SnX + RSnMe_3 + (Me_2Sn^{II})_n \text{ (264)}$$

$$Me_3PbCl + Me_3SnSnMe_3 \rightarrow Me_3SnCl + Me_4Sn + Pb^{II}Cl_2 \text{ (265)}$$

$$Me_3SnSnMe_3 \xrightarrow{Co_2(CO)_8} Me_4Sn + (Me_2Sn^{II})_n$$

A cyclic mechanism has been tentatively proposed for the reaction involving trialkyltin halides.

If the groups R in R_3SnSnR_3 are very bulky, the Sn–Sn bond is weakened by steric strain, and dissociation can now occur on heating. Hexakis(2,4,6-trimethylphenyl)- and hexakis(2,4,6-triethylphenyl)-ditin can be prepared by heating the corresponding triaryltin hydrides with azoisobutyronitrile (AIBN) (*267*).

$$2\ Ar_3SnH \xrightarrow[100^{\circ}]{AIBN} Ar_3SnSnAr_3 \rightleftharpoons 2\ Ar_3Sn\cdot$$

In addition, the former compound shows the esr spectrum of $Ar_3Sn\cdot$ at 180°, and the latter does so at 100°. The Sn–Sn bond-dissociation energies are 190 ± 8 kJ · mol^{-1} and 125 ± 5 kJ · mol^{-1}, respectively, that is, they are considerably less than that for $Me_3SnSnMe_3$ (210–240 kJ · mol^{-1}).

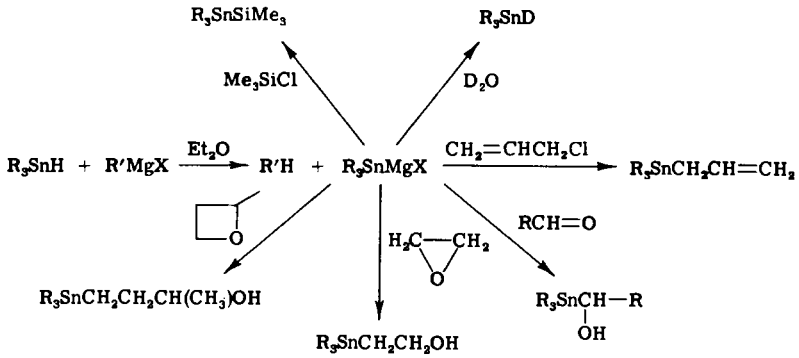
E. Tin–Metal Bonds, Sn–M

The preparation of trialkyltin compounds of lithium, R_3SnLi, and their use for preparing the organotin compounds, R_3SnR', has been discussed in a previous section.

Much interest has also been shown in compounds in which tin is bonded to a metal of Group II.

Grignard reagents having bulky alkyl groups react with trialkyltin hydrides to give compounds having a Sn–Mg bond, and are synthetically useful as a source of nucleophilic R_3Sn; in particular, they react with carbonyl compounds, oxiranes, and oxetanes to give the α-, β-, or

γ-hydroxyalkyltin compounds in good yield (*268–270*).

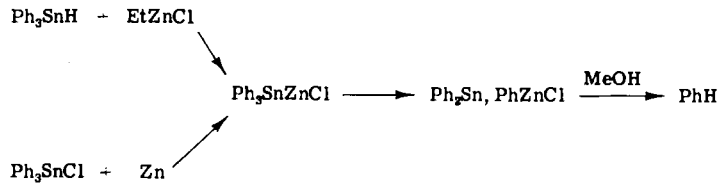


Similarly, triphenyltin hydride reacts with diethylzinc or diethylcadmium in a strongly solvating solvent, such as oxolane (tetrahydrofuran) or 1,2-dimethoxyethane, to give the solvated, metal–metal-bonded products (*271*).

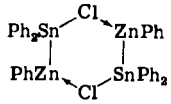
$$Ph_3SnH + Et_2Zn \rightarrow (Ph_3Sn)_2Zn$$

$$Ph_3SnH + Et_2Cd \rightarrow (Ph_3Sn)_2Cd$$

Likewise, triphenyltin hydride reacts with ethylzinc chloride, or triphenyltin chloride with metallic zinc, to give the compound $Ph_3SnZnCl$, which is stable in the presence of a strongly coordinating ligand, but, in its absence, apparently undergoes an intermetallic shift of the organic group, so that protic acids react to liberate benzene (*272*).

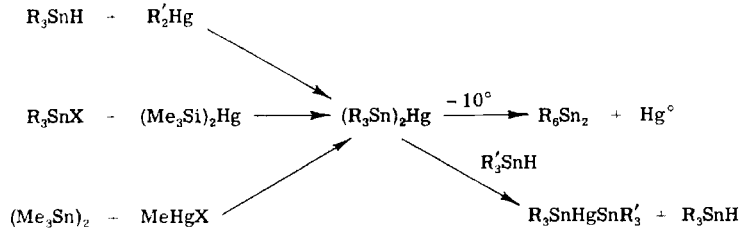


The Mössbauer spectrum of the rearranged compound corresponds with that of a Sn(IV) compound, and the most probable structure appears to be that of a chlorine-bridged dimer.



The bis(trialkyltin) compounds of mercury are formed when trialkyl-

tin hydrides react with dialkylmercury compounds, bis(trialkylsilyl)mercuries with trialkyltin halides, or hexamethylditin with methylmercuric halides (*273–276*).



The products are yellow or red solids; when R = Me, Et, Pr, or Bu, they decompose below −10°, but when R = Ph, or, particularly, when R = Me_3SiCH_2, the products are more stable. They are oxidized immediately in air to the corresponding distannoxanes, readily exchange the trialkyltin group with trialkyltin hydrides, and add across polar-substituted alkynes or azo compounds.

The compounds $R_3SnHgCR_3$ can be prepared by transmetallation with the corresponding silicon compound.

$$(Me_3Si)_2Hg + Bu^tHgX \rightarrow Me_3SiHgBu^t + Me_3SiX$$

$$Me_3SiHgBu^t + Me_3SnOMe \rightarrow Me_3SnHgBu^t + Me_3SiOMe$$

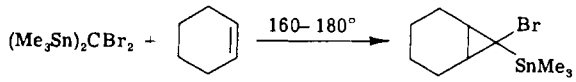
The product is a yellow oil that reacts with benzylidenemalonodinitrile by 1,4-addition of the Bu^t and $SnMe_3$ fragments, and decomposes at 37°, giving a CIDNP effect (*277, 278*).

Relatively little work has been carried out on the derivatives of the metals of Group III, but (trimethyltin)lithium has been shown to react with the trialkylmetallic compounds R_3M (M = B, Al, Ga, In, or Tl) to give the products $Me_3SnMR_3\ Li^+$, which decompose (B immediately, Ga and Zn in two days) to give $(Me_3Sn)_3SnLi$ (*279*).

F. Functionally Substituted Compounds

An improved route to iodomethylzinc iodide has made the iodomethyltin compounds, R_3SnCH_2I, more accessible (*280*). Dimetallic compounds of the types Me_3SnCBr_2MgCl (*281*), $Me_3SnCClBrLi$ (*282*), and $Me_3SnCHIZnI$ (*280, 283*), have been prepared in solution at low temperature, and thence, the ditin compounds $(Me_3Sn)_2CClBr$, $(Me_3Sn)_2CBr_2$, $(Me_3Sn)_2CHI$ (*284*).

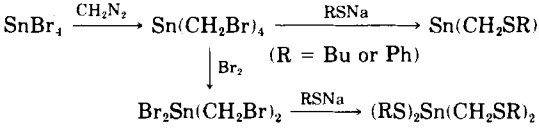
These compounds can then be used as a source of a tin-substituted carbene, e.g. (*284*),



The iodomethyltin compounds react with amines to give aminomethyltin compounds, $R_3SnCH_2NR_2$, and with phosphines to give the phosphonium ions, $Me_3SnCH_2P^+R_3$, and tris(tributylstannylmethyl)amine has been prepared from (tributyltin)lithium and tris(phenylthiomethyl)amine (*285*).

$$Bu_3SnLi + (PhSCH_2)_3N \rightarrow (Bu_3SnCH_2)_3N$$

The classic route to halogenomethyltin compounds is the methylenation of tin halides with diazomethane, and this reaction has been used as the basis for the preparation of a series of thiomethyltin compounds (*286*).



G. $R_3Sn\cdot$ Radicals

Trialkyltin radicals are important intermediates in the reduction of alkyl halides, and in the hydrostannation of alkenes (*1, 287*).

$$R_3Sn\cdot + R'X \rightarrow R_3SnX + R'\cdot$$

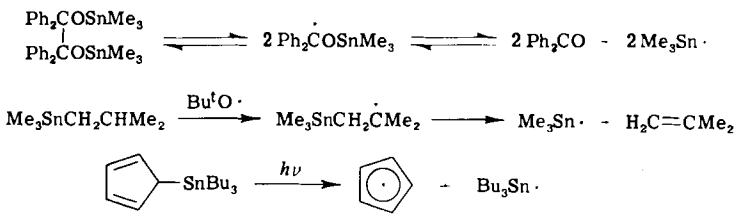
$$R'\cdot + R_3SnH \rightarrow R'H + R_3Sn\cdot$$

$$R_3Sn\cdot + C{=}C \rightarrow R_3SnCC\cdot$$

$$R_3SnCC\cdot + R_3SnH \rightarrow R_3SnCCH + R_3Sn\cdot$$

These reactions are well established, have been reviewed elsewhere (*288, 289*), and will not be considered in detail here.

New sources of $R_3Sn\cdot$ radicals that have been developed include the reversible thermal dissociation of bis(trialkylstannyl)pinacols (*290–292*), the β-scission of β-stannylalkyl radicals (*293*), and the photolysis of cyclopentadienyltin compounds (*294*).



The last two reactions are useful for esr studies involving free radicals. Until recently, the only trialkyltin radical that had been observed directly, in solution, by esr was $Me_3Sn\cdot$ (*295*), but many more have now been reported (e.g., $Et_3Sn\cdot$, $Pr_3Sn\cdot$, and $Bu_3Sn\cdot$) (*296*). Bulky ligands [e.g., $(PhCMe_2CH_2)_3Sn\cdot$] increase the persistence of the radicals, so that esr observation is easier (*297*), and tris(2,3,5-trimethylphenyl)tin and tris(2,3,5-triethylphenyl)tin radicals, at 180° and 100°, respectively, are in thermal equilibrium with the corresponding hexaarylditins (*298*).

$$Ar_3SnH \xrightarrow[100^\circ]{AIBN} 2\ Ar_3Sn\cdot \rightleftharpoons Ar_3SnSnAr_3$$
$$(Ar = 2,3,5\text{-}Me_3C_6H_2 \text{ or } 2,3,5\text{-}Et_3C_6H_2)$$

Very much more persistent radicals, with a half-life of up to a year, and with the structures $[(Me_3Si)_2CH]_3Sn\cdot$ and $[(Me_3Si)_2CH]_2RSn\cdot$ (R = Pr^i, Bu^t, Me, Et, Bu, or cyclopentadienyl) have been prepared by the photolysis of $[(Me_3Si)_2CH]_2Sn$(II), or by photolyzing a mixture of the appropriate halide $[(Me_3Si)_2CH]_2RSnX$ with an "electron rich" olefin (*299, 300*).

Homolytic substitution (SH2) by tin radicals at halogen centers (X) has been investigated extensively, the reactivity of the alkyl halides RX increasing in the sequence R = $R^p < R^s < R^t$, and X = F < Cl < Br < I (*301, 302*).

The reaction of tributyltin hydride with ring-substituted benzyl chlorides gives a Hammett ρ-factor of +0.81, confirming the "nucleophilic" character of the $Bu_3Sn\cdot$ radical (*303*).

Other centers at which the SH2 reaction by $R_3Sn\cdot$ radicals has been established include H (in R_3SnH) (*304*), N (in tetraalkyltetrazenes) (*305*), (but not P in diphosphines) (*306*), O (in peroxides) (*307–309*), S (in disulfides) (*310, 311*), and Se and Te (in diselenides and ditellurides) (*312*).

Apart from the familiar addition of $R_3Sn\cdot$ radicals to alkenes and alkynes, addition has also been shown to occur at O in C=O (in aldehydes, ketones, 1,2-diketones, and esters) (*313, 314*), S in C=S (in thioesters) (*315, 316*) and in $R_2P(S)P(S)R_2$ (*317*), and Se in C=Se (in selenoketones) (*318*).

H. R_2Sn: STANNYLENES

Like the Sn(III) radicals, the Sn(II) stannylenes are familiar both as persistent species of unlimited life and as transient, highly reactive intermediates. Many of the compounds that, in the older literature, were

referred to as monomeric R_2Sn species, are now recognized to be cyclic oligomers.

Dicyclopentadienyltin(II) is readily prepared from cyclopentadienyllithium or -sodium and tin(II) chloride, and is the best known, monomeric, R_2Sn compound. The planes of the $^5\eta$-cyclopentadienyl groups subtend an angle of $\sim 55°$, and the unshared pair of electrons can act as a ligand towards such Lewis acids as BF_3 and $AlCl_3$ (*319*).

The cyclopentadienyl groups are readily displaced by protic acids HX (e.g., alcohols, phenols, thiols, and oximes), providing a convenient route to other Sn(II) compounds (*320–323*).

$$(C_5H_5)_2Sn + 2\ HX \rightarrow SnX_2 + 2\ C_5H_6$$

Dicyclopentadienyltin also takes part in oxidative addition reactions with such reagents as iodomethane, diiodomethane, ethyl bromoacetate, and diphenyl disulfide, and there is evidence that the reactions involve a radical chain-mechanism (*324, 325*).

$$X\cdot + (C_5H_5)_2Sn \rightarrow (C_5H_5)_2\dot{S}nX$$

$$(C_5H_5)_2\dot{S}nX + XY \rightarrow (C_5H_5)_2SnXY + X\cdot$$

Another interesting organotin(II) compound is the highly sterically hindered $[(Me_3Si)_2CH]_2Sn$, which can be prepared by the reaction of $(Me_3Si)_2CHLi$ with $SnCl_2$ or $Sn[N(SiMe_3)_2]_2$ (*326–329*).

Like dicyclopentadienyltin, it undergoes oxidative addition-reactions with alkyl halides, and, again, there is evidence for a homolytic chain-mechanism (*330, 331*).

A single-crystal, X-ray diffraction analysis of the structure has recently been performed that shows that the compound is, in fact, a tin–tin bonded dimer, having an Sn–Sn bond length of 276 pm, similar to that in hexaphenylditin; this was interpreted in terms of overlap of a filled sp_zp_y orbital with the vacant p_z orbitals on the other tin atom resulting in a "bent," weak, Sn–Sn double bond (*332*).

Transient dialkylstannylene intermediates R_2Sn: (reviewed in ref. *333*) can be prepared by the thermolysis of distannanes ClR_2SnSnR_2Cl, R_3SnSnR_2Cl, or HR_2SnSnR_2H, e.g., (*334, 335*)

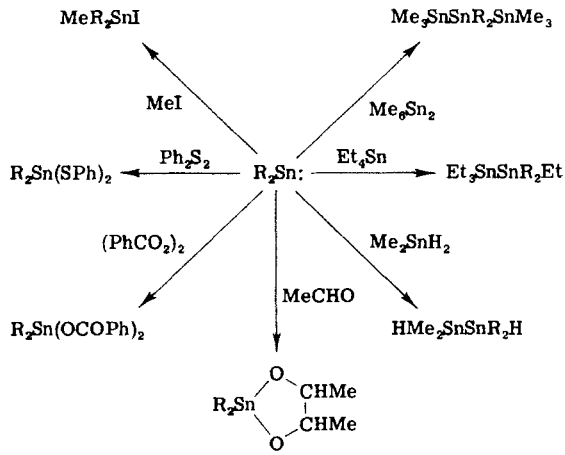
$$ClBu_2SnSnBu_2Cl \xrightarrow{120–130°} Bu_2SnCl_2 + [Bu_2Sn:]$$

$$Me_3SnSnMe_2Br \xrightarrow{20°} Me_3SnBr + [Me_2Sn:]$$

Alternatively, the oligomeric dialkylstannanes can be photolyzed (*336*).

$$(Bu_2Sn)_n \xrightarrow{h\nu} Bu_2\dot{S}n(SnBu_2)_{n-2}\dot{S}nBu_2 \rightarrow n\ Bu_2Sn:$$

The stannylenes from either source will insert into the Sn–Sn, Sn–R, or Sn–H bonds of organotin compounds, and react with alkyl halides, disulfides, or peroxides as shown in the reaction scheme below, but only the stannylenes that are generated photolytically will react with carbonyl compounds, and it appears that the stannylenes may exist in two forms, perhaps related as singlet and triplet, or a complexed and uncomplexed species.

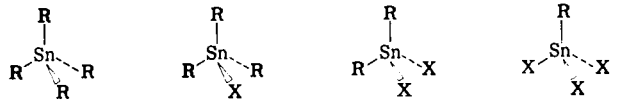


III. Structural Organotin Chemistry

Before 1963, when Hulme (*337*) used X-ray crystallography to demonstrate that the monopyridine adduct of trimethyltin chloride contains 5-coordinate tin, it had been generally assumed that most organotin(IV) compounds are simple, tetrahedral molecules containing 4-coordinate tin atoms. In recent years, however, the well established techniques of proton NMR and infrared spectroscopy have been supplemented by ^{119m}Mössbauer (*5–9*) and ^{119}Sn NMR spectroscopy (*10–12, 338*), and these have stimulated X-ray investigations of a large number of organotin compounds (*339, 340*). Many derivatives are now known that contain not only 5- and 6-, but even 7-, coordinate tin atoms, and a selection of these will be discussed in this section. This increased knowledge of the structural chemistry of organotin compounds is of considerable importance in understanding the mode of action operative in their many applications (see Section V) and explaining the variations that are observed in their toxicity (see Section IV).

A. X-Ray Investigations of Organotin(IV) Compounds

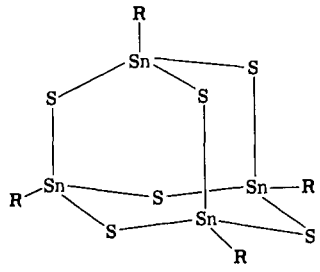
1. 4-Coordinate Compounds



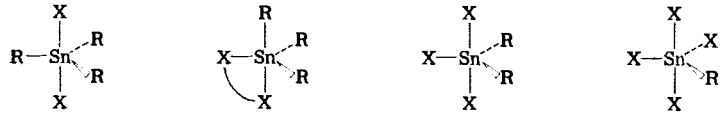
R_4Sn type R_3SnX type R_2SnX_2 type $RSnX_3$ type

The simplest bonding situation that can occur in organotin(IV) compounds consists of hybridization of the 5*s*- and three 5*p*- orbitals of the tin atom, to produce four tetrahedrally oriented bonds, and a coordination number of 4. Thus, the R_4Sn structural type is expected to be a tetrahedral molecule, as has been demonstrated for $Sn(C_6F_5)_4$ (*341*), $Sn(C_6H_4Me\text{-}3)_4$ (*342*), $Sn(C_6H_4Me\text{-}4)_4$ (*343*), Sn(2-thienyl)$_4$ (*344*), and $Sn(C_5H_5)_4$ (*345*). The absolute configuration of optically active (+)-2-triphenylstannylbutane has also been determined crystallographically (*346*).

If one (or more) alkyl or aryl groups in a tetraorganotin compound, R_4Sn, is (are) replaced by an electronegative substituent, X, the tin atom in the resulting compounds, R_nSnX_{4-n}, has a marked tendency to increase its coordination number above 4, as described in the following subsections. However, if the R or X groups are fairly bulky, the coordination number may remain 4, as in $[(Me_3Si)_2CH]_3SnCl$ (*347*), and in the triphenyltin thiophenoxides, $Ph_3SnSC_6H_4{}^tBu\text{-}4$ (*348*) and $Ph_3SnSC_6H_4Me\text{-}2$ (*349*), all of which have a regular, tetrahedral R_3SnX type of structure. Similarly, the cyclic dimethyltin sulfide trimer, $(Me_2SnS)_3$, is (*350, 351*) a six-membered ring in a boat conformation, with near-tetrahedral tin atoms of the R_2SnX_2 type. Structural data on 4-coordinate, mono-organotin compounds, $RSnX_3$, are very scarce, but an X-ray study of methyltin sesquisulfide, $(MeSnS_{1.5})_4$, in which the tin atom is in a tetrahedral $RSnX_3$ type of geometry involving one alkyl group and three sulfur atoms, showed the presence of an adamantane-like cage (*352*).



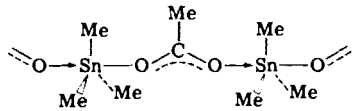
2. 5-Coordinate Compounds



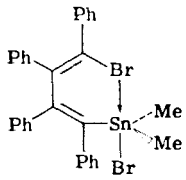
R_3SnX_2 type | *cis*-R_3SnX_2 type | *cis*-R_2SnX_3 type | $RSnX_4$ type

The tetraorganotin compounds, R_4Sn, show no tendency to increase their coordination number, owing to their weak, Lewis acidity conferred by the four electron-releasing alkyl groups. It has, however, been claimed (*353*) that trimethyl(trifluoromethyl)tin forms a 1:1 adduct with hexamethylphosphoric triamide, and that this may be isolated in the solid state.

