TIN

Annual Survey Covering the Year 1974

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Contents:

+Tin, Annual Survey covering the year 1973 see J. Organometal. Chem., 79(1974)17-174.

During 1974 a new international series of symposia was instituted to discuss advances in the organic chemistry of germanium, tin and lead. The emphasis of the first symposium clearly lay towards tin: all seven of the plenary lectures and thirty four of the forty short communications delivered being wholly or in part concerned with diverse aspects of the chemistry of this metal.[1] The second symposium is scheduled to be held in Utrecht in 1976.

1. REVIEW ARTICLES.

Several reviews have appeared which contain sections devoted to aspects of organotin chemistry. Perhaps the most interesting is that by Thayer[2] which deals with the interaction of organometallic compounds with living organisms. Other subjects which have been reviewed are stannaboroxanes[3], fluxional organotin compounds[4], organotin peroxy compounds[5], O-organotin hydroxylamine and oxime derivatives[6], cycloalkanes containing heterocyclic tin[7], the preparation and chemistry of tin free-radicals[8], the ligand characteristics of the Me_3SnCH_2- group[9], the chemistry of coordinated organotin-substituted phosphines[10], and the production and use of organotin compounds[11]. The use of organotin compounds as stabilisers for PVC has also been reviewed[12]. Mössbauer data for monoorganotin derivatives has been collected together and evaluated[287].

2. COMPOUNDS WITH FOUR TIN-CARBON BONDS.

Crystals of tetrakis(pentafluorophenyl)tin. $(C_6F_5)_4Sn$, consists of discrete molecules with exact $\bar{4}$ crystallographic symmetry (Fig. 1). The Sn-C bond distance and CSnC bond angle are 2.126(8)Å and 105.5(4)°, respectively

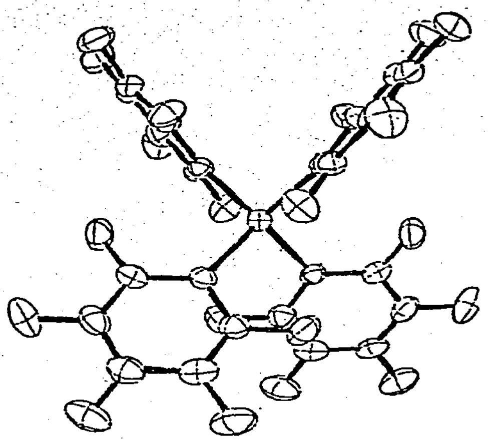


Fig. 1. View of $(C_6F_5)_4Sn$ along the molecular $\bar{4}$ axis. (Reproduced by permission of the American Chemical Society).

Transfer of methyl groups from trimethylgallium to tin films forming tetramethyltin has been observed at 190° [14]. CD_3 and CF_3 radicals abstract hydrogen atoms from tetramethyltin:

$$CX_3 \quad + \quad Me_4Sn \longrightarrow CHX_3 \quad + \quad CH_2SnMe_3$$

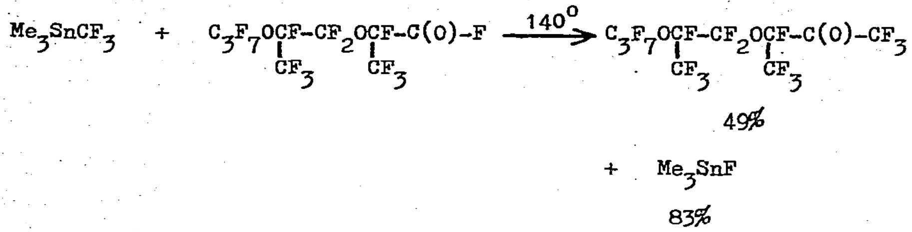
$$X = D,\ F$$

Not unexpectedly, H atom abstraction is more efficient with CF_3 radicals, the reactivity ratio R_{CF_3}/R_{CD_3} being *ca*. 58 at 373K[15]. The reaction of Me_3SnCF_3 with $CF_3HgO_2CCF_3$ proceeds with Sn-Me bond cleavage giving $Me_2Sn(CF_3)O_2CCF_3$ and CF_3HgMe:

$$Me_3SnCF_3 \quad + \quad CF_3HgO_2CCF_3 \longrightarrow Me_2Sn(CF_3)O_2CCF_3 \quad + \quad CF_3HgMe$$

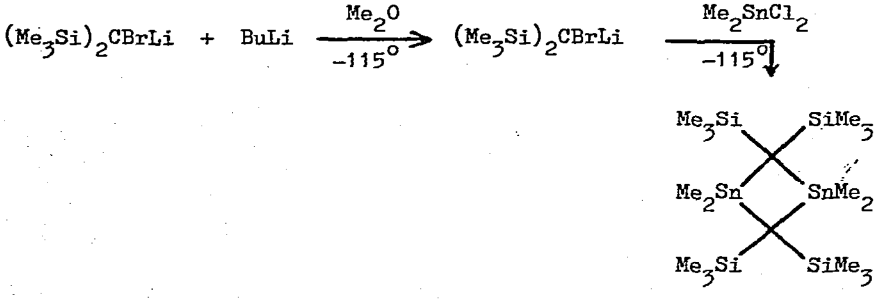
In contrast, Me_3SnCF_3 and CF_3HgCl hardly react, whilst the reaction between tetramethyltin and $CF_3HgO_2CCF_3$ is very slow[16]. No reaction occurred when

Me_3SnCF_3 and pentafluorobenzoyl fluoride were heated at either 140° or 200°, but insertion of of difluorocarbene into the terminal C-F bond took place on heating Me_3SnCF_3 with $\underline{n}$-$C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)F$ at 140° [17]:



$$\mathrm{Me_3SnCF_3} + \mathrm{C_3F_7O\underset{CF_3}{CF}\text{-}CF_2O\underset{CF_3}{CF}\text{-}C(O)\text{-}F} \xrightarrow{140^{\circ}} \underset{49\%}{\mathrm{C_3F_7O\underset{CF_3}{CF}\text{-}CF_2O\underset{CF_3}{CF}\text{-}C(O)\text{-}CF_3}} + \underset{83\%}{\mathrm{Me_3SnF}}$$

Both Seyferth[18] and Bulten[19] have published routes to small-ring stannacycloalkanes. Seyferth has synthesised the first distannacyclobutane, I, via the lithium reagent $(Me_3Si)_2CBrLi$ according to the scheme:



$$\mathrm{(Me_3Si)_2CBrLi} + \mathrm{BuLi} \xrightarrow[-115^{\circ}]{\mathrm{Me_2O}} \mathrm{(Me_3Si)_2CBrLi} \xrightarrow[-115^{\circ}]{\mathrm{Me_2SnCl_2}}$$

I 20%

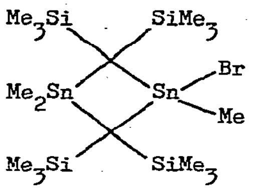
Other tin-containing products present in trace quantities were tentatively identified as $Me_2Sn\left[CBr(SiMe_3)_2\right]_2$ and $(Me_3Si)_2C(SnClMe_2)_2$. In addition to spectroscopic data, I was also characterised chemically by its reaction with an equimolecular amount of methyllithium at room temperature followed by hydrolysis with aqueous NH_4Cl. This procedure yields $(Me_3Si)_2(Me_3Sn)CH$ and $Me_3SnC(SiMe_3)_2SnMe_2C(SiMe_3)_2H$, which are the products expected to arise from hydrolysis of II and III, the expected cleavage products from the reaction of methyllithium with I:

$$\mathrm{I} \xrightarrow{\mathrm{MeLi}} \underset{\mathrm{II}}{(\mathrm{Me_3Si})_2(\mathrm{Me_3Sn})\mathrm{CLi}} + \underset{\mathrm{III}}{\mathrm{Me_3Sn(Me_3Si)_2CSnMe_2C(SiMe_3)_2Li}}$$

$$\Big\downarrow \mathrm{NH_4Cl/H_2O}$$

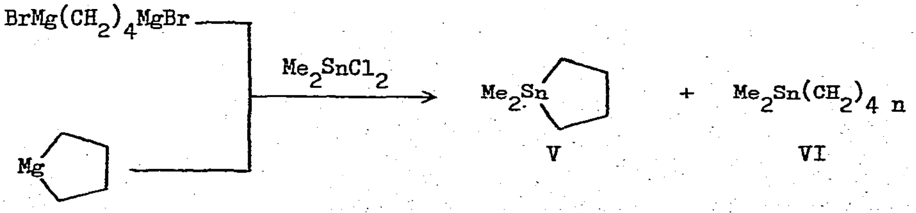
$$(\mathrm{Me_3Si})_2(\mathrm{Me_3Sn})\mathrm{CH} + \mathrm{Me_3Sn(Me_3Si)_2CSnMe_2C(SiMe_3)_2H}$$

The reaction of I with two moles of bromine in refluxing methanol results in only partial methyl group cleavage from tin yielding IV.

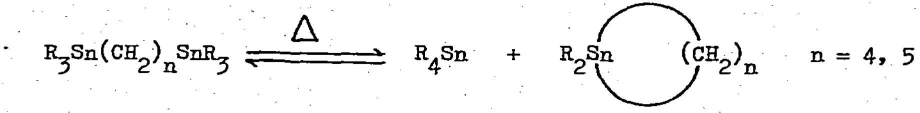


IV

The reaction of the bis-Grignard reagent $BrMg(CH_2)_4MgBr$ or magnesium cyclopentane with dimethyltin dichloride yields a 1:1 mixtures of dimethylstannacyclopentane V and polymeric products VI even under optimum reaction conditions. Treatment of 1,4-dibromobutane either with Me_2SnNa_2 in liquid ammonia or with Me_2SnLi_2 in THF or HMPT gave only traces of V:

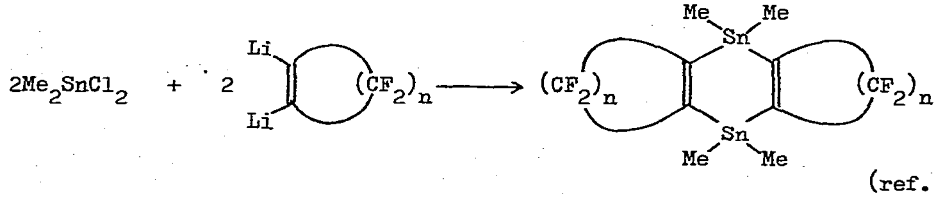


Dialkylstannacyclopentanes and -hexanes may, however, be obtained in high yields (>80%) by the disproportionation of α,ω-bis(trialkylstannyl)alkanes at 250-280°:



The reaction is enhanced by $ZnCl_2$ or $AlCl_3$ catalysis, although these catalysts also facilitate ring-opening to afford polymeric species. 1,1-Dimethylstannacycloheptane is formed in only ca. 40% yield even when the reaction is performed in great dilution. Only traces of ring compound could be detected in the case of the corresponding stannacyclooctane.[19,20]

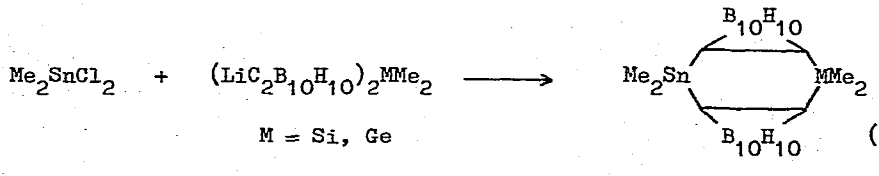
The 'lithium-salt' method has, however, been employed successfully to prepare the more sophisticated tin-containing carbocyclic compounds VII and VIII from Me_2SnCl_2 and the appropriate dilithium salt:



n = 2, 3, 4

VII

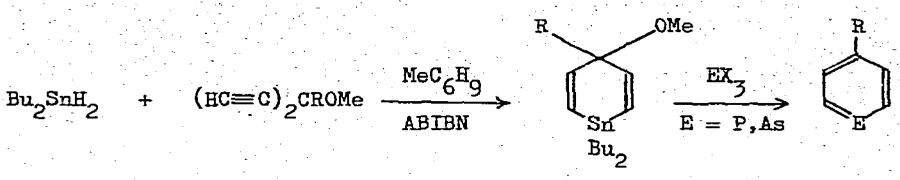
(ref. 21)



(ref. 22)

VIII

The stannacyclohexadiene IX has been obtained in 58-68% yields by the addition of dibutyltin dihydride to the diynes $(HC{\equiv}C)_2CROMe$:



IX X

The compounds IX may be converted into substituted phospha- and arsabenzenes X by treatment with phosphorus or arsenic trihalides in the presence of triphenylphosphine[23].

The synthesis and reactivity of tetraorganostannanes containing a functional group in one alkyl chain continue to be investigated. Methylsulphoxides[24] and sulphones[25] protolyse the Sn-N bond of stannylamines affording the appropriate α-stannyl derivatives:

$$Bu_3SnNEt_2 + PhSO_2Me \longrightarrow Bu_3SnCH_2SO_2Ph \qquad \text{(ref. 24)}$$

$$Bu_3SnNMe_2 + MeSOR \longrightarrow Bu_3SnCH_2SOR \qquad \text{(ref. 25)}$$

(<u>N</u>-Alkyl-<u>N</u>-methylaminomethyl)tributyltin compounds, Bu_3SnCH_2NRMe, from the reaction of Bu_3SnLi with either <u>N</u>,<u>S</u>-acetals, isoxazolidines, imidazolidines, or sodium <u>N</u>,<u>N</u>-disubstituted aminomethanesulphonates, exchange with butyllithium to afford the corresponding lithium derivative:[231]

$$\begin{tikzcd}
Bu_3SnLi + MeRNCH_2X \arrow[r] & MeRCH_2SnBu_3 + LiX \arrow[d, "BuLi"] \\
 & Bu_4Sn + LiCH_2NMeR
\end{tikzcd}$$

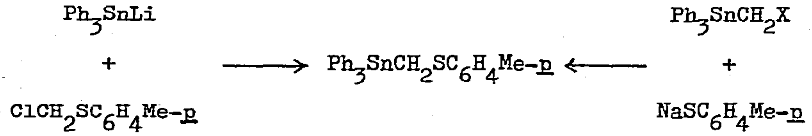
$X = SMe,\ SPh,\ OMe,\ \overset{+}{N}R'Me_2,\ SO_3Na;\quad R = PhCH_2,\ Me_2NCH_2CH_2,\ Me(OCH_2CH_2)_3$

α-Stannylamines have been used as a source of the $CH_2NR'_2$ ligand in the forma of manganese carbonyl complexes:[26]

$$R_3SnCH_2NR'_2 \quad + \quad Mn(CO)_5Br \longrightarrow R'_2NCH_2\,Mn(CO)_4$$

$$R' = Me,\ Et,\ Pr,\ Bu,\ Me_2CHCH_2$$

Wardell has investigated α- and β-sulphur-substituted stannanes[27]. The α-substituted compounds are available by metathesis of Ph_3SnLi and $ClCH_2SC_6H_4Me$-p and also of Ph_3SnCH_2X (X = Cl, I) and $NaSC_6H_4Me$-p:



$$\begin{array}{c} Ph_3SnLi \\ + \\ ClCH_2SC_6H_4Me\text{-}\underline{p} \end{array} \longrightarrow Ph_3SnCH_2SC_6H_4Me\text{-}\underline{p} \longleftarrow \begin{array}{c} Ph_3SnCH_2X \\ + \\ NaSC_6H_4Me\text{-}\underline{p} \end{array}$$

Three routes to the β-substituted derivatives are available: (a) free-radical addition of HSC_6H_4Me-p to $Ph_3SnCH{=}CH_2$:

$$Ph_3SnCH{=}CH_2 \quad + \quad HSC_6H_4Me\text{-}\underline{p} \xrightarrow{ABIBN} Ph_3SnCH_2CH_2SC_6H_4Me\text{-}\underline{p}$$

(b) free-radical addition of Ph_3SnH to $CH_2{=}CHSC_6H_4Me$-p:

$$Ph_3SnH \quad + \quad CH_2{+}CHSC_6H_4Me\text{-}\underline{p} \xrightarrow{ABIBN} Ph_3SnCH_2CH_2SC_6H_4Me\text{-}\underline{p}$$

and (c) from bis(triphenylstannyl)magnesium:

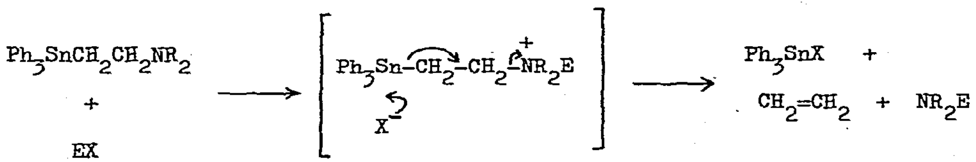
$$(Ph_3Sn)_2Mg \quad + \quad 2BrCH_2CH_2SC_6H_4Me\text{-}\underline{p} \longrightarrow Ph_3SnCH_2CH_2SC_6H_4Me\text{-}\underline{p}$$

N-(2-Triphenylstannylethyl)amines XI may also be obtained by metathesis from Ph_3SnLi and the appropriate 2-chloroethylamine in THF:

$$Ph_3SnLi + ClCH_2CH_2NRR' \longrightarrow \underset{\textstyle XI}{Ph_3SnCH_2CH_2NRR'} + Ph_6Sn_2$$

$$R = R' = Me, Et, Ph;\ R,R' = (CH_2CH_2)_2O;\ R = Me, MeCO, R' = Ph$$

$Ph_3SnCH_2CH_2NHPh$ was isolated in low yield from the reaction of N-(2-chloroethyl)acetanilide with Ph_3SnLi. The same compound was also produced by either hydrolysis (alcoholic KOH) or reduction ($LiAlH_4$) of $Ph_3SnCH_2CH_2NPhCOMe$. Reconversion to the acetanilide derivative may be accomplished using acetic anhydride. The products of the reactions with methyl halides (MeX) and hydrogen halides (HX) varied with the substituents, R and R', and the reagents MeX and HX. The quaternary ammonium salts or amine hydrohalides XII produced from $Ph_3SnCH_2CH_2NR_2$ (R = Me, Et) and MeX or HX (X = Br, I) are unstable, and decompose by nucleophilic attack of X^- at tin forming Ph_3SnX, ethylene, and alkylamines:



XII

E = Me, H

The corresponding chlorides, XII (X = Cl), are stable, but are converted quantitatively to (2-alkylaminoethyl)phenyltin dichloride hydrochlorides XIII in the presence of excess HCl by electrophilic attack of H^+ on the phenyl groups.

$$Ph_3SnCH_2CH_2\overset{+}{N}R_2H\ \ Cl^- \xrightarrow{\text{excess HCl}} \underset{\textstyle XIII}{Cl_2PhSnCH_2CH_2\overset{+}{N}R_2H\ \ Cl^-}$$

The reaction of N-(2-triphenylstannylethyl)arylamines with HCl affords mixtures of Ph_3SnCl, Ph_2SnCl_2, $PhSnCl_3$ and sec-arylamines, as a result of competition between nucleophilic attack of Cl^- at the tin atom and the electrophilic attack of H^+ on the phenyl groups[28].

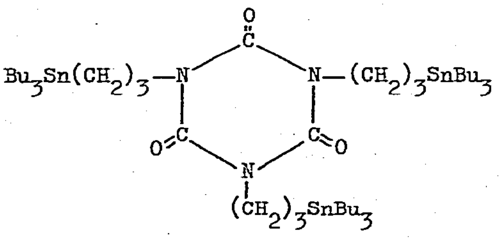
Dergunov *et al.* have studied the reactions of $Bu_3Sn(CH_2)_3NCO$ XIV with a variety of reagents. With water and isobutyl alcohol, 1,3-bis 3-(tributylstannyl)propyl urea XV and isobutyl[3-(tributylstannyl)propyl]-carbamate XVI (R = ^{iso}Bu) are produced quantitatively:

$$\underset{XV}{\left[Bu_3Sn(CH_2)_3NH\right]_2CO} \xleftarrow{H_2O} \underset{XIV}{Bu_3Sn(CH_2)_3NCO} \xrightarrow{ROH} \underset{XVI}{Bu_3Sn(CH_2)_3NHCO_2R}$$

Reaction of XIV with phenol is slower, producing XVI (R = Ph) in 65% yield. With NH_3, Et_2NH, and $PhNH_2$, the urea derivatives XVII are formed:

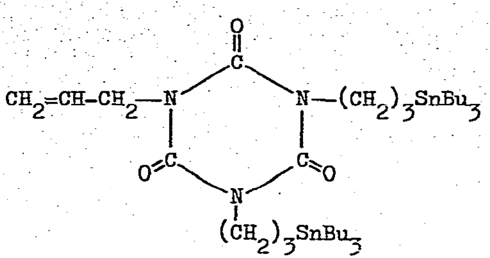
$$XIV \xrightarrow{R_2NH} \underset{XVII}{Bu_3Sn(CH_2)_3NH.CO.NR_2} \qquad R_2 = H_2,\ Et_2,\ HPh$$

XIV itself spontaneously trimerises, albeit very slowly (8.2%. 10 hr, 100°) to give the isocyanurate XVIII.



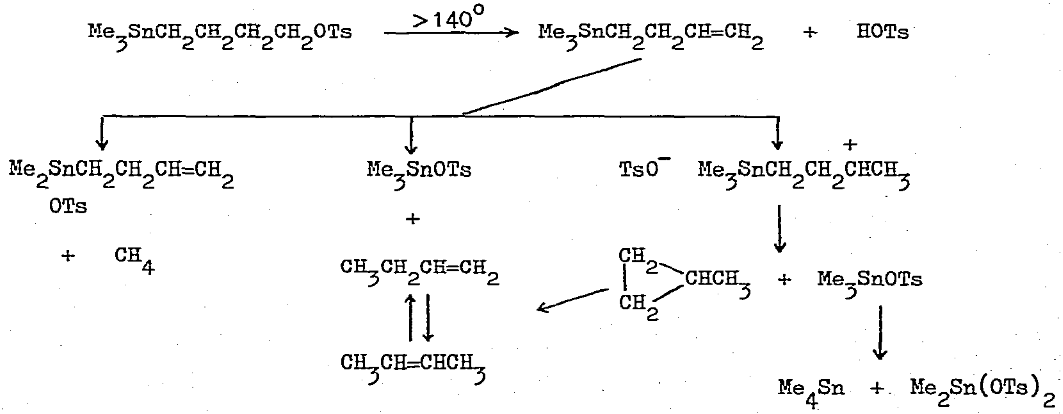
XVIII

The trimerisation is greatly accelerated in the presence of hexakishydroxymethylmelamine and ammonia. With allyl isocyanate, XIV forms the mixed isocyanurate XIX:[29]



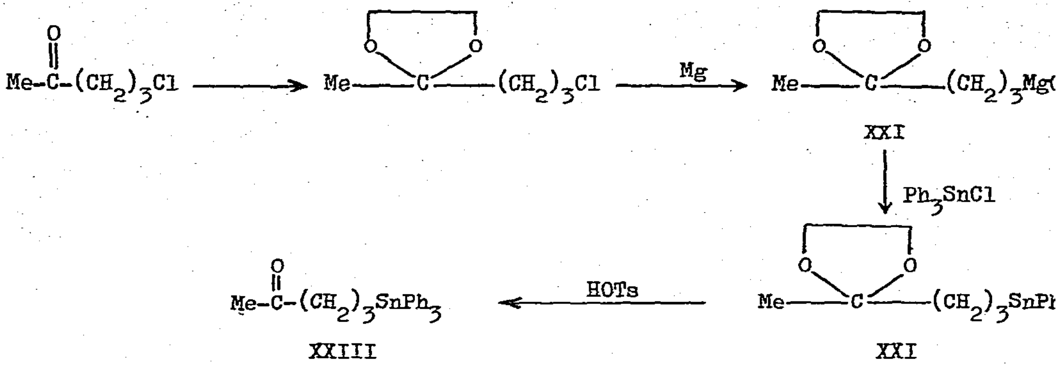
XIX

Pommier and Kuivila have investigated the thermal decomposition of 4-tosyloxybutyltrimethyltin XX. The initial decomposition step involves dehydrotosylation to form toluenesulphonic acid and 3-butenyltrimethyltin. This reaction may be arrested if sodium carbonate or 2,6-lutidine is present to neutralise the evolved acid, but in the absence of base, secondary reactions take place leading to the formation of methylcyclopropane, 1-butene, methane, trimethyltin tosylate, and 3-butenyldimethyltin tosylate. Further reactions lead to the formation of tetramethyltin, dimethyltin ditosylate, and *cis*- and *trans*- 2-butenes:[30]



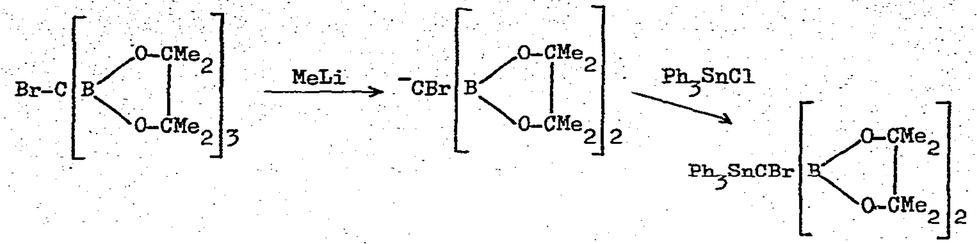
Poller has synthesised a number of 4-oxopentyltin compounds by initial protection of the carbonyl group in 1-chloropentan-4-one by dioxolan formation. Reaction of the readily formed Grignard reagent XXI with Ph_3SnCl

gave XXII, but attempts to remove the protecting ethylenedioxy-residue using hydrochloric acid also resulted in cleavage of phenyl groups from tin giving $Ph_2ClSnCH_2CH_2CH_2COMe$. Successful conversion of XXII to the 4-oxopentyltin derivative XXIII was achieved using p-toluenesulphonic acid:

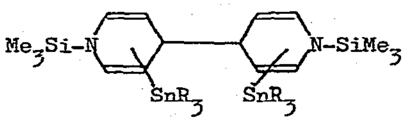


A similar procedure using Ph_2SnCl_2 afforded di(4-oxopentyl)diphenyltin XXIV and di(4-oxopentyl)tin dichloride XXV. Treatment of XXIV with bromine gave di(2-oxopentyl)tin dibromide XXVI; both XXV and XXVI formed 1:1 adducts with 2,2'-bipyridyl. The reaction of the Grignard reagent XXI with $SnCl_4$ afforded the expected tetrakis(ethylenedioxypentyl)stannane, but conversion to $Sn(CH_2CH_2CH_2COMe)_4$ was not successful. Spectroscopic data indicated intramolecular coordination of the carbonyl group to tin in the halogenotin derivatives[31].

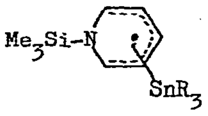
Methyllithium abstracts a boronic ester group from the bromomethanetriboronic ester, $BrC(BO_2C_2Me_4)_3$, to form the carbanion, $^{-}CBr(BO_2C_2Me_4)_2$, which reacts with Ph_3SnCl:[32]



Trialkyltin-substituted pyridines react with $(Me_3Si)_2Hg$ to give products of the type XXVII, which dissociate to give stable free-radicals of the type XXVIII[33].



XXVII



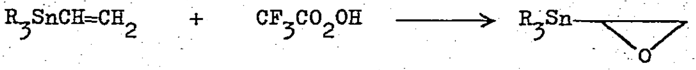
XXVIII

α-Thienyltin compounds have been synthesised from α-thienylmagnesium iodide and tin halides[34].

Reaction of tin(IV) chloride with vinylmagnesium bromide gives $Sn(CH{=}CH_2)_4$ as the major product accompanied by some $Sn_2(CH{=}CH_2)_6$[35]. A Russian patent reports the synthesis of vinyltin compounds by the treatment of alkyltin halides or alkylpolystannanes with alkali metal in liquid ammonia followed by the reaction of the resultant alkylstannide with acetylene or a vinyl halide[36]. 2-Chlorovinyltributyltin has been obtained in 86% yield by the reaction of Bu_3SnH and $(ClCH{=}CH)_2Hg$:[37]

$$Bu_3SnH \quad + \quad (ClCH{=}CH)_2Hg \xrightarrow{\text{ether}} Bu_3SnCH{=}CHCl$$

Vinyltin derivatives undergo epoxidation to give the corresponding stannyloxiranes on treatment with pertrifluoroacetic acid:[38]



R = Me, Ph

Both cis- and trans-crotyltrimethyltin react with butyl- and methyllithium in ether to give crotyllithium in high yield. Further reaction of this reagent solution with Me_3SiCl in both cases gives a ca. 3/2 mixture of trans- and cis-crotyltrimethylsilane:

$$\underset{\underline{cis}\text{ or }\underline{trans}}{Me_3SnCH_2CH{=}CHMe} \xrightarrow{BuLi} LiCH_2CH{=}CHMe \xrightarrow{Me_3SiCl} \underset{\underline{cis}\text{ and }\underline{trans}}{Me_3SiCH_2CH{=}CHMe}$$

Analysis of the tin-containing product shows the formation of Me_4Sn and Me_2SnBu_2 in addition to the expected product Me_3SnBu, illustrating the presence of alkyllithium-promoted exchange equilibria. The addition of 10 mole % of BuLi or MeLi to isomerically pure cis or trans trimethylcrotyltin results in a rapid isomerisation yielding a 3/2 trans/cis ratio of trimethylcrotyltin isomers. The isomerisation is also promoted by metallic lithium. In this case, a metal displacement mechanism is postulated, in which small amounts of crotyllithium are formed which can then equilibriate with the remaining trimethylcrotyltin:

$$MeCH{=}CHCH_2SnMe_3 + 2Li \longrightarrow MeCH{=}CHCH_2Li + Me_3SnLi$$

$$MeCH{=}CHCH_2SnMe_3 + MeCH{=}CH\overset{*}{C}H_2Li \longrightarrow MeCH{=}CH\overset{*}{C}H_2SnMe_3 + MeCH{=}CHCH_2Li$$

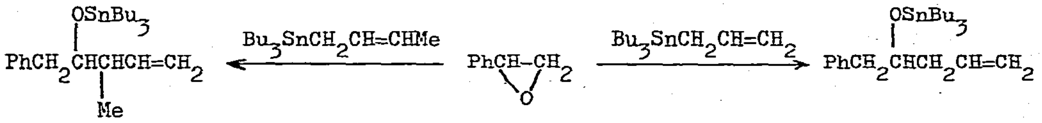
The preferred method of generation of crotyllithium is from triphenylcrotyltin and phenyllithium in ether. Tetraphenyltin precipitates in high yield leaving crotyllithium in solution:[39]

$$Ph_3SnCH_2CH{=}CHMe + PhLi \xrightarrow{ether} Ph_4Sn + MeCH{=}CHCH_2Li$$

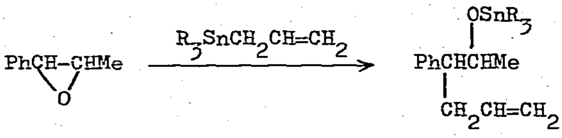
cis/trans mixture

gem-Dichloroallyllithium reacts with Me_3SnBr to give $Me_3SnCH_2CH{=}CCl_2$ in 97% yield. No evidence for the formation of $Me_3SnCCl_2CH{=}CH_2$ was obtained[40].

Allyltin compounds react with epoxides giving as the principal products alkoxytin derivatives produced from addition to the carbonyl compound resulting from isomerisation of the epoxide:



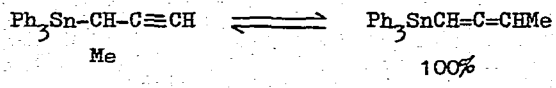
The reaction with cis and trans 1-phenyl-1,2-epoxypropane gives only a poor yield of threo and erythro isomers:[41]



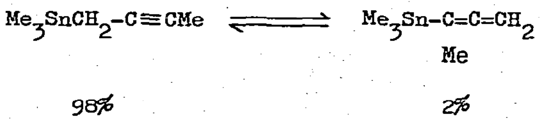
threo and erythro

Guillerm et al. have demonstrated that propargyltin compounds can exist in equilibrium with their allenic isomers when the tautomerisation is catalysed by electron-donating solvents or by Lewis acids. The predominance of each particular isomer depends strongly on the substituents, eg:

$$\underset{2\%}{Ph_3SnCH_2{-}C{\equiv}CH} \rightleftharpoons \underset{98\%}{Ph_3SnCH{=}C{=}CH_2}$$



$$Ph_3Sn{-}\underset{Me}{CH}{-}C{\equiv}CH \rightleftharpoons \underset{100\%}{Ph_3SnCH{=}C{=}CHMe}$$



$$\underset{98\%}{Me_3SnCH_2{-}C{\equiv}CMe} \rightleftharpoons \underset{2\%}{Me_3Sn{-}\underset{Me}{C}{=}C{=}CH_2}$$

Exchange of the unsaturated groups is apparent when a mixture of equal amounts of all four possible allenic products is obtained from ether mixtures of $Me_3SnCH_2C{\equiv}CD$ and $Et_3SnCH_2{-}C{\equiv}CH$ or $Me_3Sn{-}CD{=}C{=}CH_2$ and $Et_3{=}CH{=}C{=}CH_2$ in the presence of mercury(II) chloride:

$$\begin{matrix} Me_3SnCH_2C{\equiv}CD \\ + \\ Et_3SnCH_2C{\equiv}CH \end{matrix} \xrightarrow[\text{ether}]{HgCl_2;\ 20^{\circ}} \begin{matrix} Et_3Sn{-}CH{=}C{=}CH_2 & 25\% \\ Et_3Sn{-}CD{=}C{=}CH_2 & 25\% \\ Me_3Sn{-}CH{=}C{=}CH_2 & 25\% \\ Me_3Sn{-}CD{=}C{=}CH_2 & 25\% \end{matrix} \xleftarrow[\text{ether}]{HgCl_2;\ 20^{\circ}} \begin{matrix} Me_3SnCD{=}C{=}CH_2 \\ + \\ Et_3Sn{-}CH{=}C{=}CH \end{matrix}$$

and by the reactions:

$$Ph_3Sn{-}CH_2{-}C{\equiv}CPh \xrightarrow{BrMgCH_2C{\equiv}CMe} Ph_3Sn{-}CH_2{-}C{\equiv}CMe$$

$$Ph_3Sn{-}CH{=}C{=}CH_2 \xrightarrow[\text{ether}]{Me_3SnCH{=}C{=}CHMe} Ph_3SnCH{=}C{=}CHMe$$

$$Me_3SnCH{=}C{=}CHMe \xrightarrow[HgCl_2,\ \text{ether}]{Et_3SnCH{=}C{=}CH_2} \begin{matrix} Me_3Sn{-}CH{=}C{=}CH_2 & 12\% \\ Me_3Sn{-}CH{=}C{=}CHMe & 38\% \\ \text{allenic compounds with} & \\ \text{ethyl substituents} & 5\% \end{matrix}$$

The rate of the $Ph_3SnCH_2C\equiv CH \rightleftharpoons Ph_3SnCH{=}C{=}CH_2$ interconversion is dependent on the solvent used and on added Lewis acid ($MgBr_2$ $HgCl_2$ $ZnCl_2$). In a variety of solvents used, the rate decreased in the order DMSO MeOH EtOH pyridine 2-methylpyridine, MeCN, PhCN, HMPT 2,2'-dimethylpyridine, *t*-BuOH. An ion-pair mechanism involving solvent or Lewis acid was proposed[42].

A patent reports the addition of mixed carbon tetrahalides across the C≡C triple bond of alkynyltin compounds:[43]

$$R_3SnC\equiv CH \quad + \quad YCX_3 \xrightarrow[40\text{-}50^\circ]{UV} R_3SnCY{=}CHCX_3$$

X, Y = Cl, Br

The free-radical addition of butane thiol to triethylethynyltin affords a mixture of products:[44]

$$Et_3SnC\equiv CH \quad + \quad BuSH \xrightarrow{h\nu} \underset{\underline{trans}}{Et_3SnCH{=}CHSnEt_3} \quad + \quad (Et_3Sn)_2C{=}CH_2$$

$$+ \quad BuSCH{=}CHSBu \quad + \quad Et_3SnSBu$$

The alkynyl-tin bond of XXIX is cleaved by halogen in organic solvents:[45]

$$R_3Sn\text{-}C\equiv C\text{-}CO_2SnR_3 \xrightarrow{X_2} XC\equiv C\text{-}CO_2SnR_3$$

XXIX

$Ph_3SnC\equiv CPh$ displaces carbon monoxide from $cpNb(CO)_4$ forming XXX:[46]

$$Ph_3SnC\equiv CPh \quad + \quad cpNb(CO)_4 \xrightarrow{pentane} cpNb(CO)(Ph_3SnC\equiv CPh)_2$$

2-fold excess

XXX

Cyclopentadienyltin compounds and organotin chlorides undergo facile redistribution at room temperature to yield mixed cyclopentadienyltin chlorides:

$$\mathrm{RSnCl_3} + \mathrm{2RSncp_3} \longrightarrow \underset{90\%}{\mathrm{Rcp_2SnCl}} \qquad \text{(ref. 47)}$$

$$\mathrm{2RSnCl_3} + \mathrm{RSncp_3} \longrightarrow \underset{95\%}{\mathrm{RcpSnCl_2}} \qquad \text{(ref. 47)}$$

$$\mathrm{R_2SnCl_2} + \mathrm{R_2Sncp_2} \longrightarrow \underset{100\%}{\mathrm{R_2cpSnCl}} \qquad \text{(ref. 48)}$$

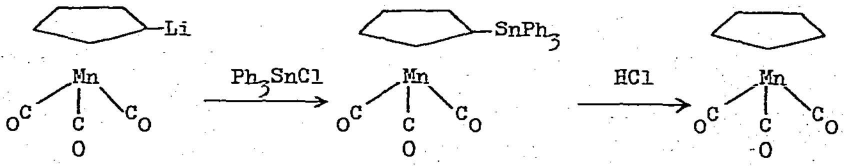
$\mathrm{R = Me, Et}$

Carboxylic acids cleave cyclopentadienyl groups of $\mathrm{cp_4Sn}$ to give cyclopentadienyltin tris(carboxylates) XXXI:[49]

$$\mathrm{cp_4Sn} + \mathrm{3RCO_2H} \xrightarrow{90^\circ} \mathrm{cpSn(O_2CR)_3} \quad \text{XXXI } 95\%$$

$\mathrm{R = Et, Me_2CH}$

The treatment of the lithium salt XXXII with $\mathrm{Ph_3SnCl}$ in ether at -60° gives the complex XXXIII which undergoes Sn-cp bond cleavage with dry HCl.



XXXII XXXIII

After removal of the solvent from the solution of XXXIII, treatment of the dry residue with $NaMn(CO)_5$ in THF gave an 8% yield of $(OC)_3Mn(C_5H_4)SnPh_3Mn(CO)_5$. $Ph_3Sn(C_5H_4)Re(CO)_3$ is similarly cleaved by dry HCl affording $cpRe(CO)_3$.[50]

Mixed alkylphenyltin dichlorides are conveniently prepared by the treatment of triphenylalkylstannanes with an ethereal solution of hydrogen chloride:[28]

$$Ph_3SnR \xrightarrow{\text{HCl in ether}} \underset{100\%}{RPhSnCl_2} + 2PhH$$

$R = Me, Et, {}^{n}Pr, {}^{iso}Pr, {}^{n}Bu, PhCH_2$

McLean has investigated the synthetic utility of the reaction of tetraorganostannanes with iodine monochloride and monobromides in CCl_4[51]. The following reactions gave very high yields of product, and were considered to be of preparative importance:

$$Ph_4Sn + 2ICl \xrightarrow{30^\circ/5\ \text{mins}} Ph_2SnCl_2 + 2PhI$$

$$Ph_4Sn + IBr \xrightarrow{30^\circ/30\ \text{mins}} Ph_3SnBr + PhI$$

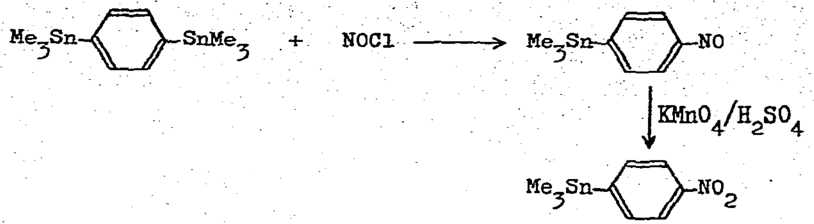
$$Ph_4Sn + 2IBr \xrightarrow{77^\circ/4\ \text{hr}} Ph_2SnBr_2 + 2PhI$$

$$Bu_4Sn + ICl \xrightarrow{30^\circ/30\ \text{mins}} Bu_3SnCl + BuI$$

$$Bu_4Sn + 2ICl \xrightarrow{30^\circ/15\ \text{mins}} Bu_2SnCl_2 + 2BuI$$

$$Bu_4Sn + IBr \xrightarrow{30^\circ/5\ \text{mins}} Bu_3SnBr + BuI$$

Cleavage of aryltrimethylstannanes by nitrosyl chloride followed by oxidation of the resulting nitroso compounds provides a useful route to some aromatic nitro compounds, eg:[52]



Aromatic sulphenyl halides and thiocyanates, RSX, cleave aryl-tin bonds when the aryl groups contain a strongly electron-releasing group forming unsymmetrical sulphides:

$$\mathrm{Bu_3SnC_6H_4Y\text{-}\underline{p}} \quad + \quad \mathrm{RSX} \longrightarrow \mathrm{RSC_6H_4Y\text{-}\underline{p}} \quad + \quad \mathrm{Bu_3SnX'}$$

X = X' = Cl, Br; X = SCN, X' = NCS; Y = OMe, OEt, O^{i}Pr, SMe

A much smaller yield (22%) of the appropriate sulphide was obtained when Y = Me. Cleavage of allyl groups from tin by o-nitrobenzene sulphenyl chloride occurs more readily than aryl-tin bond fission:

$$\mathrm{Ph_3SnCH_2CH{=}CH_2} \; + \; \mathrm{\underline{o}\text{-}O_2NC_6H_4SCl} \longrightarrow \left[\mathrm{Ph_3SnCl}\right] \; + \; \underset{67\%}{\mathrm{CH_2{=}CHCH_2SC_6H_4NO_2\text{-}\underline{o}}}$$

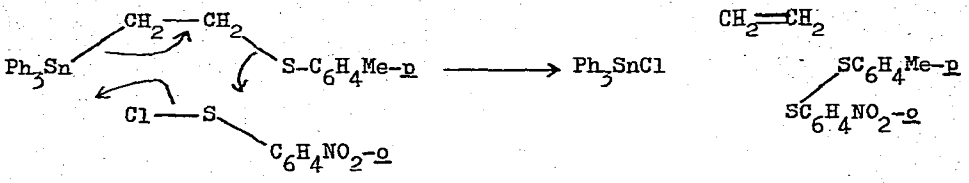
$$\underline{\mathrm{trans}}\text{-}\mathrm{Ph_3SnCH_2CH{=}CHPh} \xrightarrow{\mathrm{\underline{o}\text{-}O_2NC_6H_4SCl}} \underset{13\%}{\mathrm{PhCH{=}CHCH_2SC_6H_4NO_2\text{-}\underline{o}}}$$

$$+ \quad \underset{52\%}{\mathrm{CH_2{=}CHCHPhSC_6H_4NO_2\text{-}\underline{o}}}$$

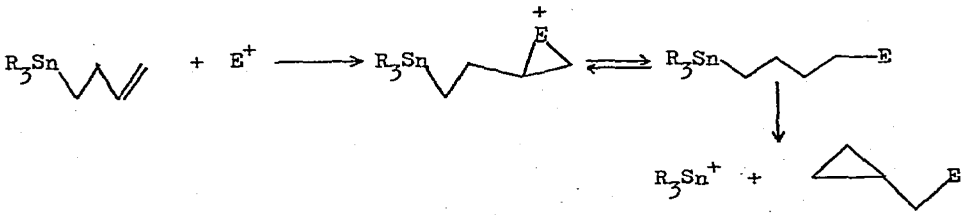
The reaction of $\mathrm{\underline{o}\text{-}O_2NC_6H_4SCl}$ with $\mathrm{Ph_3SnCH{=}CH_2}$ gave both the cleavage and addition products:

$$\mathrm{Ph_3SnCH{=}CH_2} \xrightarrow{\mathrm{\underline{o}\text{-}O_2NC_6H_4SCl}} \underset{44\%}{\mathrm{Ph_3SnCHClCH_2SC_6H_4NO_2\text{-}\underline{o}}} \; + \; \underset{39\%}{\mathrm{CH_2{=}CHSC_6H_4NO_2\text{-}\underline{o}}}$$

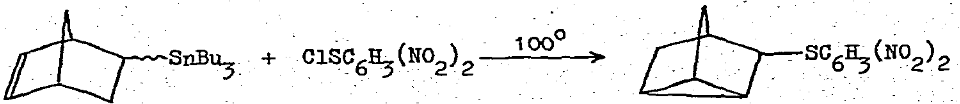
Loss of ethylene occurs in the reaction with the β-stannylsulphide $Ph_3SnCH_2CH_2SC_6H_4Me$-p:[53]



Electrophilically-induced destannylation of alk-3-en-1-yltin compounds has been employed in the synthesis of cyclopropylcarbinyl compounds. A variety of electrophiles, Cl_2, Br_2, I_2, SO_3, $HgCl_2$, SCl_2, ArSCl, react with $R_3SnCH_2CH_2CH{=}CH_2$ compounds by initial addition to the double bond forming electron-deficient carbon atoms γ to tin. These incipient carbonium ions then electrophilically induce heterolytic fragmentations of the Sn-C bonds with concurrent ring formation:

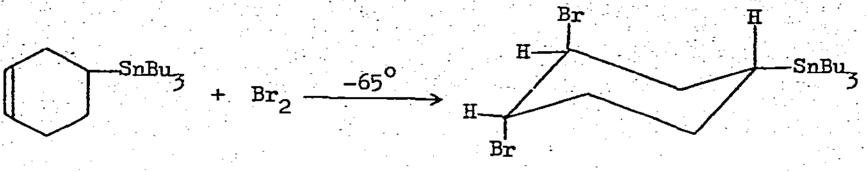


In some cases, small amounts of R-Sn bond cleavage was detected, but use of tetra(but-3-enyl)tin gave surprisingly small yields (~50%). The reaction of norborn-2-en-5-yltributyltin XXXIV with 2,4-dinitrobenzenesulphenyl chloride in glacial acetic acid at 100° gave a 75% yield of the strained nortricyclic product XXXV:



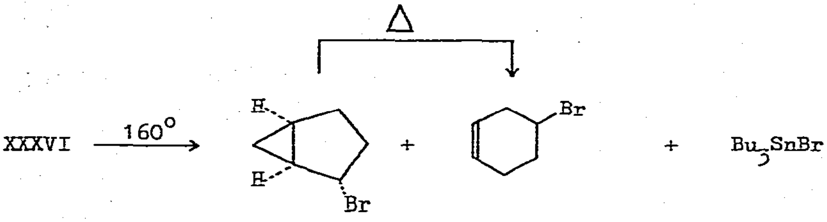
XXXIV XXXV

but bromination of cyclohex-3-en-1-yltributyltin at -65° only resulted in the bromination of the double bond:

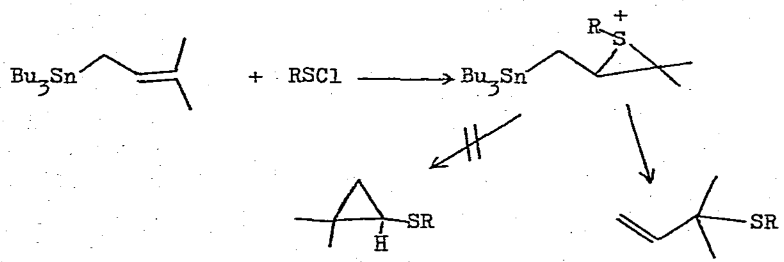


XXXVI

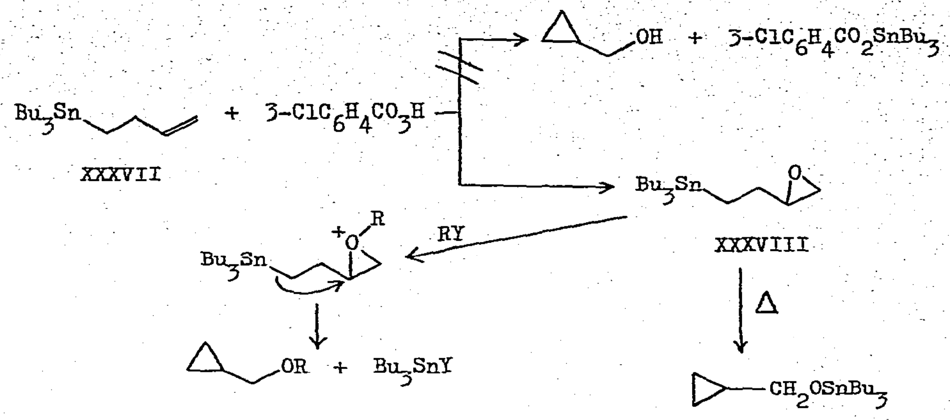
Heating the adduct XXXVI to *ca.* 160° caused fragmentation to give approximately equal quantities of *trans*-2-bromobicyclo 3,1,0 hexane and 4-bromocyclohexane; the latter compound probably arising from the rearrangement of the former:



An attempt to effect cyclodestannylation of 3-methyl-but-2-en-1-yltributyltin failed: instead an S_E2' reaction took place:



m-Chloroperbenzoic acid also does not induce cyclodestannylation. Rather reaction with XXXVII produced the epoxycompound XXXVIII. Cyclodestannylation could, however, be induced in XXXVIII by HCl, picrylsulphonic acid, $BF_3.OEt_2$, or methyl fluorosulphonate, or thermally:[54]



$Ph_3C^+ X^-$ ($X = HgBr_3$, ClO_4, $ZnCl_2Br$) salts abstract hydrogen from tetraorganostannanes XXXIX giving Ph_3CH and mixtures of alkenes:[55]

$$Ph_3C^+ X^- + RCH_2CHMeSnR'_3 \xrightarrow{CH_2Cl_2} \underset{75\text{-}95\%}{Ph_3CH} + RCH_2CH{=}CH_2 + \underset{\underline{cis}\ +\ \underline{trans}}{RCH{=}CHMe}$$

Tetraphenyltin undergoes complete dearylation by alkali metal amides in liquid ammonia to afford the amido-stannates XL:[56]

$$\underset{M\,=\,K,\ Rb,\ Cs}{Ph_4Sn + MNH_2} \xrightarrow{\text{liq. } NH_3} \underset{XL}{M_2Sn(NH_2)_6}$$

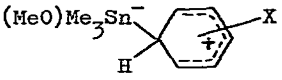
Several kinetic studies of Sn-C bond cleavage have been reported. Eaborn <u>et al</u>. have studied solvent isotope effects in various systems. For the cleavage of the aryl-tin bond of $X.C_6H_4.SnMe_3$ compounds by sodium methoxide in methanol at 21°, the kinetic data indicate the reaction sequence:

$$\mathrm{MeO^- \;+\; Me_3Sn.C_6H_4X \rightleftharpoons (MeO)Me_3Sn^-.C_6H_4.X} \quad \text{XLI} \quad \text{(fast)}$$

$$\mathrm{(MeO)Me_3Sn^-.C_6H_4.X \;+\; MeOH \longrightarrow \underset{XLII}{(MeO)Me_3Sn^-.C_6H_5^+.X} \;+\; MeO^-} \quad \text{(slow)}$$

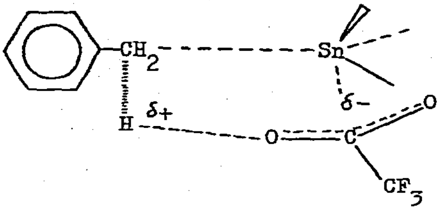
$$\mathrm{(MeO)Me_3Sn^-.C_6H_5^+.X \longrightarrow MeOSnMe_3 \;+\; C_6H_5X} \quad \text{(fast)}$$

in which proton transfer from the solvent to the carbon atom of the Sn-aryl bond in involved in the rate-determining step, which is probably the conversion of the pentavalent species XLI into the Wheland intermediate XLII.[57]



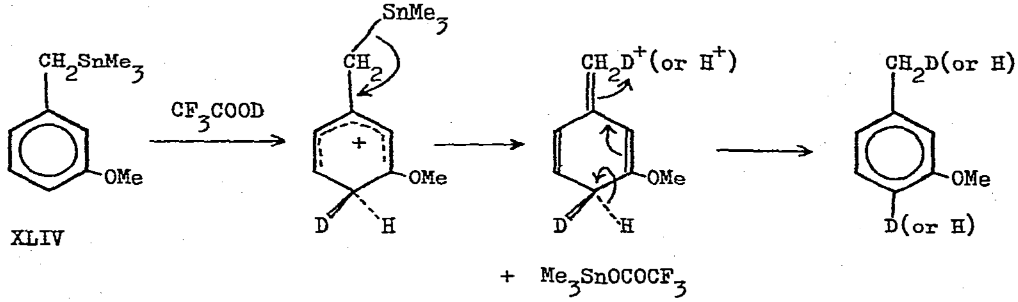
XLII

In the cleavage of $XC_6H_4SnMe_3$ compounds by acetic acid at 50°, the data suggest that proton transfer to form the Wheland intermediate is rather more than half complete[58]. The cleavage of the benzyl-tin bond by sodium methoxide in methanol[59], excess trifluoroacetic acid in benzene[60], and also by aqueous methanolic perchloric acid[61] has been investigated. Solvent isotope effects in the cleavage of the substituted benzyl-tin compounds $XC_6H_4CH_2SnMe_3$ by sodium methoxide in methanol indicate that a free carbanion is not formed, but favour a rate-determining step again involving proton transfer from the solvent to the carbon atom af the breaking $Sn\text{-}CH_2C_6H_4X$ bond, with the MeO-Sn bond fully or almost fully formed in the transition state. Initial formation of the pentavalent intermediate $\left[(MeO)Me_3Sn.CH_2.C_6H_4.X^-\right]$ is proposed[59]. Both benzyl-tin and methyl-tin bond cleavage is observed in the cleavage with trifluoroacetic acid in benzene, although the rate of disappearance of stannane is strictly first-order. For the m- and p-Cl, m- and p-CF_3, p-Me and p-OMe-substituted compounds, a transition state XLIII is proposed in which C-H bond formation is well advanced and oxygen coordination of the molecular acid to the tin being important.



XLIII

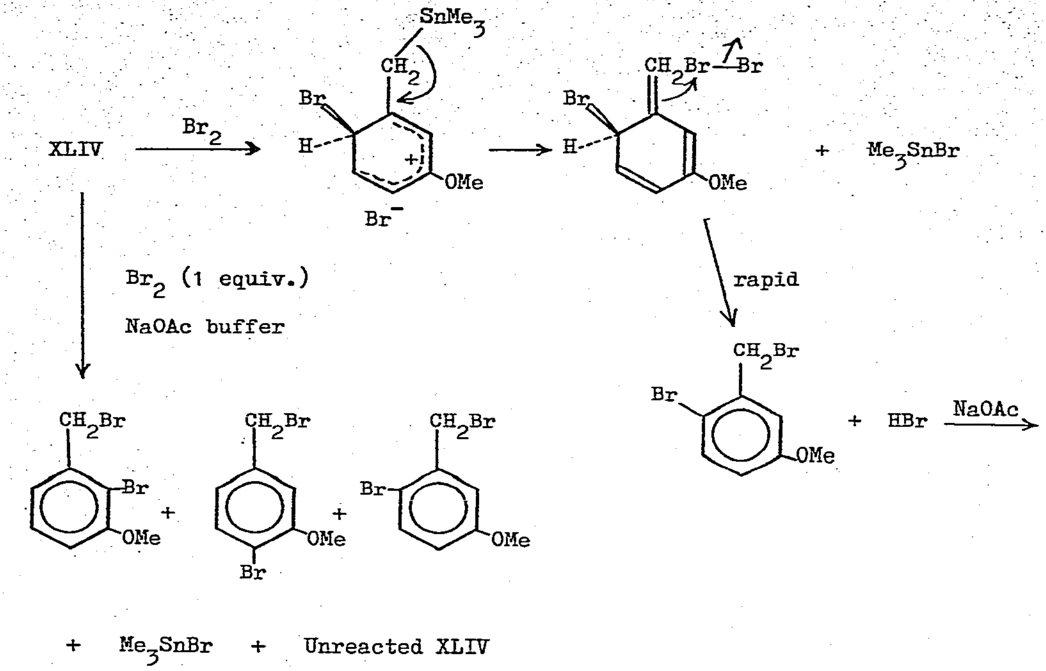
The rates for the m-Me and m-OMe substituted derivatives are abnormally fast and are not accompanied by any Sn-Me bond cleavage, and in these cases a mechanism involving protonation of the ring was proposed:



XLIV

Brominolysis of XLIV also results in ring substitution by an analogous mechanism[60].

Very similar results were obtained for the cleavage of $XC_6H_4CH_2SnMe_3$ compounds by aqueous methanolic perchloric acid. For X = H, p-Me, o-Me, p-^{t}Bu, o-, m- and p-F and -Cl, and o-Br, the cleavage of the benzyl-tin bond involves attack of the acid at the benzylic carbon atom, and is not much faster than Sn-Me bond cleavage, but the ring-protonation mechanism

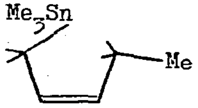


is important for X = *m*-Me, and greatly predominant for X = *m*-OMe[61]. The second-order rate constants for the S_E2 substitution of tetraethyltin by mercury(II) carboxylates, $Hg(O_2CR)_2$, in methanol increase along the series $R = {}^tBu < Et < Me < Ph < ClCH_2CH_2 < MeOCH_2 < ClCH_2$. *Ca.* 60% of the reaction takes place through the species $Hg(O_2CR)_2$. Rate constants for attack of $Hg(O_2CR)_3^-$, $Hg(O_2CR)_2$, and $Hg(O_2CR)^+$ are in the order $0:1:10^2$. The substitution by $Hg(O_2CR)_2$ in methanol was deduced to take place via a S_E2(open), rather than a cyclic, transition state.[62] Kinetic and product studies of the solvolysis of γ-R_3Sn-substituted sulphonates indicate a concerted 1,3-elimination mechanism rather than reaction pathways involving intermediate ions or ion-pairs[63].

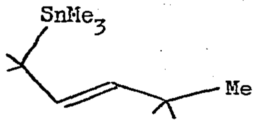
3. HYDRIDES.