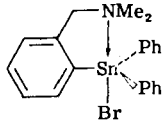
Replacement of one of the organic groups by an electronegative radical, X, decreases the electron density at the tin atom, and thus increases its ability to act as an electron acceptor. Compounds of the type R_3SnX readily form 5-coordinate, trigonal, bipyramidal complexes of the R_3SnX_2 type, in which the three organic groups are situated in an equatorial plane at right angles to the linear X—Sn—X axis. The 1:1 adduct of trimethyltin chloride with triphenylphosphine-acetylmethylene, $Me_3SnCl, Ph_3P{:}CHCOMe$, has been shown to be of this type (*354*). Trimethyltin acetate also has a tin atom that is pentacoordinate with an R_3SnX_2 geometry, but the structure is polymeric, with planar, Me_3Sn units linked by bridging, bidentate, acetate groups (*355*).



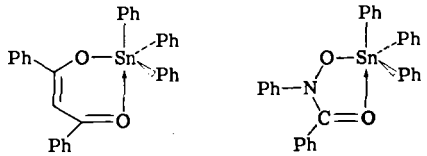
Many other R_3SnX compounds adopt this self-associated, infinite-chain structure in the solid state, and examples of common bridging atoms or groups include X = F, NCS, NCO, OMe, NO_3, or OH. Rather more unusual, however, are triorganotin compounds that have the same R_3SnX_2 geometry, but contain a tin atom that is pentacoordinate through intramolecular coordination via one of the R groups. Two compounds that are known to have a structure of this type are the mixed triorganotin bromides, dimethyl(4-bromo-1,2,3,4-tetraphenyl-*cis,cis*-1,-3-butadienyl)tin bromide (*356*)



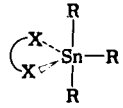
and *C,N*-{2-[(dimethylamino)methyl]phenyl} diphenyltin bromide (*357*).



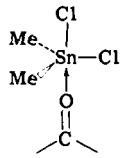
If the ligand X_2 in a pentacoordinate triorganotin compound is potentially bidentate, such as the anion of 1,3-diphenyl-1,3-propanedione or of *N*-benzoyl-*N*-phenylhydroxylamine, the tin atom is constrained to a *cis*-R_3SnX_2 type of geometry, e.g., the triphenylstannyl derivatives of



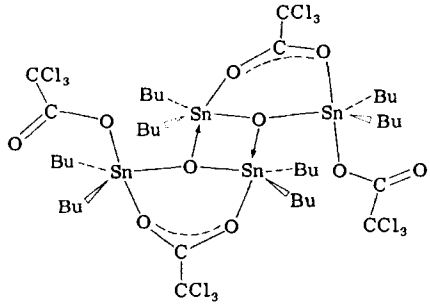
these anions (*358, 359*). No examples of triorganotin compounds that have a *meridional* -R_3SnX_2 type of geometry have yet been demonstrated crystallographically.



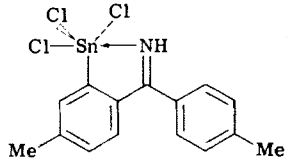
The diorganotin compounds, R_2SnX_2, are stronger Lewis acids than the triorganotins, R_3SnX; and the 5-coordinate complexes, R_2SnX_3, which result from the addition of a donor atom or group to the R_2SnX_2 compound, are not very common, mainly because of the tendency of the tin atom in these compounds to increase its coordination number to 6 by accepting *two* donor molecules (and, in some cases, even up to 7, as will be described later). However, the existence of a number of pentacoordinate complexes having a *cis*-R_2SnX_3 geometry has been demonstrated by X-ray crystallography. The anion in quinolinium dimethyltrichlorostannate, $(C_9H_8N)^+$ $(Me_2SnCl_3)^-$, is a distorted, trigonal bipyramid having the two methyl groups occupying equatorial positions (*360*). Salicylaldehyde forms a 1:1 complex with dimethyltin dichloride, and X-ray studies revealed (*361*) a similar tinatom geometry, with two methyl groups occupying equatorial positions of a trigonal bipyramid and the other three sites taken up by the two chlorine atoms and a donor



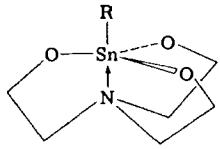
carbonyl oxygen atom from the aldehyde. Dimeric tetrabutyl-1,3-bis(trichloroacetoxy)distannoxane, $[(Cl_3CO{\cdot}O{\cdot}Bu_2Sn)^2O]_2$, has a ladder structure involving both monodentate and bidentate carboxylate groups, with the tin atoms occupying a *cis* R_2SnX_3 geometry (*362*).



Monoorganotin compounds, $RSnX_3$, also show a marked tendency to increase their coordination number from 4 to 6, or 7, and there are few examples of compounds of the type $RSnX_4$ (which contain pentacoordinate tin). The anion in tetraphenylarsonium tetrachloromonomethylstannate, $(Ph_4As)^+(MeSnCl_4)^-$, is one such example, and consists of a trigonal bipyramid with the methyl group occupying an equatorial site (*363*). A similar $RSnX_4$ type of geometry, with the organic group again occupying an equatorial position, was found (*364*) in the intramolecularly pentacoordinate, ketiminotin trichloride.

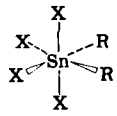


It is quite probable that, in the monoorganostannatranes, $RSn(OCH_2CH_2)_3N$, the tin atom also occupies a trigonal, bipyramidal geometry, but with the organic group forced into an axial site (*195*,

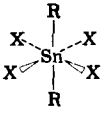


198). This configuration has not yet been demonstrated by X-ray studies, perhaps due to the difficulty in obtaining good crystalline samples. Recently, Tzschach reviewed the whole field of intramolecularly pentacoordinate, organotin compounds (*198*), including the stannatranes.

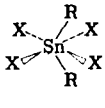
3. 6-Coordinate Compounds



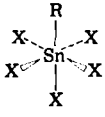
cis-R_2SnX_4 type



trans-R_2SnX_4 type



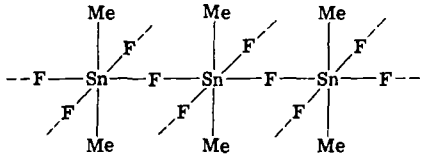
distorted *trans*-R_2SnX_4 type



$RSnX_5$ type

In triorganotin compounds of the type R_3SnX, as mentioned previously, the tin atom is only a weak acceptor, and these compounds tend to increase their coordination number only to 5. Consequently, examples of 6-coordinate, triorganotin complexes containing three inorganic groups or ligands, R_3SnX_3, have not yet been demonstrated crystallographically. The 1:1 adducts of trimethyltin chloride with 2,2-bipyridyl, and of trimethyltin isothiocyanate with 1,10-phenanthroline are believed to contain 6-coordinate tin on the basis of the infrared-spectral properties (*365*).

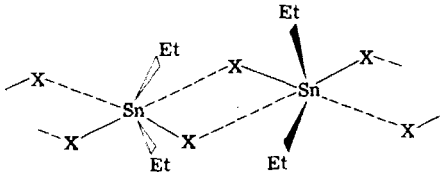
In contrast, the diorganotin compounds, R_2SnX_2, show a strong tendency to increase their coordination number to 6 by accepting two donor molecules, thus leading to octahedral complexes of the type R_2SnX_4, which can exist as the cis or trans isomers, as already illustrated. The *cis*-R_2SnX_4 orientation is often found to be sterically favorable when two bidentate ligands are present, as in Me_2Snox_2 (*366*), $Me_2Sn(O{\cdot}NH{\cdot}CO{\cdot}Me)_2$ (*367*), and $Ph_2Sn(S{\cdot}CS{\cdot}NEt_2)_2$(*368*). Dimethyltin bis(acetylacetonate), however, has a *trans*-R_2SnX_4 geometry (*369*), as have the two diphenyltin dichloride adducts Ph_2SnCl_2,bipy (*370*) and Ph_2SnCl_2,$2Me_2SO$ (*371*). Dimethyltin difluoride consists of an infinite, two-dimensional network of tin and fluorine atoms, with each tin linearly bridged to its four neighbors by one, symmetrically disposed, fluorine atom, and the methyl groups situated above and below this plane, thus completing a regular, octahedral *trans*-R_2SnX_4 type of coordination of the tin atom (*372*).



Dimethyltin bis(fluorosulfonate), $Me_2Sn(SO_3F)_2$, has a similar, polymeric structure (*373*).

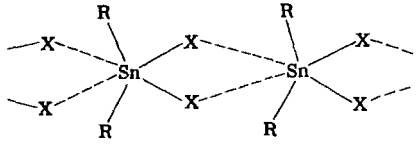
Interesting variations of this *trans*-R_2SnX_4 structure exist; they usually take the form of a distorted geometry in which the C–Sn–C

bond angle is lessened below 180°, and the four inorganic groups remain in a plane about the tin atom, but two pairs of groups are at different distances from the central tin atom. (This was illustrated at the beginning of this subsection.) This type of structure is exemplified by diethyltin dichloride and dibromide (*374*), which consist of chains of molecules, with each tin atom in a distorted, *trans*-R_2SnX_4 environment of two ethyl groups and coplanar chlorine, and bridging chlorine atom pairs.



(X = Cl or Br)

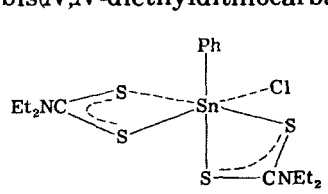
Dimethyltin dichloride has a similar chain structure (*375*). In diethyltin diiodide (*374*), dimethyltin diisothiocyanate (*376, 377*), and dichloro bis(chloromethyl)stannane (*378*), however, the distorted, *trans*-R_2SnX_4 geometry of each tin atom is completed by two bridging bonds involving the halogen or pseudohalogen atoms on the same, neighboring molecule.



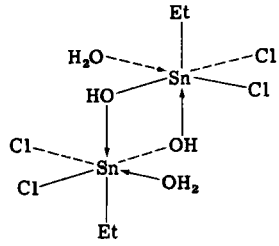
(R = Me, X = NCS; R = Et, X = I;
R = CH_2Cl, X = Cl)

The same, distorted, octahedral geometry is also found in a number of monomeric diorganotin complexes having two bidentate ligands, such as $Me_2Sn(O{\cdot}NMe{\cdot}CO{\cdot}Me)_2$ (*379*) and $Me_2Sn(S{\cdot}CS{\cdot}NMe_2)_2$ (*380*), or one tetradentate group, such as Me_2Sn(salen) (*381*).

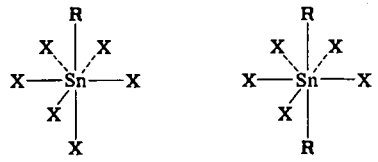
Monoorganotin compounds, $RSnX_3$, like the diorganotin derivatives, have a strong tendency to increase their coordination number up to 6 by accepting two donor molecules, leading to octahedral complexes of the $RSnX_5$ type. Two examples of molecules having this geometry are chloromonophenyltin bis(*N*,*N*-diethyldithiocarbamate) (*382*)



and the dimeric, monoethyltin hydroxide dichloride hydrate, $EtSn(OH)Cl_2 \cdot H_2O$ (*383*).



4. 7-Coordinate Compounds



$RSnX_6$ type R_2SnX_5 type

Monoorganotin compounds having three bidentate, donor ligands, such as $MeSn(NO_3)_3$ (*384*) and $MeSn(SCSNEt_2)_3$ (*385*), contain a tin atom occupying a pentagonal, bipyramidal geometry, as just illustrated. Certain diorganotin complexes have also been shown to possess a tin atom in a pentagonal, bipyramidal structure of the R_2SnX_5 type, namely, $Me_2Sn(NCS)_2$, terpy (*386*), $[Ph_2Sn(NO_3), 3Me_2SO]^+ NO_3^-$ (*387*), $(^nPr_2SO)Ph_2Sn(NO_3) \cdot O \cdot CO \cdot CO \cdot O \cdot SnPh_2(NO_3)$ ($^nPr_2SO$) (*388*), and $Ph_2Sn(NO_3)_2$, Ph_3PO (*461*).

5. Survey of Organotin(IV) Crystal Structures

The X-ray crystal structures of organotin compounds that have been described since Ho and Zuckerman's earlier compilation (*339*) are listed systematically in Table I.[1]

The following abbreviations are used: $salenH_2$ = bis(salicylaldehyde)ethylenediimine, salH = salicylaldehyde, SAB = 2-hydroxy-*N*-(2-hydroxybenzylidine)aniline dianion, SAT = 2-(*o*-hydroxyphenyl)benzothiazoline dianion, SAP = *N*-(2-hydroxyphenyl)salicyladldimine dianion, and HMPT = hexamethylphosphoric triamide, and structures marked with an asterisk (*) are polymeric, usually by intermolecular association.

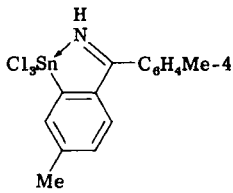
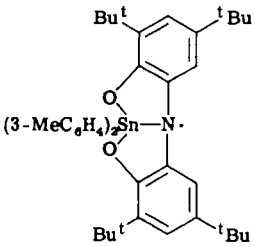
[1] Since this review was written, Zuckerman has up-dated his earlier compilation (*339*) to 1978 [Zubieta, J. A., and Zuckerman, J. J., *Progr. Inorg. Chem.*, **24**, 251 (1978)].

TABLE I

THE STEREOCHEMISTRIES OF ORGANOTIN(IV) COMPOUNDS THAT HAVE BEEN DETERMINED BY X-RAY CRYSTALLOGRAPHY

Compound	Geometry of Sn Atom	Ref.
Mono-, Di-, and Tri-methyltin Compounds, Me_nSnX_{4-n}		
$MeSn(SCSNEt_2)_3$	Distorted $RSnX_6$	*385*
$Me_2Sn(acac)_2$	*trans*-R_2SnX_4	*369*
$Me_2Sn(salen)$	Distorted *trans*-R_2SnX_4	*381*
$Me_2SnSCH_2CH_2S$	Distorted R_2SnX_2	*389*
$Me_2Sn(O{\cdot}NMe{\cdot}CO{\cdot}Me)_2$	Distorted *trans*-R_2SnX_4	*379*
$Me_2Sn(O{\cdot}NH{\cdot}CO{\cdot}Me)_2$	*cis*-$R_2SnX_4^*$	*367*
$Me_2Sn(O{\cdot}NH{\cdot}CO{\cdot}Me)_2{\cdot}H_2O$	Distorted *trans*-$R_2SnX_4^*$	*367*
$Me_2Sn(SCSNMe_2)_2$	Distorted *trans*-R_2SnX_4	*380*
$Me_2Sn(SAB)$	Distorted *cis*-R_2SnX_3 (dimeric)	*390*
$Me_2Sn(SAP)$	Distorted *cis*-R_2SnX_3	*391*
$Me_2Sn(OH)NO_3$	Distorted *cis*-R_2SnX_3 (dimeric)	*392*
$(Me_2Sn)_3(PO_4)_2{\cdot}\ 8\ H_2O$		*393*
inner Sn atoms	*trans*-$R_2SnX_4^*$	
outer Sn atoms	Distorted *trans*-$R_2SnX_4^*$	
Me_3SnOMe	$R_3SnX_2^*$	*394*
$Me_3SnONC_6H_{10}$	$R_3SnX_2^*$	*395*
$Me_3SnN(Me)NO_2$	$R_3SnX_2^*$	*396*
Me_3SnNCO, Me_3SnOH	$R_3SnX_2^*$	*397*
$Me_3SnOCHO$	$R_3SnX_2^*$	*398*
$Me_3SnOCOMe$	$R_3SnX_2^*$	*355*
$Me_3SnOCOCF_3$	$R_3SnX_2^*$	*355*
$Me_3SnOCOCH_2NH_2$	$R_3SnX_2^*$	*399*
$Me_3SnOCOPy\text{-}2{\cdot}H_2O$	$R_3SnX_2^*$	*400*
Me_3SnNO_3	$R_3SnX_2^*$	*401*
Me_3SnSO_2Me	$R_3SnX_2^*$	*402,403*
$Me_3SnSO_2CH_2C{:}CH$	$R_3SnX_2^*$	*404*
$Me_3SnSO_3Ph{\cdot}H_2O$	$R_3SnX_2^*$	*405*
$(Me_3Sn)_3(OH)CrO_4$	$R_3SnX_2^*$	*406*
Mono- and Di-ethyltin Compounds, $EtSnX_3$ and Et_2SnX_2		
$EtSn(OH)Cl_2{\cdot}H_2O$	$RSnX_5$ (dimeric)	*383*
Et_2SnCl_2	Distorted *trans*-$R_2SnX_4^*$	*374*
Et_2SnBr_2	Distorted *trans*-$R_2SnX_4^*$	*374*
Et_2SnI_2	Distorted *trans*-$R_2SnX_4^*$	*374*
Di- and Tri-n-butyltin Compounds, Bu_2SnX_2 and Bu_3SnX		
$Bu_2SnO(CH_2)_3O$	Distorted *trans*-$R_2SnX_4^*$	*407*
$Bu_2SnSCH_2CH_2S$	Space-group and unit-cell data only	*408*

TABLE I (*Continued*)

Compound	Geometry of Sn Atom	Ref.
Bu_3SnF	Incomplete determination	*409*
$(Bu_3Sn)_2SO_4$	Incomplete determination	*450*
Mono-, Di- and Tri-phenyltin Compounds, Ph_nSnX_{4-n}		
$PhSn(SCSNEt_2)_2Cl$	Distorted $RSnX_5$	*382*
$(^nPr_2SO)Ph_2Sn(NO_3)O{\cdot}CO{\cdot}CO{\cdot}OSnPh_2(NO_3)(^nPr_2SO)$	R_2SnX_5	*388*
$Ph_2Sn(SCSNEt_2)_2$	Distorted *cis*-R_2SnX_4	*368*
$Ph_2Sn[SPS(OEt)_2]_2$	Distorted *trans*-R_2SnX_4	*465*
$Ph_2Sn(glygly)$	Distorted *cis*-R_2SnX_3	*410*
$Ph_2Sn(SAT)$	Distorted *cis*-R_2SnX_3	*411*
$Ph_2Sn(SAB)$	Distorted *cis*-R_2SnX_3	*412*
Ph_3SnOH	$R_3SnX_2^*$	*413*
$Ph_3SnO{\cdot}CPh{\cdot}CH{\cdot}CO{\cdot}Ph$	*cis*-R_3SnX_2	*358*
$Ph_3SnO{\cdot}NPh{\cdot}CO{\cdot}Ph$	*cis*-R_3SnX_2	*359*
$Ph_3SnSPy\text{-}4$	$R_3SnX_2^*$	*414*
Ph_3SnNCS	$R_3SnX_2^*$	*415*
Ph_3SnNCO	$R_3SnX_2^*$	*416*
$Ph_3SnSC_6H_4{}^tBu\text{-}4$	R_3SnX	*348*
$Ph_3SnSC_6H_2Me_3\text{-}2,4,6$	R_3SnX	*349*
$Ph_3SnSC_6H_4Me\text{-}2$	R_3SnX	*349*
$Ph_3SnSC_6H_2F\text{-}4,Br_2\text{-}2,6$	R_3SnX	*349*
Other Mono-, Di-, and Tri-organotin Compounds, R_nSnX_{4-n}		
	$RSnX_4$	*364*
$(ClCH_2)_2SnCl_2$	Distorted *trans*-$R_2SnX_4^*$	*378*
$(Ferrocenyl)_2SnCl_2$	R_2SnX_2	*417*
	Distorted *cis*-R_2SnX_3	*418*

(*continued*)

TABLE I (*Continued*)