The molecular structures of $\mathrm{Me_3SnH}$ and $\mathrm{Me_2SnH_2}$ have been studied by gas phase electron diffraction. Both molecules are approximately tetrahedral with Sn-C bond distances of 2.147(4)A $[\mathrm{Me_3SnH}]$ and 2.150(3)A $[\mathrm{Me_2SnH_2}]$ and Sn-H bond distances of 1.705(67)A $[\mathrm{Me_3SnH}]$ and 1.680(15)A $[\mathrm{Me_2SnH_2}]$[64].

The 1,4-concerted addition of $\mathrm{Me_3SnH}$ to the singlet excited penta-1,3-dienes yield both cis- and trans-adducts XLVa and XLVb according to a stereochemistry which is incompatible with an allylmethylene relaxed

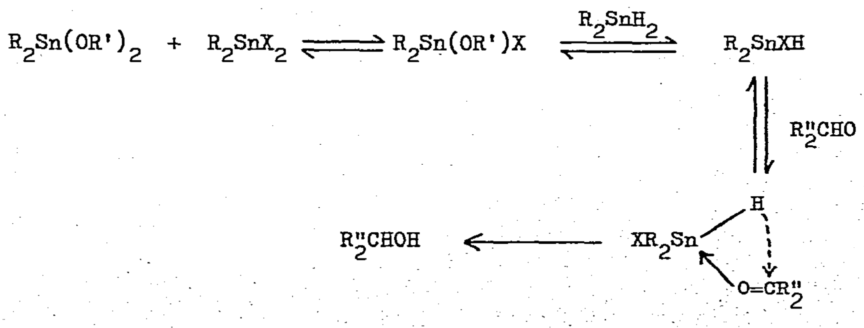


XLVa



XLVb

configuration, and suggests a doubly twisted state[65]. Triorganotin hydrides add to the C≡C triple bonds of alkynylamines[66] and propargyl glycidyl ether[67] to yield $\mathrm{R_3SnCR'{=}CHNEt_2}$ compounds and 1-(trialkylstannyl)-3-(glycidyloxy)propene, respectively. Knocke and Neumann have demonstrated that small amounts of mixtures of $\mathrm{R_2Sn(OR')_2}$ and $\mathrm{R_2SnX_2}$ (X = halide, acylate, or acetylacetonate) strongly accelerate the addition of $\mathrm{R_2SnH_2}$ to aldehydes and ketones. A mechanism involving the intermediacy of the mixed species $\mathrm{R_2Sn(OR')X}$ and $\mathrm{R_2Sn(OR')H}$ was proposed.

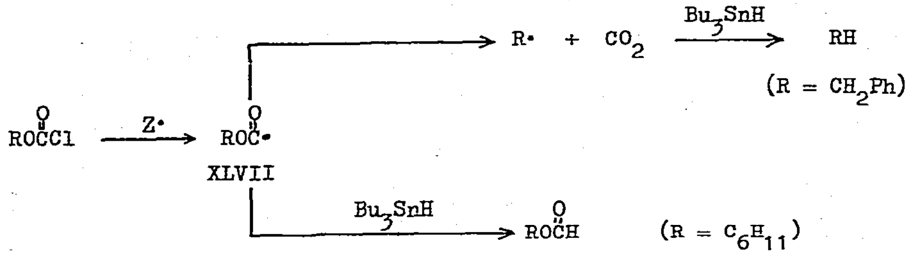


The same systems also catalyse the addition of R_2SnH_2 and R_3SnH to cyclohexanone yielding the alkoxides XLVI in high yield[68].

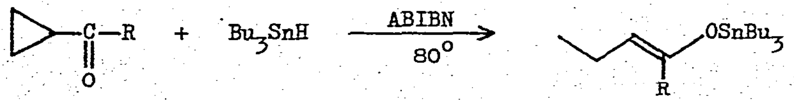
$$R_{4-n}SnH_n \quad + \quad nC_6H_{10}O \longrightarrow R_{4-n}Sn(OC_6H_{10})_n$$

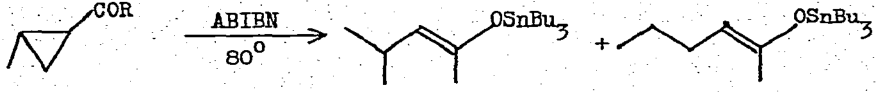
$$n = 1,2 \qquad\qquad\qquad \text{XLVI}$$

The Bu_3SnH-reduction of benzyl and cyclohexylchloroformates under free-radical conditions (ABIBN/hexane) affords toluene and cyclohexyl formate, respectively, as the only product in each case. Rationalisation of these results in terms of the alkoxycarbonyl radical XLVII is consistent, since its rate of fragmentation is determined by the stability of the incipient radical $\dot{R}$. Thus, in the case of R = $PhCH_2$, decarboxylation to $PhCH_2\cdot$ is favoured, and toluene is formed, whilst, when R = C_6H_{11}, the $C_6H_{11}O\overset{O}{C}\cdot$ survives to be reduced[69].

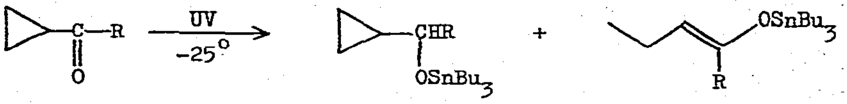


Pereyre has determined the stereochemistry of the reduction of acyclic ketones by Bu_3SnH under both ionic and free-radical conditions. The stereochemistry of the products is little affected by the mechanism of the hydrostannation, and the stereochemistry in both cases is minor[70]. The reaction of Bu_3SnH with cyclopropyl-[71] and cyclobutylketones[72] under free-radical conditions lead to both cyclic and acyclic products. At 80°, cyclopropylketones give exclusively ring-opening:

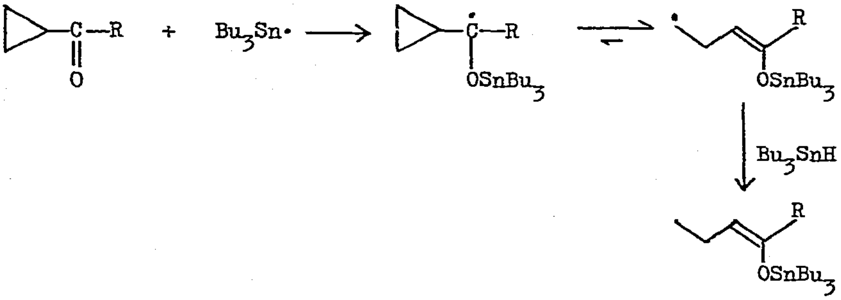




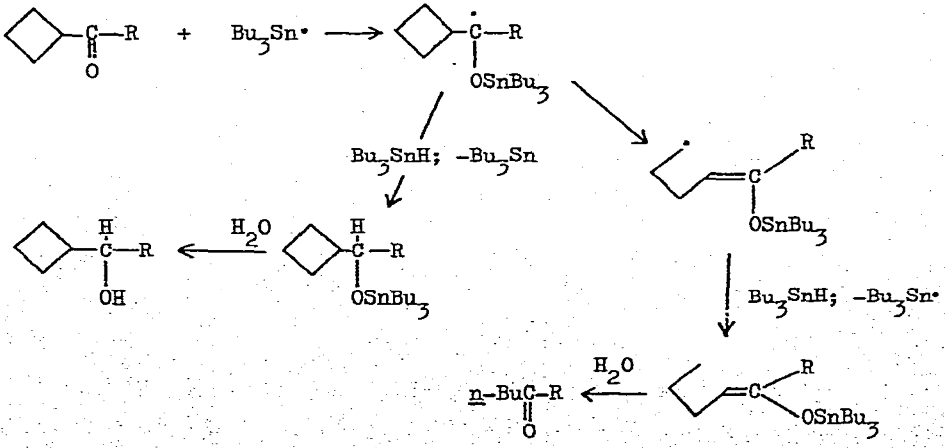
but at 25°, cyclopropanoxytributyltin is obtained:



These results are consistent with a mechanism involving the rearrangement of the intermediate radical:



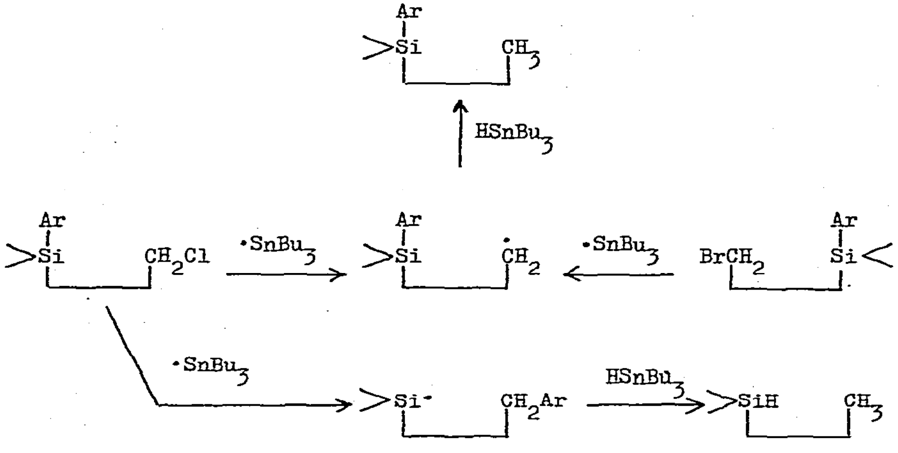
Cyclobutylketones also give both reduction and ring-opening by an identical mechanism:



The amount of ring-opening increases with increase in temperature, diminution in hydride concentration, and is also favoured when R = Ph.[72] Complete loss of stereochemistry occurs during the Bu_3SnH-reduction of 2-substituted 2-halonorbornanes[73]. The extent of aryl group migration from silicon to carbon during the Bu_3SnH-reduction of γ-silyl halides:

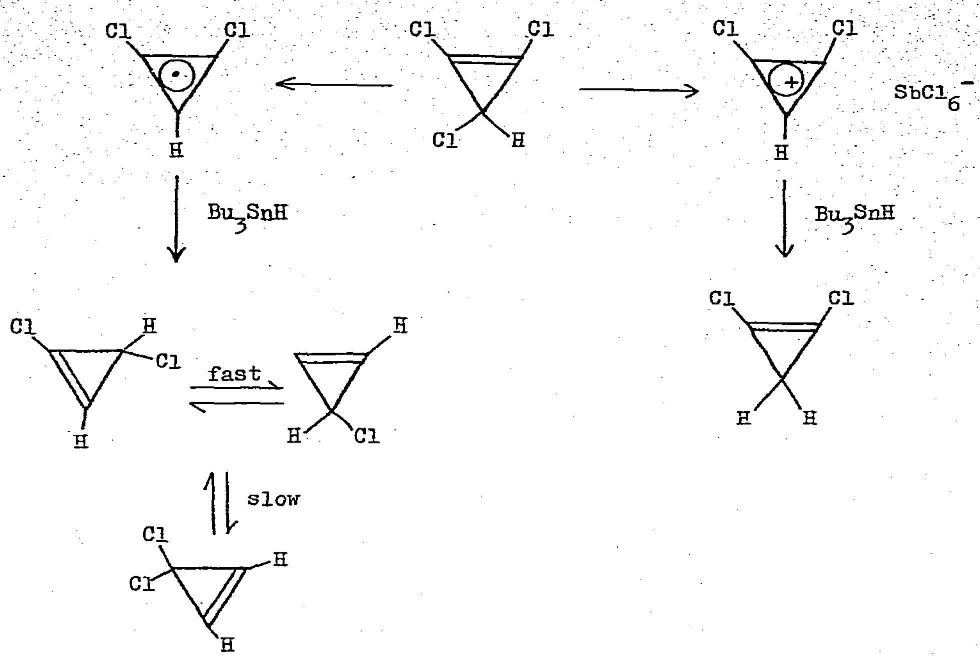
$$ArMe_2SiCH_2CH_2CH_2X \xrightarrow{Bu_3SnH/DTBP} ArMe_2SiCH_2CH_2Me \ + \ HMe_2SiCH_2CH_2CH$$

depends on the halogen in the order Cl Br, the effect being more pronounced at higher reactant concentrations. In order to rationalise this observation, the rearranged radical XLV was proposed also to arise directly from the γ-silyl chloride but not the bromide:[74]



XLV

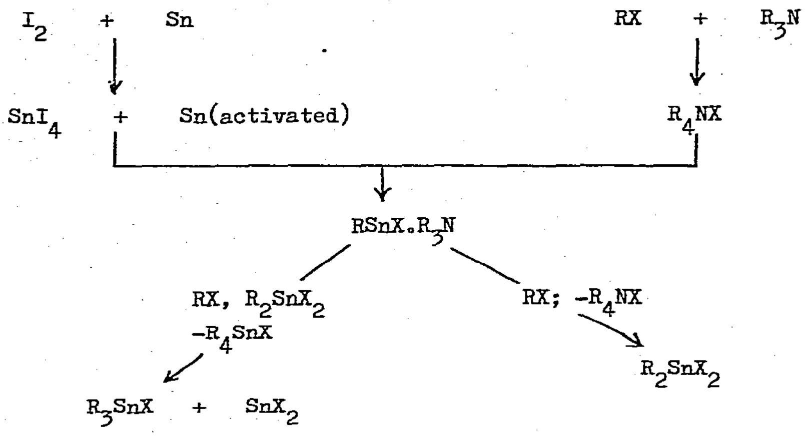
The addition of a very small excess of Bu_3SnH to a solution of dichlorocyclopropenyl hexachloroantimonate in tetramethylene sulphone solution gives 1,2-dichlorocyclopropene as the only reduction product:[304]



In contrast, the reduction of 1,2,3-trichlorocyclopropene by Bu$_3$SnH under free-radical conditions affords a mixture of 1,3- and 3,3-dichlorocyclopropenes. The different behaviour was attributed to contrasting substituent effects of chlorine in the stabilisation of the two transition states. In the radical intermediate, the chlorine atom stabilises the radical localised on an adjacent carbon atom, reaction with which Bu$_3$SnH will produce 1,3-dichlorocyclopropene. In the corresponding cation however, a localized transition state for hydride transfer will preferentially put positive charge on the carbon atom bearing hydrogen, not chlorine.[304]

4. HALIDES.

As usual, considerable attention has been devoted to the synthesis of organotin halides. Several patents report procedures for the 'direct' synthesis of organotin halides from metallic tin and alkyl halide in the presence of various catalyst systems[75-77], whilst one describes an apparatus for their continuous preparation by percholating alkyl halide or epichlorohydrin through a column containing tin granules and interstitial phosphonium or ammonium salt as catalyst[78]. The 'direct' synthesis of butyltin bromides from elemental tin and butyl bromide in the presence of various catalysts has been investigated in detail. Tetraalkylammonium salts were found to be the most efficient catalysts, giving quantitative or near-quantitative conversion of tin in 24 hrs at 101° in the presence of iodine. The following reaction scheme was proposed for the catalysis:[79]



The alkylation of tin(II) halides has also been studied as a route to monoorganotin trihalide derivatives. Dialkylmercurials react with tin(II) fluoride to form $RSnF_3$ compounds:[80]

$$R_2Hg \quad + \quad SnF_2 \longrightarrow RSnF_3$$

$$R = Et,\ Pr,\ Bu,\ Me(CH_2)_4,\ Me(CH_2)_5$$

Methyltin trichloride may be obtained in high yield by the reaction of tin(II) chloride and methyl chloride using cyclic sulphones as solvents at ca. 160–180° in the presence of Bu_3P, iodine, and $FeCl_3$ as catalysts[81]. The reaction of tin(II) halides with halomethylsilanes at 140-180° in a solvating solvent or in an inert gas affords $H_3SiCH_2SnX_3$[82]. Chloromethylsilane compounds in general react similarly with tin(II) chloride in the absence of catalysts in solvating solvents such as THF or DME:

$$RR'R''SiCH_2Cl \quad + \quad SnCl_2 \xrightarrow{140\text{–}200^0} RR'R''SiCH_2SnCl_3$$

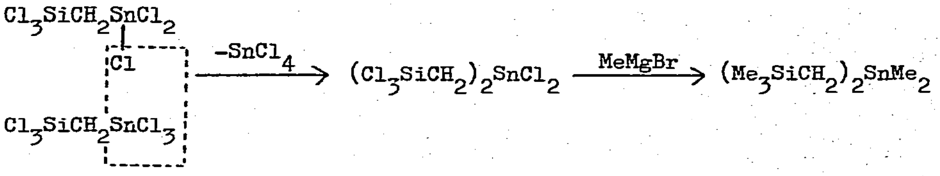
$$R,\ R',\ R'' = R,\ Ar,\ RO$$

Chloro(chloromethyl)silanes react analogously with $SnCl_2$, but the corresponding trichloro(chlorosilylmethyl)stannanes could not be isolated because of reaction with the ether solvent. These compounds, however, could be obtained using 'onium salts as catalysts with the exclusion of solvating solvents:

$$Cl_nMe_{3-n}SiCH_2Cl \quad + \quad SnCl_2 \xrightarrow[140\text{–}180^0]{R_4EX} Cl_nMe_{3-n}SiCH_2SnCl_3$$

$$E = N,\ P,\ As,\ Sb;\ X = Cl,\ Br;\ n = 1,\ 2,\ 3$$

The preparation of $Cl_3SiCH_2SnCl_3$ was accompanied by the formation of some $(Cl_3SiCH_2)_2SnCl_2$, which was characterised by further methylation:[83]



$$\begin{matrix} Cl_3SiCH_2SnCl_2 \\ Cl \\ Cl_3SiCH_2SnCl_3 \end{matrix} \xrightarrow{-SnCl_4} (Cl_3SiCH_2)_2SnCl_2 \xrightarrow{MeMgBr} (Me_3SiCH_2)_2SnMe_2$$

The decomposition of $TiPh_4$ at room temperature in the presence of tin(II) chloride affords a mixture of phenyltin(IV) chlorides:

$$TiPh_4 \xrightarrow{SnCl_2} \underset{90\%}{TiCl_3} + \text{Biphenyl} + \underset{10\text{–}15\%}{Ph_2SnCl_2} + \underset{15\text{–}20\%}{Ph_3SnCl} + \underset{10\text{–}15\%}{Ph_4Sn}$$

The analogous decomposition in the presence of hexaphenylditin gave $TiPh_3$ (85%), benzene, biphenyl, and Ph_4Sn[84].

Alkylation and dealkylation of (organo)tin(IV) halides has been employed particularly in the synthesis of monoorganotin trihalides and mixed tri- and diorganotin halides:

$$SnCl_4 + R_2AlOR' \text{ or } ClAlROR' \longrightarrow RSnCl_3 \qquad \text{(ref. 85)}$$

$$R'SnCl_3 + Me_3SiR \xrightarrow[\text{catalyst}]{AlCl_3} RR'SnCl_2 \qquad \text{(ref. 86)}$$

$$SnX_4 + (PhCH_2)_2Hg \xrightarrow{\text{benzene}} PhCH_2HgX + PhCH_2SnX_3 \qquad \text{(ref. 87)}$$

$$X = Cl, Br, I$$

$$SnCl_4 \xrightarrow{C_6H_{11}MgX} (C_6H_{11})_3SnCl \xrightarrow{H_2O} (C_6H_{11})_3SnOH \qquad \text{(ref. 88)}$$

$$\begin{array}{c} R_3SnCl \\ \text{or} \\ R_2SnCl_2 \end{array} \xrightarrow{R'MgCl} \begin{array}{c} R_3R'Sn \\ \text{or} \\ R_2R'_2Sn \end{array} \xrightarrow{SnCl_4} R_2R'SnCl \qquad \text{(ref. 89)}$$

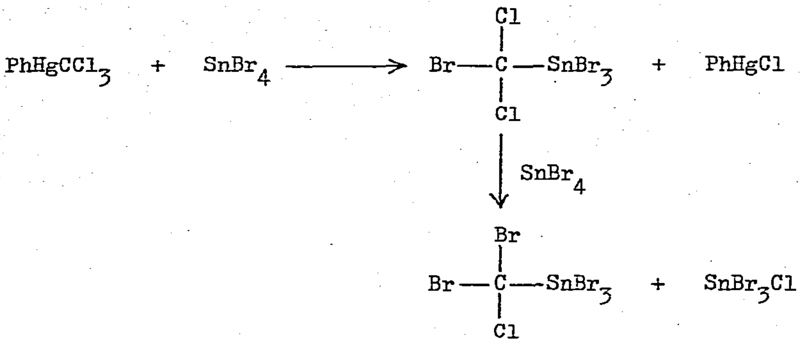
$$R_2SnX_2 + X_2 \longrightarrow RSnX_3 \qquad \text{(refs.90,91)}$$

$$R = C_1\text{–}C_{20};\ X = Cl, Br, I$$

$$R_2SnI_2 + I_2 \xrightarrow[120\text{–}130^{\circ}]{8\ \text{hr}} RSnI_3 \xrightarrow{NaOH/H_2O} RSn(OH)O \xrightarrow{HCl} RSnCl_3$$

$$R = Bu,\ (CH_2)_7Me,\ CHMe_2 \qquad \text{(ref. 90)}$$

Substituted monoaryltin trichlorides have also been obtained by diazotisation of the appropriate substituted aniline, followed by subsequent stannylation using $SnCl_4$[92]. Dichlorocarbene, derived from $PhHgCCl_3$, inserts into the Sn-Br bond of tin(IV) bromide. The actual product isolated, however, was XLVI due to halogen exchange:[93]



$$PhHgCCl_3 + SnBr_4 \longrightarrow Br{-}\overset{Cl}{\underset{Cl}{C}}{-}SnBr_3 + PhHgCl \xrightarrow{SnBr_4} Br{-}\overset{Br}{\underset{Cl}{C}}{-}SnBr_3 + SnBr_3Cl$$

XLVI

Monoorganotin trifluorides may be obtained in high yield by treating the corresponding tris(carboxylates) with HF in benzene:[94]

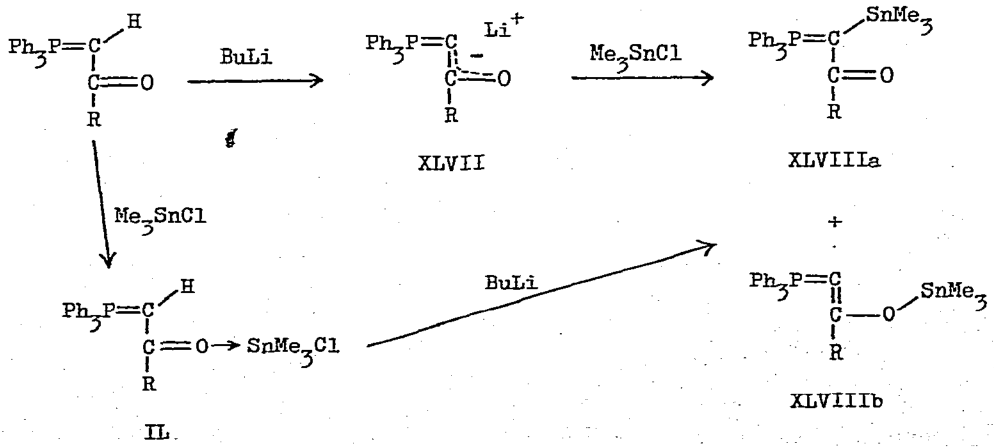
$$RSn(O_2CR')_3 \quad + \quad 3HF \xrightarrow[20\text{-}25^{\circ}]{\text{benzene}} RSnF_3 \quad + \quad 3R'CO_2H$$

R = alkyl, aryl, alkenyl; R' = alkyl

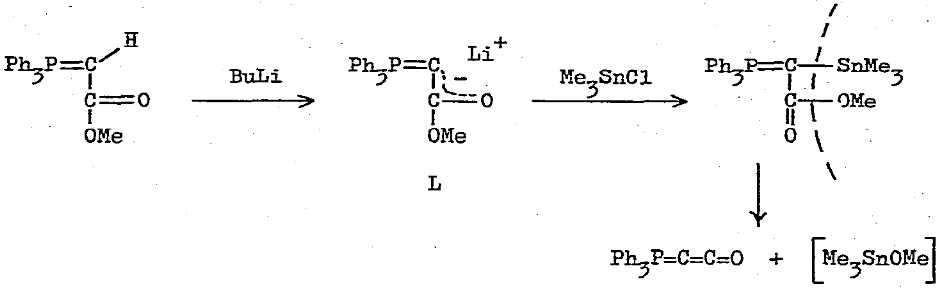
Seyferth has described an improved synthesis of $Me_2Sn(CH_2I)I$ by the reaction of Me_2SnCl_2 with one mole of $IZnCH_2I$ in THF. The formation of the organotin iodide rather than the chloride is rationalised in terms of halogen exchange between tin and zinc. With magnesium metal in THF, $Me_2Sn(CH_2I)I$ reacted readily to give hexamethyltristannacyclohexane in 22% yield. The involatile residue from this reaction appeared to be material of composition $(Me_2SnCH_2)_n$:[302]

$$Me_2SnCl_2 \xrightarrow[THF]{IZnCH_2I} Me_2Sn(CH_2I)I \xrightarrow{Mg/THF} (Me_2SnCH_2)_3$$

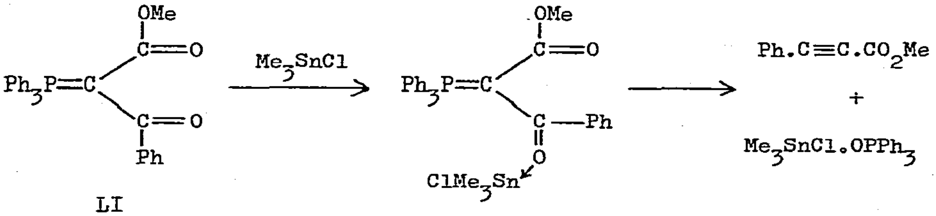
The molecular structures of $MeSnCl_3$ and Me_3SnCl in the gas phase have been reinvestigated by electron diffraction. Both compounds are approximately tetrahedral, and have very similar Sn-C bond distances [2.108(6)A (Me_3SnCl) and 2.105(16)A ($MeSnCl_3$)]. Increased chlorine substitution leads to a contraction of the Sn-Cl bond distance [2.354(8)A (Me_3SnCl) and 2.306(3)A ($MeSnCl_3$)][64]. ^1H and ^{119}Sn nmr data indicate that rapid exchange of halogen and SMe groups takes place at room temperature in binary mixtures of $Me_{4-n}SnX_n/Me_{4-n}Sn(SMe)_n$ (X = halogen, n = 1-4). The rate of exchange is slowest when X = I[95]. Birchall et al. have studied the solvolysis of methyltin chlorides $Me_{4-n}SnCl_n$ in highly acidic media using nmr and Mössbauer spectroscopy. Solvated cations such as $[Me_3Sn]^+$, $[Me_2Sn]^{2+}$, $[MeSnCl_2]^+$, and $[MeSnCl]^{2+}$ were detected[96]. The formation of complexes between alkyltin(IV) cations and fluoride ions has been studied in a constant ionic medium (1M $NaClO_4$) at 25° by potentiometric and solubility methods. In the concentration range examined only mononuclear complexes were found[97]. Treatment of the lithium salt XLVII with Me_3SnCl leads to a mixture of C- and O-stannylated isomers XLVIIIa and XLVIIIb. The same product mixture is obtained by treating the ylid-Me_3SnCl complex IL with butyllithium:



Elimination of Me_3SnOMe occurs during the reaction of Me_3SnCl with the lithium salt L:

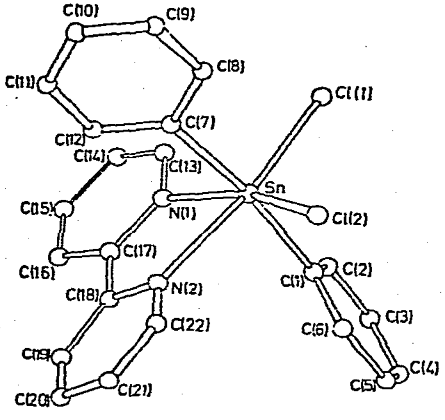


whilst during attempted complex formation between the disubstituted ylid LI and Me_3SnCl, the complex $Me_3SnCl.OPPh_3$ was formed:[98]



The complexation of methyltin halides in donor solvents such as acetone, dioxan, DME, pyridine, DMF, DMSO, HMPT, and tetramethylethylenediamine have been studied by means of ^1H nmr spectroscopy, and equilibrium constants evaluated for the $Me_3SnX.D$ complexes[99]. The $Me_3SnCl_3^-$ anion has been obtained as the tetramethylammonium salt by heating a mixture of Me_4NCl and excess Me_3SnCl in a sealed tube at 140° for 4 hrs. The complex is stable when stored under anhydrous conditions, but probably releases chloride in solution. The Mössbauer data are consistent with T-shaped $SnCl_3$ units in an octahedral configuration.[100] Elegbede and McLean have prepared the 1:1 complexes $Ph_3SnX.HMPA$ (X = Cl, Br, I, N_3, CN). Reaction of the $Ph_3SnCl.HMPA$ complex with F^- or OH^- ions caused dissociation to give Ph_3SnF and Ph_3SnOH, respectively but exchange occurred with I^- and N_3^- giving the corresponding $Ph_3SnX.HMPA$ ($X = I, N_3$) complexes. No reaction occurred with Br^- or CN^- [101].

The crystal structure of Ph_2SnCl_2.bipyridyl shows that the tin atoms are octahedrally coordinated with <u>trans</u> phenyl groups (Sn-C = 2.152Å) and <u>cis</u> chlorine atoms (Sn-Cl = 2.509Å) (Fig. 2). The bipyridyl group is not planar, one C_5H_4N ring is slightly twisted (4.2°) with respect to the other, with the two Sn-N bond distances being unequal (2.344 and 2.375Å)[102]. The similar complex $Ph_2SnCl_2.2DMSO$ has an almost identical structure (Fig. 3) with Sn-C = 2.116Å, Sn-Cl = 2.474, 2.355Å and Sn-O = 2.355 and 2.280Å. One of the methylsulphoxide groups is disordered into two positions[148]. Novel 1:1 adducts



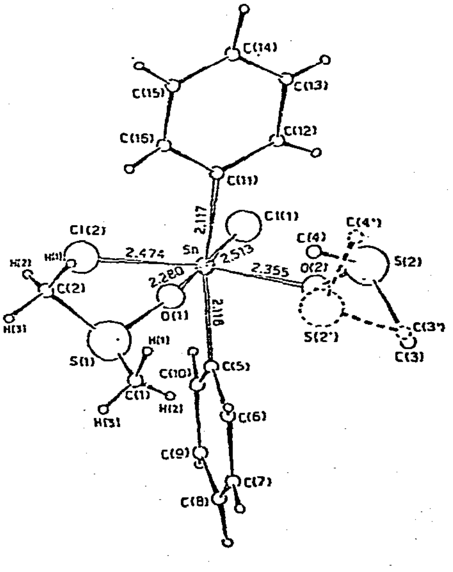


Fig. 2. The molecular structure of Ph_2SnCl_2. bipyridyl. (Reproduced by permission of the Chemical Society).

Fig. 3. The molecular structure of $Ph_2SnCl_2.2DMSO$.

have been obtained from the nickel complex *N,N'*-ethylenebis(salicylideneiminato)nickel(II) (Nisalen) with di- and monoorganotin(IV) chlorides. Spectroscopic data show that the square planar configuration around nickel is maintained, and the coordination to tin involves 3-coordinate phenolic oxygen atoms resulting in octahedrally-coordinated tin[103]. The *trans*-R_2, *cis*-Cl_2 configuration deduced spectroscopically for the $R_2SnCl_2Nisalen$ complex has been confirmed when R = Me by a crytsallographic study[104]. The structure is shown in Fig. 4, and is distorted significantly from regular octahedral coordination (CSnO = 161.0(7)°, OSnO = 61.3(3)°). The two Sn-C distances are equal ($2.12_5(1)$Å), but the Sn-O and Sn-Cl distances are not equivalent [Sn-O = 2.40, 2.55(1)Å; Sn-Cl = 2.403, 2.523(4)Å]. Far-infra-red spectra of the complexes $Ar_2SnX_2 \cdot 2L$ (Ar = aryl; X = Cl, Br, I; L = amide) indicate *cis*-aryl and *trans*-halogen arrangements about tin. The amide is coordinated via the carbonyl oxygen rather than the nitrogen atom[105]. Mono-, di-, and triethanolamines form complexes of the general type $Ar_2SnX_2 \cdot nL$

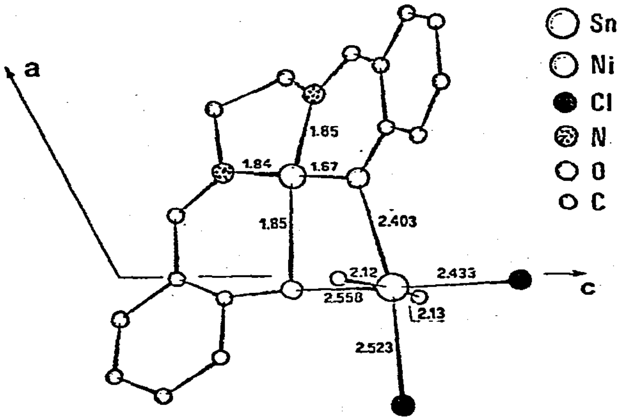


Fig. 4. Projection of $Me_2SnCl_2 \cdot Ni(salen)$ along the *b* axis.

(Ar = aryl, n = 1 for L = MEA and DEA, and n = 2 for TEA) with diaryltin dihalides. Again a cis-aryl-trans-halogen arrangement about octahedral tin is indicated. Both MEA and DEA function as bidentate ligands, bonding through both oxygen and nitrogen atoms, whilst TEA acts as a unidentate ligand via the oxygen atom[106].

5. PSEUDOHALIDES.

Crystals of triphenyltin isothiocyanate consist of infinite zig-zag =S...Sn-N=C=S...Sn- chains similar to those in Me$_3$SnNCS, but with slightly longer Sn-N (2.22(5)Å), shorter Sn-S (2.92(6)Å) bond distances, and almost planar SnC$_3$ units (Sn-C =2.09(3)Å) (Fig. 5)[107].

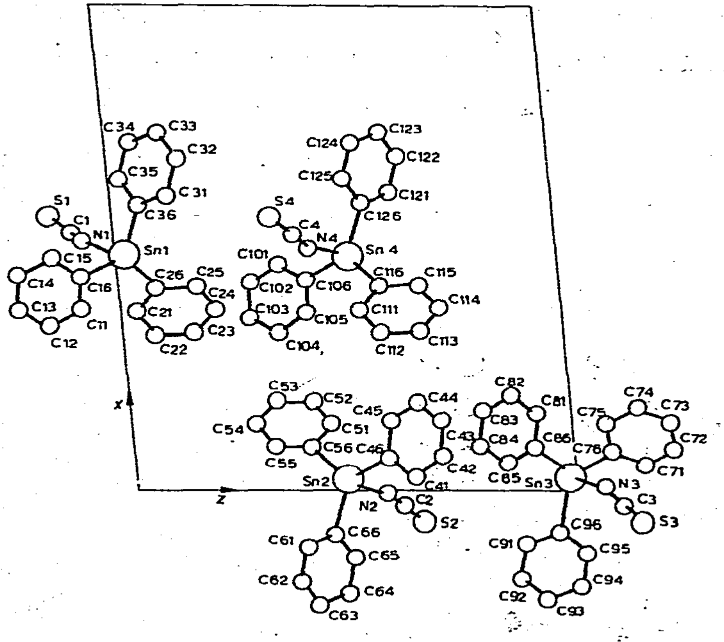
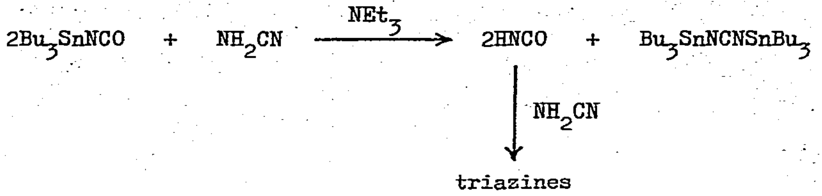


Fig. 5. The asymmetric unit of Ph$_3$SnNCS projected perpendicular to Y.

Tributyltin isocyanate reacts with cyanamide in triethylamine to form bis(tributyltin)carbodiimide and a mixture of triazines[108].



$$2Bu_3SnNCO + NH_2CN \xrightarrow{NEt_3} 2HNCO + Bu_3SnNCNSnBu_3$$
$$2HNCO \xrightarrow{NH_2CN} \text{triazines}$$

Dergunov *et al.* have studied the thermal decompositions of R_3SnNCO and $R_3SnN{=}C{=}NSnR_3$ (R = Bu, Ph). Bu_3SnNCO decomposes to metallic tin, CO, N_2, butane, and butylene:

$$Bu_3SnNCO \xrightarrow[6\ hr]{250^\circ} \underset{58\%}{Sn} + \underset{60\%}{N_2} + \underset{57\%}{CO} + \underset{95\%}{\text{butane}} + \underset{90\%}{\text{butylene}}$$

In contrast, Ph_3SnNCO undergoes disproportionation:

$$Ph_3SnNCO \xrightarrow{200^\circ} \underset{70\text{–}73\%}{Ph_4Sn} + Ph_2Sn(NCO)_2$$

Similarly, $Bu_3SnNCNSnBu_3$ decomposes at 250–270° to metallic tin and a mixture of butane and butylene, but only Ph_4Sn (90%) was isolated from the thermolysis of $Ph_3SnNCNSnPh_3$[109]. Pseudohalide derivatives of the type $R_nSn\left[C(CN)_2COMe\right]_{4-n}$ may be obtained from the organotin chloride and the silver salt $AgC(CN)_2COMe$ in acetone. Triphenyltin acetyldicyanomethanide results from the reaction of dicyanoacetone and tetraphenyltin in CCl_4. The Mössbauer spectra of the pseudohalide derivatives Ph_3SnX $\left[X = NCC(CN)_2, NCNCN, ONC(CN)_2, C(CN)_2COMe\right.$, $\left.Et_3Sn\ C(CN)_2COMe\right]$, Me_2SnX_2 $\left[X = NCNCN, C(CN)_2COMe\right]$, and $(Bu_2SnNCN)_4$ indicate polymeric structures with coordination numbers greater than four. The spectrum of $(PhCH_2)_2Sn\left[C(CN)_2COMe\right]_2$ shows two different types of tin ascribed to the presence of six-coordinate polymeric and four-coordinate monomeric species[110].

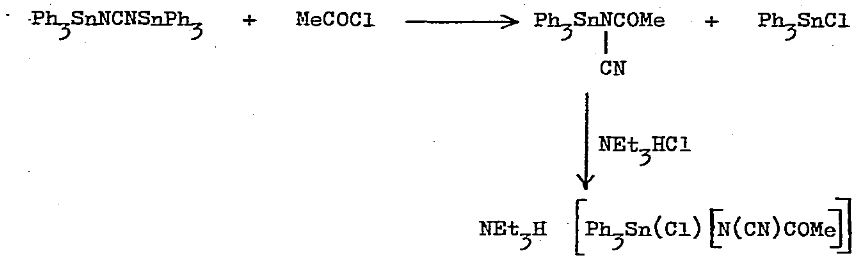
Triphenyltin cyanamide reacts with acyl chlorides, chlorocarbonates, and benzenesulphonyl chloride in the presence of excess triethylamine to give high yields of the corresponding triethylammonium (organocyanoamino)-chlorotriphenylstannates LII:

$$Ph_3SnNHCN \quad + \quad RCl \quad + \quad NEt_3 \longrightarrow Et_3\overset{+}{N}H \left[Ph_3Sn(Cl)\left[N(CN)R\right]\right]^-$$

LII

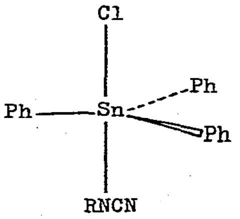
R = MeCO, EtCO, PhCO, MeOCO, EtOCO,
$PhCH_2OCO$, $PhSO_2$

LII (R = MeCO) was also obtained from the reaction of $\overset{+}{N}Et_3H\ Cl^-$ with $Ph_3SnN(CN)COMe$, itself prepared by treating $Ph_3SnNCNSnPh_3$ with MeCOCl:



$$\begin{tikzcd}[column sep=small] Ph_3SnNCNSnPh_3 + MeCOCl \arrow[r] & Ph_3SnN(CN)COMe \arrow[d, "NEt_3HCl"] + Ph_3SnCl \\ & NEt_3H\left[Ph_3Sn(Cl)\left[N(CN)COMe\right]\right] \end{tikzcd}$$

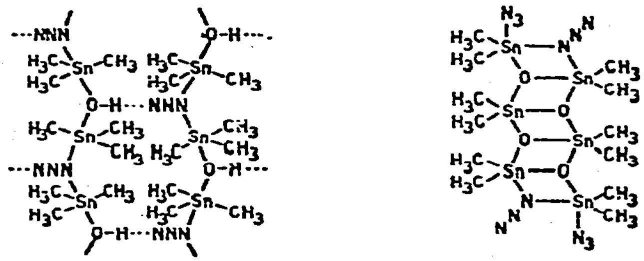
The Mössbauer spectra indicate the five-coordinate trigonal bipyramidal structure LIII for the complexes[111].



LIII

5. OXIDES, ALKOXIDES, AND RELATED DERIVATIVES.

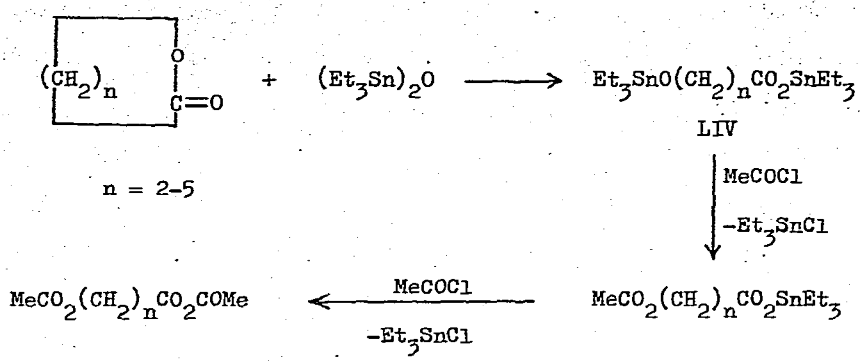
Tetrabutyl-1,3-diacyloxydistannoxanes $(RCO_2)Bu_2SnOSnBu_2(O_2CR)$ LIV and/or tetrabutyl-1-acyloxy-3-hydroxydistannoxanes $(RCO_2)Bu_2SnOSnBu_2OH$ LV may be prepared from equimolecular amounts of dibutyldiallyltin and the carboxylic acid RCOOH (R = H, Me, CH_2Cl, $CHCl_2$, CCl_3, CF_3) in moist methanol or acetone/water (50/50). Isolation of compounds LIV or LV depends on the hydrolysing power of the medium and the nature of R[112]. The solid-state structures of $(Me_3Sn)_2(OH)N_3$ and hexamethyl-1,5-diazidotristannoxane have been investigated by Mössbauer, infra-red and Raman spectroscopy. Proposed structures are shown in Fig. 6. $(Me_3Sn)_2(OH)N_3$ is thought to consist of infinite chains of planar Me_3Sn groups bridged alternately by OH and N_3 groups.. Hydrogen bonding links adjacent chains. The diazidotristannoxane is considered to be dimeric through oxygen and terminal azide bridges. All the tin atoms are five coordinate[113]. Hexaethyldistannoxane and its chloro-derivatives react with lactones containing four to seven-membered rings to form 1:1 adducts with ring-opening. With $Et_3SnOSnEt_3$, the adduct formed LIV is thermally unstable, and reverts to the reactants on attempted



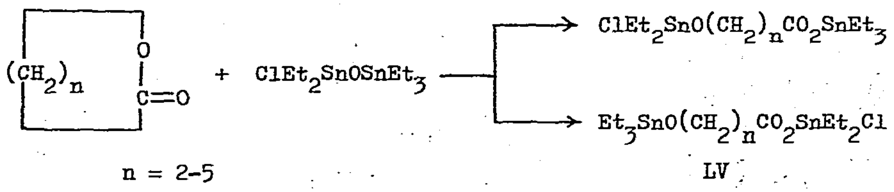
(a) (b)

Fig. 6. Proposed structures for (a) $(Me_3Sn)_2(OH)N_3$ and (b) $N_3Me_2Sn[OSnMe_2\ _2N_3]_2$.

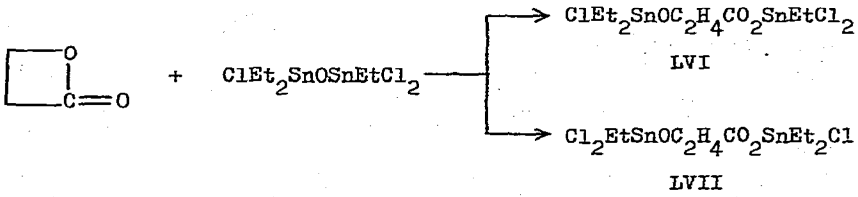
distillation, but treatment with either one or two moles of acetyl chloride yields the isolable mono- or diacetate:



$ClEt_2SnOSnEt_2Cl$ reacts similarly giving $ClEt_2SnO(CH_2)_nCO_2SnEt_2Cl$, which could also be converted to the diacetate. The reaction with chloropentaethyl distannoxane appeared to proceed largely to form LV:



but the reaction of β-propiolactone and $Cl_2EtSnOSnEt_2Cl$ gave approximately equal amounts of LVI and LVII:



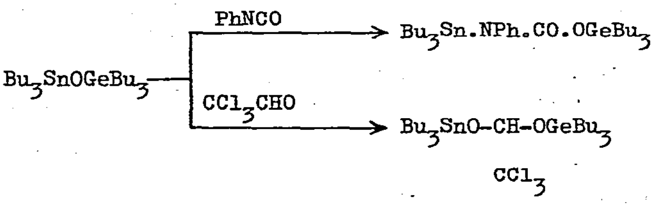
Kinetic measurements of the reactions gave the following orders of reactivity: ε-caprolactone > δ-valerolactone > β-propiolactone > γ-butyrolactone;

$Cl_2EtSnOSnEt_2Cl > Et_3SnOSnEt_3 > ClEt_2SnOSnEt_3 > ClEt_2SnOSnEt_2Cl$; monomeric > dimeric stannoxanes; and non-polar > polar or basic solvent[114]. Heating mixtures of bis(trialkyltin) oxides and bis(trialkylgermyl) oxides affords mixed germastannoxanes LVIII:

$$(R_3Sn)_2O \quad + \quad (R'_3Ge)_2O \longrightarrow \underset{\text{LVIII}}{2R_3SnOGeR'_3}$$

R = Bu; R' = Me, Bu

The reaction of hexabutylgermastannoxane with phenyl isocyanate and chloral is considered to take place exclusively at the Sn-O bond:[115,116]



$$\begin{tikzcd} & Bu_3Sn.NPh.CO.OGeBu_3 \\ Bu_3SnOGeBu_3 \arrow[ur, "PhNCO"] \arrow[dr, "CCl_3CHO"'] & \\ & Bu_3SnO\text{-}\underset{CCl_3}{CH}\text{-}OGeBu_3 \end{tikzcd}$$

Similarly, $Bu_3SnOSiMe_3$ was also considered to react with PhNCO solely at the Sn-O bond:[117]

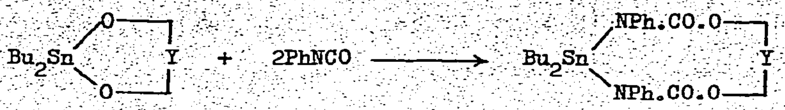
$$Bu_3SnOSiMe_3 \quad + \quad PhNCO \longrightarrow Bu_3Sn.NPh.CO.OSiMe_3$$

The addition reactions of monoorganotin tris(alkoxides) and alkoxide halides with isocyanates and isothiocyanates, and of dibutyltin glycolates have been briefly reported:[117]

$$RSn(O^iPr)_3 \quad + \quad nR'NCE \longrightarrow RSn(NR'.CO.O^iPr)_n(O^iPr)_{3-n}$$

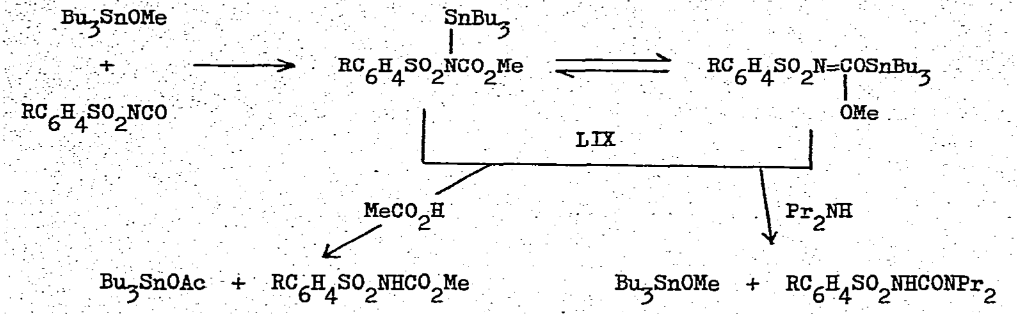
$$RSn(O^iPr)_{3-n}Cl_n \quad +(3-n)PhNCO \longrightarrow RSn(NPh.CO.O^iPr)_{3-n}Cl_n$$

R = Et, Bu; R' = Ph, α-Np; E = O, E

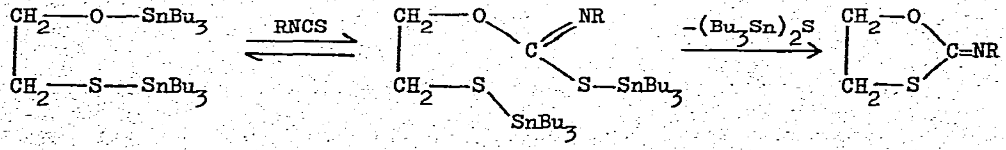


Y = CH_2CH_2, $CHMeCH_2CMe_2$

Tributyltin methoxide adds to arenesulphonyl isocyanates to form the adducts LIX as a tautomeric mixture:

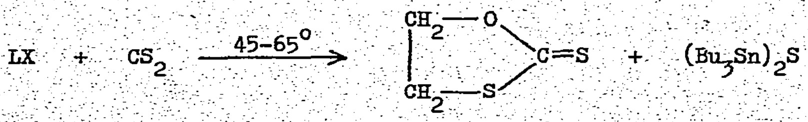


The adducts undergo protolysis with both acetic acid and dipropylamine[118]. Bis(tributylstannyl)mercaptoethanolate reacts with isothiocyanates at room temperature to afford an adduct LXI, which eliminates bis(tributyltin) sulphide on heating:

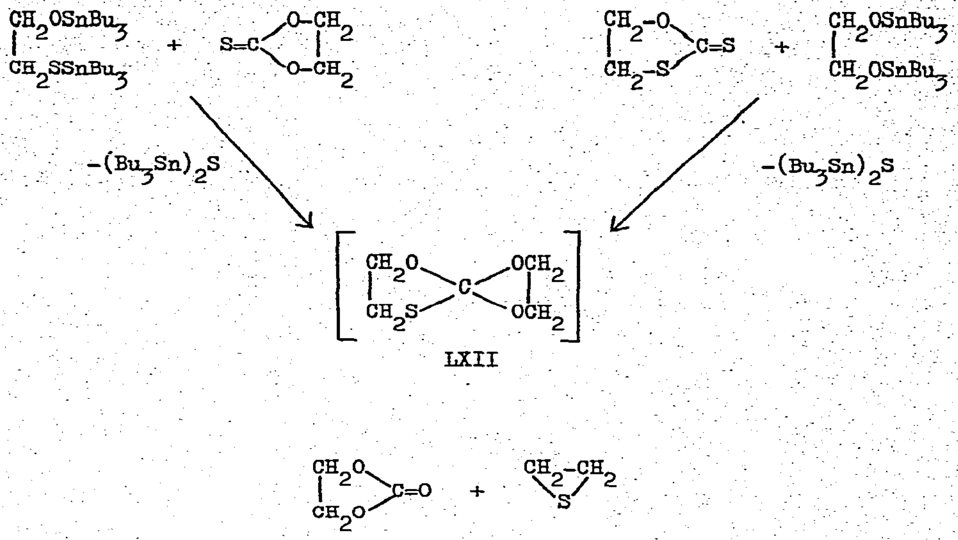


LX LXI

Treatment of LX with CS_2 for 20 hrs at 60° yielded ethylene dithiocarbamate

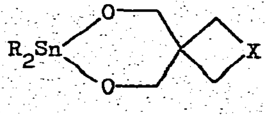


The formation of identical products, bis(tributyltin) sulphide, and ethylene sulphide, from both the thione-carbonate and bis(tributylstannyl)mercapto-ethanolate, and from the dithiocarbonate and bis(tributylstannyl)glycolate suggests that the spiro compound LXII is a common intermediate. Attempts to isolate LXII failed[119].

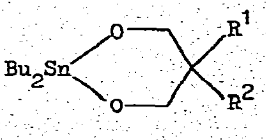


LXII

A patent reports the synthesis of some diorganotin glycolates of the types LXIII and LXIX from dialkyltin oxide and the appropriate diol[120].

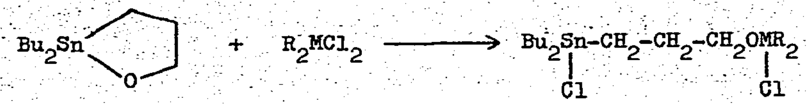


LXIII

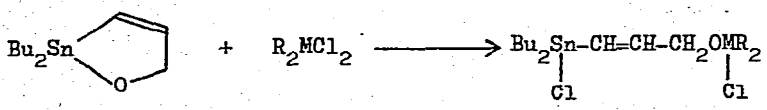


LXIX

Diorganotin oxacyclopentanes and pentenes react with dialkyldichlorosilanes or germanes with Sn-O bond fission:



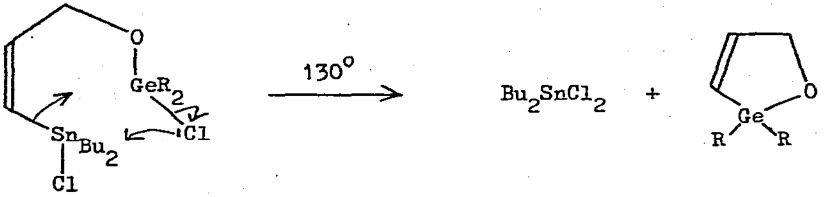
LXX

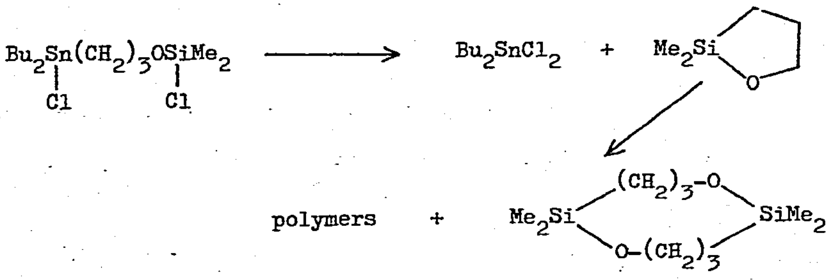


LXXI

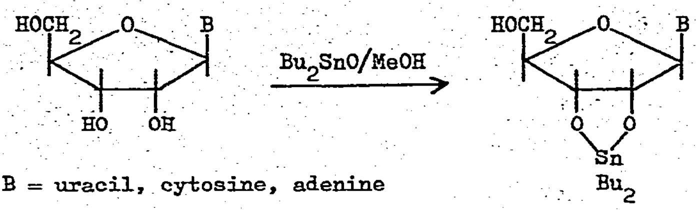
M = Si, R = Me; M = Ge, R = Me, Et

Heating the linear derivatives LXX and LXXI above ca. 130° causes cyclisation with the elimination of Bu_2SnCl_2:[121]





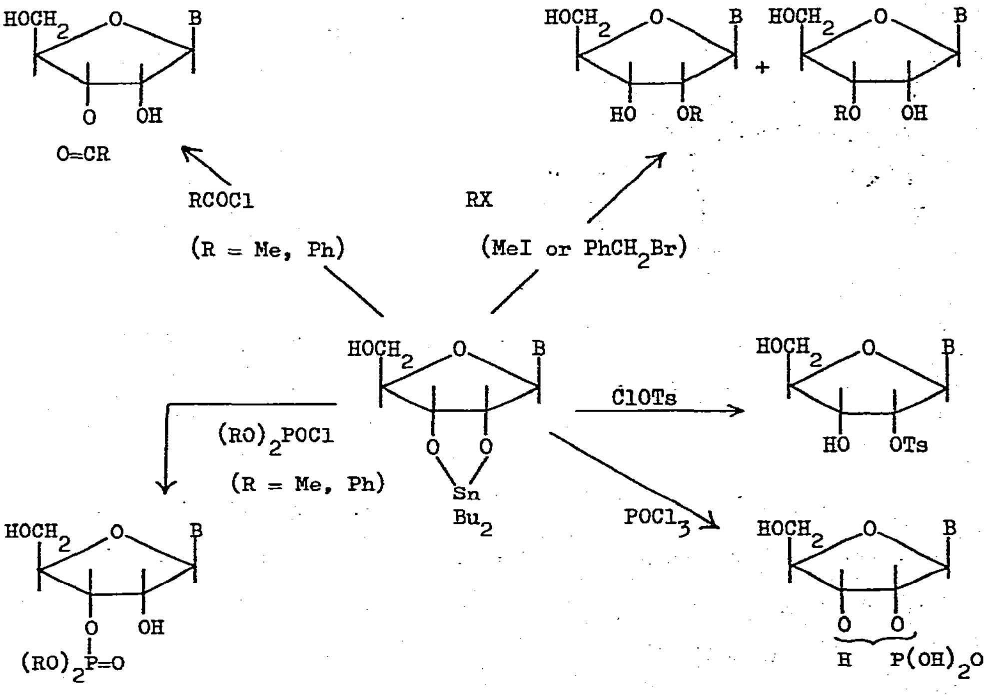
2',3'-O-(dibutylstannylene)nucleosides LXXII have been obtained as crystalline solids by heating methanol suspensions of the nucleoside and dibutyltin oxide:



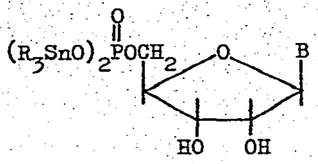
B = uracil, cytosine, adenine
hypoxanthine

LXXII

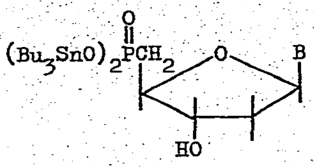
The derivatives LXXII react with acyl, alkyl, sulphonyl, and phosphonyl chlorides resulting in preferential substitution at the 2'(3') positions, with no substitution at the 5 position:



Bis(trialkyltin)nucleoside 5'-phosphates LXXIIIa and LXXIIIb result from reaction of bis(tributyltin) oxide and the nucleoside 5'-phosphate[122].