Compound	Geometry of Sn Atom	Ref.
2-$(Me_2NCH_2)C_6H_4SnPh_2Br$	R_3SnX_2	*357*
2,6-$(Me_2NCH_2)_2C_6H_3SnMe_2^+Br^-$	R_3SnX_2	*463*
2-$(Me_2NCHMe)C_6H_4SnMePhBr$	R_3SnX_2	*464*
$[(Me_3Si)_2CH]_3SnCl$	R_3SnX	*347*
Symmetrical and Unsymmetrical Tetraorganotins, R_4Sn and R_3SnR^1		
$Sn(C_6F_5)_4$	R_4Sn	*341*
$Sn(C_6H_4Me\text{-}3)_4$	R_4Sn	*342*
$Sn(2\text{-thienyl})_4$	R_4Sn	*344*
$Sn(C_5H_5)_4$	$R_4Sn(-60°)$	*345*
1,1-$(Me_3Sn)_2C_5H_4$	$R_3SnR^1(-60°)$	*419*
$Ph_3SnC_7H_7$	R_3SnR^1	*420*
$Ph_3SnCHMeEt$	R_3SnR^1	*346*
Ph_3SnCH_2I	R_3SnR^1	*346a*
Compounds Containing Tin–Metal Bonds		
$Ph_3SnSnPh_3$	R_3SnX	*422*
$Ph_3Sn^aSnNO_3(AsPh_3)$ Tin a	R_3SnX (dimeric)	*421*
$(Ph_3Sn^a)_3^bSnNO_3$ Tin a	Distorted R_3SnX	*423*
Tin b	See ref.	*423*
$Ph_3^bSnSnNO_3$ Tin a	Distorted R_3SnX	*423*
$[Me_3SnRu_4(CO_4)]_2$	R_3SnX	*424*
$[Me_2SnFe(CO_4]_2$	Distorted R_2SnX_2	*425*
$\{Me_2Sn\ Fe(CO_4)\}_2Sn\{Fe(CO_4\}_2SnMe_2$	R_2SnX_2	*426*
$\{(\sigma\text{-}C_5H_5)_2SnFe(CO)_4\}_2$	Distorted R_2SnX_2	*427*
$Ph_3Sn\{Fe(CO)(\pi\text{-}C_5H_5)(\pi\text{-}PhC{:}CPh)\}$	R_3SnX	*428*
cis-$(Ph_3Sn)_2Fe(CO)_4$	R_3SnX	*429*
$\{Me_2SnCo(CO)(\pi\text{-}C_5H_5)\}_2$	Distorted R_2SnX_2	*430*
$Ph_2Sn\{Co(CO)_2(\pi\text{-}C_7H_8)\}_2$	Distorted R_2SnX_2	*431*
trans-$(Me_3Sn)_2Ni(PPh_3)_2Cl_2$	R_3SnX	*432*
trans-$(Ph_3Sn)_2Os(CO)_4$	R_3SnX	*433*
$PhCl_2SnMo(CO)_2(C_7H_7)$	Distorted $RSnX_3$	*434*
$Ph_2ClSnMo(CO)_2(C_7H_7)$	Distorted R_2SnX_2	*434*
$(CH_2{:}CH)_2Sn\{Mn(CO)_5\}_2$	R_2SnX_2	*435*
$^tBu_2(Py)SnCr(CO)_5$	Flattened tetrahedron	*436*
$[Ph_3SnNi\{N(CH_2CH_2PPh_2)_3\}]^+BPh_4^-$	R_3SnX	*451*
Organotin Oxides and Sulfides		
$Ph_3SnOSiPh_3$	Unit-cell data only	*437*
$(Bu_2SnOCOCCl_3)_2O$	Distorted *cis*-R_2SnX_3 (dimeric)	*362*
$Ph_3SnSSnPh_3$	R_3SnX	*462*

TABLE I (*Continued*)

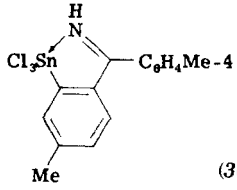
Compound	Geometry of Sn Atom	Ref.
$Ph_3SnSPbPh_3$	R_3SnX	*438*
$(Me_2SnS)_3$		
tetragonal form	R_2SnX_2	*350*
monoclinic form	R_2SnX_2	*351*
Ionic Organotin Halide Complexes		
$(Ph_4As)^+ (MeSnCl_4)^-$	$RSnX_4$	*363*
$(C_5H_5N)^+ (Me_2SnCl_3)^-$	Distorted *cis*-R_2SnX_3	*360*
$(PyH)_2^+(Me_2SnCl_4)^{2-}$	*trans*-R_2SnX_4	*439*
$[Ph_3Sn(NO_3), 3\ DMSO]^+ NO_3^-$	R_2SnX_5	*389*
$(BzPPh_3)^+(Bu_3SnCl_2)^-$	R_3SnX_2	*440*
$[Me_3Sn(HMPT)_2]^+ (Me_3SnBr_2)^-$	R_3SnX_2	*440a*
Covalent Organotin Halide, Pseudohalide, Carboxylate, and Nitrate Complexes		
Me_2SnCl_2, 2 DMF	*trans*-R_2SnX_4	*441*
Me_2SnCl_2, 2 HMPT	*trans*-R_2SnX_4	*441*
Me_2SnBr_2, 2 HMPT	*trans*-R_2SnX_4	*441*
Me_2SnCl_2, $salenH_2$	*trans*-R_2SnX_4*	*442*
Me_2SnCl_2,salH	*cis*-R_2SnX_3	*361*
Me_2SnCl_2, 2 DMSO	*trans*-R_2SnX_4	*441,443*
Me_2SnBr_2, 2 DMSO	*trans*-R_2SnX_4	*441*
$Me_2Sn(NCS)_2$, terpy	R_2SnX_5	*386*
Me_2SnCl_2, Ni(salen)	Distorted *trans*-R_2SnX_4	*444*
Me_3SnCl, Ph_3P:CHCOMe	R_3SnX_2	*354*
$(CH_2{:}CH)_2Sn(OCOCF_3)_2$, bipy	Distorted *trans*-R_2SnX_4	*445*
$Ph_2Sn(NO_3)_2$, Ph_3PO	R_2SnX_5	*461*
Ph_2SnCl_2, bipy	*trans*-R_2SnX_4	*370*
Ph_2SnCl_2, 2 DMSO	*trans*-R_2SnX_4	*371*
Ph_3SnNO_3, Ph_3PO	R_3SnX_2	*446*
Ph_3SnNO_3, Ph_3AsO	R_3SnX_2	*447*
Ph_3SnNO_3, PyO		
monoclinic form	Distorted R_3SnX_2	*448*
triclinic form	Distorted R_3SnX_2	*449*
$MeSnCl_3$, 2 HMPT	$RSnX_5$	*441*
$MeSnBr_3$, 2 HMPT	$RSnX_5$	*441*
$MeSnCl_3$, 2 DMF	$RSnX_5$	*441*
Me_3SnCl, HMPT	R_3SnX_2	*440a*
Ph_2SnCl_2, benzothiazole	*cis*-R_2SnX_3	*440b*

B. ^{119}Sn Mössbauer Spectroscopy

The various, solid-state stereochemistries just described may often be distinguished fairly readily by ^{119}Sn Mössbauer spectroscopy (*5–9, 452*), particularly from the value of the quadrupole splitting parameter, ΔE_Q (see Table II).

TABLE II

^{119}Sn Mössbauer Quadrupole Splittings for Organotin Compounds of Known Stereochemistry

Stereochemistry	Example	ΔE_Q (mm·sec^{-1})	Ref.
$RSnX_3$	$(MeSnS_{1.5})_4$ (*352*)	1.40	*195*
R_2SnX_2	$(Me_2SnS)_3$ (*350,351*)	1.82	*453*
R_3SnX	$[(Me_3Si)_2CH]_3SnCl$ (*347*)	2.18	*454*
R_4Sn	$(C_6F_5)_4Sn$ (*341*)	0.00	*455*
cis-R_3SnX_2	$Ph_3SnO{\cdot}NPh{\cdot}CO{\cdot}Ph$ (*359*)	1.94	*400*
R_3SnX_2	$Me_3SnOCOMe$ (*355*)	3.00–4.00[a]	
R_2SnX_3	Me_2SnCl_2, salH (*361*)	3.32	*456*
			
$RSnX_4$	(*364*)	1.59	*364*
cis-R_2SnX_4	$Ph_2Sn(SCSNEt_2)_2$ (*368*)	1.74	*457*
trans-R_2SnX_4	$Me_2Sn(acac)_2$ (*369*)	4.02	*400*
distorted *trans*-R_2SnX_4	Me_2Sn(salen) (*381*)	3.10–3.70[b]	
$RSnX_5$	$PhSn(SCSNEt_2)_2Cl$ (*382*)	1.66	*457*
$RSnX_6$	$MeSn(SCSNEt_2)_3$ (*385*)	1.97	*458*
R_2SnX_5	$Me_2Sn(NCS)_2$, terpy (*386*)	4.29	*459*

[a] Lower end of ΔE_Q range for symmetrical X—Sn · · · X unit.
[b] ΔE_Q increases as CSnC opens.

For example, octahedral *trans*-R_2SnX_4 complexes give approximately twice the quadrupole splitting observed for the cis-octahedral analogs (*7, 8*). More recently, temperature-dependent Mössbauer measurements have been used in conjunction with Raman spectroscopy to determine molecular weights (*453*) and lattice rigidity (*460*) of various organotin compounds.

IV. Biological and Environmental Aspects

A. Biological Activity and Mode of Toxic Action

1. R_4Sn Compounds

The biological effects of tetraorganotins, R_4Sn, in mammals appear to be caused principally by the R_3SnX compound, which is produced by their *in vivo* (*466*) and *in vitro* (*466, 467*) conversion, particularly in the liver. Studies in mice and dogs (*468*) showed that tetraethyltin was the most toxic, followed by tetramethyltin, and, thereafter, the toxicity decreased with increasing alkyl chain-length. A similar pattern of toxicity was found for the R_3SnX, R_2SnX_2, and $RSnX_3$ compounds (*469–471*). Following administration of the R_4Sn compound, delayed development of toxic symptoms is usually observed (*468*), due to the *in vivo* formation of the more toxic R_3SnX derivative.

2. R_3SnX Compounds

Progressive introduction of organic groups at the tin atom in any member of the R_nSnX_{4-n} series produces a maximum biological activity when $n = 3$, i.e., for the triorganotin compounds, R_3SnX (*469–471*). If the chain length of the *n*-alkyl group is increased within any trialkyltin series, R_3SnX, the highest mammalian toxicity is attained when R = Et (*471*). For insects, however, the trimethyltins are usually the most toxic (*472*); for Gram-negative bacteria, the tri-*n*-propyltins (*473*), and for Gram-positive bacteria and fungi, the tributyltins show the highest activity (*473, 474*) (see Fig. 1). Further increase in the *n*-alkyl chain-length produces a sharp drop in the biological activity, and the tri-*n*-octyltin compounds are essentially nontoxic to all living species.

Variation of the inorganic radical, X, within any particular series of R_3SnX compounds usually has very little effect on the biological activity, and it is the nature of the R_3Sn moiety that is of prime importance. The triphenyltin compounds also show a high fungicidal activity (*473, 474*), and tricyclohexyl- (*475*) and trineophyl-tin (*476*) derivatives are very active against mites. In addition, bulky R groups, such as those in bis(trineophyltin) oxide, appear to lessen the mammalian toxicity (*476*).

The lower trialkyltin compounds are able to inhibit mitochondrial, oxidative phosphorylation (*471, 477*) and, therefore, disrupt the funda-

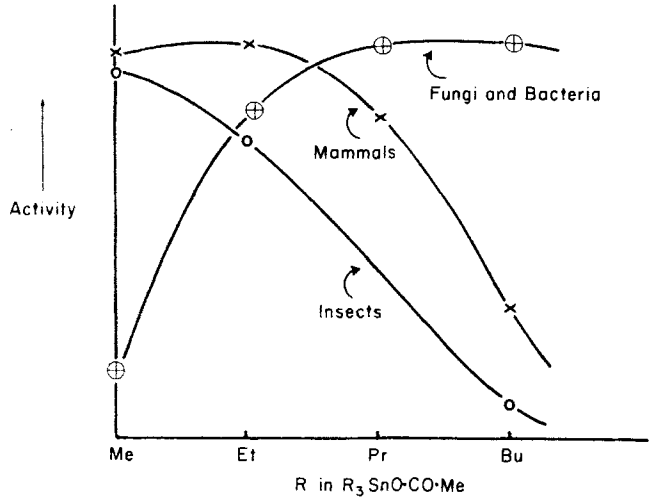


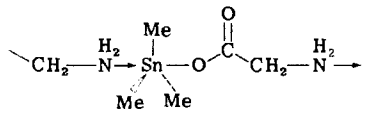
FIG. 1. Dependence of the biological activity of tri-*n*-alkyltin acetates on the nature of the alkyl group for different species.

mental energy processes in living systems. Their remarkable biological activity pattern may be dependent upon the effectiveness of their interaction at an active site (or sites) which involves coordination to an amino acid (*478*). The exact, chemical nature of these high-affinity binding-sites has recently been the focus of much attention (*477, 479, 480*).

In the case of simple amino acids and dipeptides, esterification of the carboxyl groups occurs on heating in toluene with the appropriate bis(triorganotin) oxide or triorganotin hydroxide (*481, 482*), the water being removed azeotropically.

$$2\ H_2NCHR^1CO_2H + (R_3Sn)_2O \rightarrow 2\ H_2NCHR^1CO_2SnR_3 + H_2O$$

The resulting derivatives, unlike most organotin carboxylates, are hydrolyzed relatively readily in air. An X-ray crystallographic study (*399*) showed that trimethyltin glycinate has an intermolecularly associated, polymeric structure, with bridging amino groups.



In trimethyltin acetate, however, bridging occurs through the carboxylate group (*355*), as described in Section III. An X-ray study of the di-

phenyltin derivative of the dipeptide glycylglycine was also reported recently (*410*).

Limouzin and Maire (*66*) used ESCA spectroscopy to study complex-formation between tributyltin chloride and a number of amino acids. They concluded that, although the $-NH_2$ groups are not basic enough to coordinate to tin, complexation does occur at the $-SH$ group of cysteine. It has also been found that the Sn–S–C linkage in *S*-(tributylstannyl)cysteine, $Bu_3SnSCH_2CH(NH_3^+)CO_2^-$, is quite stable to hydrolysis (*483*). Another possible point of attachment of trialkyltins to amino acids is via N-1 of the imidazole ring in histidine (*484, 485*).

On a macromolecular scale, trialkyltins are known to bind to a number of proteins (see Table III).

Studies *in vitro* with bis(tributyltin) oxide in snail protein indicated a high order of activity with a number of amino acids (as well as lipids), and it has been suggested that mortality arises from direct reaction of the organotin with proteins (*489*). Elliott and Aldridge (*486*) found that two molecules of triethyltin chloride bind to one molecule of either rat or cat hemoglobin, and that at least one of these binding sites involves histidine residues. Recent work by Maire (*66*), Griffiths (*490*), and Tan (*490a*) and their co-workers suggested that $-SH$ groups may also be involved in binding the trialkyltins.

The ^{119m}Sn Mössbauer spectra of triethyltin compounds bound to high-affinity, protein sites indicate that the quadrupole splitting, ΔE_Q, is less than 2.3 $mm \cdot sec^{-1}$ (*479, 491*), which would be consistent with tetrahedral, R_3SnX, tin-atom geometry, or a 5-coordinate, *cis*-R_3SnX_2 chelated structure. However, the trialkyltin–histidine complex, having a planar, R_3Sn unit, suggested earlier by Rose and Lock (*485*,

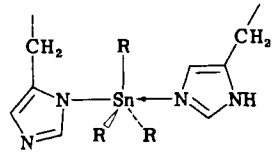


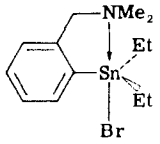
TABLE III

SOME PROTEINS THAT BIND TRIALKYLTIN COMPOUNDS

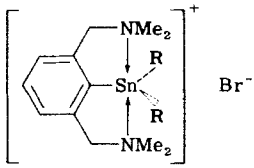
Protein	R_3SnX Compound	Ref.
1. Cat hemoglobin	$(Et_3Sn)_2SO_4/Et_3SnCl$	*486*
2. Rat hemoglobin	$(Et_3Sn)_2SO_4/Et_3SnCl$	*486*
3. Rat-brain myelin	Et_3SnCl	*487*
4. Protein fraction from guinea pig liver	Et_3SnCl	*488*
5. Snail-tissue protein	$(Bu_3Sn)_2O$	*489*
6. Yeast mitochondrial membrane	Et_3SnCl	*480*

488), may be excluded (*479*), as this R_3SnX_2 tin-atom geometry would be expected to give a $\Delta E_Q \geq 3$ mm·sec^{-1} (*400*).

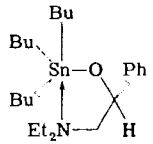
Farrow and Selwyn (*479*) found that the intramolecularly 5-coordinate, mixed triorganotin bromide, prepared by Nöltes and his co-workers (*63, 492*), namely,



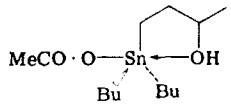
is more effective as an inhibitor of the mitochondrial ATPase than the simple triorganotin compounds, but that 5-coordinate, triorganotin compounds having two intramolecular Sn ← N bonds (*63, 463, 492*)



are feeble inhibitors. Tzschach and co-workers (*493*) observed that the tributyltin derivative



which contains a chelating diethylamino alcohol group, was approximately one-eighth as toxic orally to mice as the 4-coordinate bis(tributyltin) oxide, and this was ascribed to the lack of affinity of the chelated tributylstannyl complex for the active sites on the protein. 4-Hydroxybutyldibutyltin acetate, in which the hydroxyl group may also be in-



tramolecularly coordinated to tin, was found by Aldridge and co-work-

ers (*494*) to be about half as toxic to mice (treated intraperitoneally) as the 4-coordinate, tributyltin chloride.

As the intramolecularly 5-coordinate, mixed triorganotin bromides have no tendency to react with monodentate, donor ligands, such as pyridine (*492*), these observations would appear to indicate that the halogen of the triorganotin bromide undergoes a chemical exchange-reaction at the active sites on the protein; this is in line with the toxicity, relatively independent of X, of trialkyltin compounds that contain simple, nonchelating X groups. An exchange with thiol groups of the type

$$R_3SnX + HS— \rightarrow R_3SnS— + HX$$

would give tetrahedral, $R_3SnS—$ groups having a ΔE_Q of the observed magnitude.

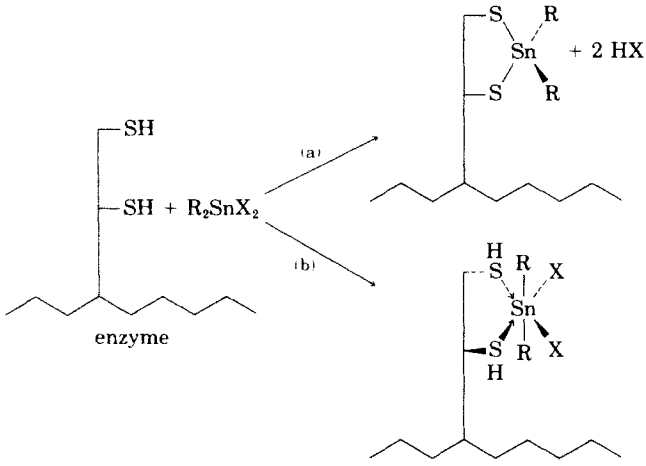
Ascher and Nemny (*495*) found that residues of triphenyltin acetate on glass, resulting from the evaporation of acetone solutions thereof, were, on contact to houseflies, less toxic with rising concentration. As triphenyltin acetate is likely to be a self-associated polymer in the solid state [similar to trimethyltin acetate (*355*)] and in concentrated solutions, it was suggested (*495*) that the monomer, which exists in dilute solutions, is toxic to insects, and the polymer, nontoxic. Interestingly, in this connection, a triphenyltin methacrylate copolymer has (*470*) a very low mammalian toxicity (acute, oral LD_{50} for mice >2000 mg/kg).

3. R_2SnX_2 Compounds

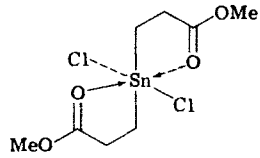
The dialkyltin compounds show a similar trend of decreasing toxicity with increasing length of the alkyl chain, and certain di-*n*-octyltin derivatives have been used for many years in food-contact applications, as described in Section V.

The toxic action of the lower di-*n*-alkyltins in mammals, which is quite different from that of the tri-*n*-alkyltin analogs, is due to their ability to combine with enzymes (such as lipoic acid or lipoyl dehydrogenase) possessing two thiol groups in the correct positions, and thereby to interfere with α-keto acid oxidation (*477*). Two possible reactions may be envisaged. Here, the dialkyltin compound (a) combines with the dithiol groups to form a tetrahedral, dialkylstannadithiaheterocyclic derivative, with the elimination of HCl, or (b) forms an octahedral complex in which the dithiol group acts as a neutral, bidentate ligand. The observed toxicological data for the dialkyltin de-

rivatives may be most readily rationalized in terms of reaction pathway (b).



For example, the decrease in toxicity of the dialkyltin dichlorides with increasing alkyl chain-length (see Table IV) is paralleled by a drop in their Lewis acidity and, hence, a lowered tendency to complex the dithiol ligand. Although diethyltin dichloride has a relatively high mammalian toxicity, introduction of a 2-methoxycarbonyl substituent renders the resulting compound, $(MeOCOCH_2CH_2)_2SnCl_2$, essentially nontoxic (see Table II). In all probability, the latter has an octahedral structure with intramolecular, chelating, carboxylate groups (*77*), a structure found for other carbonyl-substituted, alkyltin compounds



(*496–498*), and, therefore, it has no tendency to complex the dithiol groups. Further substitution of the two chlorine atoms by isooctylthioglycolate groups produces the compound, $(MeOCOCH_2CH_2)_2Sn(SCH_2COO^iOct)_2$, in which the carbonyl groups are now likely to be free (cf. *496, 498*) and, in common with other dialkyltin bis(isooctylthioglycolates), the mammalian toxicity is still very low

TABLE IV

ACUTE, ORAL TOXICITIES OF DIALKYLTIN DICHLORIDES (*470*)

R in R_2SnCl_2	LD_{50} (rats) (mg/kg)
Me	74–237
Et	66–94
^{n}Bu	112–219
^{n}Oct	4000–7000
$C_{16}H_{33}$	10,000
$MeOCOCH_2CH_2$—	2350

(*470*). In this case, the diminution in Lewis acidity caused by the introduction of the two, less-electronegative, sulfur ligands prevents any reaction with the dithiol enzyme, regardless of the nature of the alkyl group.

It may, therefore, be seen that the mammalian toxicity of the lower dialkyltin compounds, unlike that of their trialkyltin counterparts, is markedly dependent upon the nature of the X groups; this is probably true for species other than mammals (e.g., fungi) if the mode of action is similar.