LXXIIIa



LXXIIIb

The structure of trimethyltin methoxide consists of chains of methoxy-bridged planar trimethyltin groups [Sn–C = 2.14(2)Å; Sn–O = 2.23(3)Å; OSnO = 172.4(7)°; SnOSn' = 131.2(12)°] (Fig. 7)[123]. Van den Berghe and van der Kelen have investigated the structure of methyltin alkoxides $\mathrm{Me_{4-n}Sn(OR)_n}$ (n = 1–3; R = Me, Et) by ^{1}H and ^{119}Sn nmr. The trimethyltin alkoxides are monomeric and tetrahedral in solution, but the data for the dimethyltin dialkoxides and methyltin tris(alkoxides) indicate the presence of polymeric species such as LXXIX[124].

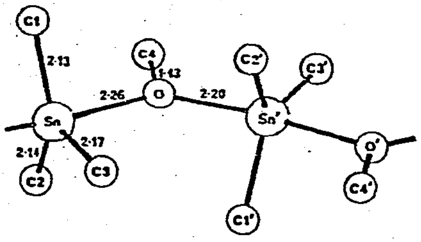
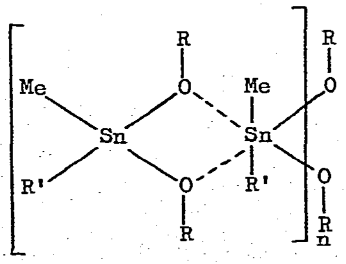


Fig. 7. The repeat unit of the chains of $[\mathrm{Me_3SnOMe}]_\infty$. (Reproduced with permision from Acta Cryst.).



LXXIX R' = Me, OR

Exchange reactions between triethyltin alkoxides with pentafluorophenylgermanium[203] and -tin[202] bromides have been described:

$$(C_6F_5)_{4-n}GeBr_n + nEt_3SnOMe \xrightarrow{100^\circ} (C_6F_5)_{4-n}Ge(OMe)_n + nEt_3SnBr$$

$n = 1, 2$

$$(C_6F_5)_3SnBr + Et_3SnOR \xrightarrow{100^\circ} (C_6F_5)_3SnOR + Et_3SnBr$$

$R = Me, Et$

Triorganotin alkoxides react with polyhalomethylmethanes under free-radical conditions giving the corresponding carbonyl compounds. Two secondary reactions also occur giving an alcohol and perhalo derivatives of pentane. The mechanism of the reaction proceeds by the abstraction of a hydrogen atom on the α-carbon atom of the alkoxy group followed by the rapid elimination of a trialkyltin radical:

$$>CHOSn< + \cdot CCl_3 \longrightarrow >\dot{C}-OSn< + HCCl_3$$

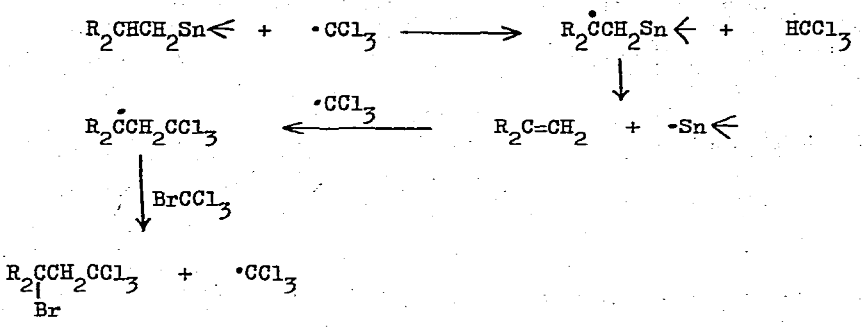
$$>\dot{C}-OSn< \longrightarrow >C{=}O + \cdot Sn<$$

$$>Sn\cdot + BrCCl_3 \longrightarrow >SnBr + \cdot CCl_3$$

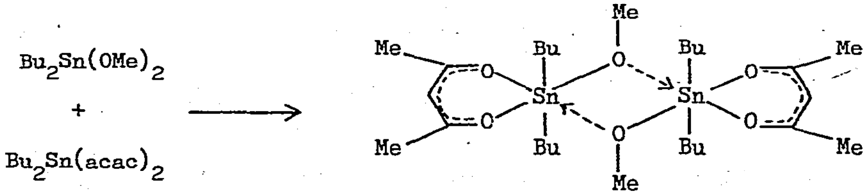
The formation of alcohol and perhalo derivatives of pentane occurs by attack of a $\cdot CCl_3$ radical either on the tin atom with subsequent elimination of a RO• radical or abstraction of a hydrogen atom on the β-carbon atom of the tributyltin group leading to an olefin which adds a polyhalomethane molecule:[125]

$$>\!Sn\text{-}OR \; + \; \cdot CCl_3 \longrightarrow \; >\!SnCCl_3 \; + \; RO\cdot$$

$$RO\cdot \; + \; QH \longrightarrow ROH \; +$$



Dibutyltin dimethoxide and dibutyltin bis(acetylacetonate) disproportionate in hexane forming the dimer LXXX:[68]



LXXX

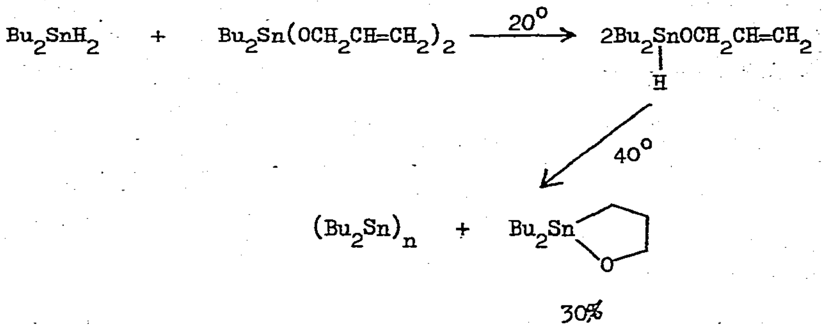
Dibutyltin dialkoxides also disproportionate with dibutyltin dihydride at low temperatures forming mixed dibutyltin hydride alkoxides, but at higher temperatures elimination of alcohol occurs:[68,126]

$$Bu_2SnH_2 \; + \; Bu_2Sn(OR)_2 \xrightarrow{< 25^\circ} 2Bu_2SnH(OR)$$

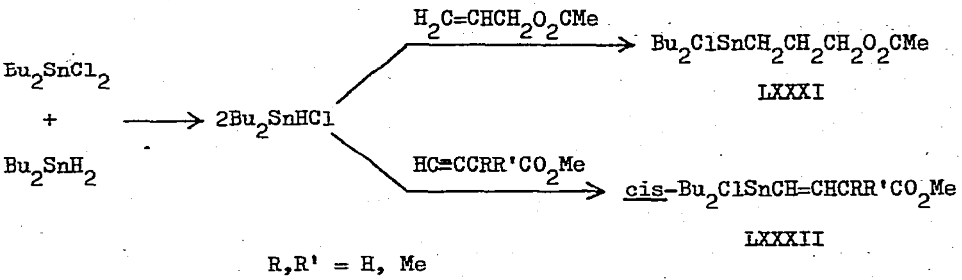
$$R = Me, Et$$

$$nBu_2SnH(OMe) \xrightarrow{60\text{–}70^\circ} nMeOH \; + \; (Bu_2Sn)_n$$

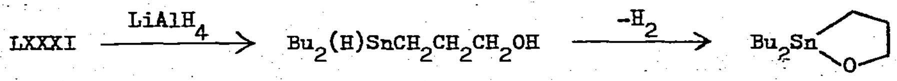
The attempted addition of $Bu_2Sn(H)OMe$ to allyl alcohol resulted only in the decomposition to methanol and $(Bu_2Sn)_n$. $Bu_2Sn(H)Oallyl$ can, however, be obtained by exchange at low temperature, but mild heating results in cyclisation accompanied by elimination:



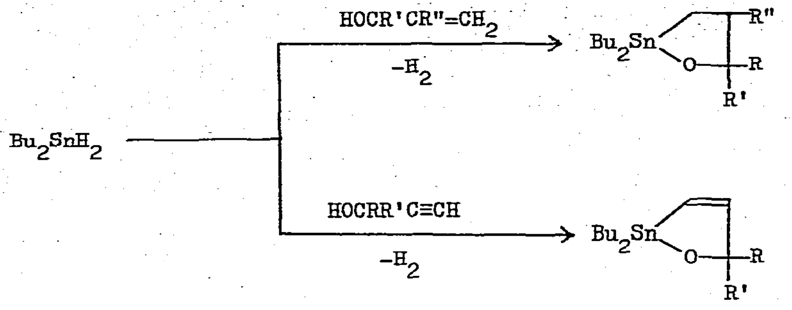
Dibutyltin hydride chloride adds to allyl and propargyl acetates forming LXXXI and LXXXII, respectively:



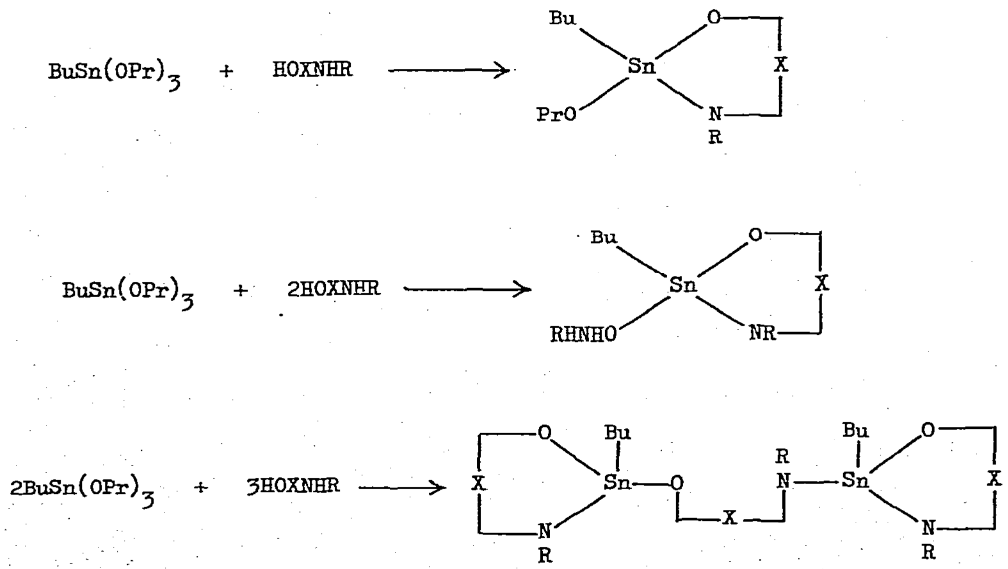
Attempted reduction of LXXXI to $Bu_2(H)Sn(CH_2)_3OH$ by $LiAlH_4$ yielded an ether phase which evolved hydrogen gas even at 0^o as cyclisation takes place:



Cyclostannaoxapentanes and -pentenes may be formed directly by the reaction of Bu_2SnH_2 with allyl or propargyl alcohols:[126]



Mehrotra has investigated the products of reaction of butyltin tris(isopropoxide) with alkanolamines[127] and β-diketones[128]. Various products are obtained depending on the molar ratio of the reactants, viz.:

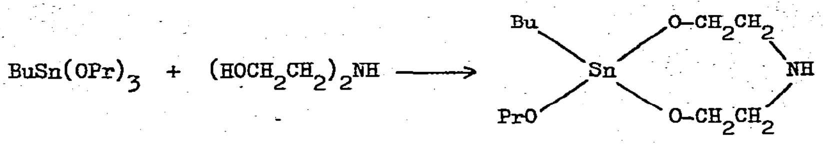


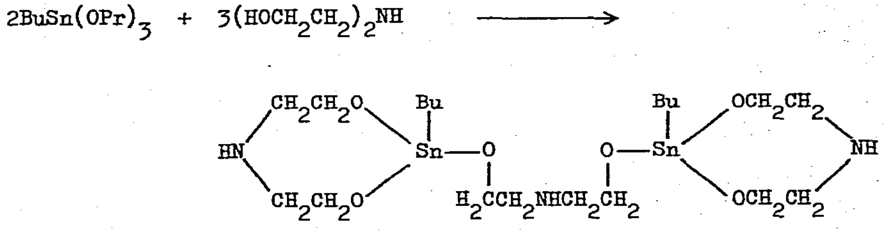
$$BuSn(OPr)_3 \quad + \quad 3HOXNHR \longrightarrow BuSn(OXNHR)_3$$

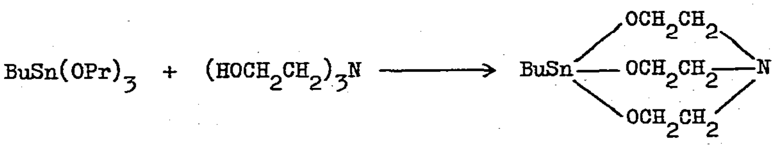
$$BuSn(OPr)_3 + nHOXNMe_2 \longrightarrow BuSn(OPr)_{3-n}(OXNMe)_n$$

$n = 1-3;$ $R = H;$ $X = CH_2CH_2, CH_2CH_2CH_2$

$R = Me;$ $X = CH_2CH_2$

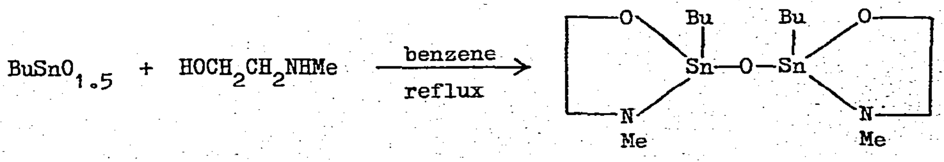




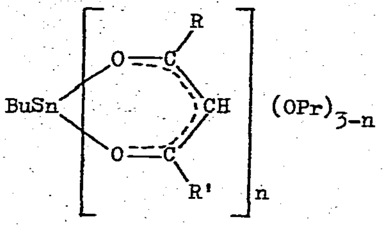


The same products could, in general, also be obtained using butylstannonic acid. Higher reaction temperatures caused condensation of N-H bonds:

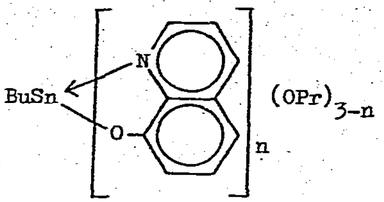
$$BuSn(OPr)_3 + HOCH_2CH_2NH_2 \xrightarrow[\text{xylene}]{139^\circ} BuSn(OCH_2CH_2N)$$



-Diketones and 8-hydroxyquinoline also afford derivatives of the types LXXXIII and LXXXIV depending on the molar ratio of reactants.



LXXXIII



LXXXIV

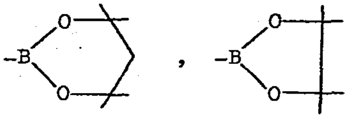
Mehrotra[129-131] and Gupta[132] have investigated the chemistry of compounds containing the Sn-O-B linkage. Several synthetic methods were employed:

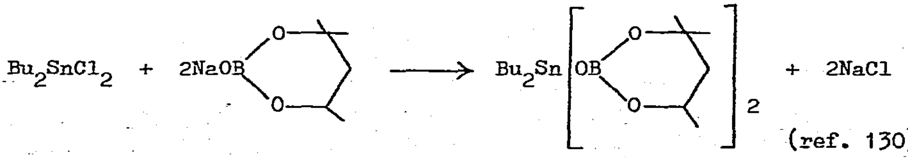
$$2B(OH)_3 + 3(R_3Sn)_2O \longrightarrow 2(R_3SnO)_3B + 3H_2O$$ (ref. 129)

$$B_2O_3 + (R_3Sn)_2O \longrightarrow (R_3SnOBO)_3 \underset{+B_2O_3;\ 120\text{–}240^\circ}{\overset{\text{in vacuo; } -B_2O_3}{\rightleftharpoons}} (R_3SnO)_3B$$ (ref. 129)

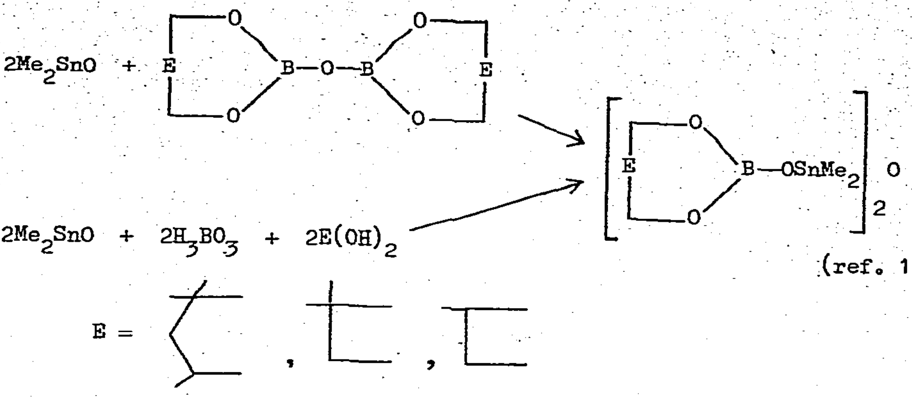
$$2Bu_2SnO + 2H_3BO_3 + 2\text{diol} \longrightarrow QOSnBu_2OSnBu_2OQ$$ (ref. 130)

Q =

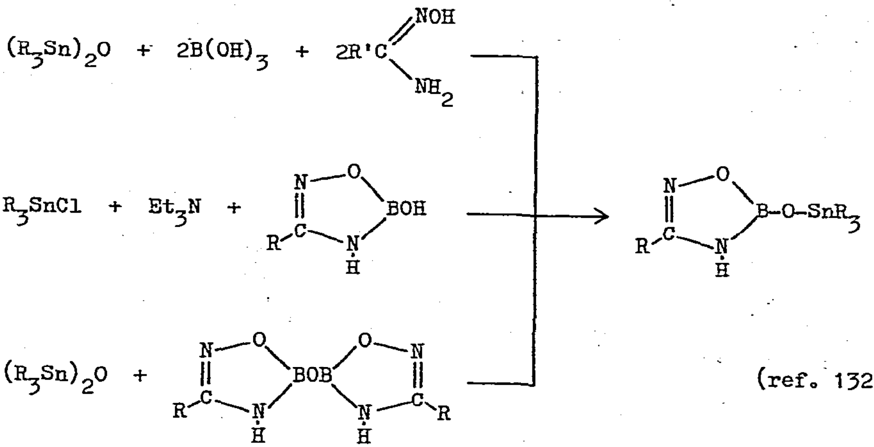




(ref. 130)

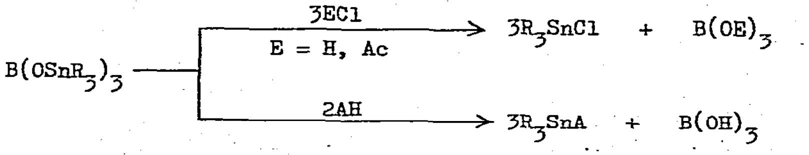


(ref. 130)



(ref. 132)

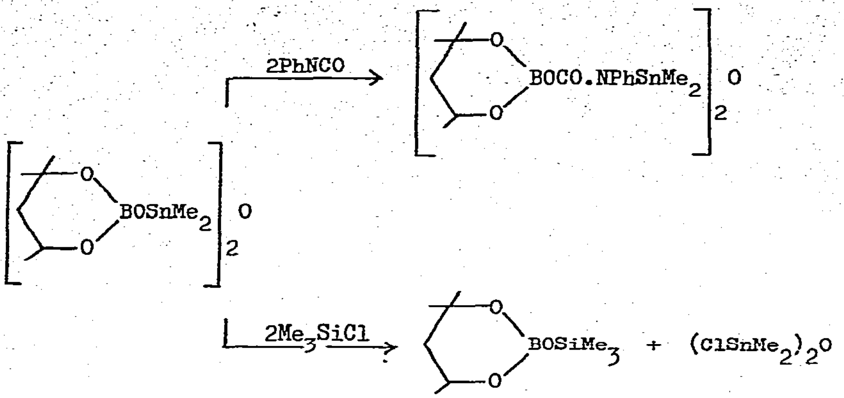
These types of compound undergo reaction with a variety of reagents at the Sn–O bond:



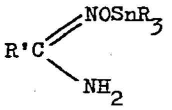
$$B(OSnR_3)_3 \xrightarrow[E\ =\ H,\ Ac]{3ECl} 3R_3SnCl + B(OE)_3$$

$$B(OSnR_3)_3 \xrightarrow{2AH} 3R_3SnA + B(OH)_3$$

A = AcO, SBu, SPh, OPh



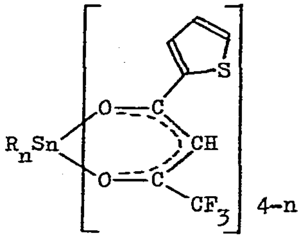
O-Triorganostannylamidoximes LXXXV [133] and diorganotin derivatives of 2-thenoyltrifluoroacetone LXXXVI[134] have also been synthesised by similar methods.



R = Me, Bu, Ph

R' = Me, Et, Pr, Ph

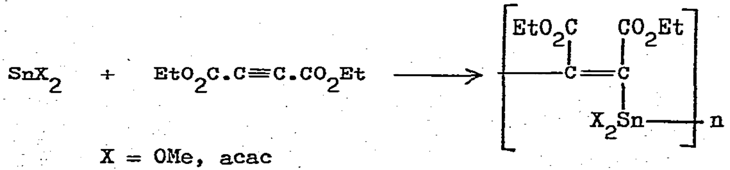
LXXXV



n = 2, 3; R = Me, Et, Bu, Ph

LXXXVI

Organotin alkoxide and acetylacetonate derivatives have been obtained by oxidative-addition reactions of tin(II) bis(alkoxides), bis(β-ketoenolates) and bis(β-ketoesters):[226,227,230]



X = OMe, acac

$$\mathrm{Sn(acac)_2} + \mathrm{RX} \longrightarrow \mathrm{RSn(acac)_2X}$$

$\mathrm{RX} = \mathrm{MeI}, \mathrm{BrCH_2CH{=}CH_2}, \mathrm{PhCH_2Br}$

$$\mathrm{Sn(OR)_2} + \mathrm{R'I} \longrightarrow \mathrm{R'Sn(OR)_2I}$$

$\mathrm{R} = \mathrm{MeC{=}CHCO_2Et}, \mathrm{PhC{=}CHCOPh}, \underline{o}\text{-}\mathrm{C_6H_4CO_2Et}$

$\mathrm{R'} = \mathrm{Me}, \mathrm{Et}, \mathrm{Bu}$

Serpone and his coworkers have investigated the mechanism of intermolecular ligand exchange and configurational rearrangements in organotin acetylacetonates. Acetylacetonate exchange between $Ph_2Sn(acac)_2$ and $Me_2Sn(acac)_2$ is first-order in $Ph_2Sn(acac)_2$ but zero-order in $Me_2Sn(acac)_2$ concentration. A mechanism was proposed in which the rate-determining step is tin-oxygen bond rupture in $Ph_2Sn(acac)_2$ to yield a five-coordinate tin species with a 'dangling' unidentate acetylacetonate ligand. This species is then thought to react with a similar five-coordinate species formed from a rapid equilibrium step from $Me_2Sn(acac)_2$[135]. Configurational rearrangements in $RClSn(acac)_2$ (R = Me, Ph) complexes probably proceed via twist motions through trigonal-prismatic transition states, if the exchange process occurs by a sole reaction pathway[136]. In $CDCl_3$ and $CHBr_3$ solutions these compounds have predominantly the <u>cis</u> structures with only a small amount of the <u>trans</u> isomer. When R = Ph, the complex is <u>ca</u>. 95% <u>cis</u> and <u>ca</u>. 5% <u>trans</u>. Kinetics of configurational rearrangements which exchange acac ring protons between the two non-equivalent sites in $ClRSn(acac)_2$ (R = Me, Ph), along with exchange of methyl groups in $Ph_2Sn(acac)_2$ have also been studied. Substitution of chloride in $Cl_2Sn(acac)_2$ by phenyl or methyl groups increase the lability in the order $Cl_2Sn < PhClSn < MeClSn < Ph_2Sn$[137].

Ruddick and Sams[138] have investigated the structures of organotin oxine and related derivatives by magnetically-perturbed Mössbauer spectroscopy.

$RSnCl(ox)_2$ (R = Bu, Ph) compounds have the cis-$RSnXY_4$ octahedral structure, whilst $BuSn(ox)_3$ is seven-coordinate with three equivalent bidentate oxine groups. The complexes $R_2SnCl(ox)$ (R = Me, Ph) and the dimethyltin derivatives of N-(2-hydroxyphenyl)salicylaldimine, $Me_2Sn(sal\text{-}N\text{-}2OC_6H_4)$, have five-coordinate structures. The data for Me_3SnO_2CMe and $Ph_3Sn(ox)$ are consistent with the previously deduced trans and cis-R_3SnXY five-coordinate stereochemistries, but the complex $Ph_3Sn(sal\text{-}N\text{-}2\text{-}HOC_6H_4)$ appears to possess the novel mer-octahedral configuration. Nmr and uv data indicate that coordinating solvents such as pyridine, trimethylphosphate, DMSO, or HMPA do not interact with the substituted dimethyltin bis(oxinates) $Me_2Sn(ox\text{-}Y)_2$ (Y = Me, Et)[139]. Full details of the crystal structure of $Ph_3SnONPh.CO.Ph$ have been published[140]. The tin atoms are five-coordinated with a distorted cis-Ph_3SnX_2 configuration (Fig. 8). The value of the Mössbauer quadrupole splitting is satisfactorily explained using the point charge approximation.

Several organotin derivatives of tri- and tetradentate Schiff bases have been investigated. The diphenyltin derivative of 2-(o-hydroxyphenyl)-

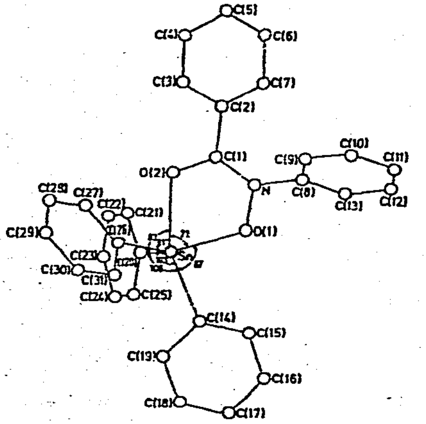
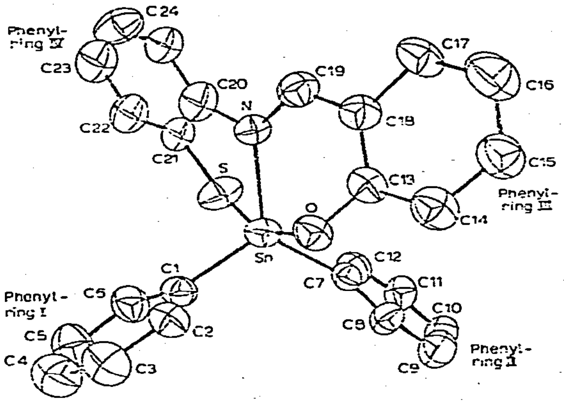


Fig. 8. The molecular structure of $Ph_3SnO.NPh.CO.Ph$. (Reproduced by permission of the Chemical Society).

benzothiazoline, Ph$_2$SnSAT, has heavily distorted trigonal-bipyramidal geometry. The nitrogen atom and the two phenyl groups occupy equatorial positions, with the sulphur and oxygen atoms occupying the axial sites (Sn-S = 2.496(1)Å; Sn-O = 2.093(2)Å; Sn-N = 2.217(3)Å; Sn-C = 2.123(3)Å) (Fig. 9)[141]. The structure of the dimethyltin derivative of 2-hydroxy-N-(2-hydroxybenzylidene)aniline, Me$_2$SnSAB, is similar, although weak intermolecular Sn...O coordination (Sn...O = 2.881(8)Å) occurs to form rather loose dimers (Fig. 10). Each individual molecule, however, also possesses the distorted trigonal bipyramidal stereochemistry, again with the nitrogen and both carbon atoms occupying equatorial sites and the oxygen atoms the axial sites (Sn-C = 2.117(14)Å; Sn-O = 2.112(9)Å; Sn-N = 2.229(11)Å)[142]. Organochlorotin derivatives of similar ONO and SNO Schiff bases, RClSn(trid), have also been synthesised and investigated spectroscopically. The data indicate polymeric



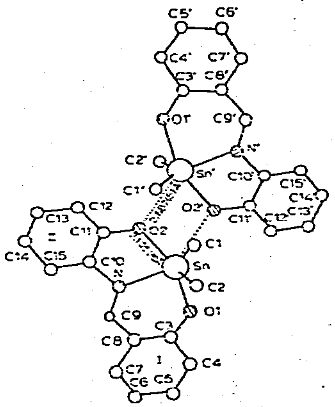
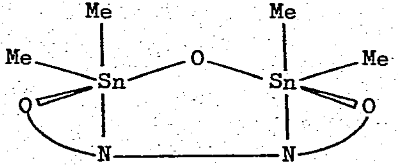


Fig. 9. The molecular structure of Ph$_2$SnSAT. (Reproduced with permission from Z anorg. allg. Chem.).

Fig. 10. The molecular structure of Me$_2$SnSAB. (Reproduced with permission from Z. anorg. allg. Chem.).

trigonal bipyramidal structures, although five-coordinated monomers and octahedral dimers cannot be ruled out[143]. Diorganotin derivatives of ONNO tetradentae Schiff bases derived from salicylaldehyde and its derivatives and ethylene-, propylene-, or phenylene diamine have been synthesised. The representative compound, dimethyltin bis(salicylaldehyde)ethylenediiminate) $Me_2SnBSED$, may be isolated in two isomeric forms in the solid state. Spectroscopic data show that these have six-coordinate cis and trans geometries with, respectively, a bent CSnC moiety and a non-planar BSED ligand and nearly linear CSnC moiety and a symmetric BSED ligand. The two forms undergo cis-trans isomerisation in solution, the cis isomer being favoured in non-coordinating solvents (CH_2Cl_2) and $PhNO_2$) and the trans form by coordinating solvents (DMF and HMPA). The trans isomer is also favoured at higher temperatures. In air, the complex is converted to, initially, $(Me_2Sn)_2O(BSED)$, for which structure LXXXVII is proposed, and ultimately to the ligand and dimethyltin oxide[144].



LXXXVII

Mössbauer data for the diphenyltin and phenylchlorotin derivatives of the tetradentate ligand diacetylbis(benzoylhydrazone) indicate octahedral geometries for both, with linear CSnC and CSnCl skeletons, respectively[145]

7. CARBOXYLATES AND OXYACID DERIVATIVES.

Me_3SnO_2CMe and $Me_3SnO_2CCF_3$ are isostructural, consisting of chains of carboxylate-bridged planar Me_3Sn groups (Fig. 11). The carboxyl bridging

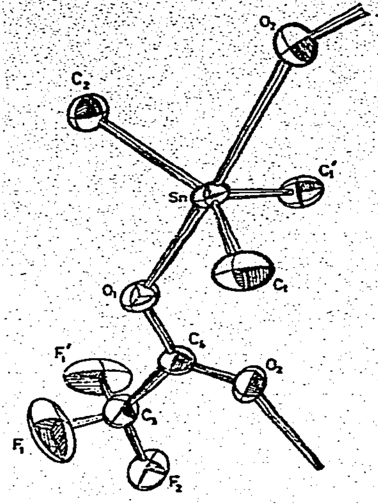
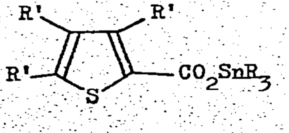
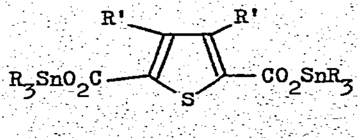


Fig. 11. The repeat unit of the polymeric chain of $Me_3SnO_2CCF_3$. (Reproduced with permission from J. Cryst. Mol. Struct.).

is not equal; the tin-oxygen bond distances being 2.205(3) and 2.391(4)Å for the acetate and 2.177(14) and 2.458(15)Å for the trifluoracetate[146]. Osmometric and infra-red data for trivinyltin formate in carbon tetrachloride solution suggest the presence of a monomer⇌dimer equilibrium[147]. Garner and Hughes have shown that divinyltin bis(trifluoroacetate) is monomeric with unidentate trifluoroacetate groups[149]. The patent literature reports the synthesis of dialkyltin maleates from maleic anhydride and R_2SnO in an organic solvent[150], the compounds LXXXVIIIa and LXXXVIIIb from R_3SnOH or $(R_3Sn)_2O$ and the corresponding carboxylic acid[151], and $R_3SnO_2CCH{=}C(OR')CH_2R''$



LXXXVIIa



LXXXVIIb

from R_3SnOR' and $HO_2CCH_2C{\equiv}CR'$ at temperatures in excess of 100°[152]. Mono- and bis-trialkyltin esters of the unsaturated carboxylic acids, $HO_2CCMe{=}CHCO_2H$ and $CH_2C(CO_2H)CH_2CO_2H$, may also be obtained by reaction with the triorganotin (hydr)oxide. The derivatives readily polymerize, and copolymerised with styrene and methyl methacrylate[153]. Triorganotin esters of bicyclo[2,2,1]hept-2-ene-5-carboxylates may be obtained by the Diels-Alder addition of $R_3SnO_2CR'{=}CH_2$ to cyclopentadiene at 150-250°[154].

Bis(trialkyltin) oxides disproportionate in liquid sulphur dioxide at and above room temperature giving diorganotin sulphites, R_2SnSO_3, and triorganotin monosulphinates, R_3SnO_2SR, or diorganotin disulphinates, respectively[155].

$$R_3SnOSnR_3 \;+\; 2SO_2 \xrightarrow[\text{1 day}]{\text{liquid } SO_2} R_3SnO_2SR \;+\; R_2SnSO_3$$

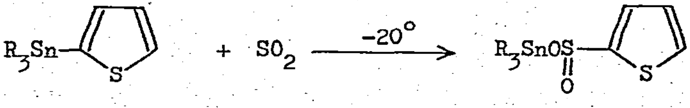
R = Me; T = 60°

R = Et, Ph; T = 25°

$$R_3SnOSnR_3 \;+\; 3SO_2 \xrightarrow[\text{1 day}]{\text{liquid } SO_2} R_2Sn(O_2SR)_2 \;+\; R_2SnSO_3$$

R = Et, Ph; T = 60°

α-Thienyltriorganotin compounds react with SO_2 at -20° exclusively at the tin-thienyl bond:[34]



Triphenylmethyltin reacts with liquid SO_2 at -30° to give a mixture of mono- and di-insertion products IXC and XC:

$$\begin{tikzcd}
\mathrm{Ph_3SnMe} + \mathrm{SO_2} \arrow[r, "-30^\circ"] \arrow[dd, "20\text{–}60^\circ"] & \mathrm{Ph_2MeSnO_2SPh} & + \ \mathrm{PhMeSn(O_2SPh)_2} \\
 & \text{IXC} \quad 11\% & \text{XC} \quad 48\% \\
\mathrm{PhMeSn(O_2SPh)_2} & \mathrm{Ph_3MeSn} \arrow[l, "\text{aqueous } \mathrm{SO_2}"'] & \\
\text{XC} & &
\end{tikzcd}$$

but at temperatures of 20–60°, or using aqueous sulphur dioxide, only XC was formed. In no case was the Sn-Me bond attacked[156]. Similar studies with perfluoroorganotin derivatives demonstrate that $(C_6F_5)_4Sn$ is inert and $(CF_2{=}CF)_4Sn$ shows only slight reactivity. In mixed derivatives such as $Ph_3SnC_6F_5$ and $Ph_3SnCF{=}CF_2$, reaction takes place only at the phenyl-tin bond:

$$\mathrm{Ph_3SnL} + 2\mathrm{SO_2} \xrightarrow[\text{liq. } \mathrm{SO_2}]{20\text{–}60^\circ} \mathrm{Ph(L)Sn(O_2SPh)_2}$$

$$L = C_6F_5,\ CF{=}CF_2$$

The presence of the C_6F_5 group in $Me_3SnC_6F_5$ deactivates the molecule to attack, and the tin sulphate XCI is produced after 14 days at 90°:

$$\mathrm{Me_3SnC_6F_5} \xrightarrow[\text{liquid } \mathrm{SO_2}]{90^\circ/14 \text{ days}} \underset{\text{XCI}}{\mathrm{(Me_3Sn)\ Me_2(C_6F_5)Sn\ SO_4}}$$

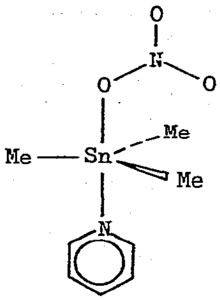
Perfluoromethanesulphinate derivatives have been obtained from the organotin halides and the sodium sulphinate:[157]

$$\mathrm{R_{4-n}SnX_n} + n\mathrm{NaO_2SCF_3} \xrightarrow{20^\circ/\mathrm{THF}} \mathrm{R_{4-n}Sn(O_2SCF_3)_n} + n\mathrm{NaX}$$

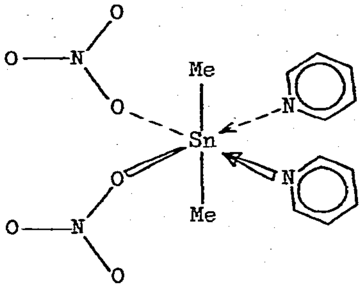
$$R = \mathrm{Me,\ Et,\ Ph,}\ \underline{p}\text{-}C_6H_4Me;\ X = Cl,\ Br;\ n = 1,\ 2$$

Arguments favouring an S_E2 mechanism for the SO_2 insertion reactions of tetraorganostannanes have been presented by Kunze and Koola[158].

The adducts $Me_2Sn(NO_3)_2(py)_2$ and $Me_3SnNO_3(py)$ are formed by the addition of pyridine to chloroform suspension of the appropriate anhydrous methyltin nitrate. Mössbauer, infra-red, and Raman data indicate structures XCII and XCIII with unidentate nitrate groups for the two complexes.

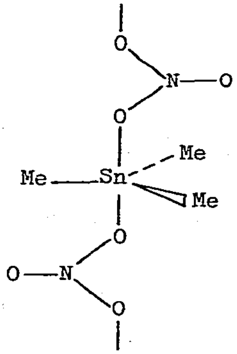


XCII



XCIII

Structures XCIV involving bridging nitrate groups was proposed for anhydrous Me_3SnNO_3[159].



XCIV

Dimethyltin nitrate hydroxide is dimeric in the crystal. Each tin atom enjoys trigonal bipyramidal geometry with the methyl groups occupying equatorial sites (Sn-C = 2.13(4) Å) and the nitrate group bonding in a unidentate fashion via an axial site (Sn-O = 2.30(3) Å). Two hydroxy bridges link adjacent tin atoms via the remaining equatorial and axial sites (Sn-O = 2.18(3) Å) (Fig. 12)[160].

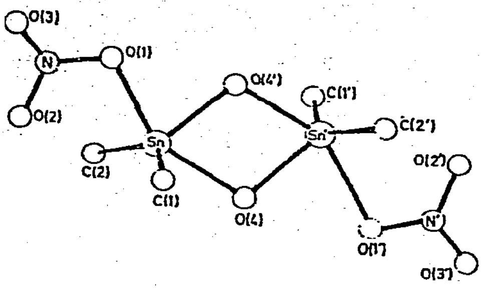


Fig. 12. The structure of $Me_2Sn(OH)NO_3$. (Reproduced by permission of the Chemical Society).

The structure of $(Me_2Sn)_3(PO_4)_2.8H_2O$ consists of infinite 'ribbons' through the crystal (Fig. 13). One tin atom has a regular octahedral environment with trans methyl groups, whilst the other two enjoy highly distorted (CSnC = 147, 150°) tetrahedral geometries due to weak coordination of two water molecules. All the water molecules are involved in hydrogen bonding to each other and to phosphate oxygen atoms[161]. The compounds

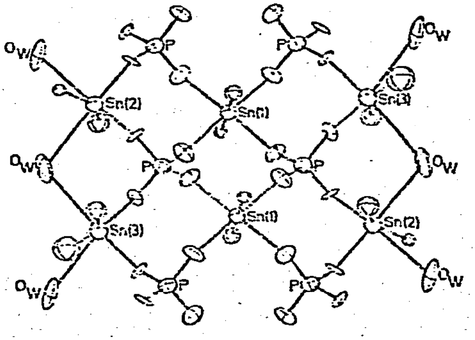


Fig. 13. The structure of $(Me_2Sn)_3(PO_4)_2.8H_2O$. (Reproduced by permission of the Chemical Society).

$Me_3SnO_2PCl_2$ and $Me_2Sn(O_2PCl_2)_2$ have been synthesised from the appropriate methyltin chloride and $P_2O_3Cl_4$. Ir and Mössbauer data suggest that the compounds are associated through OPO bridges[162]. Dibutyltin butoxide diethylphosphate has been prepared from diethylphosphate and $Bu_2Sn(OBu)_2$[163]. Polymeric dibutyltin arsonates, Bu_2SnO_3AsAr, have been obtained from Bu_2SnO and the arsonic acid[164].

The crystal structure of polymeric tris(trimethyltin) chromate hydroxide has been determined. Each of three crystallographically independent tin atoms has approximately trigonal bipyramidal geometry with approximately planar Me_3Sn groups. The oxygen atoms of the chromate groups are bonded to tin, and the hydroxide group bridges two Me_3Sn groups, and is also probably hydrogen-bonded to one of the chromate oxygen atoms. The $Sn-O_{chromate}$ bond distances are longer (2.48(5)Å and 2.51(4)Å) than the Sn-OH bond distances (2.14(3)Å and 2.51(4)Å) (Figs. 14a and 14b)[165].

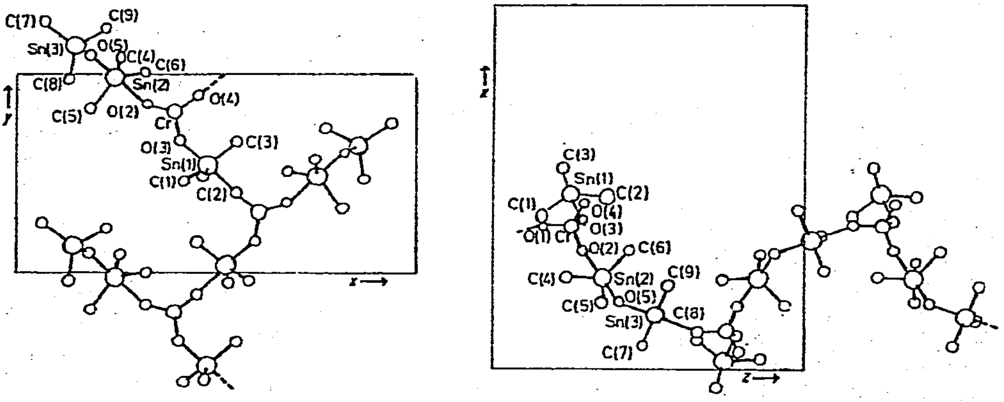


Fig. 14. (a) Projection of part of the structure of basic trimethyltin chromate perpendicular to Z, showing the chains in the Y axis direction. (b) Projection of part of the structure perpendicular to Y, showing the chains in the Z axis direction. (Reproduced by permission of the Chemical Society).

8. SULPHUR DERIVATIVES.

Syntheses of organotin sulphides and thiolates are reported in various patents. Trimeric ethylhydrotin sulphide, $(EtHSnS)_3$, is formed in 56% yield by the action of sodium thiosulphate on ethyltin trichloride[166]. Mixed vinylalkyltin sulphides[167], $Bu_2Sn\left[SCH_2CH_2O(CH_2)_{17}Me\right]_2$[168], and alkyltin (isooctyloxycarbonyl)methanethiolates[169] have also been synthesised by standard procedures. Heating mixtures of organotin alkoxides or oxides with thioesters affords the corresponding organotin thiolates in yields upto 95%:

$$R_nSn(OR')_{4-n} + MeCOSR'' \longrightarrow R_nSn(SR'')_{4-n} + MeCO_2R$$

$$R_nSnO_{\frac{1}{2}(4-n)} + MeCOSR'' \longrightarrow R_nSn(SR'')_{4-n} + R_nSn(O_2CMe)_{4-n}$$

R,R' = alkyl; R" = alkyl, aryl, alkenyl

Triethyltin thioacetate reacts similarly with triethyltin methoxide:[170]

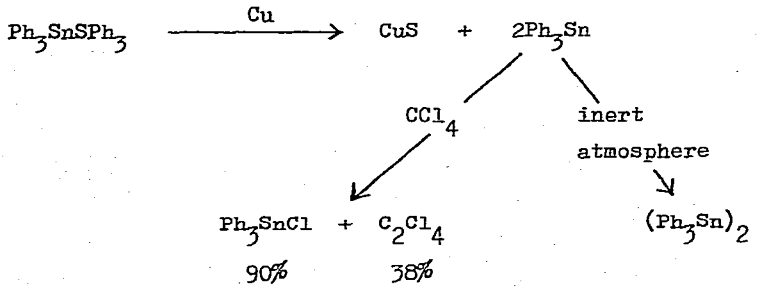
$$Et_3SnSCOMe + Et_3SnOMe \longrightarrow Et_3SnSSnEt_3 + MeCO_2Me$$

Stapfer and Herber have investigated the synthesis and structures of organotin mercaptoesters, $R_nSn\left[S(CH_2)_{1-2}CO_2R'\right]_{4-n}$[171]. The compounds were prepared by the condensation of the organotin chloride and thiocompound with or without an HCl acceptor such as sodium bicarbonate or triethylamine. The trialkyltin mercaptoesters $Bu_3SnSCH_2CO_2R$ (R = Me, C_8H_{17}, Na) all appear to be isostructural with four-coordinated tin atoms. The structures of the dialkyltin bis(mercaptoesters), however, depend on the nature and size of the ligands and also on the method of preparation. Generally, the two mercaptoester groups are not equivalent; one functioning as a unidentate and the other as a bidentate ligand through intramolecular carbonyl ⟶ tin coordination. Butyltin tris(isooctylthioglycolate) has five-coordinate tin when prepared in an aqueous medium, but six-coordinated tin when obtained under non-aqueous conditions. Again both unidentate and bidentate mercapto-ester groups are present.

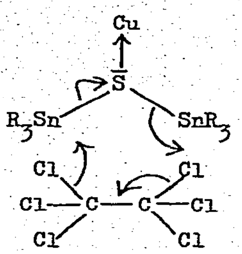
Treatment of dibutyltin bis(thiobenzoate) with dilute aqueous hydrochloric acid results in the cleavage of one thiobenzoate group from tin forming XCV:[172]

$$\mathrm{Bu_2SnO} + \mathrm{2PhCOSH} \longrightarrow \mathrm{Bu_2Sn(SCOPh)_2} \xrightarrow{\mathrm{HCl}} \underset{\substack{93\% \\ \mathrm{XCV}}}{\mathrm{Bu_2SnCl(SCOPh)}}$$

Razuvaev[173] has investigated the inluence of freshly precipitated copper on the reaction of organotin sulphides. With bis(triphenyltin) sulphide, $Ph_3Sn\cdot$ radicals are generated which dimerize in an atmosphere of inert gas. In carbon tetrachloride, chlorine abstraction takes place:



In the presence of freshly precipitated copper, hexachloroethane reacts more vigourously with bis(trialkyltin) sulphides than CCl_4. A heterolytic process was proposed:



$$\longrightarrow \underset{98\%}{2R_3SnCl} + \underset{60\%}{C_2Cl_4} + \underset{92\%}{CuS}$$

In the absence of copper, the reaction did not proceed, even after prolonged heating. Hexaorganodistannanes also react with C_2Cl_6 with the formation of R_3SnCl. $Bu_3SnSSnBu_3$ and di-tert-butylperoxide (300% excess) at 65° in the presence of copper gave copper sulphide and Bu_3SnO^tBu as the major products:

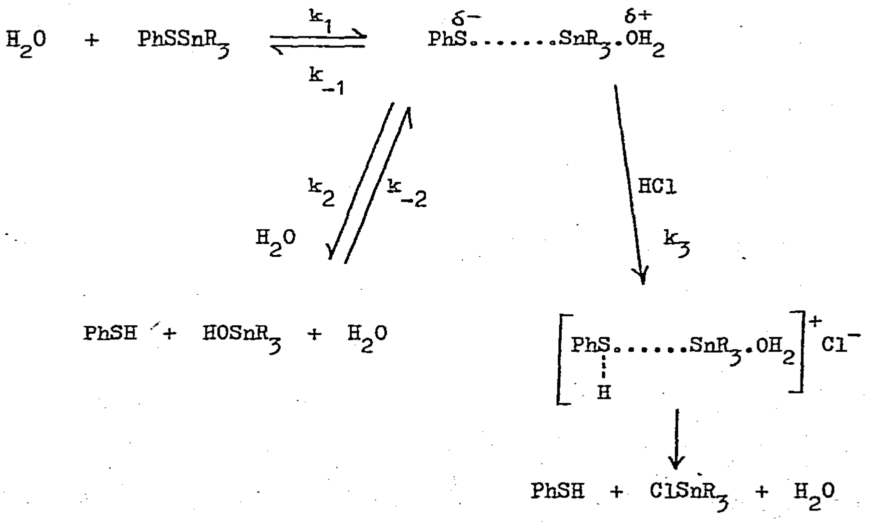
$$(Bu_3Sn)_2S + {}^tBuOO^tBu \xrightarrow{Cu} \underset{50\%}{CuS} + \underset{50\%}{Bu_3SnO^tBu} + \underset{10\%}{(Bu_3Sn)_2} + \text{acetone}$$

No reaction was observed between $R_3SnSSnR_3$ (R = Et, Bu) and triphenylphosphine, but $Bu_3SnSSnBu_3$ and Ph_3PCl_2 underwent exchange:

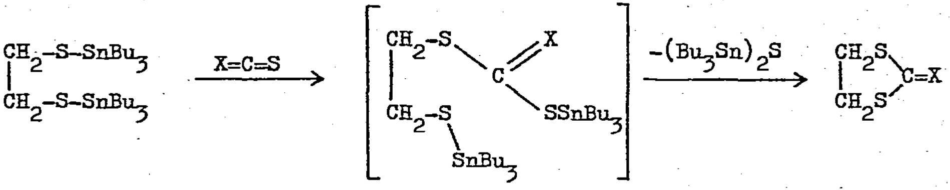
$$Bu_3SnSSnBu_3 + Ph_3PCl_2 \longrightarrow \underset{90\%}{2Bu_3SnCl} + \underset{80\%}{Ph_3PS}$$

Tributyltin p-tolylsulphide reacts with triphenylmethylchloride and phenylmercuric chloride to form triphenylmethyl p-tolylsulphide and phenylmecury p-tolylsulphide[174]. Kravtsov *et al.*[175,176] have studied the kinetics of metal-proton exchange and metal-metal exchange between triphenyltin arylmercaptides and the corresponding phenylmercury, triphenyllead arylmercaptides or the free (substituted) thiophenol. In chlorobenzene, metal-metal exchange proceeds at a greater rate than metal-proton exchange, whilst pyridine accelerates the metal-proton exchange to a greater extent than the metal-

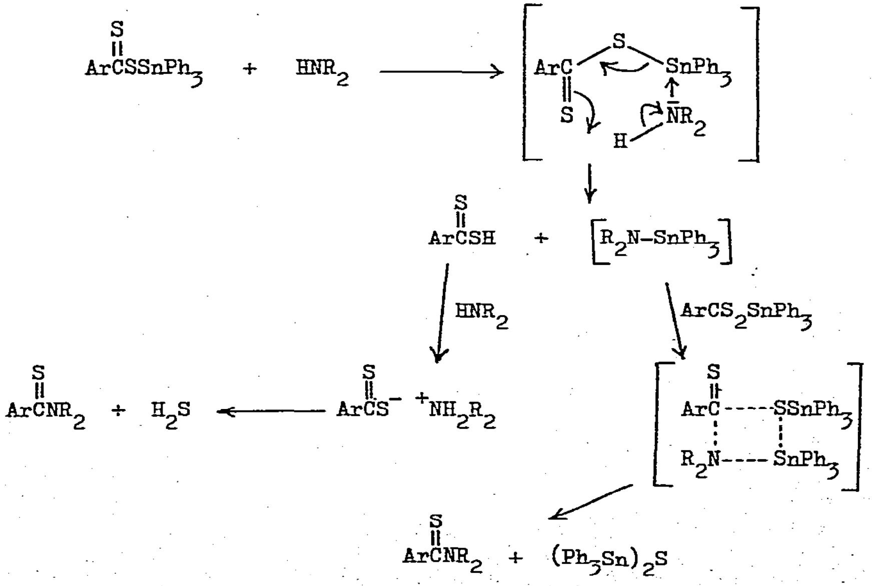
metal exchange. The most probable mechanism for the exchange reactions involves an associative pathway, the rate of exchange being mainly determined by the ability of the migrating group to form a cyclic transition state with delocalised bonds. The rates of cleavage of triorganotin thiophenolates have been measured in neutral and acidic aqueous dioxan. The driving force for the Sn–S bond cleavage was suggested to be a stretching of the bond by nucleophilic assistance of water. The fast reverse reaction $(k_{-2} \gg k_2)$ between thiol and R_3SnOH, which instantly gives R_3SnSPh, stabilizes the intermediate with respect to the final products and accounts for the stability of the R_3SnSPh derivatives in neutral aqueous dioxan. For the acid hydrolysis, the mechanism which best accommodates the data involves a rate-determining attack (k_3) of a proton on the sulphur atom:[177]

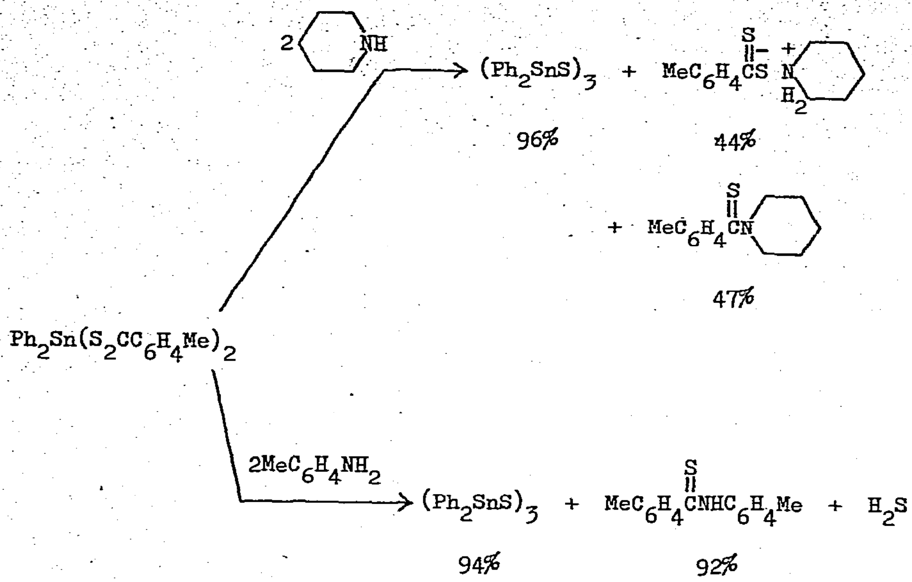


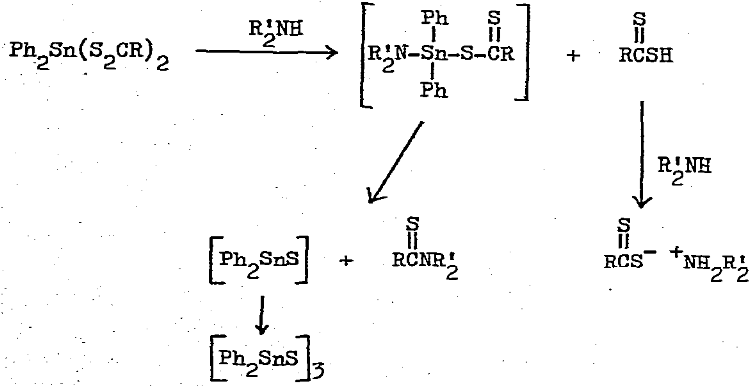
Potentiometric, spectrophotometric, and polarographic studies indicate that the dissolution of ethyltin sesquisulphide in aqueous solution, in the presence of sulphide ion at pH values between 8 and 11, is due to the formation of the two complexes $[EtSnS_3]^{3-}$ and $[(EtSn)_3(OH)_6(HS)_8]^{5-}$[178]. Bis(tributylstannyl)-ethane dithiolate reacts with CS_2 and methyl or phenyl isothiocyanates over a period of several days at 40-90° to afford 2-thio- and 2-methylimino- or 2-phenylimino-1,3-dithiolanes, respectively:[119]



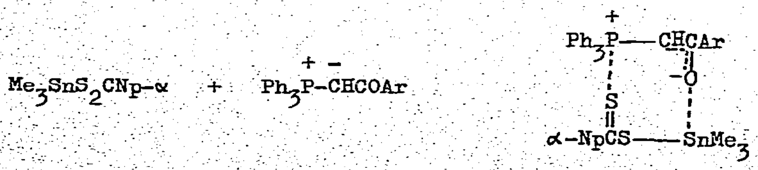
Ishii et al. have synthesised di- and triphenyltin esters of dithiocarboxylic acids from the phenyltin chloride and the piperidinium dithiocarboxylate. The products are crystalline, and are unreactive towards methanol, but with primary or secondary amines, however, the organotin sulphide, thioamides, and amine salts, or their decomposition products (thioamide and hydrogen sulphide) were produced:



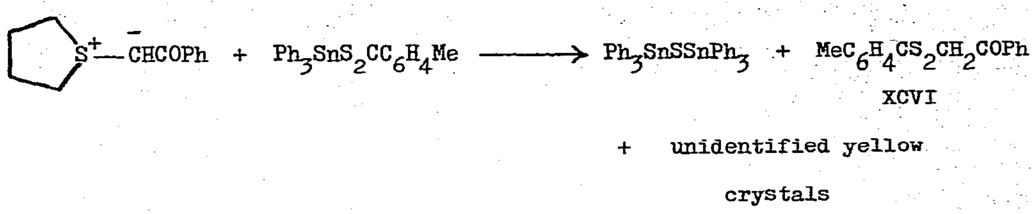




Phenacylidenetriphenylphosphoranes did not react with Ph_3SnS_2CAr compounds, but with Me_3SnS_2CNp-α a monomeric 1:1 adduct was obtained:



Treatment of $Ph_3SnS_2CC_6H_4Me$ with phenacylidene-tetramethylene sulphurane afforded XCVI:



Sodium methoxide displaced the thiobenzoate group:[179]

$$Ph_3SnS_2CC_6H_4Me + Na^+\ {}^-OMe \longrightarrow Ph_3SnOMe + Na^+\ {}^-S_2CC_6H_4Me$$

Diphenyltin bis(N,N'-diethyldithiocarbamate) possesses a distorted cis octahedral geometry (Fig. 15). The angle subtended at the tin atom by

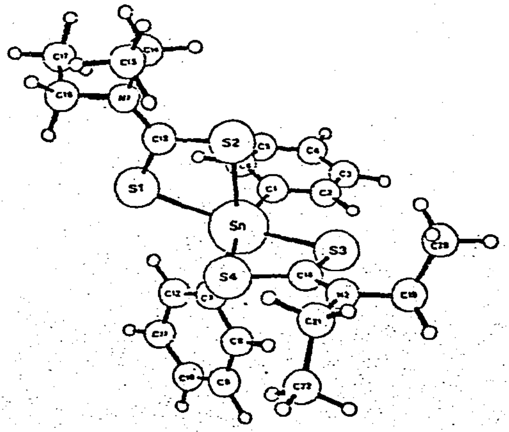
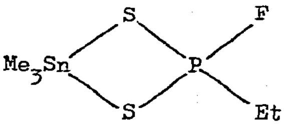


Fig. 15. The molecular structure of $Ph_2Sn(S_2CNEt_2)_2$. (Reproduced with permission from J. Mol. Cryst. Struct.).

the groups is 101.4(6)°, with the two Sn-C bond distances equal (2.176(17)Å). The Sn-S bond distances of one ligand are approximately equal (2.613(5) and 2.637(5)Å), but differ significantly in the other (2.548(5) and 2.790(6)Å)[180].