4. *$RSnX_3$ Compounds*

The monoorganotins do not appear to have any important toxic action in mammals (*469, 470, 471*), but they show the familiar pattern of decreasing toxicity with increasing alkyl chain-length, with the maximum again falling at the monoethyltin derivative (see Table V).

TABLE V

VARIATION OF TOXICITY OF MONOALKYLTIN TRICHLORIDES WITH ALKYL CHAIN LENGTH (*470, 499*)

R in $RSnCl_3$	Acute, oral LD_{50} (rats) (mg/kg)
Me	1370
Et	200 (LD_{100})
^{n}Bu	2200
^{n}Oct	3800

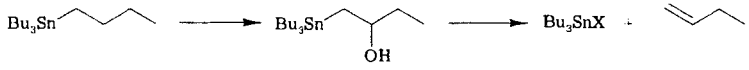
B. Environmental Degradation

1. Metabolic Breakdown

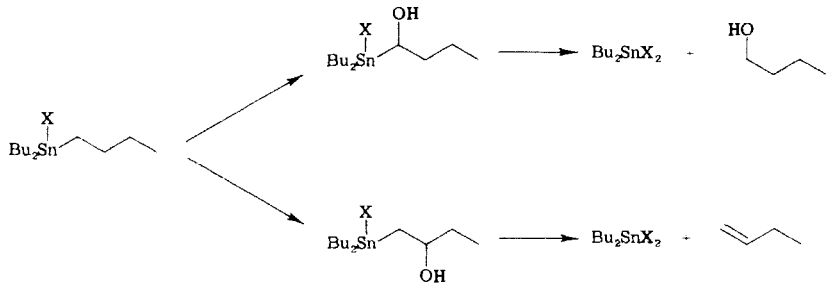
In view of the increasing number of industrial applications of organotins, which are described in the next section, a knowledge of their metabolic fate in mammals is obviously of considerable importance.

The earliest work in this field, by Cremer (*466*), showed that tetraethyltin is metabolized *in vitro* and *in vivo* (rats) to a triethyltin derivative and, later, it was further demonstrated that triethyltin compounds are converted *in vitro* into diethyltin derivatives (*500*). The latter are broken down *in vivo* to monoethyltins, which are eliminated from the body within a short time (*501*). Other trialkyltins appear to behave similarly (*500*).

However, very recent studies by Fish and his co-workers (*467*) with butyltin compounds showed that the primary, metabolic reaction is not Sn–C bond-cleavage but carbon hydroxylation of the *n*-butyl group. Using [1-^{14}C]tetrabutyltin in an *in vitro* study, the major, primary metabolite was identified as a 2-hydroxybutyltributyltin derivative that underwent a rapid β-elimination reaction to afford 1-butene and a tributyltin compound (*467*).



A similar approach with [1-^{14}C]tributyltin acetate showed that carbon hydroxylation occurred at the α-, as well as at the β-, carbon atoms, followed by Sn–C bond-cleavage, to afford dibutyltin derivatives.



Studies with the same compound in mice showed an essentially identical pattern of breakdown (*467*).

It was suggested that the greater susceptibility of the α- and β-carbon–hydrogen bonds to hydroxylation is consistent with a free-radical

pathway for this reaction. In line with this concept, it is known, for example, that an α- or β-trialkylstannyl substituent confers an enhanced reactivity on a CH group towards the abstraction of hydrogen by *tert*-butoxy radicals (*132*).

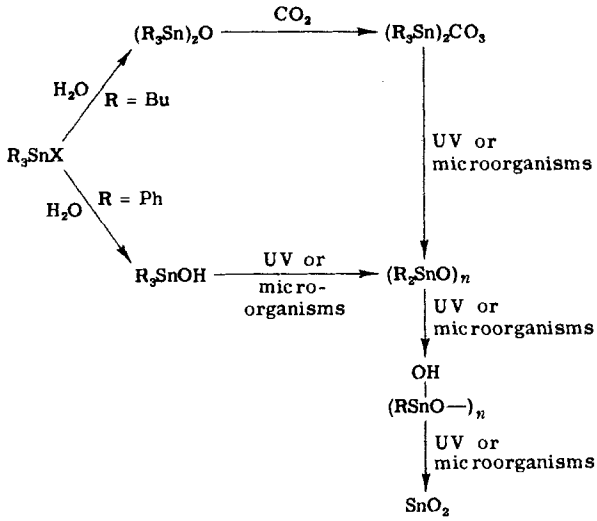
Tricyclohexyltin hydroxide is metabolized *in vivo* to inorganic tin via di- and monocyclohexyltin derivatives (*502*), and *in vitro* studies suggested that the major, metabolic reaction is carbon-hydroxylation of the cyclohexyl group (*503*). Studies *in vivo* using either triphenyl[^{113}Sn]tin acetate (*467*) or triphenyl[^{113}Sn]tin chloride (*504*) in rats showed that these compounds are metabolized to yield substantial amounts of di- and monophenyltin derivatives, although no significant quantities of hydroxylated metabolites have been identified (*503*) in this case.

2. *Photolytic and Microbiological Breakdown*

It has been well established that triphenyltin compounds are broken down photochemically to inorganic tin via the di- and monophenyltin derivatives both under laboratory (*505, 506*) and natural (*507*) conditions. In soil, triphenyltin acetate is converted microbiologically (*505*) into inorganic tin, as is tricyclohexyltin hydroxide (*502*). The latter compound is also photochemically broken down to inorganic tin (*502, 508*).

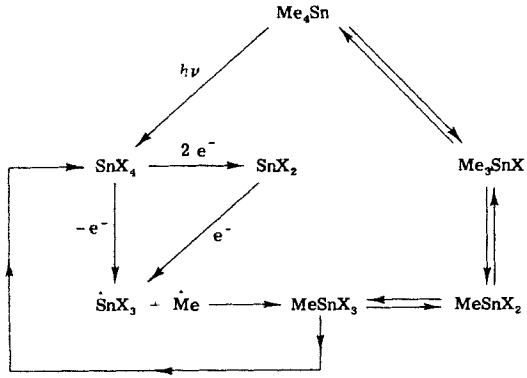
Bis(tributyltin) oxide is known to break down to inorganic tin under UV irradiation in laboratory conditions (*509, 510*), and the decomposition may be accelerated by absorbing the organotin compound on a cellulosic matrix (*511*). As bis(tributyltin) oxide is known to react rapidly with carbon dioxide (atmospheric, or trapped in various cellulosic materials, such as cotton or wood) (*512*), to form bis(tributyltin) carbonate, $(Bu_3SnO)_2CO$, the observed UV degradation pattern may be rationalized in terms of more-ready breakdown of the carbonate than of the oxide, due to the presence of the carbonyl chromophore. The half-life of bis(tributyltin) oxide in pond water has recently been given as 16 days (*513*). Diorganotin compounds have also been shown to decompose to inorganic tin under UV irradiation (*514, 515*).

It may, therefore, be concluded that, within a generally consistent pattern of behavior, organotins are degraded in the environment to afford nontoxic, inorganic tin species. A generalized, environmental-breakdown scheme for the commercially used tributyl- and triphenyltin derivatives (*516*), that is probably applicable to other triorganotins, is illustrated in Scheme 1.



SCHEME 1. Environmental-degradation scheme for tributyl- and triphenyltin compounds (*516*).

The possibility of biomethylation of inorganic tin residues in the environment has recently been discussed by Wood and co-workers (*517–519*), who found that methylation of certain tin(II) salts (e.g., $SnCl_3^-$) by methylcobalamin in aqueous solution at pH 1 requires the presence of an oxidizing agent, such as Co(III) or Fe(III), and that monomethyltin(IV) species are formed. No reaction was observed between Sn(II) and methylcobalamin in the absence of an oxidizing agent (*518*), or between Sn(IV) and methylcobalamin under a variety of conditions of pH and complexing ligands (*519*). It was suggested that the $SnCl_3^-$ species is oxidized to a trichlorostannyl radical, $\dot{S}nCl_3$, which could then cleave the Co–C bond homolytically to produce $MeSnCl_3$. The following biological cycle for tin was proposed (*517*).



Brinckman and his co-workers, using a strain of *Pseudomonas* bacteria isolated from the Chesapeake Bay (*520*), obtained evidence of a biomethylation of $SnCl_4$ to a dimethyltin species under laboratory conditions. At the present time, however, very little is known about (a) the distribution of methyltin compounds in the environment,[2] (b) whether they bioaccumulate in food chains (*521*), and (c) the chemical nature and oxidation state of inorganic tin residues. The toxicity pattern of the Me_nSnX_{4-n} series is obviously very important in this context. All monomethyltins, $MeSnX_3$, so far studied have a low mammalian toxicity (*470*), whereas, with dimethyltin compounds, Me_2SnX_2, the nature of the X group is of considerable importance, as mentioned previously. For example, dimethyltin bis(isooctylthioglycolate) has a low mammalian toxicity (*470*), and is approved in a number of countries for use as a stabilizer in PVC food-packaging (see Section V,B,1). The trimethyltins, Me_3SnX, are the most toxic members of the series, regardless of the nature of X, and show acute, oral, LD_{50} values (rats) in the range of 10 to 20 mg/kg (*470*).

V. Industrial Applications

Although the first organotin compound was prepared by Frankland as long ago as 1849 (*522*), it is only during the last decade that their use in industry has risen dramatically—from ~5000 tons in 1965 to at least 30,000 tons at the present time. Some two-thirds of the current total of organotins are used for nontoxic types of applications (R_2SnX_2 and $RSnX_3$ derivatives), and the remaining 7000–10,000 tons are used as biocides (R_3SnX derivatives) (see Table VI). This rapid increase in the industrial consumption of organotins may be attributed principally to the remarkable diversity of their applications, coupled with their favorable toxicological and environmental properties, as described in the preceding section.

The tetraorganotins, R_4Sn, are used primarily as intermediates in the industrial synthesis of organotins from $SnCl_4$ (see Section II), and have no large industrial application.

A. Biological Uses (R_3SnX Compounds)

The pioneering work that paved the way for the widespread industrial use of organotins as pesticides was conducted in 1954 at the Insti-

[2] Recent analytical studies have indicated that mono-, di-, and trimethyltin compounds are present in environmental samples at nanogram levels [Braman, R. S., and Tompkins, M.A., *Analyt. Chem.* **51**, 12 (1979); Hodge, V. F., Seidel, S. L., and Goldberg, E. D., *ibid.* **51**, 1256 (1979)].

TABLE VI

APPROXIMATE WORLD PRODUCTION OF ORGANOTIN CHEMICALS

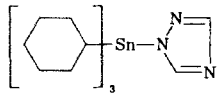
Compounds	Uses	Tons
A. R_2SnX_2 and $RSnX_3$ compounds	1. PVC stabilizers	
	United States	8000
	Japan	5500
	United Kingdom and Western Europe	6500
	2. Homogeneous Catalysts	1000
B. R_3SnX compounds	1. Triphenyltin agrochemicals	1000
	2. Others (see Table VII)	8000
	Total	30,000

tute of Organic Chemistry, TNO, Utrecht, Holland, by van der Kerk and Luijten (*474*), who demonstrated the high fungicidal and bactericidal activity of tributyl- and triphenyltin compounds (*473, 474*). Table VII summarizes the major biocidal applications of various triorganotin compounds in current use.

1. Agrochemicals

The first organotin compound to reach commercialization in agriculture, namely, triphenyltin acetate ("Brestan"), was introduced in the early 1960s by Farbwerke Hoechst A. G. in West Germany for control of the potato-blight fungus *Phytophthora infestans,* and the sugar-beet fungus *Cercospora beticola.* This was soon followed by another triphenyltin fungicide, triphenyltin hydroxide ("Duter"), developed by Philips–Duphar, N. V., in Holland and having a spectrum of activity similar to that of the acetate. It has recently been estimated (*523*) that the consumption of these two organotin agrochemicals alone in Europe and Japan is of the order of ~1000 tons per annum.

The next major discovery in this field, which was the result of a joint research effort in 1968 between M and T Chemicals, Inc., and the Dow Chemical Company in the United States (*475, 524*), was that tricyclohexyltin hydroxide ("Plictran") possesses a very high activity against certain types of mites, and this compound was subsequently introduced by Dow as an acaricide for use on apple, pear, and citrus-fruit trees. A second triorganotin acaricide, bis(trineophyltin) oxide ("Vendex" or "Torque"), has recently been introduced by Shell Chemical Company (*476*). Two other tricyclohexyltin compounds are currently under de-



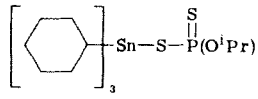


TABLE VII

BIOCIDAL USES OF R_3SnX COMPOUNDS

Compound	Application
Ph_3SnOAc Ph_3SnOH	Agrochemical fungicides
(*cyclo*-$C_6H_{11})_3SnOH$ $[(PhCMe_2CH_2)_3Sn]_2O$	Agrochemical miticides
$Bu_3SnOCOPh$	Disinfectant
Bu_3SnF Ph_3SnX (X = Cl, F, OH, or OAc) $(—CHMe{\cdot}CHCO_2SnBu_3—)_n$	Biocides in marine antifouling paints
$Bu_3SnOSnBu_3$	Wood preservation Stone preservation Textile preservation Slimicide in paper industry Biocide in antifouling rubbers In-can fungicide for paints

velopment (*524, 525*) as acaricides. Tris(2-norbornyltin) hydroxide also shows a high acaricidal activity (*524*).

As only one compound in approximately 10,000 tested will actually reach commercialization as a plant-protection agent (*526*) it is quite remarkable for one metal to have four of its organic compounds in commercial use. The main advantages of the organotin agrochemicals are their low phytotoxicity, their generally low toxicity to nontarget organisms, and their relatively rapid breakdown in the environment to nontoxic, inorganic tin residues.

2. *Tributyltin Disinfectants*

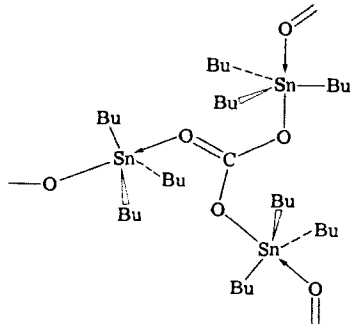
The high antibacterial activity of tributyltin derivatives, particularly against Gram-positive bacteria (*473*), has led to their use as disinfectants, although a second chemical toxicant is usually added to extend the biological activity spectrum to cover Gram-negative bacteria. One such product ("Incidin"), containing tributyltin benzoate and formaldehyde, was developed by Henkel in West Germany (*527*). Various combinations of tributyltin benzoate and a quaternary ammonium salt have been evaluated as bactericides for use on hospital floors (*528*).

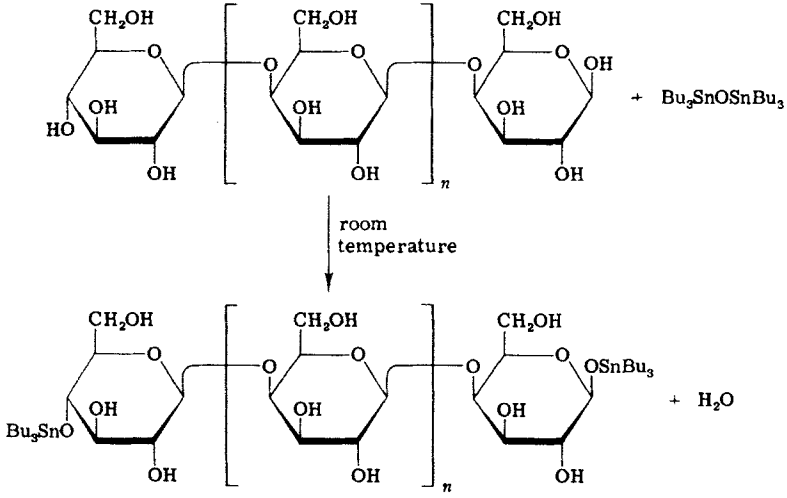
3. *Preservation of Cellulosic Materials and Stonework*

Bis(tri-*n*-butyltin) oxide, $Bu_3SnOSnBu_3$, is an organotin chemical very effective in, and widely used for, the protection of such cellulosic materials as cotton textiles, wood, and cellulose-based household-

fillers against fungal attack (*529–531*). In the case of wood, for example, fungal protection may be achieved by dipping, brushing, or vacuum-impregnating the material with a 1% (w/w) solution of the organotin compound in an organic solvent, such as white spirit (*531*). An organic insecticide is usually added to the solution to prevent attack by wood-destroying insects (*530*).

The high retentive capacity of cellulosic materials for the organotin oxide was originally considered (*530, 532*) to be due to its chemical reaction with the terminal hydroxyl groups of the cellulose chains (see Scheme 2). Very recent work has, however, shown (*512*) that, in fact, bis(tributyltin) oxide reacts rapidly with the carbon dioxide trapped in wood, to form bis(tributyltin) carbonate, $(Bu_3SnO)_2CO$, which, unlike the trialkyltin oxide, is a polymeric, self-associated species containing 5-coordinate tin, probably having the following structure.



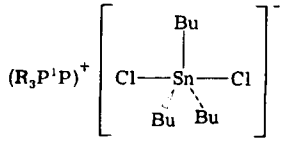


SCHEME 2. Proposed reaction between bis(tributyltin)oxide and cellulose (*530, 532*).

The polymeric organotin carbonate is less volatile than the oxide and, in this connection, tris(tributylstannyl) phosphate, $(Bu_3Sn)_3PO_4$, which is likely to have a similarly self-associated structure [cf., $(Me_2Sn)_3(PO_4)_2 \cdot 8\ H_2O$ (*393*)], is also being used as a wood preservative (*533*) in Holland.

Recently, there has been much interest in developing water-soluble tributyltin biocides to lessen the costs of application, and to prevent fire hazards when treating material in confined spaces. Bis(tributyltin) oxide itself has a very low aqueous solubility (~0.001%), but it may be made water-dispersible by the addition of certain (*534, 535*) quaternary ammonium salts. Formulations of this type, although currently under development[3] as wood preservatives (*534*), have been used extensively in the United Kingdom for the treatment of stonework to eradicate fungal growths, algae, mosses, and lichens (*535*).

In order to avoid the necessity of adding a quaternary ammonium compound to solubilize the organotin derivative, a number of new, anionic, tributyltin salts of the type $(R_3R^1P)^+$ $(Bu_3SnCl_2)^-$, where R = R^1 = ^{n}Bu or Ph; R = Ph, R^1 = Bz, were prepared (*440, 536*). Although these contain discrete, trigonal, bipyramidal tributyldichlorostannate anions (*440*), their solubility in water was found to be very low.



Similarly, the cationic tributyltin complexes (*537*), $(Bu_3SnL_2)^+BPh_4^-$, where L = Me_2SO, Ph_3PO, Ph_3AsO, or PyO, are also insoluble in water. However, tributyltin alkanesulfonates, Bu_3SnSO_3R (particularly where R = Me, Et, ^{n}Bu, or ^{t}Bu), dissolve in water to the extent of 0.8 to 1.5% (*538, 539*), which is a remarkably high solubility for a tributyltin compound, and a concentration quite adequate for most biocidal applications (see the foregoing). The resulting, aqueous solutions appear to be quite stable on standing in normal daylight for 2 to 3 months.

4. *Marine Antifouling Paints and Related Systems*

Marine fouling, namely, the attachment of such marine organisms as barnacles, algae, tubeworms, hydroids, and sponges to a surface im-

[3] One such formulation has recently been approved for use in Sweden (Anonymous, "Wood Preservatives Approved by the Swedish Wood Preservation Institute," Svenska Traskyddinstitutet, Stockholm, 1 Jan., 1979).

mersed in sea water, can cause serious problems. In the case of large tankers and other ocean-going vessels, marine fouling increases hull friction as the ship moves through the water, fuel consumption goes up, and the maximum speed attainable is decreased. Fouling may also cause severe mechanical damage to marine instruments and outboard-motor engines.

The most realistic method of dealing with this fouling problem is to protect the ship's hull with an antifouling, coating system that functions by releasing chemicals toxic to marine organisms, and thus prevents their attachment to the hull surface. The two vital components of such an antifouling system are: (a) a toxicant that (*i*) is effective against a wide range of fouling species at low concentrations, (*ii*) will constitute only a minimum toxic hazard during application to a vessel, and (*iii*) will not contribute significantly to environmental pollution, and (b) a coating medium that will release the toxicant at a low, but steady, rate and preserve its film integrity on the hull surface.

Conventional, organotin-based, antifouling paints containing up to 20% (by weight) of a tributyl- or triphenyl-tin derivative incorporated in a standard paint-vehicle have been in use for many years (*540–542*). The most common triorganotin compounds employed are those that have a polymeric, intermolecularly anion-bridged, R_3SnX_2 type of structure, such as tributyltin fluoride, triphenyltin fluoride, and triphenyltin hydroxide (*541, 543*). Bis(tributyltin) oxide is also used, and, in some cases, is known (*543*) to react with carboxylic acids in the paint matrix to form the corresponding tributyltin carboxylate. The colorlessness of these triorganotin additives allows the use of any color in the paints, and, additionally, they are not subject to bimetallic corrosion problems when used on lightweight, aluminum hulls (*541*).

Poller (*498, 544*) prepared a number of tributyl- and triphenyl-stannyl esters of sucrose hydrogenphthalate and succinate, and found that, as potential antifoulants, these were at least three times as effective against the marine alga, *Enteromorpha,* as bis(tributyltin) oxide, even though they contain almost one third the tin (see Table VIII). A new antifouling paint that also contains tributyltin compounds has recently been developed in Norway (*545*).