Tetramethyltin undergoes Sn-C bond cleavage with HSP(S)FEt giving monomeric $Me_3SnSP(S)FEt$ for which nmr data suggest the five-coordinate structure XCVII[181].



XCVII

Petridis and Fitzsimmons have synthesised anionic diorganotin and triorganotin complexes of the sulphur ligands $(CN)_2C_2S_2^{2-}$ (MNT) and $CN(CO_2Et)C_2S_2^-$ (CED), $[R_2Sn(MNT)_2]^{2-}$, $[R_2Sn(CED)_2]^{2-}$ and $[R_3Sn(MNT)]^-$ (R = Me, Bu, Ph). From Mössbauer data, it was deduced that the $[R_2Sn(MNT)_2]^{2-}$ (R = Me, Bu, Ph) and $[Bu_2Sn(CED)_2]^{2-}$ complexes possess distorted octahedral structures with chelating ligands and CSnC bond angles of *ca.* 130°. The $[Ph_2Sn(MNT)_2]^{2-}$ anions, however, appear to have four-coordinate tin atoms[182]. A similar Mössbauer study of organotin-MNT complexes has also been carried out by Allen and Brown[183]. The neutral species R_2SnMNT (R = Me, Ph) are polymeric. The MNT ligand is unidentate in R_3SnMNT^- anions, but bidentate, leading to five-coordinate tin atoms, in the $[R_2Sn(MNT)X]^-$ (R = Me; X = Cl, Br, I: R = Ph; X = Cl) anions. A *cis* octahedral structure was also assigned to the $[R_2Sn(MNT)_2]^{2-}$ (R = Me, Ph) anions, in agreement with the observations of Petridis and Fitzsimmons.

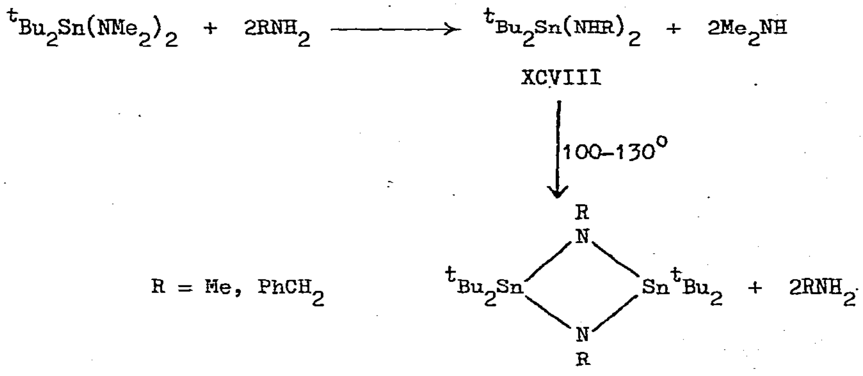
9. NITROGEN AND PHOSPORUS DERIVATIVES.

Solvolysis of $^tBu_3SnPh$ in liquid ammonia in the presence of KNH_2 affords the primary stannylamine XCVII as a moisture-sensitive liquid:

$$ {}^{t}\mathrm{Bu_3SnPh} + \mathrm{NH_3} \xrightarrow{\mathrm{KNH_2/C_6H_6}} {}^{t}\mathrm{Bu_3SnNH_2} $$

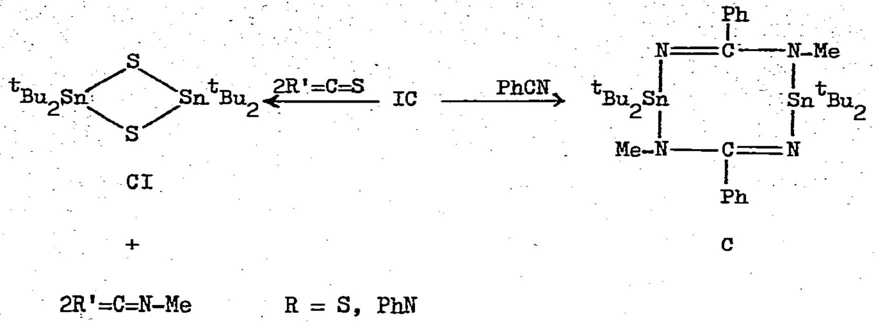
XCVII

${}^{t}\mathrm{Bu_3SnND_2}$ is similarly produced using $\mathrm{KND_2}$ in $\mathrm{ND_3}$. Both compounds form bis(tri-tert-butyltin) carbonate on reaction with wet carbon dioxide, but unlike other stannylamines, the Sn–N bond in XCVII is not cleaved by carbon tetrachloride[184]. Di-tert-butylstannylbis(dimethylamine) reacts with an excess of methyl- or benzylamine to give the stannylamines XCVIII, which themselves condense at 100–130° with loss of alkylamine to form the 1,3,2,4-diazadistannetidines IC as colourless crystals:



IC

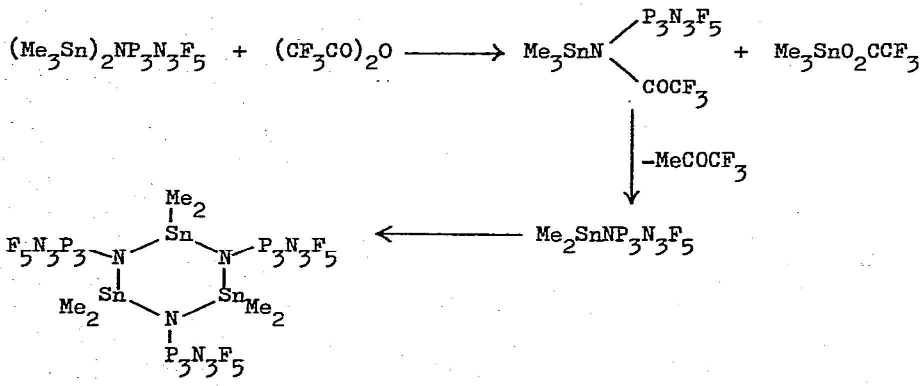
Reaction of IC with benzonitrile produces the eight-membered heterocycle C, but with sulphur-containing heterocumulenes such as $\mathrm{CS_2}$ or phenyl isothiocyanate, the cyclic dithiadistannane CI is formed:[185]



CI

C

The phosphonitrilic-substitued tristannazane CII has been obtained by the following route:[186]



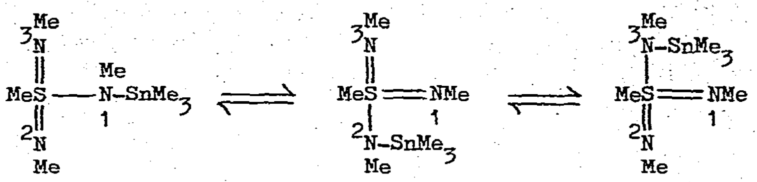
CII

Methanesulphonobis(methylimide)methylamidostannanes of the general composition $Me_nSn\left[NMeSMe(NMe)_2\right]_{4-n}$ (n = 0-3) CIII have been synthesised by transamination of the corresponding stannylamines with $MeS(NMe)_2NHMe$:

$$Me_nSn(NMe_2)_{4-n} + (4-n)MeS(NMe)_2NHMe \longrightarrow Me_nSn\left[NMeSMe(NMe)_2\right]_{4-n}$$

CIII

The same compounds can also be synthesised by substitution using $MeS(NMe)_2\bar{N}MeNa^+$. Proton nmr spectra indicate the occurrence of intramolecular exchange processes in solution such as:[187]



The trimethyltin derivative of 7,7,8,8-tetracyanoquinodimethane, $Me_3SnTCNQ$, has been obtained from Me_3SnCl and $Li^+(TCNQ)^-$ in water as an intense blue, air-stable solid with five-coordinated tin atoms[188]. The preparation of trialkyltin triazole derivatives from $R_3SnOSnR_3$ ($R = C_6H_{11}$, Bu, ^{i}Pr, ^{t}Bu, C_5H_9) and 1,2,4-triazole has been reported in a patent[189].

The crystal structure of $Me_3SnNMeNO_2$ consists of planar Me_3Sn groups linked by planar N-nitromethylamine groups (Fig. 16) (Sn-C = 2.16(7)Å, Sn-N = 2.33(4)Å, Sn-O = 2.36(5)Å)[190].

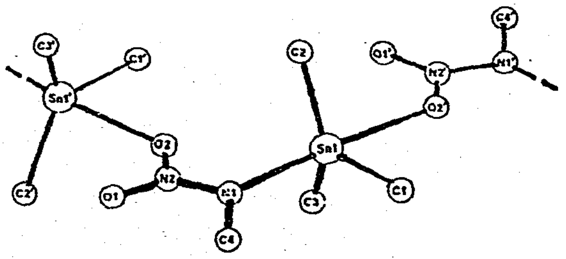


Fig. 16. The repeat unit of the chains of $[Me_3SnNMeNO_2]$.

Tris(trimethylstannyl)amine reacts with the methylchlorosilanes $Me_{4-n}SiCl_n$ (n = 1-4) to afford mixed stannylsilylamines CIV:

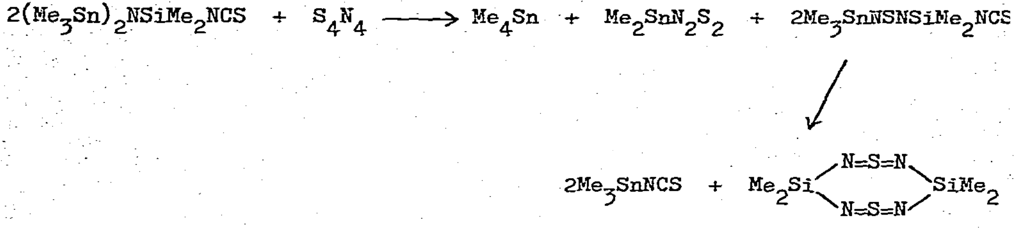
$$(Me_3Sn)_3N + Me_{4-n}SiCl_n \longrightarrow (Me_3Sn)_2NSiMe_{4-n}Cl_{n-1}$$

CIV (n = 1-4)

The complexes CIV (n = 2, 3) react with AgNCO and AgNCS to give the corresponding pseudohalide derivatives. With S_4N_4, $(Me_3Sn)_3N$ gives the distannylsulphodiimide, $Me_3SnNSNSnMe_3$, which is also produced, together with $Me_3SnNSNSiMe_3$, from the reaction of CIV (n = 1) with S_4N_4:

$$2(Me_3Sn)_2NSiMe_3 + S_4N_4 \longrightarrow Me_3SnNSNSnMe_3 + S + 2Me_3SnNSNSiMe_3$$

$(Me_3Sn)_2NSiMe_2NCS$ also reacts with S_4N_4:[191]



Lehnig[303] has studied the mechanism of the photochemical decomposition of Me_3SnNEt_2 using CIDNP. The following reaction scheme was proposed:

$$\begin{tikzcd}
 & & Me_3SnH + Me\text{–}CH{=}NEt \\
Me_3SnNEt_2 \arrow[r] & \overline{Me_3Sn\cdot \quad \cdot NEt_2}^{\,s} \arrow[ur] \arrow[dr] & \\
 & & Me_3Sn\cdot + Et_2N\cdot
\end{tikzcd}$$

$$Me_3SnH + Me_3SnNEt_2 \longrightarrow Me_3SnSnMe_3 + Et_2NH$$

$$2Me_3Sn\cdot \longrightarrow Me_3SnSnMe_3$$

$$2Et_2N\cdot \longrightarrow MeCH{=}NEt + Et_2NH$$

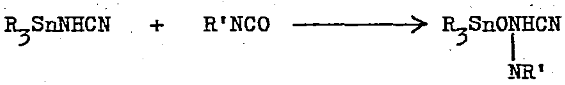
$$Me_3Sn\cdot + Et_2N\cdot \longrightarrow Me_3SnH + MeCH{=}NEt$$

giving the overall reaction:

$$2Me_3SnNEt_2 \xrightarrow{h\nu} Me_3SnSnMe_3 + Et_2NH + MeCH{=}NEt$$

The addition of excess tert-butyl chloride to the system greatly suppresses the formation of $Me_3SnSnMe_3$, and instead Me_3SnCl is formed.

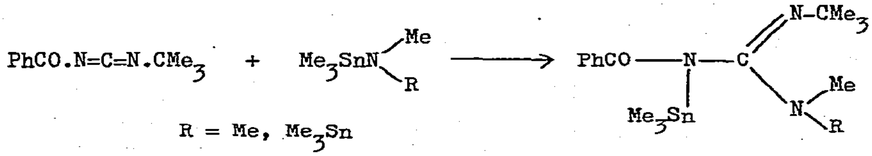
The expected insertion products CV are obtained from the reaction of triorganotin cyanamides with isocyanates:[192]



$$R_3SnNHCN + R'NCO \longrightarrow R_3SnO\underset{\displaystyle NR'}{\underset{|}{C}}NHCN$$

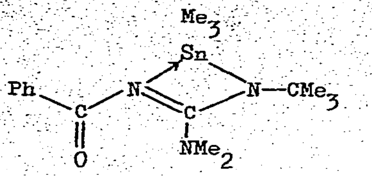
CV

Ishii has described the reactions of benzoyl-tert-butylcarbodiimide with Me_3SnNMe_2 and $(Me_3Sn)_2NMe$[193]. 1:1 Adducts are obtained from an exothermic reaction at room temperature:

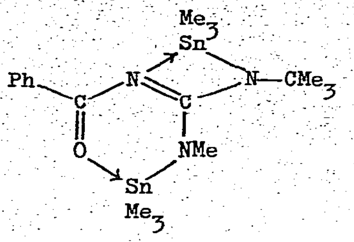


CVI

Spectroscopic and molecular weight data suggest the intramolecularly coordinated structures CVII and CVIII for the two compounds, although proton nmr spectra indicate that Me_3Sn group exchange occurs with CVIII at >50°[193].



CVII



CVIII

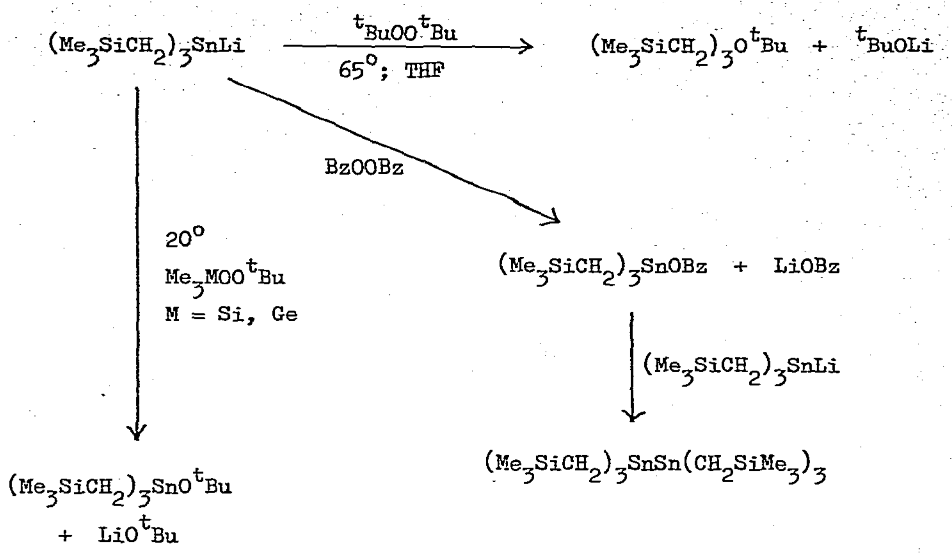
10. TIN-MAIN GROUP METAL BONDED DERIVATIVES.

Weibel and Oliver have shown that in solutions of $LiSnMe_3$ and $KSnMe_3$ an equilibrium exists between contact and solvent-separated ion pairs of these species. HMPA strongly solvates the alkali metal ion, and shifts the equilibrium:

$$M,SnMe_3 \rightleftharpoons M \,||\, SnMe_3$$

strongly to the right. Decreasing solvating ability is shown by DME and bis(β-ethoxyethyl)ether, until with THF the equilibrium is strongly displaced to the left. The addition of two moles of HMPA to a THF solution of $LiSnMe_3$ causes a displacement of the equilibrium to the right. A lowering in temperature also results in a shift to the right. No attack of the solvent by Me_3SnLi was observed, but on heating the compound rearranges to Me_4Sn and $LiSn(SnMe_3)_3$, a process which is aided by added HMPA[195]. The same authors have reported proton nmr data for the species $Li\left[Me_3SnMMe_3\right]$ (M = Al, Ga, In, Tl) and $Li\left[(Me_3Sn)_nTlMe_{4-n}\right]$. The presence of tin-metal bonds in these complexes was confirmed by the observation of tin-across-metal coupling, and for the thallium derivatives by the additional observation of thallium-across-tin coupling[201].

Vyanzankin et al.[196] have investigated the reactions of tris(trimethylsilylmethyl)stannyllithium with peroxy compounds. Lithium and tris(trimethylsilyl)stannyl *tert*-butoxides or benzoates were obtained:



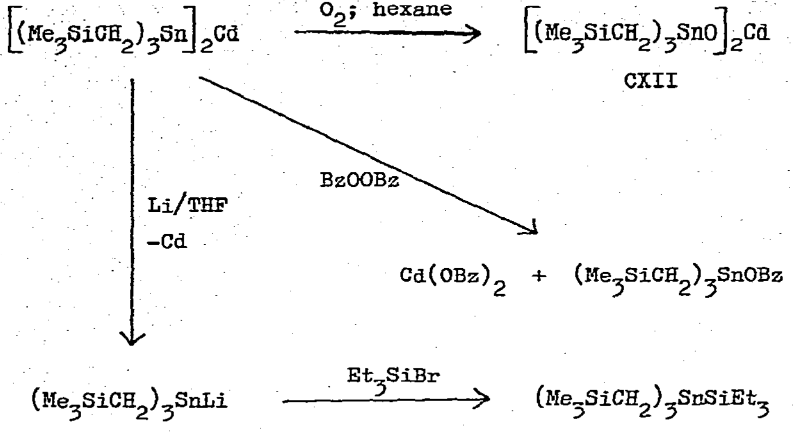
Thermally-stable stannylmercury and stannylcadmium compounds have been obtained by hydrostannolysis:[197,198]

$$2(Me_3SiCH_2)_3SnH \quad + \quad Et_2Cd \xrightarrow{-2C_2H_6} \underset{\text{CX}}{\left[(Me_3SiCH_2)_3Sn\right]_2Cd}$$

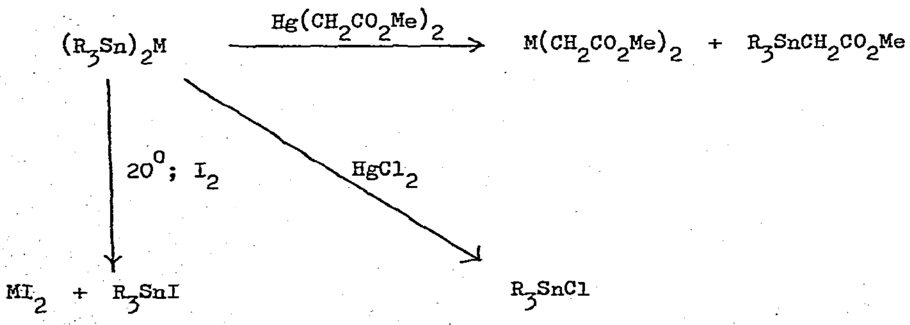
$$\underset{M\,=\,\text{Cd, Hg}}{2(Me_3CCH_2)_3SnH \quad + \quad Et_2M} \xrightarrow[-2C_2H_6]{2\text{hr}/20^\circ} \underset{\text{CXI}}{\left[(Me_3CCH_2)_3Sn\right]_2 M}$$

The derivatives CX and CXI are very reactive. CX is readily oxidised by molecular oxygen in hexane solution to the stannyloxycadmium compound CXII, and with benzoyl peroxide to give the organotin and cadmium benzoates.

Lithium metal displaces cadmium forming $(Me_3SiCH_2)_3SnLi$.

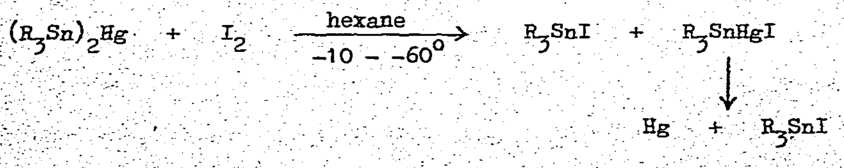


Both CX and CXI are oxidised by iodine and mercury(II) compounds:



$R = Me_3SiCH_2,\ Me_3CCH_2;\quad M = Cd,\ Hg$

When the reaction of CXI (M = Hg) with iodine in a 1:1 molar ratio is carried out at temperatures of -10 - -60° in hexane, mercury (97%) and triorganotin iodide (81%) are produced:



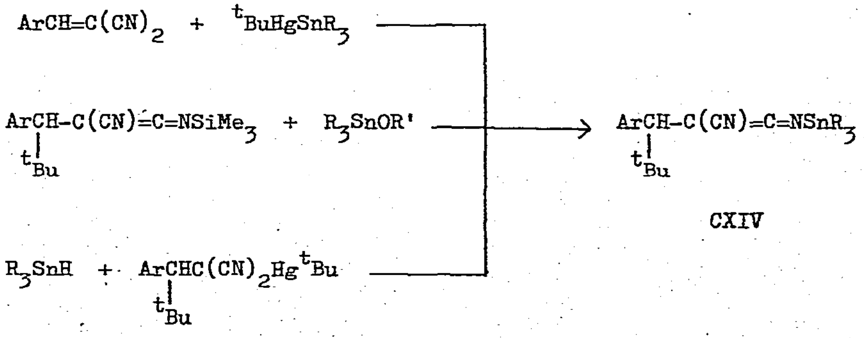
Mitchell has synthesised stannylmercury compounds of the type $RHgSnR'_3$ by the exchange of triorganotin methoxide with the corresponding silylmercurials:

$$RHgSiMe_3 + R'_3SnOMe \longrightarrow \underset{\text{CXIII}}{RHgSnR'_3} + Me_3SiOMe$$

$R' = Et$; $R = Et, Pr, Bu, {}^tBu$

$R = {}^tBu$; $R' = Bu, {}^iBu, Me$

When $R = R' = Me$ or $R = Et$, $R' = Me$, the desired product CXIII is unstable, and mercury and Me_4Sn or Me_3EtSn are produced. The observation of CIDNP signals in the nmr during thermolysis for the ${}^tBuHgSnR'_3$ compounds indicates homolytic cleavage of the C–Hg bond. Photolysis of CXIII also involves free-radical intermediates[199]. The reaction between ${}^tBuHgSnR_3$ and benzylidenemalononitrile leads to the formation of *N*-trialkylstannylketeneimines CXIV:



CXIV

The same compounds may also be obtained from the corresponding silylketeneimine and triorganotin alkoxide or from triorganotin hydride and the adduct between benzylidedmalononitrile and ${}^tBu_2Hg$[200]. Irradiation of toluene solutions of $(C_6F_5)_3SnBr$ and bis(triethylgermyl)mercury or $Et_3GeHgGe(C_6F_5)_3$

leads to the formation of bis(tripentafluorophenylstannyl)mercury CXV and the mixed stannylgermylmercurial CXVI:

$$2(C_6F_5)_3SnBr + (Et_3Ge)_2Hg \xrightarrow{h\nu} 2Et_3GeBr + \underset{\text{CXV}}{\left[(C_6F_5)_3Sn\right]_2Hg}$$

$$(C_6F_5)_3SnBr + Et_3GeHgGe(C_6F_5)_3 \xrightarrow{h\nu} Et_3GeBr + \underset{\text{CXVI}}{(C_6F_5)_3SnHgGe(C_6F_5)_3}$$

Without arradiation, mercury and the ditin compound are formed:

$$2(C_6F_5)_3SnBr + (Et_3Ge)_2Hg \xrightarrow{20^{\circ}} 2Et_3GeBr + Hg + (C_6F_5)_6Sn_2$$

CXV shows the usual reactions of this type of compound, eg:

$$\begin{matrix} 2(C_6F_5)_3SnCl \\ + \\ 2Hg \end{matrix} \xrightarrow[THF]{HgCl_2} \underset{\text{CXV}}{\left[(C_6F_5)_3Sn\right]_2Hg} \xrightarrow[50^{\circ}]{BzOOBz} \begin{matrix} 2(C_6F_5)_3SnOBz \\ + \\ Hg \end{matrix}$$

The tripentafluorophenyltin alkoxides $(C_6F_5)_3SnOR$, formed by exchange condense with triethyltin hydride to give the mixed distannane CXVI, which itself exchanges with $(C_6F_5)_3SnBr$ forming the symmetrical distannane CXVII:

$$\begin{tikzcd}
(C_6F_5)_3SnBr + Et_3SnOR \arrow[r, "100^{\circ}"] & Et_3SnBr + (C_6F_5)_3SnOR \arrow[d, "50^{\circ}"', "\begin{matrix} Et_3SnH \\ -MeOH \end{matrix}"] \\
\underset{\text{CXVII}}{Et_3SnBr + (C_6F_5)_3SnSn(C_6F_5)_3} & \underset{\text{CXVI}}{Et_3SnSn(C_6F_5)_3} \arrow[l, "(C_6F_5)_3SnBr"', "100^{\circ}"]
\end{tikzcd}$$

R = Me, Et

Hexaethyldistannanereacts much more slowly with $(C_6F_5)_3SnBr$ producing Et_3SnBr, CXVI and CXVII:[202]

$$\begin{tikzcd} Et_6Sn_2 + (C_6F_5)_3Br \arrow[r, "100^\circ"] & Et_3SnBr + Et_3SnSn(C_6F_5)_3 \arrow[d, "(C_6F_5)_3SnBr"] \\ & Et_3SnBr + (C_6F_5)_6Sn_2 \end{tikzcd}$$

Germanium-tin bonded derivatives may also be obtained by hydrostannolysis:[203]

$$(C_6F_5)_3GeH + Et_3SnNEt_2 \xrightarrow{100^\circ} (C_6F_5)_3GeSnEt_3 + Et_2NH$$

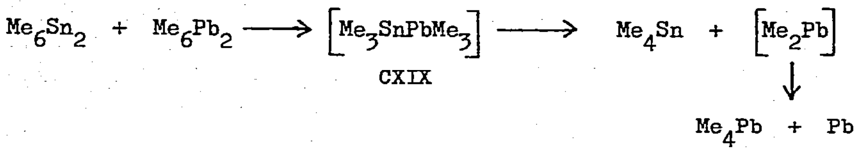
$$(C_6F_5)_2GeH_2 + 2Et_3SnNEt_2 \xrightarrow{100^\circ} Et_3SnGe(C_6F_5)_2SnEt_3 + 2Et_2NH$$

Triphenylstannyl and tributylstannyl radicals generated photochemically from the corresponding hexaorganodistannanes abstract halogen atoms from alkyl halides. The fate of the resulting alkyl radicals depends largely on the nature and concentration of the hydrogen atom donors present in the system[204]. Mixtures of symmetrical hexaorganodistannanes rapidly equilibriate in HMPT to afford the mixed distannanes CXVIII as distillable oils:

$$R_3SnSnR_3 + R'_3SnSnR'_3 \rightleftharpoons \underset{\text{CXVIII}}{2R_3SnSnR'_3}$$

$R = Me; R' = Et, Pr, Bu, {}^iBu$

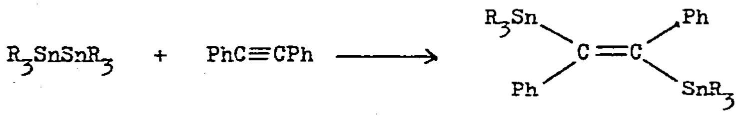
With the Me_6Sn_2/Me_6Pb_2 system in THF (with 5% MeMgBr as catalyst) only the decomposition of Me_6Pb_2 into Me_4Pb and lead was observed. In HMPT and without a catalyst, however, equimolecular amounts of Me_6Sn_2 and Me_4Sn, together with Me_4Pb and lead, resulting from the decomposition of the intermediately formed stannaplumbane CXIX:



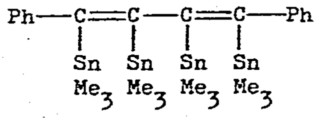
$$Me_6Sn_2 + Me_6Pb_2 \longrightarrow \underset{\text{CXIX}}{[Me_3SnPbMe_3]} \longrightarrow Me_4Sn + [Me_2Pb]$$

$$[Me_2Pb] \longrightarrow Me_4Pb + Pb$$

Hexaalkyldistannanes react readily under polar conditions with C≡C triple bonds and N=N double bonds. Hexamethyl- and hexaethylditin with diphenylacetylene in HMPT with 5 mole % NaOMe catalyst affords 70% of trans-1,2-bis(trimethylstannyl)-1,2-diphenylethylene:

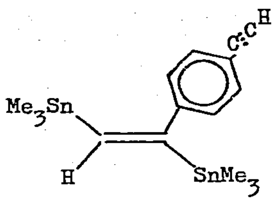


A trans-adduct was also obtained with phenylacetylene, but only a very small amount of reaction occurred with 1-hexyne. Diphenylbutadiyne reacts with Me_6Sn_2 in either a 1:1 or 1:2 molar ratio to give CXX.