As mentioned earlier, water-based, tributyltin-based biocides are attracting much interest at the present time, and one such formulation has been developed in the United Kingdom for the prevention of fouling in sea-water cooling-systems (*546*).

For the majority of merchant ships, which dry-dock at intervals of about 12 to 18 months, the conventional paint-formulations containing simple triorganotin additives are quite satisfactory, and provide adequate protection over this period. However, giant tankers involve capital investment that runs into millions of pounds, and their economical

TABLE VIII

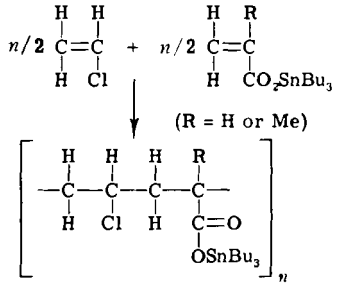
ACTIVITY OF TRIBUTYL- AND TRIPHENYL-STANNYLSUCROSE COMPOUNDS AGAINST *Enteromorpha* IN SEA WATER MODIFIED WITH ALGAL NUTRIENTS (*498*, *544*)

Compound	Concentration[a] 1 ppm	0.1 ppm
$Bu_3SnOCOC_6H_4COO$sucrose	+	+
$Ph_3SnOCOC_6H_4COO$sucrose	+	+
$Bu_3SnOCOCH_2CH_2COO$sucrose	+	+
$Ph_3SnOCOCH_2CH_2COO$sucrose	+	+

[a] Key: + = effective [minimum concentration at which $(Bu_3Sn)_2O$ is effective = 0.3 ppm].

operation requires that they spend a high proportion of their time at sea, with a period of at least 2 to 2.5 years (preferably 4 to 5 years) between dry-docking periods. A long-term, antifouling coating is even more essential for naval vessels, and many of the more recent developments in this field have originated in the laboratories of the United States and Australian Navies, whose ships spend considerable periods in tropical environments conducive to marine fouling.

The first approach in the search for longer-life, or "second generation," antifouling coatings has been to incorporate the triorganotin moiety in an organometallic polymer system. This has been achieved by co-polymerizing tributyltin acrylate (or methacrylate) with other co-monomers, such as vinyl chloride (*547–549*), to give linear poly-



mers having trialkylstannyl groups chemically bound to the polymer backbone, cf., the simple R_3SnX additives, where the toxic R_3SnX species are weakly held together in the solid state by self-association. The resulting polymers are then formulated into marine coatings, and tested in immersion trials at marine sites. Foul-free periods of at least four years have been observed with these slow-release, polymeric systems (*549*).

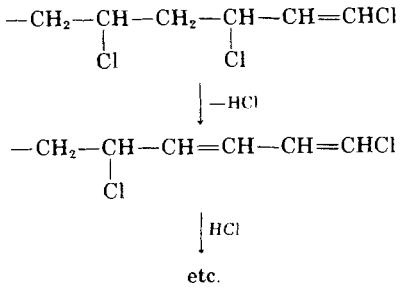
A second, parallel approach, has been to incorporate the tributyltin toxicant into an elastomeric matrix to produce long-life, antifouling,

rubber coatings. The precursor for these systems was the "Nofoul" antifouling rubber-sheet marketed by B. F. Goodrich in the United States and described in detail by Cardarelli (*550*). Although originally developed as a protective coating for ships' hulls, these controlled-release, bis(tributyltin) oxide-containing rubbers, in the form of pellets, have been extensively investigated as molluscicides (*489, 550*) for use against the vector snails that transmit the notorious, water-borne, tropical disease, schistosomiasis (*551*). The safe concentration level of bis(tributyltin) oxide wherein the snails may be destroyed in infected tropical waters with minimal damage to the fish life has recently been estimated (*552*) at 0.12–0.27 μg/liter.

B. Nonbiological Uses (R_2SnX_2 and $RSnX_3$ Compounds)

1. PVC Stabilizers

The largest single use for organotin compounds is the stabilization of PVC (*553*), some 20,000 tons of chemicals currently being used. PVC is degraded both by heat (to which it is subjected during processing at 180–200°) and by long-term exposure to sunlight, producing severe discoloration, a rapid deterioration in physical properties, and progressive embrittlement until the polymer completely disintegrates. This phenomenon is caused by the elimination of hydrogen chloride from the polymer, starting from the labile, allylic chlorine atoms, and resulting in the formation of a polyene. The degradation may be prevented by the addition of 1–1.5% of certain dialkyltin compounds (see Table IX) to the polymer before processing.



In general, the diorganotin bis(isooctylthioglycolates) are used in applications that require good stability to heat, e.g., PVC drink-bottles and food packaging, whereas the dialkyltin bis(carboxylates) are useful for providing long-term stability to light, e.g., in PVC roofing. Di-*n*-octyltin bis(isooctylthioglycolate) and maleate have a low mammalian toxicity and are used in many countries as stabilizers for PVC food-

TABLE IX

SOME ORGANOTIN STABILIZERS FOR PVC

R	X	Ref.
	(a) $R_2Sn(SCH_2COO^iOct)_2$	
Me	SCH_2COO^iOct	*554*
$^n BuOCH_2CH_2$	SCH_2COO^iOct	*78,555*
$^n Bu$	SCH_2COO^iOct	*553*
$^n Oct$	SCH_2COO^iOct	*556*
$PhCH_2$	SCH_2COO^iOct	*557*
	(b) $R_2Sn(OCOR^1)_2$	
$^n Bu$	$(OCOCHCHCOO)_n$	*553*
$^n Bu$	OCOCHCHCOOR	*553*
$^n Bu$	$OCO^nC_{11}H_{23}$	*553*
$^n Oct$	$(OCOCHCHCOO)_n$	*556*

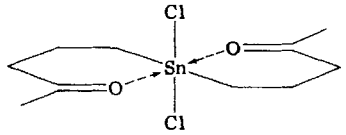
packaging and drink containers; dimethyltin bis(isooctylthioglycolate) is also approved in some European countries, e.g., West Germany, for stabilizing food-contact, PVC packaging, and in the United States as a heat stabilizer for use in PVC, potable-water piping; di-*n*-butyl- and di-(2-butoxycarbonylethyl)-tin stabilizers are currently used in non-food-contact PVC. In most cases, up to 60% of the corresponding monoalkyltin compound, $RSnX_3$, is added to the dialkyltin stabilizer, R_2SnX_2, as it is found that this combination gives a synergistic improvement in the stabilizing activity (*553*). Monobutyltin sesquisulfide, $(BuSnS_{1.5})_4$, is used as a stabilizer in its own right for certain grades of PVC in West Germany (*558*), and dilauryltin compounds also show promise (*559*).

The di- and monoalkyltin compounds are considered to be effective as stabilizers because they (*i*) inhibit the onset of the dehydrochlorination reaction by exchanging their anionic groups, X, with the reactive, allylic chlorine atoms in the polymer; (*ii*) react with, and thereby scavenge, the hydrogen chloride that is produced and that would otherwise induce further elimination; (*iii*) produce the compound HX, which may also help to inhibit other undesirable side reactions; and (*iv*) prevent breakdown of the polymer initiated by atmospheric oxidation, i.e., by acting as antioxidants.

The dialkyltin dichloride formed[4] by reaction of the dialkyltin stabilizer with the polymer, or with the hydrogen chloride liberated, is itself

[4] A Mössbauer study of PVC stabilized with 4% di-*n*-butyltin bis(isooctylthioglycolate) indicates that the tin species formed in the polymer is $Bu_2Sn(Cl)SCH_2COO^iOct$ [Allen, D. W., Brooks, J. S., Clarkson, R. W., Mellor, M. T. J., and Williamson, A. G., *Chem. Ind. (London)* 663 (1979)].

a Lewis acid catalyst for further dehydrochlorination (*496, 498*). Poller (*496*) synthesized the stabilizer di-(4-oxopentyl)tin bis(isooctylthioglycolate), in which the Lewis acidity of the resulting diorganotin dichloride was suppressed because of intramolecular coordination of the two carbonyl groups to tin. Subsequent tests showed (*416*) that the

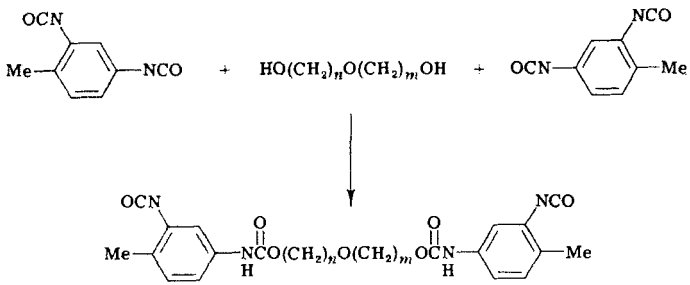


stabilizer was more than twice as effective as the corresponding butyltin derivatives. In this connection, it is interesting that di-(2-methoxycarbonyl)ethyltin dichloride, produced from the corresponding isooctylthioglycolate stabilizer, also contains chelated carbonyl groups (*77, 78*).

2. Homogeneous Catalysts

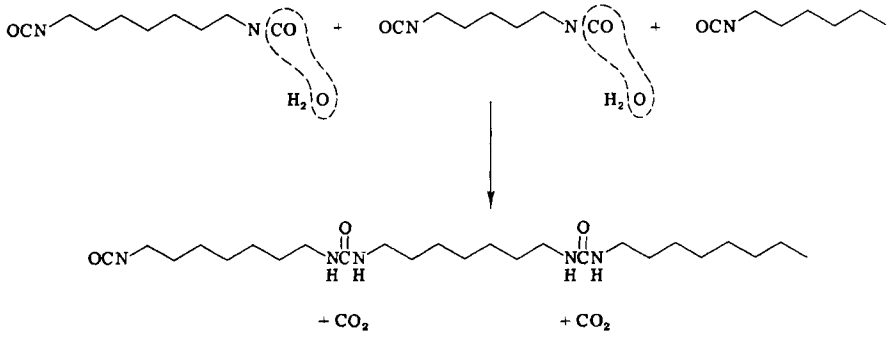
Dibutyltin diacetate, dilaurate, and di-(2-ethylhexanoate) are used as homogeneous catalysts for room-temperature-vulcanizing (RTV) silicones. The dialkyltin compounds bring about the cross-linking of the oligomeric siloxanes, to produce flexible, silicone rubbers having a host of different uses, such as electrical insulators and dental-impression molds. Recent work has also shown (*560*) that various dibutyltin dicarboxylates catalyze both the hydrolysis and gelation of ethyl silicate under neutral conditions.

The same dibutyltin compounds are used in the industrial manufacture of poly(urethane) foams, the first step in which involves the addition of a polyether glycol to 2,4-diisocyanotoluene, to produce the urethane prepolymer having isocyanate end-groups.



In the second, or "foaming," stage, water is added to the prepolymer to produce the polyurethane and carbon dioxide gas. The organotin com-

pounds catalyze both reaction steps in the manufacturing process.



Certain monobutyltin compounds have recently been introduced (*561*) as esterification catalysts, e.g., in the reaction of phthalic anhydride with octanol to produce dioctyl phthalate.

3. *Treatment of Glass*

Dimethyltin dichloride is used in the glass industry as an alternative to stannic chloride for coating glass with a thin film of stannic oxide (*562*). The dialkyltin compound vapor is brought into contact with the glass surface at temperatures of 500–600°C, where decomposition and oxidation occurs.

$$Me_2SnCl_2 + O_2 \rightarrow SnO_2 + 2\ MeCl$$

The thickness of the film of SnO_2 varies from ~10.0 nm to several μm, depending on the desired application (*563*).

At the low end of the thickness scale (<100.0 nm), films of SnO_2 are used in the glass industry for strengthening glasses, bottles, jars, and other items subjected to vigorous usage. If thickness of the film on the glass is of the same order as the wavelength of visible light (~100.0–1000.0 nm), thin-film interference occurs, to give the article an iridescent, decorative coating. Finally, very thick films of SnO_2 on glass are useful when electrical conductivity combined with optical transparency is required, e.g., for de-icing aircraft windscreens (*563*). Other organotin compounds have also been investigated recently for this application (*564, 565, 566*).

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References

1. Neumann, W. P., "The Organic Chemistry of Tin." Wiley, New York, 1970.
2. Poller, R. C., "The Chemistry of Organotin Compounds." Logos, London and Academic Press, New York, 1970.
3. A. K. Sawyer, ed., "Organotin Compounds," Vols. 1, 2, and 3. Dekker, New York, 1971, 1972.
4. Pereyre, M., and Pommier, J.-C., *J. Organomet. Chem. Library* **1,** 161 (1976).
5. Smith, P. J., *Organomet. Chem. Rev., Sect. A* **5,** 373 (1970).
6. Ruddick, J. N. R., *Rev. Silicon, Germanium, Tin, Lead Compd.* **2,** 115 (1976).
7. Parish, R. V., *Prog. Inorg. Chem.* **15,** 101 (1972).
8. Bancroft, G. M., and Platt, R. H., *Adv. Inorg. Chem. Radiochem.* **15,** 59 (1972).
9. Zuckerman, J. J., *Adv. Organomet. Chem.* **9,** 22 (1970).
10. Smith, L., and Smith, P. J., *Inorg. Chim. Acta Rev.* **7,** 11 (1973).
11. Kennedy, J. D., and McFarlane, W., *Rev. Silicon, Germanium, Tin, Lead Compd.* **1,** 235 (1974).
12. Smith, P. J., and Tupčiauskas, A. P., *Annu. Rep. NMR Spectrosc.* **8,** 291 (1978).
13. Ingham, R. K., Rosenberg, S. D., and Gilman, H. *Chem. Rev.* **60,** 459 (1960).
14. Kocheshkov, K. A., Zemlyanskii, N. N., Sheverdina, N. I., and Panov, E. M., "Metodi Elementoorganicheskoi Khimii. Germanii, Olovo, Svenets." Nauka, Moscow, 1968 (in Russian).
15. Coates, G. E., and Wade, K., "Organometallic Compounds," Vol. 1: The Main Group Elements. Methuen, London, 1967.
16. Coates, C. E., Aylett, B., and Wade, K., "Organometallic Compounds," Vol. 1: The Main Group Elements, Methuen, London, 1978.
17. Emeleus, H. J., and Aylett, eds., "Organometallic Derivatives of the Main Group Elements," MTP *Int. Rev. Sci., Ser. One* **4** (1972).
18. P. G. Harrison, *MTP Int. Rev. Sci., Ser. Two* **4** (1972), Chapter 3.
19. Bulten, E. J., "Tin: Annual Survey Covering the Year 1970." *Organomet. Chem. Rev.* **9,** 248 (1972).
20. Bulten, E. J., "Tin: Annual Survey Covering the Year 1971." *J. Organomet. Chem.* **53,** 1 (1973).
21. Harrison, P. G., "Tin: Annual Survey Covering the Year 1972." *J. Organomet. Chem.* **58,** 49 (1973).
22. Harrison, P. G., "Tin: Annual Survey Covering the Year 1973." *J. Organomet. Chem.* **79,** 17 (1974).
23. Harrison, P. G., "Tin: Annual Survey Covering the Year 1974." *J. Organomet. Chem.* **109,** 363 (1976).
24. Harrison, P. G., "Tin: Annual Survey Covering the Year 1975." *J. Organomet. Chem. Library* **4,** 367 (1977).
25. Armitage, D. A., *Chem. Soc. Spec. Period. Rep.: Organomet. Chem.* **1,** Chapter 5 (1972).
26. Armitage, D. A., *Chem. Soc. Spec. Period. Rep.: Organomet. Chem.* **2,** Chapter 6 (1973).
27. Armitage, D. A., *Chem. Soc. Spec. Period. Rep.: Organomet. Chem.* **3,** Chapter 6 (1974).
28. Armitage, D. A., *Chem. Soc. Spec. Period. Rep.: Organomet. Chem.* **4,** Chapter 6 (1975).
29. Armitage, D. A., *Chem. Soc. Spec. Period. Rep.: Organomet. Chem.* **5,** Chapter 6 (1976).

30. Armitage, D. A., *Chem. Soc. Spec. Period. Rep.: Organomet. Chem.* **6,** Chapter 6 (1977).
31. Zuckerman, J. J., ed., "Organotin Compounds: New Chemistry and Applications." *Adv. Chem. Ser.* **157,** 227 (1976).
32. Crompton, T. R., ed., "Chemical Analysis of Organometallic Compounds," Vol. 3: Elements of Group IV–B, Chapter 9. Academic Press, New York, 1974.
33. Price, J. W., and Smith, R., "Gmelin Handbuch der Analytischen Chemie" W. Fresenius, ed. Teil 3, Band 49: Tin Springer-Verlag, Berlin and New York, 1977.
34. Bokranz, A., and Plum, H., "Industrial Manufacture and Use of Organotin Compounds," Schering, A. G., D-4619, Bergkamen, Germany, 1975; *Fortschr. Chem. Forsch.* **16,** 365 (1971).
35. Luijten, J. G. A., and van der Kerk, G. J. M., Synthesis and properties of the tin–carbon bond, *in* "Organometallic Compounds of the Group IV Elements," (A. G. MacDiarmid, ed.), Vol. 1, Part 2. Arnold, New York, 1968.
36. Schumann, H., and Schumann, I., Zinn-organische Verbindungen SnR_4, *in* "Gmelin Handbuch der Anorganischen Chemie," Band 26, Teil 1. Springer and New York, Berlin, 1975.
37. Schumann, H., and Schumann, I., Zinn-organische Verbindungen, R_3SnR', *in* "Gmelin Handbuch der Anorganischen Chemie," Band 26, Teil 2. Springer-Verlag, Berlin and New York, 1975.
38. Schumann, H., and Schumann, I., Zinn-organische Verbindurgen, $R_2SnR'_2$, $R_2SnR'R''$, $RR'SnR''R'''$, *in* "Gmelin Handbuch der Anorganischen Chemie," Band 26, Teil 3. Springer-Verlag, Berlin and New York, 1975.
39. Poller, R. C., and Murphy, J., *J. Organomet. Chem. Library,* **9,** 189 (1979).
40. Galli, R., Giannaccari, B. M., and Cassar, L., *J. Organomet. Chem.* 25, 429 (1970).
41. Matschiner, H., Voigtländer, R., and Tzschach, A., *J. Organomet. Chem.,* **70,** 387 (1974).
42. Matsuda, S., and Nomura, M., *J. Organomet. Chem.,* **25,** 101 (1970).
43. Fostein, P., and Pommier, J.-C., *J. Organomet. Chem.,* **114,** C7 (1976).
44. Bos, K. D., Budding, H. A., Bulten, E. J., and Noltes, J. G., *Inorg. Nucl. Chem. Lett.* **9,** 963 (1973).
45. Bos, K. D., Bulten, E. J., and Noltes, J. G., *J. Organomet. Chem.* **99,** 397 (1975).
46. Wakeshima, I., and Kijima, I., *J. Organomet. Chem.* **76,** 37 (1974).
47. Bulten, E. J., *J. Organomet. Chem.* **97,** 167 (1975).
48. Kandil, S. A., and Allred, A. L., *J. Chem. Soc. A* p. 2987 (1970).
49. Glockling, F., Lyle, M. A., and Stobart, S. A., *J. Chem. Soc., Dalton Trans.* p. 2537 (1974).
50. Killian, L., and Wrackmeyer, B., *J. Organomet. Chem.* **132,** 213 (1977).
51. Corey, J. Y., Duebar, M., and Malaizde, M., *J. Organomet. Chem.* **36,** 49 (1972).
52. Meinema, H. A., and Noltes, J. G., *J. Organomet. Chem.* **63,** 243 (1973).
53. Matteson, D. S., and Larson, G. L., *J. Organomet. Chem.* **57,** 225 (1973).
54. Matteson, D. S., and Wilcsek, R. J., *J. Organomet. Chem.* **57,** 231 (1973).
55. Seyferth, D., and Lefferts, J. L., *J. Am. Chem. Soc.* **96,** 6237 (1974).
56. Gröbel, B. T., and Seebach, D., *Chem. Ber.* **110,** 852 (1977).
57. Seyferth, D., Armbrecht, F. M., Lambert, R. L., and Tronich, W., *J. Organomet. Chem.* **44,** 299 (1972).
58. Seyferth, D., and Lambert, R. L., *J. Organomet. Chem.* **54,** 123 (1973).
59. Seyferth, D., Lambert, R. L., and Massol, M., *J. Organomet. Chem.* **88,** 255 (1975).
60. Seyferth, D., and Lambert, R. L., *J. Organomet. Chem.* **88,** 287 (1975).
61. Seyferth, D., and Andrews, S. B., *J. Organomet. Chem.* **30,** 151 (1971).

62. Mengoli, G., and Daolio, S., *J. Chem. Soc., Chem. Commun.* p. 76 (1976).
63. van Koten, G., Schaap, C. A., and Noltes, J. G., *J. Organomet. Chem.* **99,** 157 (1975).
64. Itoh, K., Kato, S., and Ishii, Y., *J. Organomet. Chem.* **34,** 293 (1972).
65. Bulten, E. J., and Budding, H. A., *J. Organomet. Chem.* **110,** 167 (1976).
66. Limouzin, Y., and Maire, J. C., ref. *31,* p. 227.
67. Kuivila, H. G., Kennedy, J. D., Tien, R. Y., Tyminiski, I. J., Pelczar, F. L., and Khan, O. R., *J. Org. Chem.* **36,** 2083 (1971).
68. Kennedy, J. D., Kuivila, H. G., Pelczar, F. L., Tien, R. Y., and Considine, J. L., *J. Organomet. Chem.* **61,** 167 (1973).
69. Juenge, E. C., Hawkes, S. J., and Snider, T. E., *J. Organomet. Chem.* **51,** 189 (1973).
70. Leusink, A. J., Budding, H. A., and Noltes, J. G., *J. Organomet. Chem.* **24,** 375 (1970).
71. Ashe, A. J., and Shu, P., *J. Am. Chem. Soc.* **93,** 1804 (1971).
72. Jutzi, P., and Baumgärtner, J., *J. Organomet. Chem.* **148,** 247 (1978).
73. Märkl, G., Baier, H., and Heinrich, S., *Angew. Chem., Int. Ed. Engl.* **14,** 710 (1975).
74. Märkl, G., and Rampal, J. B., *Tetrahedron Lett.* p. 2325 (1977).
75. Massol, M., Barreau, J., Satgé, J., and Bonyssieres, B., *J. Organomet. Chem.* **80,** 47 (1974).
76. Rahm, A., and Pereyre, M., *J. Organomet. Chem.* **88,** 79 (1975).
77. Hutton, R. E., and Oakes, V., *J. Chem. Soc., Chem. Commun.* 803 (1976).
78. Hutton, R. E., and Oakes, V., ref. *31,* p. 227.
79. Kuivila, H. G., ref. *31,* p. 41.
80. Davis, D. D., and Gray, C. L., *Organomet. Chem. Rev.* **6,** 283 (1970).
81. Roberts, R. M. G., *J. Organomet. Chem.* **63,** 159 (1973).
81a. Still, W. C., *J. Am. Chem. Soc.* **100,** 1481 (1978).
82. Kuivila, H. G., and Di Stefano, F. V., *J. Organomet. Chem.* **122,** 171 (1976).
83. Juenge, E. C., Snider, T. E., and Lee, Y.-C., *J. Organomet. Chem.* **22,** 403 (1970).
84. Jensen, F. R., and Davis, D. D., *J. Am. Chem. Soc.* **93,** 4047 (1971).
85. Koermer, G. S., Hall, M. L., and Traylor, T. G., *J. Am. Chem. Soc.* **94,** 7205 (1972).
86. Kuivila, H. G., Considine, J. L., and Kennedy, J. D., *J. Am. Chem. Soc.* **94,** 7206 (1972).
87. Jones, C. H. W., Jones, R. C., Partington, P., and Roberts, R. M. G., *J. Organomet. Chem.* **32,** 201 (1971).
88. Kuivila, H. G., and Wursthorne, K. R., *Tetrahedron Lett.* p. 4357 (1975).
89. Kuivila, H. G., and Wursthorne, K. R., *J. Organomet. Chem.* **105,** C6 (1975).
90. Quintard, J.-P., Hauvette, S., and Pereyre, M., *J. Organomet. Chem.* **112,** C11 (1976).
91. Lahournère, J.-C., and Valade, J., *C. R. Hebd. Acad. Sci., Ser. C* **270,** 2080 (1970).
92. Lahournère, J.-C., and Valade, J., *J. Organomet. Chem.* **22,** C3 (1970).
93. Lahournère, J.-C., and Valade, J., *J. Organomet. Chem.,* **33,** C4 (1971).
94. Abraham, M. H., "Electrophilic Substitution at a Saturated Carbon Atom" (C. H. Bamford and C. F. H. Tipper, eds.). Elsevier, Amsterdam, 1973.
95. Eaborn, C., Cleavages of aryl–silicon and related bonds by electrophiles, *J. Organomet. Chem.* **100,** 43 (1975).
96. Reutov, O. A., The mechanisms of the substitution reactions of non-transition metal organometallic compounds, *J. Organomet. Chem.* **100,** 219 (1975).
97. Eaborn, C., *Pure Appl. Chem.,* **19,** 375 (1969).
98. Eaborn, C., Thompson, A. R., and Walton, D. R. M., *J. Organomet. Chem.* **29,** 257 (1971).

99. Eaborn, C., Jones, J. R., and Seconi, G., *J. Organomet. Chem.* **116,** 83 (1976).
100. Eaborn, C., and Seconi, G., *J. Chem. Soc., Perkin Trans. 2* p. 925 (1976).
101. Alexander, R., Eaborn, C., and Traylor, T. G., *J. Organomet. Chem.* **21,** P65 (1970).
102. Wardell, J. L., ref. *31,* p. 113.
103. Kuivila, H. J., and Scarpa, N. M., *J. Am. Chem. Soc.* **92,** 6990 (1970).
104. Abraham, M. H., Dadjour, D. F., Gielen, M., and de Poorter, B., *J. Organomet. Chem.* **84,** 317 (1975).
105. Abraham, M. H., and Dadjour, D. F., *J. Chem. Soc., Perkin Trans. 2* p. 233 (1974).
106. Abraham, M. H., and Dorrell, F. J., *J. Chem. Soc., Perkin Trans. 2* p. 444 (1973).
107. Abraham, M. H., Dadjour, D. F., and Holloway, C. J., *J. Organomet. Chem.* **52,** C27 (1973).
108. Abraham, M. H., and Hogarth, M. J., *J. Chem. Soc. A* p. 1474 (1971).
109. Abraham, M. H., *J. Chem. Soc. A* p. 1061 (1971).
110. Abraham, M. H., and Grellier, P. L., *J. Chem. Soc., Perkin Trans. 2* p. 623 (1975).
111. Bartlett, E. H., Eaborn, C., and Walton, D. R. M., *J. Organomet. Chem.* **46,** 267 (1972).
112. Folaranni, A., McLean, R. A. N., and Wadibia, N., *J. Organomet. Chem.* **73,** 59 (1974).
113. Bhattacharya, S. N., Raj, P., and Srivastava, R. C., *J. Organomet. Chem.* **105,** 45 (1976).
114. Rahm, A., and Pereyre, M., *J. Am. Chem. Soc.* **99,** 1672 (1977).
115. Jensen, F. R., and Davis, D. D., *J. Am. Chem. Soc.* **93,** 4049 (1971).
116. Kunze, U., Lindner, E., and Koola, J. D., *J. Organomet. Chem.* **57,** 319 (1973).
117. Lindner, E., and Frembs, D., *J. Organomet. Chem.* **49,** 425 (1973).
118. Lindner, E., Ritter, G., and Haag, A., *J. Organomet. Chem.* **24,** 119 (1970).
119. Vitzthum, G., Kunze, U., and Lindner, E., *J. Organomet. Chem.* **21,** P38 (1970).
120. Lindner, E., *Rev. Silicon, Germanium, Tin, Lead Compd.* **1,** 35 (1972).
121. Fong, C. W., and Kitching, W., *J. Organomet. Chem.* **22,** 95 (1970).
122. Moore, C. J., and Kitching, W., *J. Organomet. Chem.* **59,** 225 (1973).
123. Koola, J. D., and Kunze, U., *J. Organomet. Chem.* **77,** 325 (1974).
124. Fong, C. W., and Kitching, W., *J. Organomet. Chem.* **59,** 213 (1973).
125. Fong, C. W., and Kitching, W., *J. Am. Chem. Soc.* **93,** 3791 (1971).
126. Fong, C. W., and Kitching, W., *J. Organomet. Chem.* **59,** 213 (1973).
127. Moore, C. J., and Kitching, W., *J. Organomet. Chem.* **59,** 225 (1973).
128. Bulten, E. J., and Budding, H. A., *J. Organomet. Chem.* **137,** 165 (1977).
129. Hänssgen, D., and Odenhause, E., *J. Organomet. Chem.* **124,** 143 (1977).
130. Ingold, K. U., and Roberts, B. P., "Free Radical Substitution Reactions." Wiley-Interscience, New York, 1971.
131. Davies, A. G., and Roberts, B. P., *in* "Free Radicals" (J. Kochi, ed.), Vol. 1, p. 547. Wiley-Interscience, New York, 1973.
132. Davies, A. G., ref. *31,* Chap. 2.
133. Boué, S., Gielen, M., and Nasielski, J., *J. Organomet. Chem.* **9,** 461 (1967).
134. Davies, A. G., Roberts, B. P., and Smith, J. M., *J. Chem. Soc., Perkin Trans. 2* p. 2221 (1971).
135. Davies, A. G., Roberts, B. P., and Scaiano, J. C., *J. Chem. Soc., Perkin Trans. 2* p. 223 (1972).
136. Davies, A. G., and Scaiano, J. C., *J. Chem. Soc., Perkin Trans. 2* p. 1777 (1973).

137. Davies, A. G., Muggleton, B., Roberts, B. P., Tse, M.-W., and Winter, J., *J. Organomet. Chem.* **118,** 289 (1978).
138. Davies, A. G., Roberts, B. P., and Tse, M.-W., *J. Chem. Soc., Perkin Trans. 2* p. 1499 (1977).
139. Abel, E. W., and Rowley, R. I., *J. Organomet. Chem.* **84,** 199 (1975).
140. Albert, H.-J., Neumann, W. P., Kaiser, W., and Ritter, H.-P., *Chem. Ber.* **103,** 1372 (1970).
141. Schröer, U., and Neumann, W. P., *J. Organomet. Chem.* **105,** 183 (1976).
142. Hannon, S. J., and Traylor, T. G., *J. Chem. Soc., Chem. Commun.* p. 630 (1975).
143. Fishwick, M. F., and Wallbridge, M. G. H., *J. Organomet. Chem.* **25,** 69 (1973).
144. Fishwick, M. F., and Wallbridge, M. G. H., *J. Organomet. Chem.* **136,** C46 (1977).
145. Schweig, A., Weidner, U., and Manuel, G., *J. Organomet. Chem.* **54,** 145 (1973).
146. Schweig, A., Weidner, U., and Manuel, G., *J. Organomet. Chem.* **54,** 145 (1973).
147. Peruzzo, V., Plazzogna, G., and Tagliavini, G., *J. Organomet. Chem.* **40,** 121 (1972).
148. Puruzzo, V., and Tagliavini, A., *J. Organomet. Chem.* **66,** 437 (1974).
149. Magravite, J. A., Verdona, J. A., and Kuivila, H. G., *J. Organomet. Chem.* **104,** 303 (1976).
150. Bullpitt, M. L., and Kitching, W., *J. Organomet. Chem.* **84,** 321 (1972).
151. Roberts, R. M. G., *J. Organomet. Chem.* **24,** 675 (1970).
152. Servens, C., and Pereyre, M., *J. Organomet. Chem.* **35,** C20 (1970).
153. Servens, C., and Pereyre, M., *J. Organomet. Chem.* **26,** C4 (1971).
154. Abel, E. W., and Rowley, R. I., *J. Organomet. Chem.* **84,** 199 (1975).
155. Albert, H.-J., Neumann, W. P., and Ritter, H.-P., *Justus Liebigs Ann. Chem.* **737,** 152 (1970).
156. Schröer, U., and Neumann, W. P., *J. Organomet. Chem.* **105,** 183 (1976).
157. Kosigi, M., Kurimo, K., Takayama, K., and Migita, T., *J. Organomet. Chem.* **56,** C11 (1973).
158. Grignon, J., Servens, C., and Pereyre, M., *J. Organomet. Chem.* **96,** 225 (1975).
159. Guillerm, G., Maganem, F., Lequan, M., and Brower, K. R., *J. Organomet. Chem.* **67,** 43 (1974).
160. Simo, M. S., Jean, A., and Lequan, M., *J. Organomet. Chem.* **35,** C23 (1970).
161. Lequan, M., and Guillerm, G., *J. Organomet. Chem.* **54,** 153 (1973).
162. Kison, A. V., Korenevsky, V. A., Sergeyev, N. M., and Ustynyuk, Yu. A., *J. Organomet. Chem.* **34,** 93 (1972).
163. Grishin, Yu. K., Sergeyev, N. M., and Ustynyuk, Yu. A., *J. Organomet. Chem.* **34,** 105 (1972).
164. Curtis, M. D., and Fink, R., *J. Organomet. Chem.* **38,** 299 (1972).
165. Larrabee, R. B., *J. Am. Chem. Soc.* **93,** 1510 (1971).
166. Boche, G., and Haidenhain, F., *J. Organomet. Chem.* **121,** C49 (1976).
167. Abel, E. W., Dunster, M. O., and Waters, A., *J. Organomet. Chem.* **49,** 287 (1973).
168. Larrabee, R. B., *J. Organomet. Chem.* **74,** 313 (1974).
169. Schröer, U., Albert, H.-J., and Neumann, W. P., *J. Organomet. Chem.* **102,** 291 (1975).
170. Davies, A. G., and Tse, M.-W., *J. Chem. Soc., Chem. Commun.* p. 353 (1978).
170a. Schumann, H., and Schumann, I., "Organotin Hydrides," "Gmelin Handbuch der Anorganischen Chemie," Band 35, Teil 4. Springer-Verlag, Berlin and New York, 1976.
171. Pereyre, M., and Pijselman, J., *J. Organomet. Chem.* **25,** C27 (1970).
172. Pijselman, J., and Pereyre, M., *J. Organomet. Chem.* **32,** C72 (1971).
173. Pijselman, J., and Pereyre, M., *J. Organomet. Chem.* **63,** 139 (1973).

174. Brum, J. E., May, G. S., Sawyer, A. K., Schofield, R. E., and Sprague, W. E., *J. Organomet. Chem.* **124,** 13 (1977).
175. Pereyre, M., and Pommier, J.-C., *J. Organomet. Chem. Library* **1,** 161 (1976).
176. Corey, E. J., and Suggs, J. W., *J. Organomet. Chem.* **40,** 2554 (1975).
177. Lipowitz, J., and Bowman, S. A., *Aldrichimica Acta* **6,** 1 (1973).
178. Knocke, P., and Neumann, W. P., *Justus Liebigs Ann. Chem.* p. 1486 (1974).
179. Weinshenker, N. M., Crosby, G. A., and Wong, J. Y., *J. Org. Chem.* **40,** 1966 (1975).
180. Bulten, E. J., and Budding, H. A., *J. Organomet. Chem.* **111,** C33 (1976).
181. Clark, H. C., and Puddephatt, R. J., Synthesis and properties of the tin–halogen and tin–halogenoid bond, *in* "Organometallic Compounds of the Group IV Elements" (A. G. MacDiarmid, ed.), Vol. 2, Part 2, Chapter 3. Arnold, New York, 1968.
182. Knips, U., and Huber, F., *J. Organomet. Chem.* **107,** 9 (1976).
183. Garner, C. D., and Hughes, B., *J. Chem. Soc. D* p. 1306 (1974).
184. Batchelor, R. J., Riddick, J. N. R., Sams, J. R., and Aubke, F., *Inorg. Chem.* **16,** 1414 (1977).
185. Peruzzo, V., Plazzogna, G., and Tagliavini, G., *J. Organomet. Chem.* **24,** 347 (1970).
186. Peruzzo, V., Plazzogna, G., and Tagliavini, G., *J. Organomet. Chem.* **40,** 121 (1972).
187. Wang, C. S., and Shreeve, J. M., *J. Chem. Soc., Chem. Commun.* p. 151 (1970).
188. Wang, C. S., and Shreeve, J. M., *J. Organomet. Chem.* **38,** 287 (1972).
189. Christen, U., and Neumann, W. P., *J. Organomet. Chem.* **39,** C58 (1972).
190. Gaur, D. P., Srivastava, G., and Mehrotra, R. C., *J. Organomet. Chem.* **63,** 221 (1973).
191. Kennedy, J. D., McFarlane, W., Smith, P. J., White, R. F. M., and Smith, L., *J. Chem. Soc., Perkin Trans. 2* p. 1785 (1973).
192. Davies, A. G., Kleinschmidt, D. C., Palan, P. R., and Vasishtha, S. C., *J. Chem. Soc. C* p. 3972 (1971).
193. Lutzenko, I. F., Baukov, Y. I., and Belavin, I. Yu., *J. Organomet. Chem.* **24,** 359 (1970).
194. Baukov, Yu. I., and Lutzenko, I. F., *Organomet. Chem. Rev.* **6,** 355 (1970).
195. Davies, A. G., Smith, L., and Smith, P. J., *J. Organomet. Chem.* **39,** 279 (1972).
196. Zschunke, A., Tzschach, A., and Pönicke, K., *J. Organomet. Chem.* **51,** 197 (1973).
197. Tzschach, A., and Pönicke, K., Korecz, I., and Burger, K., *J. Organomet. Chem.* **59,** 199 (1973).
198. Tzschach, A., and Pönicke, K., *Kem. Kozl.* **41,** 141 (1974).
199. Tzschach, A., and Pönicke, K., *Z. Anorg. Allg. Chem.* **404,** 121 (1974).
200. Tzschach, A., and Pönicke, K., *Z. Anorg. Allg. Chem.* **413,** 136 (1975).
201. Zeldin, M., and Ochs, J., *J. Organomet. Chem.* **86,** 369 (1975).
202. Zschunke, A., Tzschach, A., and Jurkschat, K., *J. Organomet. Chem.* **112,** 273 (1976).
203. Delmond, B., and Pommier, J.-C., *J. Organomet. Chem.* **26,** C7 (1971).
204. Delmond, B., Pommier, J.-C., and Valade, J., *J. Organomet. Chem.* **34,** 91 (1972).
205. Delmond, B., Pommier, J.-C., and Valade, J., *J. Organomet. Chem.* **47,** 337 (1973).
206. Delmond, B., Pommier, J.-C., and Valade, J., *J. Organomet. Chem.* **50,** 121 (1973).
207. Wagner, D., Verheyden, J. P. H., and Moffatt, J. G., *J. Org. Chem.* **39,** 24 (1974).
208. Auge, C., David, S., and Veyrières, A., *J. Chem. Soc., Chem. Commun.* p. 375 (1976).
209. Nashed, M. A., and Anderson, L., *Tetrahedron Lett.* p. 3503 (1976).
210. Munavu, R. M., and Szmant, H. H., *J. Org. Chem.* **10,** 1832 (1976).
211. Crowe, A. J., and Smith, P. J., *J. Organomet. Chem.* **110,** C57 (1976).
211a. Ogawa, T., and Matsui, M., *Carbohydrate Res.* **62,** C1 (1978).

211b. Nashed, M. A., and Anderson, L. *Carbohydrate Res.* **56,** 325 (1977).
212. Brown, J. M., Chapman, A. C., Harper, R., Mowthorpe, D. J., Davies, A. G., and Smith, P. J., *J. Chem. Soc. D* p. 338 (1972).
213. Stapfer, C. H., Dworkin, R. D., and Weisfeld, L. B., *J. Organomet. Chem.* **24,** 355 (1970).
214. Salomon, M. F., and Salomon, R. G., *J. Am. Chem. Soc.* **99,** 3500 (1977).
215. Sannley, R. L., Aue, W. A., and Shubber, A. K., *J. Organomet. Chem.* **38,** 281 (1972).
216. Brandes, D., and Blaschette, A., *J. Organomet. Chem.* **78,** 1 (1974).
217. Bishop, M. E., and Zuckerman, J. J., *J. Am. Chem. Soc.* **16,** 1749 (1977).
218. Armitage, D. A., and Sinden, A. W., *J. Organomet. Chem.* **44,** C43 (1972).
219. Pommier, J.-C., and Roubineau, A., *J. Organomet. Chem.* **50,** 101 (1973).
220. Brocas, J.-M., and Pommier, J.-C., *J. Organomet. Chem.* **121,** 45 (1976).
221. Roubineau, A., and Pommier, J.-C., *J. Organomet. Chem.* **107,** 63 (1976).
222. Brocas, J.-M., de Jeso, B., and Pommier, J.-C., *J. Organomet. Chem.* **120,** 217 (1976).
223. de Jeso, B., and Pommier, J.-C., *J. Organomet. Chem.* **122,** C1 (1976).
224. Cardona, R. A., and Kupchik, E. J., *J. Organomet. Chem.* **34,** 129 (1972).
225. Feiccabrino, J. A., and Kupchik, E. J., *J. Organomet. Chem.* **56,** 167 (1973).
226. Feiccabrino, J. A., and Kupchik, E. J., *J. Organomet. Chem.* **73,** 319 (1974).
227. Feiccabrino, J. A., and Kupchik, E. J., *J. Organomet. Chem.* **93,** 325 (1975).
228. Hänssgen, D., and Roelle, W., *J. Organomet. Chem.* **56,** C14 (1973).
229. Harris, S. J., and Walton, D. R. M., *J. Organomet. Chem.* **127,** C1 (1977).
230. Cragg, R. H., and Taylor, A., *J. Organomet. Chem.* **99,** 391 (1975).
231. Breitschneider, E. S., and Allen, C. W., *J. Organomet. Chem.* **38,** 43 (1972).
232. Armitage, D. A., and Tarassoli, A., *Inorg. Chem.* **14,** 1210 (1975).
233. Levchuk, L. E., Sams, J. R., and Aubke, F., *Inorg. Chem.* **11,** 43 (1972).
234. Yeats, P. A., Sams, J. R., and Aubke, F., *Inorg. Chem.* **11,** 2634 (1972).
235. Chapman, A. C., Davies, A. G., Harrison, P. G., and McFarlane, W., *J. Chem. Soc. C* p. 821 (1970).
236. Davies, A. G., and Kennedy, J. D., *J. Chem. Soc. C* p. 759 (1970).
237. Schumann, H., du Mont, W. W., and Kooth, H.-J., *Chem. Ber.* **109,** 237 (1976).
238. Schumann, H., du Mont, W.-W., Corvan, P. J., and Zuckerman, J. J. *J. Organomet. Chem.* **128,** 187 (1977).
239. Wang, C. S., and Shreeve, J. M., *J. Chem. Soc., Chem. Commun.* p. 151 (1970).
240. Wang, C. S., and Shreeve, J. M., *J. Organomet. Chem.* **38,** 287 (1972).
241. Cohen, A. D., and Dillard, C. R., *J. Organomet. Chem.* **25,** 421 (1970).
242. Gaur, D. P., Srivastava, G., and Mehrotra, R. C., *J. Organomet. Chem.* **63,** 221 (1973).
243. Stapfer, C. H., Dworkin, R. D., and Weisfeld, L. B., *J. Organomet. Chem.* **24,** 355 (1970).
244. Gaur, D. P., Srivastava, G., and Mehrotra, R. C., *J. Organomet. Chem.* **63,** 213 (1973).
245. Chu, C. K., and Murray, J. D., *J. Chem. Soc. A* p. 360 (1971).
246. Matsuda, H., Mori, F., Kashiwa, A., Matsuda, S., Kasai, N., and Jitsumori, K., *J. Organomet. Chem.* **34,** 341 (1972).
247. Davies, A. G., Harrison, P. G., and Palan, P. R., *J. Chem. Soc. C* p. 2030 (1970).
248. Davies, A., and Harrison, P. G., *J. Chem. Soc. C* p. 2035 (1970).
249. Davies, A. G., and Kennedy, J. D., *J. Chem. Soc. C* p. 759 (1970).

250. Davies, A. G., and Harrison, P. G., *J. Chem. Soc. C* p. 1769 (1971).
251. Mehrotra, S. K., Srivastava, G., and Mehrotra, R. C., *J. Organomet. Chem.* **65,** 361 (1974).
252. Mehrotra, S. K., Srivastava, G., and Mehrotra, R. C., *J. Organomet. Chem.* **65,** 367 (1974).
253. Hännsgen, D., Kuna, J., and Ross, B., *Angew. Chem., Int. Ed. Engl.* **13,** 607 (1974).
254. Davies, A. G., and Kennedy, J. D., *J. Chem. Soc. D* p. 759 (1970).
255. Mathiasch, B., *J. Organomet. Chem.* **122,** 345 (1976).
256. Mitchell, T. N., and El-Bahairy, M., *J. Organomet. Chem.* **141,** 43 (1977).
257. Plazzogna, G., Puruzzo, V., and Tagliavinni, G., *J. Organomet. Chem.* **24,** 667 (1970).
258. Plazzogna, G., Puruzzo, V., and Tagliavinni, G., *J. Organomet. Chem.* **66,** 57 (1974).
259. Bulten, E. J., Budding, H. A., and Noltes, J. G., *J. Organomet. Chem.* **22,** C5 (1970).
260. Bulten, E. J., and Budding, H. A., *J. Organomet. Chem.* **78,** 385 (1974).
261. Weibel, A. T., and Oliver, J. P., *J. Organomet. Chem.* **57,** 313 (1978).
262. McWilliam, D. C., and Wells, P. R., *J. Organomet. Chem.* **85,** 335 (1975).
263. McWilliam, D. C., and Wells, P. R., *J. Organomet. Chem.* **85,** 347 (1975).
264. McWilliam, D. C., and Wells, P. R., *J. Organomet. Chem.* **85,** 165 (1975).
265. Arnold, D. P., and Wells, P. R., *J. Organomet. Chem.* **108,** 345 (1975).
266. Bulten, E. J., and Budding, H. A., *J. Organomet. Chem.* **82,** 121 (1974).
267. Buschhaus, H. U., and Neumann, W. P., *Angew. Chem., Int. Ed. Engl.* **17,** 60 (1978).
268. Lahournère, J.-C., and Valade, J., *C. R. Hebd. Acad. Sci. Ser. C.* **270,** 1080 (1970).
269. Lahournère, J.-C., and Valade, J., *J. Organomet. Chem.* **22,** C3 (1970).
270. Lahournère, J.-C., and Valade, J., *J. Organomet. Chem.* **33,** C4 (1971).
271. des Tombe, F. J. A., van der Kerk, G. J. M., Creemers, H. M. J. C., Corey, N. A. D., and Noltes, J. G., *J. Organomet. Chem.* **44,** 247 (1972).
272. des Tombe, F. J. A., van der Kerk, G. J. M., and Noltes, J. G., *J. Organomet. Chem.* **43,** 323 (1977).
273. Kruglaya, O. A., Kalinina, G. S., Petrov, B. I., and Vyazankin, N. S., *J. Organomet. Chem.* **46,** 51 (1972).
274. Blaukat, U., and Neumann, W. P., *J. Organomet. Chem.* **63,** 27 (1973).
275. Mitchell, T. N., *J. Organomet. Chem.* **92,** 311 (1975).
276. McWilliam, D. C., and Wells, P. R., *J. Organomet. Chem.* **85,** 347 (1975).
277. Mitchell, T. N., *J. Organomet. Chem.* **71,** 29 (1974).
278. Mitchell, T. N., *J. Organomet. Chem.* **71,** 39 (1974).
279. Weibel, A. T., and Oliver, J. P., *J. Am. Chem. Soc.* **94,** 8590 (1972).
280. Seyferth, D., and Andrews, S. B., *J. Organomet. Chem.* **30,** 151 (1971).
281. Seyferth, D., Armbrecht, F. M., Lambert, R. L., and Tronich, W., *J. Organomet. Chem.* **44,** 299 (1972).
282. Seyferth, D., Lambert, R. L., and Hanson, E. M., *J. Organomet. Chem.* **24,** 647 (1970).
283. Seyferth, D., Andrews, S. B., and Lambert, R. L., *J. Organomet. Chem.* **37,** 69 (1972).
284. Seyferth, D., and Lambert, R. L., *J. Organomet. Chem.* **91,** 31 (1975).
285. Abel, E. W., and Rowley, R. J., *J. Organomet. Chem.* **97,** 159 (1975).
286. Brasington, R. D., and Poller, R. C., *J. Organomet. Chem.* **40,** 115 (1972).
287. Kuivila, H. G., *Acc. Chem. Res.* **1,** 299 (1968).
288. Davies, A. G., ref. *1,* p. 26.

289. Poller, R. C., *Rev. Silicon, Germanium, Tin, Lead Compd.* **3,** 243 (1978).
290. Hillgartner, H., Schroeder, B., and Neumann, W. P., *J. Organomet. Chem.* **42,** C83 (1972).
291. Hillgärtner, H., Neumann, W. P., and Schroeder, B., *Justus Liebigs Ann. Chem.* p. 586 (1975).
292. Neumann, W. P., Schroeder, B., and Ziebarth, M., *Justus Liebigs Ann. Chem.* p. 2279 (1975).
293. Davies, A. G., and Tse, M.-W., *J. Chem. Soc., Perkin Trans. 2* p. 145 (1978).
294. Davies, A. G., and Tse, M.-W., *J. Chem. Soc., Chem. Commun.* p. 353 (1978).
295. Watts, G. B., and Ingold, K. U., *J. Am. Chem. Soc.* **94,** 491 (1972).
296. Lehnig, M., *Tetrahedron Lett.* p. 3663 (1977).
297. Buschhaus, H. A., Lehnig, M., and Neumann, W. P., *J. Chem. Soc., Chem. Commun.* p. 129 (1977).
298. Buschhaus, H. A., and Neumann, W. P., *Angew. Chem., Int. Ed. Engl.* **17,** 59 (1978).
299. Davidson, P. J., Hudson, A., Lappert, M. F., and Lednor, P. W., *J. Chem. Soc., Chem. Commun.* p. 829 (1973).
300. Gynane, M. J. S., Harris, D. H., Lappert, M. F., Power, P. P., Riviere, P., and Riviere-Baudet, M., *J. Chem. Soc., Dalton Trans.* p. 2004 (1977).
301. Cooper, J., Hudson, A., and Jackson, R. A., *J. Chem. Soc., Perkin Trans. 2* p. 1056 (1973).
302. Coates, D. A., and Tedder, J. M., *J. Chem. Soc., Perkin Trans. 2* p. 1570 (1973).
303. Grady, G. L., Danyliw, T. J., and Rabidaux, P., *J. Organomet. Chem.* **142,** 67 (1977).
304. Lehnig, M., *Tetrahedron Lett.* p. 3663 (1977).
305. Hollaender, J., Neumann, W. P., and Lind, H., *Chem. Ber.* **106,** 2395 (1973).
306. Avar, G., and Neumann, W. P., *J. Organomet. Chem.* **131,** 207 (1977).
307. Albert, H. J., Neumann, W. P., and Schneider, K., *Chem. Ber.* **106,** 411 (1973).
308. Christen, U., and Neumann, W. P., *Chem. Ber.* **106,** 421 (1973).
309. Rotenberg, K., Neumann, W. P., and Avar, G., *Chem. Ber.* **110,** 1628 (1977).
310. Neumann, W. P., and Schwindt, J., *Chem. Ber.* **108,** 1339 (1975).
311. Lehnig, M., Schwindt, J., and Neumann, W. P., *Chem. Ber.* **108,** 1355 (1975).
312. Scaiano, J. C., Schmid, P., and Ingold, K. U., *J. Organomet. Chem.* **121,** C4 (1976).
313. Cooper, J., Hudson, A., and Jackson, R. A., *J. Chem. Soc., Perkin Trans. 2* p. 1933 (1973).
314. Schroeder, B., Neumann, W. P., and Hillgärtner, H., *Chem. Ber.* **107,** 3494 (1974).
315. Neumann, W. P., and Schwindt, J., *Chem. Ber.* **108,** 1346 (1975).
316. Barton, D. H. R., and McCombie, S. W., *J. Chem. Soc., Perkin Trans. 2* p. 1574 (1975).
317. Avar, G., and Neumann, W. P., *J. Organomet. Chem.* **131,** 215 (1977).
318. Scaiano, J. C., and Ingold, K. U., *J. Am. Chem. Soc.* **99,** 2079 (1977).
319. Harrison, P. G., and Richards, J. A., *J. Organomet. Chem.* **108,** 35 (1976).
320. Harrison, P. G., *J. Chem. Soc., Chem. Commun.* 544 (1972).
321. Harrison, P. G., and Stobart, S. R., *J. Chem. Soc., Dalton Trans.* p. 940 (1973).
322. Ewings, P. F. R., and Harrison, P. G., *J. Chem. Soc., Dalton Trans.* p. 1719 (1975).
323. Ewings, P. F. R., and Harrison, P. G., *J. Chem. Soc., Dalton Trans.* p. 2015 (1975).
324. Bos, K. D., Bulten, E. J., and Noltes, J. F., *J. Organomet. Chem.* **99,** 397 (1975).
325. Albert, H.-J., and Schröer, U., *J. Organomet. Chem.* **60,** C6 (1973).
326. Davidson, P. J., and Lappert, M. F., *J. Chem. Soc., Chem. Commun.* p. 317 (1973).
327. Davidson, P. J., Harris, D. H., and Lappert, M. F., *J. Chem. Soc., Dalton Trans.* p. 2269 (1976).

328. Cotton, J. D., Davidson, P. J., Lappert, M. F., Donaldson, J. D., and Ger, J. S., *J. Chem. Soc., Dalton Trans.* p. 2286 (1976).

329. Cotton, J. D., Davidson, P. J., and Lappert, M. F., *J. Chem. Soc., Dalton Trans.* p. 2275 (1976).

330. Gynane, M. J. S., Lappert, M. F., Miles, S. J., and Power, P. P., *J. Chem. Soc., Chem. Commun.* p. 256 (1973).

331. Gynane, M. J. S., Lappert, M. F., Miles, S. J., and Power, P. P., *J. Chem. Soc., Chem. Commun.* p. 192 (1978).

332. Goldberg, D. E., Harris, D. H., Lappert, M. F., and Thomas, K. M., *J. Chem. Soc., Chem. Commun.* p. 261 (1976).

333. Neumann, W. P., *Rev. Silicon, Germanium, Tin, Lead Compd.* In press.

334. Schröer, U., and Neumann, W. P., *Angew. Chem., Int. Ed. Engl.* **14,** 246 (1975).

335. Grugel, C., Neumann, W. P., and Seifert, P., *Tetrahedron Lett.* p. 2205 (1977).

336. Neumann, W. P., and Schwarz, A., *Angew. Chem., Int. Ed. Engl.* **14,** 812 (1975).

337. Hulme, R., *J. Chem. Soc.* p. 1524 (1963).

338. Petrosyan, V. S., *Prog. Nucl. Magn. Reson. Spectrosc.* **11,** 115 (1977).

339. Ho, B. Y. K., and Zuckerman, J. J., *J. Organomet. Chem.* **49,** 1 (1973).

340. Bokii, N. G., *Itogi Nauki Tekh. Kristallokhim.* **10,** 94 (1974).

341. Karipides, A., Forman, C., Thomas, R. H. P., and Reed, A. T., *Inorg. Chem.* **13,** 811 (1974).

342. Karipides, A., and Oertel, M., *Acta Crystallogr., Sect. B* **33,** 683 (1977).

343. Karipides, A., and Wolfe, K., *Acta Crystallogr., Sect. B* **31,** 605 (1975).

344. Karipides, A., Reed, A. T., Haller, D. A., and Hayes, F., *Acta Crystallogr., Sect. B* **33,** 950 (1977).

345. Kulishov, V. I., Bokii, N. G., Prikhot'ko, A. F., and Struchkov, Yu. T., *Zh. Strukt. Khim.* **16,** 252 (1975).

346. Barrans, Y., Pereyre, M., and Rahm, A., *J. Organomet. Chem.* **125,** 173 (1977).

346a. Harrison, P. G., and Molloy, K., *J. Organomet. Chem.* **152,** 53 (1978).

347. Gynane, M. J. S., Lappert, M. F., Miles, S. J., Carty, A. J., and Taylor, N. J., *J. Chem. Soc., Dalton Trans.* p. 2009 (1977).

348. Clarke, P. L., Cradwick, M. E., and Wardell, J. L., *J. Organomet. Chem.* **63,** 279 (1973).

349. Bokii, N. G., Struchkov, Yu. T., Kravtsov, D. N., and Rokhlina, E. M., *J. Struct. Chem. (USSR)* **15,** 424 (1974).

350. Menzebach, B., and Bleckmann, P., *J. Organomet. Chem.* **91,** 291 (1975).

351. Jacobsen, H.-J., and Krebs, B., *J. Organomet. Chem.* **136,** 333 (1977).

352. Kobelt, D., Paulus, E. F., and Scherer, H., *Acta Crystallogr., Sect. B* **28,** 2323 (1972).

353. Petrosyan, V. S., and Reutov, O. A., *Pure Appl. Chem.* **37,** 147 (1974).

354. Buckle, J., Harrison, P. G., King, T. J., and Richards, J. A., *J. Chem. Soc., Dalton Trans.* p. 1552 (1975).

355. Chih, H., and Penfold, B. R., *J. Cryst. Mol. Struct.* **3,** 285 (1973).

356. Boer, F. P., Doorakian, G. A., Freedman, H. H., and McKinley, S. V., *J. Am. Chem. Soc.* **92,** 1225 (1970).

347. Van Koten, G., Noltes, J. G., and Spek, A. L., *J. Organomet. Chem.* **118,** 183 (1976).

358. Bancroft, G. M., Davies, B. W., Payne, N. C., and Sham, T. K., *J. Chem. Soc., Dalton Trans.* p. 973 (1975).

359. King, T. J., and Harrison, P. G., *J. Chem. Soc., Dalton Trans.* p. 2298 (1974).

360. Buttenshaw, A. J., Duchêne, M., and Webster, M., *J. Chem. Soc., Dalton Trans.* p. 2230 (1975).

361. Cunningham, D., Douek, I., Frazer, M. J., McPartlin, M., and Matthews, J. D., *J. Organomet. Chem.* **90,** C23 (1975).
362. Graziani, R., Bombieri, G., Forsellini, E., Furlan, P., Peruzzo, V., and Tagliavini, G., *J. Organomet. Chem.* **125,** 43 (1977).
363. Webster, M., Mudd, K. R., and Taylor, D. J., *Inorg. Chim. Acta* **20,** 231 (1976).
364. Fitzsimmonds, B. W., Othen, D. G., Shearer, H. M. M., Wade, K., and Whitehead, G., *J. Chem. Soc., Chem. Commun.* p. 215 (1977).
365. Holloway, J. H., McQuillan, G. P., and Ross, D. S., *J. Chem. Soc. A* p. 2505 (1969).
366. Schlemper, E. O., *Inorg. Chem.* **6,** 2012 (1967).
367. Harrison, P. G., King, T. J., and Phillips, R. C., *J. Chem. Soc., Dalton Trans.* p. 2317 (1976).
368. Lindley, P. F., and Carr, P., *J. Cryst. Mol. Struct.* **4,** 173 (1974).
369. Miller, G. A., and Schlemper, E. O., *Inorg. Chem.* **12,** 677 (1973).
370. Harrison, P. G., King, T. J., and Richards, J. A., *J. Chem. Soc., Dalton Trans.* p. 1723 (1974).
371. Coghi, L., Pelizzi, C., and Pelizzi, G., *Gazz. Chim. Ital.* **104,** 873 (1974).
372. Schlemper, E. O., and Hamilton, W. C., *Inorg. Chem.* **5,** 995 (1966).
373. Allen, F. H., Lerbscher, J. A., and Trotter, J., *J. Chem. Soc. A* p. 2507 (1971).
374. Alcock, N. W., and Sawyer, J. F., *J. Chem. Soc., Dalton Trans.* p. 1090 (1977).
375. Davies, A. G., Milledge, H. J., Puxley, D. C., and Smith, P. J., *J. Chem. Soc. A* p. 2862 (1970).
376. Chow, Y. M., *Inorg. Chem.* **9,** 794 (1970).
377. Foder, R. A., and Sheldrick, G. M., *J. Organomet. Chem.* **22,** 611 (1970).
378. Bokii, N. G., Struchkov, Yu. T., and Prokof'ev, A. K., *J. Struct. Chem.* **13,** 619 (1972).
379. Harrison, P. G., King, T. J., and Richards, J. A., *J. Chem. Soc., Dalton Trans.* p. 826 (1975).
380. Kimura, T., Yasuoka, N., Kasai, N., and Kakudo, M., *Bull. Chem. Soc. Jpn.* **45** 1649 (1972).
381. Calligaris, M., Nardin, G., and Randaccio, L., *J. Chem. Soc., Dalton Trans.* p. 2003 (1972).
382. Harrison, P. G., and Mangia, A., *J. Organomet. Chem.* **120,** 211 (1976).
383. Lecomte, C., Protas, J., and Devaud, M., *Acta Crystallogr., Sect. B* **32,** 923 (1976).
384. Brownlee, G. S., Walker, A., Nyburg, S. C., and Szymański, J. T., *J. Chem. Soc., Chem. Commun.* p. 1073 (1971).
385. Schlemper, E. O., personal communication, quoted in: Naik, D. V., and Curran, C., *Inorg. Chem.* **10,** 1017 (1971).
386. Naik, D. V., and Scheidt, W., *Inorg. Chem.* **12,** 272 (1973).
387. Coghi, L., Pelizzi, C., and Pelizzi, G., *J. Organomet. Chem.* **114,** 53 (1976).
388. Mangia, A., Pelizzi, C., and Pelizzi, G., *J. Chem. Soc., Dalton Trans.* p. 2557 (1973).
389. Mackay, C. A., Ph.D. Thesis, University of London, 1973.
390. Preut, H., Huber, F., Haupt, H.-J., Cafalù, R., and Barbieri, R., *Z. Anorg. Allg. Chem.* **410,** 88 (1974).
391. Evans, D. L., and Penfold, B. R., *J. Cryst. Mol. Struct.* **5,** 93 (1975).
392. Domingos, A. M., and Sheldrick, G. M., *J. Chem. Soc., Dalton Trans.* p. 470 (1974).
393. Ashmore, J. P., Chivers, T., Kerr, K. A., and van Roode, J. H. G., *Inorg. Chem.* **16,** 191 (1977).
394. Domingos, A. M., and Sheldrick, G. M., *Acta Crystallogr., Sect. B* **30,** 519 (1974).
395. Ewings, P. F. R., Harrison, P. G., King, T. J., Phillips, R. C., and Richards, J. A., *J. Chem. Soc., Dalton Trans.* p. 1950 (1975).

396. Domingos, A. M., and Sheldrick, G. M., *J. Organomet. Chem.* **69,** 207 (1974).
397. Hall, J. B., and Britton, D., *Acta Crystallogr., Sect. B* **28,** 2133 (1972).
398. Okawara, R., and Wada, M., *Adv. Organomet. Chem.* **5,** 150 (1967).
399. Ho, B. Y. K., Zubieta, J. A., and Zuckerman, J. J., *J. Chem. Soc., Chem. Commun.* p. 88 (1975).
400. Harrison, P. G., ref. *31,* p. 258.
401. Clark, H. C., personal communication, quoted in: Potts, D., Sharma, H. D., Carty, A. J., and Walker, A., *Inorg. Chem.* **13,** 1205 (1974).
402. Hengel, R., Kunze, U., and Straehle, J., *Z. Anorg. Allg. Chem.* **423,** 35 (1976).
403. Sheldrick, G. M., and Taylor, R., *Acta Crystallogr., Sect. B* **33,** 135 (1977).
404. Ginderow, G., and Huber, M. M., *Acta Crystallogr., Sect. B* **29,** 560 (1973).
405. Harrison, P. G., Phillips, R. C., and Richards, J. A., *J. Organomet. Chem.* **114,** 47 (1976).
406. Domingos, A. M., and Sheldrick, G. M., *J. Chem. Soc., Dalton Trans.* p. 477 (1974).
407. Pommier, J.-C., Mendes, F., and Valade, J., *J. Organomet. Chem.* **55,** C19 (1973).
408. Kunchur, N. R., and Borhani, S., *J. Appl. Crystallogr.* **9,** 508 (1976).
409. Williams, D., *Aust. Def. Stand. Lab. Ann. Rep.* p. 37 (1967/1968).
410. Huber, F., Haupt, H.-J., Preut, H., Barbieri, R., and Lo Giudice, M. T., *Z. Anorg. Allg. Chem.* **432,** 51 (1977).
411. Preut, H., Haupt, H.-J., Huber, F., Cefalù, R., and Barbieri, R., *Z. Anorg. Allg. Chem.* **407,** 257 (1974).
412. Preut, H., Huber, F., Barbieri, R., and Bertazzi, N., *Z. Anorg. Allg. Chem.* **423,** 75 (1976).
413. Glidewell, C., and Liles, D. C., *Acta Crystallogr., Sect. B* **34,** 129 (1978).
414. Bokii, N. G., Struchkov, Yu. T., Kravtsov, D. N., and Rokhlina, E. M., *J. Struct. Chem. (USSR)* **14,** 458 (1973).
415. Domingos, A. M., and Sheldrick, G. M., *J. Organomet. Chem.* **67,** 257 (1974).
416. Tarkhlova, T. N., Chuprunov, E. V., Simonov, M. A., and Belov, N. V., *Kristallografiya* **22,** 1004 (1977).
417. Bokii, N. G., Struchkov, Yu. T., Korolikov, V. V., and Tolstaya, T. P., *Koord. Khim.* **1,** 1144 (1975).
418. Uber, W., Stegmann, H. B., Scheffler, K., and Straehle, J., *Z. Naturforsch., Teil B* **32,** 355 (1977).
419. Kulishov, V. I., Rodé, G. G., Bokii, N. G., Prikhot'ko, A. F., and Struchkov, Yu. T., *J. Struct. Chem. (USSR)* **16,** 227 (1975).
420. Weidenborner, J. E., Larrabee, R. B., and Bednowitz, A. L., *J. Am. Chem. Soc.* **94,** 4140 (1972).
421. Pelizzi, C., Pelizzi, G., and Tarasconi, P., *J. Chem. Soc., Dalton Trans.* 1935 (1977).
422. Preut, H., Haupt, H.-J., and Huber, F., *Z. Anorg. Allg. Chem.* **396,** 81 (1973).
423. Nardelli, M., Pelizzi, C., Pelizzi, G., and Tarasconi, P., *Z. Anorg. Allg. Chem.* **431,** 250 (1977).
424. Howard, J. A., Kellett, S. C., and Woodward, P., *J. Chem. Soc., Dalton Trans.* p. 2332 (1975).
425. Gilmore, C. J., and Woodward, P., *J. Chem. Soc., Dalton Trans.* 1387 (1972).
426. Sweet, R. M., Fritchie, Jr., C. J., and Schunn, R. A., *Inorg. Chem.* **6,** 749 (1976).
427. Harrison, P. G., King, T. J., and Richards, J. A., *J. Chem. Soc., Dalton Trans.* p. 2097 (1975).
428. Shklover, V. E., Skripkin, V. V., Gusev, A. I., and Struchkov, Yu. T., *Zh. Strukt. Khim.* **13,** 744 (1972).

429. Pomeroy, R. K., Vancea, L., Calhoun, H. P., and Graham, W. A. G., *Inorg. Chem.* **16,** 1508 (1977).
430. Weaver, J., and Woodward, P., *J. Chem. Soc., Dalton Trans.* p. 1060 (1973).
431. Boer, F. P., Tsai, J. H., and Flynn, Jr., J. J., *J. Am. Chem. Soc.* **92,** 6092 (1970).
432. Folting, K., personal communication, quoted in: Garrou, P., and Hartwell, G. E., *J. Chem. Soc., Chem. Commun.* p. 881 (1972).
433. Collman, J. P., Murphy, D. W., Fleischer, E. B., and Swift, D., *Inorg. Chem.* **13,** 1 (1974).
434. Sasse, H. E., and Ziegler, M. L., *Z. Anorg. Allg. Chem.* **402,** 129 (1973).
435. McPhail, A. T., personal communication, quoted in: Garner, C. D., and Hughes, B., *J. Chem. Soc., Dalton Trans.* p. 1306 (1974).
436. Brice, M. D., and Cotton, F. A., *J. Am. Chem. Soc.* **95,** 4529 (1973).
437. Harrison, P. G., King, T. J., Richards, J. A., and Phillips, R. C., *J. Organomet. Chem.* **116,** 307 (1976).
438. Schumann, H., Schumann-Ruidisch, I., and Schmidt, M., *in* "Organotin Compounds," (A. K. Sawyer, ed.), Vol. 2, p. 318. Dekker, New York, 1971.
439. Smart, L. E., and Webster, M., *J. Chem. Soc., Dalton Trans.* p. 1924 (1976).
440. Harrison, P. G., Molloy, K., Phillips, R. C., Smith, P. J., and Crowe, A. J., *J. Organomet. Chem.* **160,** 421 (1978).
440a. Aslanov, L. A., Attiya, V. M., Ionov, V. M., Permin, A. B., and Petrosyan, V. S., *Zh. Strukt. Khim.* **18,** 1113 (1977).
440b. Harrison, P. G., and Molloy, K., *J. Organomet. Chem.* **152,** 63 (1978).
441. Aslanov, L. A., Ionov, V. M., Attiya, V. M., Permin, A. B., and Petrosyan, V. S., *J. Organomet. Chem.* **144,** 39 (1978).
442. Randaccio, L., *J. Organomet. Chem.* **55,** C58 (1973).
443. Isaacs, N. W., and Kennard, C. H. L., *J. Chem. Soc. A* p. 1257 (1970).
444. Calligaris, M., Randaccio, L., Barbieri, R., and Pellerito, L., *J. Organomet. Chem.* **76,** C56 (1974).
445. Garner, C. D., Hughes, B., and King, T. J., *J. Chem. Soc., Dalton Trans.* 562 (1975).
446. Nardelli, M., Pelizzi, C., and Pelizzi, G., *J. Organomet. Chem.* **112,** 263 (1976).
447. Nardelli, M., Pelizzi, C., and Pelizzi, G., *J. Organomet. Chem.* **125,** 161 (1977).
448. Pelizzi, C., Pelizzi, G., and Tarasconi, P., *J. Organomet. Chem.* **124,** 151 (1977).
449. Pelizzi, G., *Inorg. Chim. Acta* **24,** L31 (1977).
450. Kolakowski, A., and Kolakowski, B., *J. Appl. Crystallogr.* **10,** 494 (1977).
451. Midollini, S., Orlandini, A., and Sacconi, L., *Cryst. Struct. Commun.* **6,** 733 (1977).
452. Bancroft, G. M., "Mössbauer Spectroscopy," McGraw-Hill, New York, 1973.
453. Herber, R. H., and Leahy, M. F., ref. *31,* p. 155.
454. Cotton, J. D., Davidson, P. J., Lappert, M. F., Donaldson, J. D., and Silver, J., *J. Chem. Soc., Dalton Trans.* p. 2286 (1976).
455. Stöckler, H. A., and Sano, H., *Trans. Faraday Soc.* **64,** 577 (1968).
456. Ali, K. M., Cunningham, D., Donaldson, J. D., Frazer, M. J., and Senior, B. J., *J. Chem. Soc. A* p. 2836 (1969).
457. de Vries, J. L. K. F., and Herber, R. H., *Inorg. Chem.* **11,** 2458 (1972).
458. May, J. C., Petridis, D., and Curran, C., *Inorg. Chim. Acta* **5,** 511 (1971).
459. May, J. C., and Curran, C., *J. Organomet. Chem.* **39,** 289 (1972).
460. Harrison, P. G., Phillips, R. C., and Thornton, E. W., *J. Chem. Soc., Chem. Commun.* p. 603 (1977).
461. Nardelli, M., Pelizzi, C., and Pelizzi, G., *J. Chem. Soc., Dalton Trans.* p. 131 (1978).
462. D'yachenko, O. A., Zolotoi, A. b., Atovmyan, L. O., Mirskov, R. G., and Voronkov, M. G., *Dokl. Akad. Nauk SSSR* **237,** 863 (1977).

463. van Koten, G., Jastrzebski, J. T. B. H., Noltes, J. G., Spek, A. L., and Schoone, J. C., *J. Organomet. Chem.* **148,** 233 (1978).
464. van Koten, G., Jastrzebski, J. T. B. H., Noltes, J. G., Pontenagel, W. M. G. F., Kroon, J., and Spek, A. L., *J. Am. Chem. Soc.* **100,** 5021 (1978).
465. Liebich, W., and Tomassini, M., *Acta Crystallogr., Sect. B* **34,** 944 (1978).
466. Cremer, J. E., *Biochem. J.* **68,** 685 (1958).
467. Kimmel, E. C., Fish, R. H., and Casida, J. E., *J. Agric. Food Chem.* **25,** 1 (1977).
468. Meynier, D., Doctoral Dissertation, University of Toulouse, France (1955).
469. Smith, P. J., and Smith, L., *Chem. Br.* **11,** 208 (1975).
470. Smith, P. J., "Toxicological Data on Organotin Compounds," Int. Tin Res. Inst. Publ. No. 538 (1978).
471. Barnes, J. M., and Magos, L., *Organomet. Chem. Rev.* **3,** 137 (1968).
472. Ascher, K. R. S., and Nissim, S., *World Rev. Pest Control* **3,** 188 (1964).
473. Sijpesteijn, A. K., Luijten, J. G. A., and van der Kerk, G. J. M., *in* "Fungicides, An Advanced Treatise," (D. C. Torgeson, ed.), Vol. II, p. 331. Academic Press, New York, 1969.
474. van der Kerk, G. J. M., and Luijten, J. G. A., *J. Appl. Chem.* **4,** 314 (1954).
475. Evans, C. J., *Tin Its Uses* **86,** 7 (1970).
476. Evans, C. J., *Tin Its Uses* **110,** 6 (1976).
477. Aldridge, W. N., ref. *31,* p. 186.
478. Hall, W. T., and Zuckerman, J. J., *Inorg. Chem.* **16,** 1239 (1977).
479. Farrow, B. G., and Dawson, A. P., *Eur. J. Biochem.* **86,** 85 (1978).
480. Cain, K., and Griffiths, D. E., *Biochem. J.* **162,** 575 (1977).
481. Frankel, M., Gertner, D., Wagner, D., and Zilkha, A., *J. Org. Chem.* **30,** 1596 (1965).
482. Ho, B. Y. K., and Zuckerman, J. J., *Inorg. Chem.* **12,** 1552 (1973).
483. Wirth, H. O., Lorenz, H. J., and Friedrich, H.-H., U.S. Patent 3,933,877 (1976).
484. Luijten, J. G. A., Janssen, M. J., and van der Kerk, G. J. M., *Recl. Trav. Chim. Pays-Bas* **81,** 202 (1962).
485. Rose, M. S., *in* "Pesticide Terminal Residues," (A. S. Tahori, ed.). Butterworth, London, 1971.
486. Elliott, B. M., and Aldridge, W. N., *Biochem. J.* **163,** 583 (1977).
487. Lock, E. A., and Aldridge, W. N., *J. Neurochem.* **25,** 871 (1975).
488. Rose, M. S., and Lock, E. A., *Biochem. J.* **120,** 151 (1970).
489. Cardarelli, N. F., "Controlled Release Molluscicides," Environ. Manage. Lab. Mon., p. 34. Univ. Akron, Ohio, 1977.
490. Cain, K., Partis, M. D., and Griffiths, D. E., *Biochem. J.* **166,** 593 (1977).
490a. Tan, L. P., Ng, M. L., and Kumar Das, V. G., *J. Neurochem.* (1978). **31,** 1035 (1978).
491. Elliott, B. M., Aldridge, W. N., and Bridges, J. W., *Biochem. J.,* **177,** 461 (1949).
492. van Koten, G., and Noltes, J. G., ref. *31,* p. 275.
493. Tzschach, A., Reiss, E., Held, P., and Bollmann, W., E. Ger. Patent 63,490 (1968).
494. Aldridge, W. N., Casida, J. E., Fish, R. H., Kimmel, E. C., and Street, B. W., *Biochem. Pharmacol.* **26,** 1997 (1977).
495. Ascher, K. R. S., and Nemny, N. E., *Experientia* **32,** 902 (1976).
496. Abbas, S. Z., and Poller, R. C., *Polymer* **15,** 543 (1974).
497. Omae, I., *Rev. Silicon, Germanium, Tin, Lead Compd.* **1,** 59 (1974).
498. Poller, R. C., ref. *31,* p. 177.
499. Stoner, H. B., Barnes, J. M., and Duff, J. I., *Br. J. Pharmacol.* **10** 16 (1955).
500. Casida, J. E., Kimmel, E. C., Holm, B., and Widmark, G., *Acta Chem. Scand.* **25,** 1497 (1971).

501. Bridges, J. W., Davies, D. S., and Williams, R. T., *Biochem. J.* **105,** 1261 (1967).
502. Blair, E. H., *Environ. Qual. Saf., Suppl.* **3,** 406 (1975).
503. Fish, R. H., ref. *31,* p. 197.
504. Freitag, K. D., and Bock, R., *Pestic. Sci.* **5,** 731 (1974).
505. Barnes, R. D., Bull, A. T., and Poller, R. C., *Pestic. Sci.* **4,** 305 (1973).
506. Chapman, A. H., and Price, J. W., *Int. Pest. Control* **14,** 11 (1972).
507. Cenci, P., and Cremonini, B., *Ind. Sacc. Ital.* **62,** 313 (1969).
508. Getzendaner, M. E., and Corbin, H. B., *J. Agric. Food Chem.* **20,** 881 (1972).
509. Waggon, H., and Jehle, D., *Nahrung* **19,** 271 (1975).
510. Chapman, A. H., personal communication.
511. Klotzer, D., and Thust, U., *Chem. Tech. (Leipzig)* **28,** 614 (1976).
512. Smith, P. J., Crowe, A. J., Allen, D. W., Brooks, J., and Formstone, R., *Chem. Ind. (London)* 874 (1977).
513. Mazaev, V. T., Golovanov, O. V., Igumnov, A. S., and Tsay, V. H., *Gig. Sanit.* p. 17 (1976).
514. Woggon, H., Uhde, W.-J., and Säuberlich, H., *Ernaehrungforschung* **16,** 645 (1971).
515. Akagi, H., and Sakagami, Y., *Koshu Eiseiin Kenkyu Hokoku* **20,** No. 1 (1971).
516. Sheldon, A. W., *J. Paint Technol.* **47,** 54 (1975).
517. Ridley, W. P., Dizikes, L. J., and Wood, J. M., *Science* **197,** 329 (1977).
518. Dizikes, L. I., Ridley, W. P., and Wood, J. M., *J. Am. Chem. Soc.* **100,** 1010 (1978).
519. Wood, J. M., Cheh, A., Dizikes, L. J., Rakow, S., and Lakowicz, J. R., *Fed. Proc.* **37,** 16 (1978).
520. Huey, C., Brinckman, F. E., Grim, S., and Iverson, W. P., *Proc. Int. Conf. Transp. Persist. Chem. Aquat. Ecos., 1974,* pp. 73–78.
521. Ridley, W. P., *J. Freshwater* **1,** 7 (1977).
522. Frankland, E., *Justus Liebigs Ann. Chem.* **71,** 171, 212 (1849).
523. Kumar Das, V. G., and Cheong, C. K., *Planter (Kuala Lumpur)* **51,** 355 (1975).
524. Gitlitz, M. H., ref. *31,* p. 167.
525. Hunter, R. C., *Environ. Health Perspect.* **14,** 47 (1976).
526. Huber, G., *Tin Its Uses* **113,** 7 (1977).
527. Nösler, H. G., *Gesund. Desinfekt.* **62,** 10, 65, 175 (1970).
528. Verdicchio, R. J., *Proc. Chem. Spec. Manufact. Assoc. Ann. Meet.* **56,** 114 (1969).
529. Hueck, H. J., and Luijten, J. G. A., *J. Soc. Dyers Colour.* **74,** 476 (1958).
530. Richardson, B. A., *Proc. Br. Wood Preserv. Assoc. Annu. Conven., Cambridge* p. 37 (1970).
531. Evans, C. J., *Tin Its Uses* **115,** 11 (1978).
532. Richardson, B. A., *Proc. Int. Biodet. Symp., 1st 1968* p. 498.
533. M and T Chemicals, Inc., Ger. Offen. 2,617,821 (1976).
534. Richardson, B. A., and Cox, T. R. G., *Tin Its Uses* **102,** 6 (1974).
535. Richardson, B. A., *Stone Ind.* **8,** 2 (1973).
536. Crowe, A. J., and Smith, P. J., *Inorg. Chim. Acta* **19,** L7 (1976).
537. Crowe, A. J., Hill, R., and Smith, P. J., *Proc. Int. Control Rel. Pestic. Symp., 5th,* 1978.
538. Shioyama, H., Kuriyama, Y., and Suzuki, R., Jpn. Patent 18,489 (1976).
539. Blunden, S., Chapman, A. H., Crowe, A. J., and Smith, P. J., *Int. Pest Control* **20,** 5 (July/Aug., 1978).
540. Bennett, R. F., and Zedler, R. J., *J. Oil Colour Chem. Assoc.* **49,** 928 (1966).
541. Evans, C. J., and Smith, P. J., *J. Oil Colour Chem. Assoc.* **58,** 160 (1975).
542. Chandler, R. H., and Chandler, J., *Bibliogr. Paint Technol.* **29,** Chandler, R. H., Ltd., Braintree, Essex, England, 1977.

543. Monaghan, C. P., Hoffman, J. F., O'Brien, E. J., Frenzel, L. M., and Good, M. L., *Proc. Int. Control Rel. Pestic. Symp., 4th, 1977.*
544. Perkin, A., and Poller, R. C., *Int. Pest Control* **19,** 1 (July/Aug., 1977).
545 Frimann-Dahl, C., Technical Data Sheet: "*Combiprimer Systemet.*" Oslo, Norway, 1977.
546. King, S., *Tin Its Uses* **121,** 7 (1979).
547. Phillip, A. T., Bocksteiner, G., Pettis, R. W., and Glew, G. W., Austral. Patent 56,893 (1974).
548. Montemarano, J., and Dyckman, E. J., *J. Paint Technol.* **47,** 59 (1975).
549. Montemarano, J., Cohen, S. A., and Fischer, E. C., *Proc. Int. Control Rel. Pestic. Symp., 2nd, 1975.*
550. Cardarelli, N. F., "Controlled Release Pesticide Formulations." Chemical Rubber Co., Cleveland, Ohio, 1976.
551. Bell, D. R., *Br. J. Hosp. Med.* p. 29 (Jan., 1974).
552. Chliamovitch, Y.-P., and Kuhn, C., *J. Fish Biol.* **10,** 575 (1977); Chliamovitch, Y.-P., Ph.D. Thesis, Univ. Geneva, 1978.
553. Klimsch, P., *Plasty Kauc.* **24,** 380 (1977).
554. Weisfeld, L. B., and Witman, R. C., U.S. Patent 3,810,868 (1974).
555. Lanigan, D., and Weinberg, E. L., *ref. 31,* p. 134.
556. Luijten, J. G. A., and Pezarro, S., *Br. Plast.* **30,** 183 (1957).
557. Mazur, H., *Rocz. Pzh.* **22,** 39 (1971).
558. Frey, H. H., and Dörfelt, C., Ger. Patent 1,160,177 (1958).
559. Smith, H. V., Technical Data Sheet: "New Lauryltin Compounds." Petit-Lancy, Switzerland, June 23rd, 1976.
560. Jones, K., Biddle, K. D., Das, A. K., and Emblem, H. G., *Int. Symp. Organomet. Coord. Chem. Germanium, Tin, Lead, 2nd 1977;* Das, A. K., Jones, K., and Emblem, H. G., Br. Patent 1,494,209 (1977); Jones, K., Biddle, K. D., Das, A. K., and Emblem, H. G., *Tin Its Uses* **119,** 10 (1979).
561. M and T Chemicals Inc., Technical Data Sheet: "FASCAT 4101 Monobutyltin Esterification Catalyst." Rahway, New Jersey, 1977.
562. Suzukawa, T., *Seramikkusu* **4,** 852 (1969).
563. Fuller, M. J., *Tin Its Uses* **103,** 3 (1975).
564. Kane, J., Schweizer, H. P., and Kern, W., *J. Electrochem. Soc.* **122,** 1144 (1975).
565. Baliga, B. J., and Ghandhi, S. K., *J. Electrochem. Soc.* **123,** 941 (1976).
566. M and T Chemicals, Inc., U.S. Patent 4,130,673 (1978).