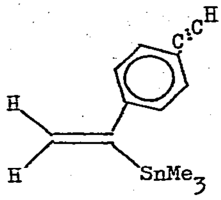


CXX

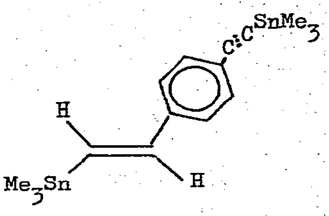
The reaction of Me_6Sn_2 with both para- and ortho-diethynylbenzene gave rather complex mixtures from which CXXI - CXXIII and CXXIV, respectively, were isolated.



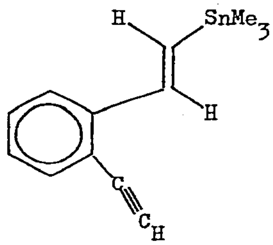
CXXI



CXXI

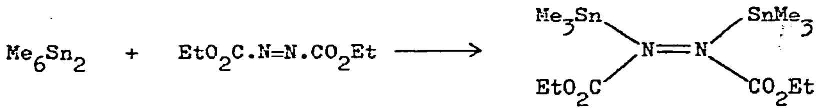


CXXIII



CXXIV

The reaction of $Me_3SnSnEt_3$ with PhC≡CPh affords all three possible adducts from both symmetrical distannanes as well as the unsymmetrical distannane. Hexamethylditin formed the addition product CXXV with diethyl azodicarboxylate:



CXXV

but no reaction was observed with C=C, C=O, or C=N double bonds, and only conversion to the isocyanurate occurred with phenyl isocyanate. Mechanisms involving stannyl Grignard reagents (MeMgBr catalysis) were proposed for the disproportionation and addition reactions[205]. Hexaalkyldistannanes are oxidised by tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) to the corresponding $R_3Sn(TCNE)$ and $R_3Sn(TCNQ)$ derivatives. With hexaphenyldistannane and TCNQ, a ($\sigma\rightarrow\pi$) charge transfer complex of composition

$(Ph_3Sn)_2(TCNQ)$ was obtained[206]. Peloso has investigated the kinetics of the oxidation of hexaorganodistannanes by tris(1,10-phenanthroline)iron(III) perchlorate[207] and substituted 1,10-phenanthroline, 2,2'-bipyridine, and 2,2',2"-terpyridine complexes of iron(III)[208]. In all the systems studied the tin-tin bond is cleaved with the concomitant reduction of two moles of iron(III) complex per mole of hexaorganodistannane. The reactions all obey a second-order rate law, being first-order with respect to both distannane and the iron(III) complex, and the reactivity increases in the order $Ph_6Sn_2 < Me_3SnSnPh_3 < Me_6Sn_2 < Bu_6Sn_2$. An outer-sphere redox mechanism involving two one-electron transfer steps was proposed, the initial electron transfer being the rate-determining step:

$$R_6Sn_2 \quad + \quad Fe^{III} \xrightarrow{slow} R_6Sn_2^{\cdot +} \quad + \quad Fe^{II}$$

$$R_6Sn_2^{\cdot +} \quad + \quad Fe^{III} \xrightarrow{fast} 2R_3Sn^{+} \quad + \quad Fe^{II}$$

$$R_6Sn_2^{\cdot +} \xrightarrow{fast} R_3Sn^{+} \quad + \quad R_3Sn^{\cdot}$$

$$R_3Sn^{\cdot} \quad + \quad Fe^{III} \xrightarrow{fast} R_3Sn^{+} \quad + \quad Fe^{II}$$

The reaction of diphenyltin dihydride with carboxylic acids, or triphenylsilane or triphenylgermane carboxylic acids, yields the 1,1,2,2-tetraphenyldicarboxylatodistannane derivatives CXXVI as monomeric species:[209]

$$2Ph_2SnH_2 \quad + \quad 2RCO_2H \longrightarrow \underset{\text{CXXVI}}{Ph_4Sn_2(O_2CR)_2}$$

R = Et, Pr, ^{i}Pr, ^{t}Bu, CH_2Ph,
$SiPh_3$, $GePh_3$

Tris(trimethylstannyl)stibine displaces carbon monoxide from nickel tetracarbonyl forming the complex CIX:[194]

$$Ni(CO)_4 + (Me_3Sn)_3Sb \xrightarrow{-CO;\ pentane} \underset{\text{CIX}}{(Me_3Sn)_3SbNi(CO)_3}$$

11. TIN-TRANSITION METAL BONDED DERIVATIVES.

The cycloheptatrienyldicarbonylmolybdenum-tin complexes $C_7H_7Mo(CO)_2SnPh_nX_{3-n}$ (X = Cl, Br; n = 0-3) have been synthesised by a number of methods:

$$C_7H_7Mo(CO)_2Br + LiSnPh_3 \longrightarrow C_7H_7Mo(CO)_2SnPh_3 + LiBr$$

$$\begin{tikzcd}
C_7H_7Mo(CO)_2SnPh_3 + HCl \arrow[r] & C_7H_7Mo(CO)_2SnPh_2Cl + C_6H_6 \arrow[d, "2HCl;\ -2C_6H_6"] \\
 & C_7H_7Mo(CO)_2SnCl_3
\end{tikzcd}$$

$$C_7H_7Mo(CO)_2SnCl_3 + Ph_2Hg \longrightarrow C_7H_7Mo(CO)_2SnPhCl_2 + PhHgCl\ .$$

The reaction of $\left[C_7H_7Mo(CO)_3\right]^+ BF_4^-$ with $NaSnPh_3$ does not lead to $C_7H_7Mo(CO)_2SnPh_3$, but rather hexaphenylditin is produced:[210]

$$\left[C_7H_7Mo(CO)_3\right]^+ BF_4^- + NaSnPh_3 \longrightarrow \left[C_7H_7Mo(CO)_3\right]_2 + NaBF_4 + Ph_6Sn_2$$

The reactions of Me_3SnCH_2I with $NaMo(CO)_3cp$, $NaFe(CO)_2cp$, $NaMn(CO)_5$, and $NaCo(CO)_4$ in THF do not lead to the $SnCH_2M$ derivatives. Instead, Sn-C bond cleavage takes place, and the corresponding $Me_3Sn\text{-}M(CO)_ncp_m$ complexes result[211]. HCl and HBr cleave organic groups from tin in trimethyltin, triphenyltin, and phenyl(pentafluorophenyl)tin-iron, -manganese, -chromium, -molybdenum, and -tungsten complexes. Reaction of the same complexes with chlorine, iodine, ICl, or CF_3I resulted in tin-transition metal bond cleavage, except in the case of Sn-Mn bonded complexes with chlorine where again only Sn-C bond cleavage occurred[212]. The complex $cpFe(CO)(CNMe)SnMe_3$ is formed from the base-catalysed reaction of Me_3SnCl with the hydride $cpFe(CO)(CNMe)H$. A mechanism involving a base-induced deprotonation of the hydride leading to the anion $[cpFe(CO)(CNMe)]^-$ was proposed[213]. The related complexes $(RMe_4C_5)Fe(CO)_2SnPh_3$ have been obtained by the reaction of the sodium salts $Na[(RMe_4C_5)Fe(CO)_2]$ with Ph_3SnCl[214]. Garner and Hughes have investigated the synthetic utility of divinyltin bis(trifluoroacetate) in the formation of tin-manganese, -iron, and -cobalt bonded derivatives. The reactions with $Na[Mn(CO)_5]$, $Na_2[Fe(CO)_4]$, and $Na[Co(CO)_4]$, afforded the complexes $(CH_2{=}CH)_2Sn(O_2CCF_3)[Mn(CO)_5]$, $(CH_2{=}CH)_2Sn[Mn(CO)_5]_2$, $\{(CH_2{=}CH)_2Sn[Fe(CO)_4]\}_2$ and $(CH_2{=}CH)_2Sn[Co(CO)_4]_2$. The structure of $(CH_2{=}CH)_2Sn[Mn(CO)_5]_2$ has four-coordinated tin with the two $Mn(CO)_5$ groups in a pseudo-staggered conformation (Fig. 17)[149]. A second complex, $(CH_2{=}CH)_2Sn_2Fe_4(CO)_{16}$, was also isolated as a biproduct from the reaction with $Na_2[Fe(CO)_4]$. The structure CXXVII was proposed on the basis of spectrscopic data[215]

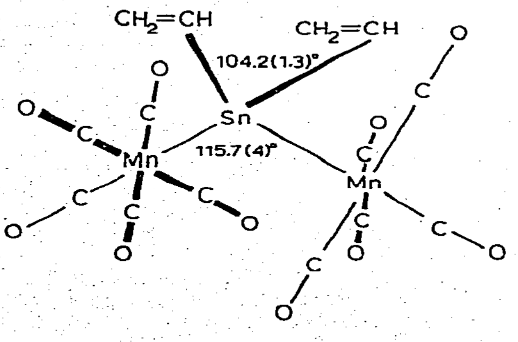
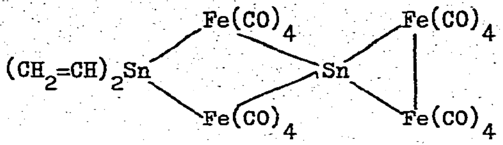


Fig. 17. The molecular structure of $(CH_2{=}CH)_2Sn[Mn(CO)_5]_2$. (Reproduced by permission of the Chemical Society).



CXXVII

Nesmeyanov et al. have studied the nucleophilic replacement of metal carbonyl groups in trphenyltin-transition metal carbonyl complexes Ph_3SnX by other carbonyl anions Y^- ($X \neq Y = Co(CO)_4$, $Mo(CO)_3cp$, $Mn(CO)_5$, $Re(CO)_5$, $Fe(CO)_2cp$)[216]. The reactivities of the phenylchlorotin-$Mn(CO)_5$ and $-Fe(CO)_2cp$ compounds, $Ph_{3-n}Cl_nSnM$ ($M = Mn(CO)_5$, $Fe(CO)_2cp$; $n = 1-3$) towards C_6F_5Li depend on M and the number of phenyl groups attached to tin[217]. Tin(II) chloride inserts into the Fe-C bond of $cpFe(CO)_2R$ (R = substituted allyl) to afford the products $cpFe(CO)_2SnCl_2R$[229].

In diethylether ditin compounds react rapidly with $Co_2(CO)_8$ to give the tin-cobalt compounds CXXVIII as the sole product:

$$X_3SnSnX_3 \quad + \quad Co_2(CO)_8 \xrightarrow{Et_2O} 2X_3SnCo(CO)_8$$

CXXVIII

$$X_3Sn \;=\; Me_3Sn,\ Et_3Sn,\ Et_2ClSn$$

but in THF, Me_6Sn_2 and $Co_2(CO)_8$ give, besides CXXVIII (X = Me), substantial amounts of Me_4Sn and $Me_2Sn\left[Co(CO)_4\right]_2$:

$$\begin{aligned} Me_6Sn_2 + Co_2(CO)_8 \xrightarrow{THF} 1.0Me_3SnCo(CO)_4 &+ 0.5Me_4Sn \\ &+ 0.3Me_2Sn\left[Co(CO)_4\right]_2 \end{aligned}$$

These additional reaction products do not arise from a disproportionation of CXXVIII (X = Me). With a catalytic amount of $Co_2(CO)_8$ in THF, less than 10% of CXXVIII (X = Me), Me_4Sn(90%) and a brown insoluble solid are produced from Me_6Sn_2.

$$Me_6Sn_2 \xrightarrow[THF]{0.1Co_2(CO)_8} Me_4Sn + \left[Me_2Sn\right] \longrightarrow \text{brown insoluble solid}$$

The extent of this catalysis disproportionation decreases with the polarity of the solvent, and no reaction at all is observed in benzene or pentane. careful bromination of the brown product afforded Me_3SnBr, Me_2SnBr_2 and $MeSnBr_3$, indicating that the dimethylstannylene polymerises during the reaction to a polytin product with a branched structure. The following mechanism, involving nucleophilic attack of $Co(CO)^-$ on $Me_3SnSnMe_3$ as the rate-determining step:

$$Co_2(CO)_8 + THF \longrightarrow Co(CO)_4^+.THF + Co(CO)_4^-$$

$$Co(CO)_4^+.THF + Me_6Sn_2 + Co(CO)_4^- \longrightarrow Me_3SnSnMe_2Co(CO)_4 + MeCo(CO)_4 + THF$$

$$Me_3SnSnMe_2Co(CO)_4 \longrightarrow Me_3SnCo(CO)_4 + \left[Me_2Sn\right]$$

$$Me_3SnCo(CO)_4 + MeCo(CO)_4 \xrightarrow{THF} Me_4Sn + Co(CO)_4^+.THF + Co(CO)_4^-$$

$Mn_2(CO)_{10}$ is also an effective catalyst for the disproportionation of Me_6Sn_2, but less so than $Co_2(CO)_8$[218]. Trimethyltin hydride reacts exothermically with $Co_2(CO)_8$ at 20° to give $Me_3SnCo(CO)_4$ in high yield. The corresponding silyl and germyl complexes may also be converted to $Me_3SnCo(CO)_4$ by reaction with Me_3SnH[219].

The unit cell of $\left[Me_2SnCo(CO)cp\right]_2$ contains two crystallographically independent, but almost geometrically identical, molecules. Each is characterised by a four-membered Sn_2Co_2 $\left[SnCoSn = 78.0(1)^\circ;\ CoSnCo = 101.8(1)^\circ;\ Sn\text{-}Co = 2.542(2)Å\right]$. The tin atoms have slightly distorted tetrahedral geometry $\left[Sn\text{-}C = 2.20(1)Å\right]$ (Fig. 18)[220].

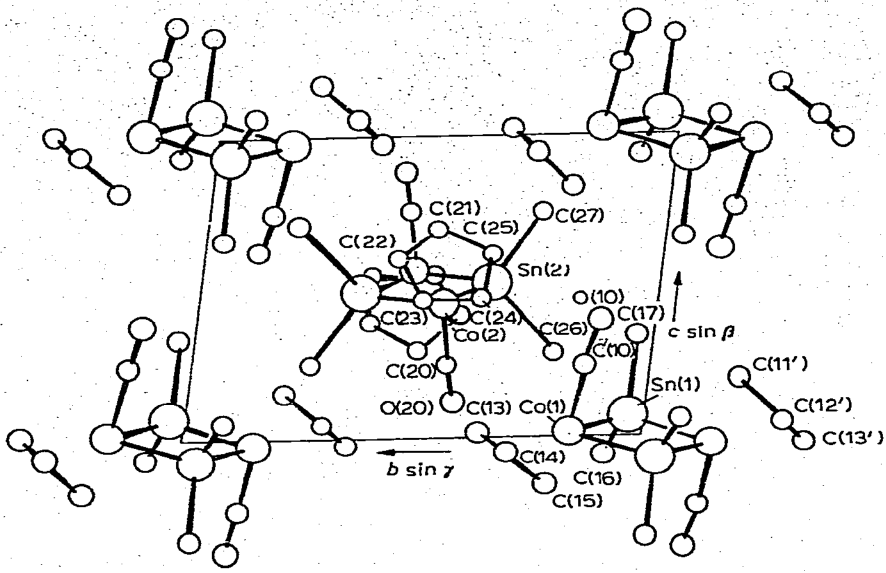


Fig. 18. The contents of the unit cell of $\left[cp(CO)CoSnMe_2\right]_2$ seen in projection along a. (Reproduced by permission of the Chemical Society).

Collman *et al.* have investigated the chemistry of some organotin complexes of tetracarbonylosmium[221]. Bis(triorganotin)osmium tetracarbonyl derivatives CXXIX are obtained in high yield from $Na_2Os(CO)_4$:

$$Os_3(CO)_{12} \xrightarrow{Na/liq.\ NH_3} Na_2Os(CO)_4 \xrightarrow{R_3SnX} \underline{trans}\text{-}(R_3Sn)_2Os(CO)_4$$

CXXIX

$R = Bu,\ Ph;\ \ R_3Sn = PhBu_2Sn$

The *trans* geometry for the osmium atom indicated by infra-red and Raman spectra, was confirmed for the triphenyltin compound by an X-ray diffraction study (Fig. 19). The Sn-Os bond distance is 2.71Å.

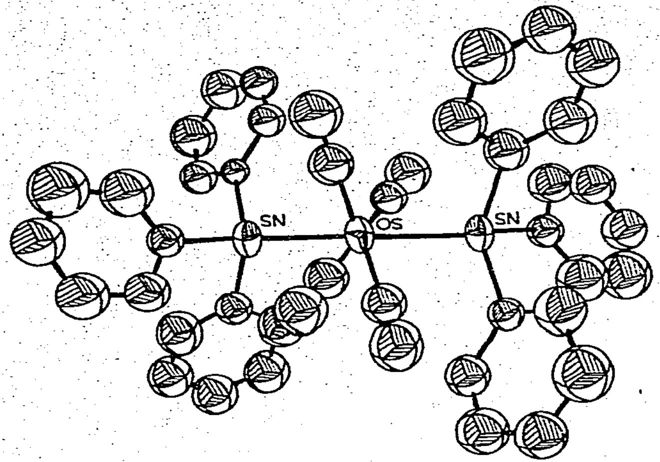


Fig. 19. The molecular structure of *trans*-$(Ph_3Sn)_2Os(CO)_4$. (Reproduced by permission of the American Chemical Society).

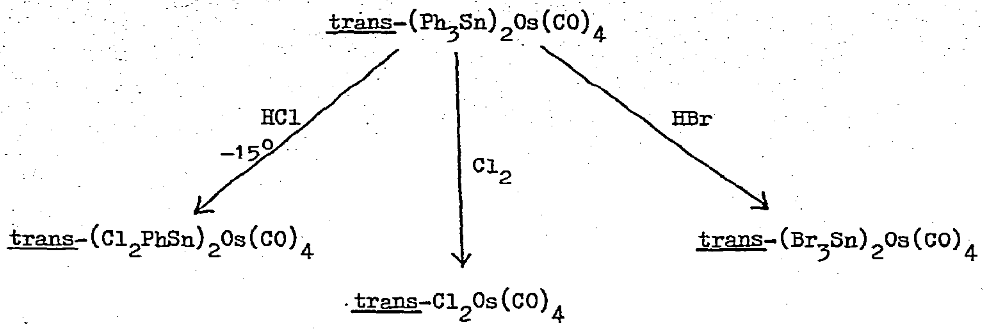
The same complexes may also be prepared from the dihydride $H_2Os(CO)_4$:

$$\begin{tikzcd} Na_2Os(CO)_4 \arrow[r, "H_3PO_4"] & H_2Os(CO)_4 \arrow[r, "B"] & (BH^+)\left[HOs(CO)_4\right]^- \arrow[rd, "Ph_3SnCl"] & \\ & & & (Ph_3Sn)_2Os(CO)_4 \end{tikzcd}$$

$$H_2Os(CO)_4 \quad + \quad 2R_3SnE \longrightarrow (R_3Sn)_2Os(CO)_4 \quad + \quad 2EH$$

$$E = \tfrac{1}{2}O.\ OR,\ NR_2$$

Treatment of the complexes CXXIX with hydrogen halides results in Sn-C bond cleavage; but chlorine causes Sn-Os bond fission:



$$\underline{trans}\text{-}(PhBu_2Sn)_2Os(CO)_4 \xrightarrow{HCl} \underline{trans}\text{-}(ClBu_2Sn)_2Os(CO)_4$$

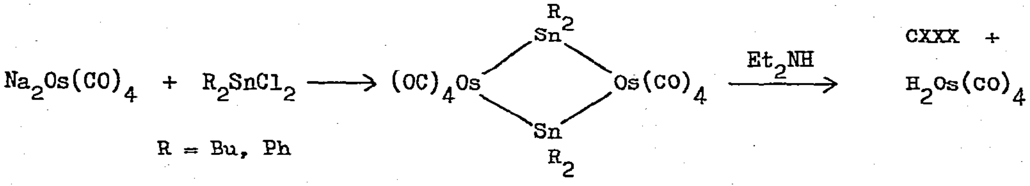
CXXX

Reaction of CXXX with $HRe(CO)_5$ affords CXXXI with the Re–Sn–Os–Sn–Re skeleton:

$$2HRe(CO)_5 \quad + \quad CXXX \xrightarrow{Et_2NH} \left[(OC)_5ReSnBu_2\right]_2OsOs(CO)_4$$

CXXXI

Cyclic Sn_2Os_2 ring systems are produced from R_2SnCl_2 with $Na_2Os(CO)_4$ and also from treatment of CXXXI with $H_2Os(CO)_4$ in the presence of base:[221]

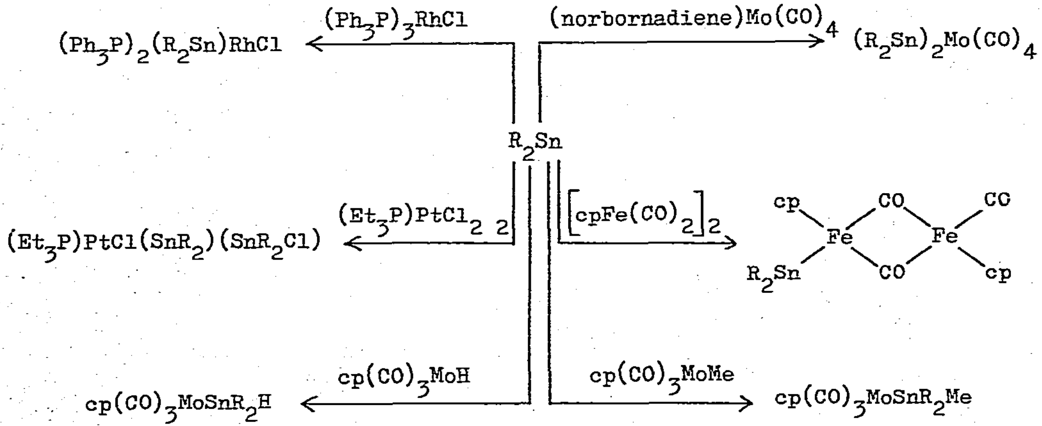


Trimethyltin hydride displaces alkane from $PtR_2\left[(Ph_2P)_2CH_2\right]$ (R = Me, Et) at room temperature, or at 50° when R = Ph. The $\underline{d}^6$ product $PtH(SnMe_3)_3\left[(Ph_2P)_2CH_2\right]$, dissociates reversibly in solution to $Pt(SnMe_3)_2\left[(Ph_2P)_2CH_2\right]$. Reaction of the analogous lead complex with Me_3SnH gives $PtH(SnMe_3)_3\left[(Ph_2P)_2CH_2\right]$ and Ph_6Pb_2. With $PtCl_2\left[(Ph_2P)_2CH_2\right]$

Me_3SnH yields the complex $PtCl(SnMe_3)_2[(Ph_2P)_2CH_2]$ which also dissociates in solution to $PtCl(SnMe_3)[(Ph_2P)_2CH_2]$. Oxidative-addition of Me_3SnH to $Pt[(Ph_2P)_2CH_2]_2$ similarly produces $Pt(SnMe_3)_2[(Ph_2P)_2CH_2]$[301].

12. DIVALENT ORGANOTIN DERIVATIVES.

Lappert, Thomas *et al.* have described the interaction of di[bis(trimethylsilyl)methyl]tin with some transition metal carbonyl and chloride complexes. The stannylene is a good nucleophile, and is able to displace CO or R_3P and cleaves the chloride bridges of the binuclear Pt^{II} complex $[(Et_3P)PtCl_2]_2$. The reactions are summarised in Scheme 1. The



R = $(Me_3Si)_2CH$

crystal structure of the pentacarbonylchromium complex of the stannylene has been determined, and is shown in Fig. 20. The tin enjoys trigonal coordination, with the two carbon atoms and the chromium atom bound to the tin, all four atoms being coplanar (sum of the angles at tin = 360°). The Sn-C bonds are not unusual (2.18, 2.19Å), but the Sn-Cr bond distance (2.562(5)Å) is considerably shorter than in the related complex $(py)^tBu_2SnCr(CO)_5$ (2.654(3)Å)[222]. $[(Me_3Si)_2CH]_2Sn$ reacts with diiron

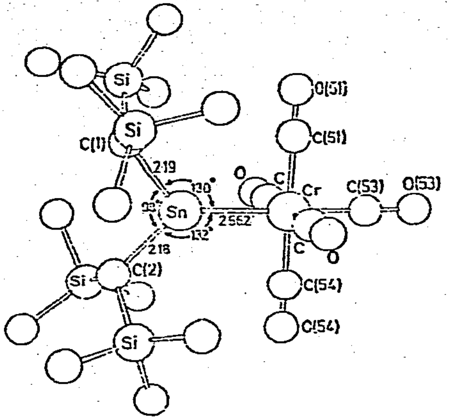
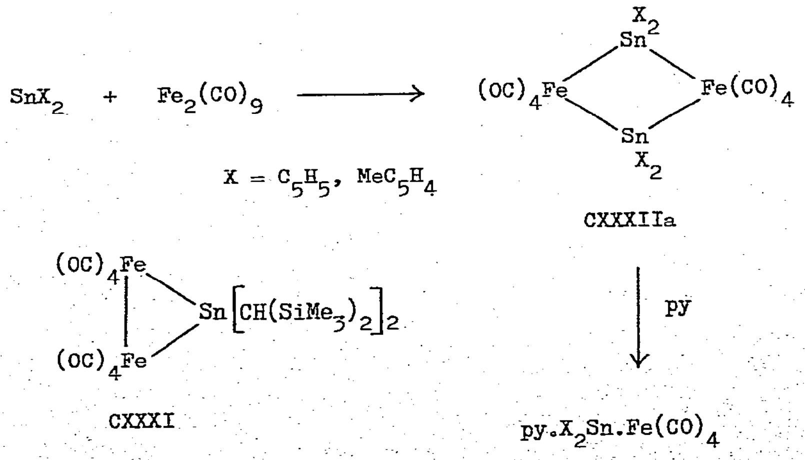


Fig. 20. The molecular structure of $\left[(Me_3Si)_2CH\right]_2SnCr(CO)_5$. (Reproduced by permission of the Chemical Society).

nonacarbonyl to give the complex CXXXI[222], but bis(cyclopentadienyl)tin compounds react to afford the cyclic dimers CXXXIIa, which undergo Sn–Fe bond cleavage in pyridine giving the monomeric species CXXXIIb:



$X = C_5H_5, MeC_5H_4$

CXXXIIa

CXXXI

CXXXIIb

The reaction of SnX_2 ($X = C_5H_5$, MeC_5H_4) with $Cr(CO)_6$ does not proceed thermally, but photolysis of SnX_2 with $M(CO)_6$ (M = Cr, Mo, W) in THF produces the complexes $X_2SnM(CO)_5$ [223,224]. Complexes of $Sn(C_5H_5)_2$ and $Sn(C_5H_4Me)_2$ with Group III trihalides have also been reported briefly[224]. Bis(methylcyclopentsdienyl)tin forms the charge transfer complexes $(MeC_5H_4)_2Sn.nTCNE$ (n = 1, 2) with tetracyanoethylene[188]. Dicyclopentadienyltin and bis[*N*,*N*-bis(trimethylsilyl)amino]tin are in equilibrium with the monocyclopentadienyltin amine CXXXIII, which is also formed from C_5H_5SnCl and $LiN(SiMe_3)_2$:[225]

$$\begin{tikzcd}
(C_5H_5)_2Sn + Sn[N(SiMe_3)_2]_2 \arrow[r, phantom, "\rightleftharpoons"] & C_5H_5SnN(SiMe_3)_2 \\
 & \text{CXXXIII} \\
 & C_5H_5SnCl + LiN(SiMe_3)_2 \arrow[u]
\end{tikzcd}$$

The reaction of $(C_5H_5)_2Sn$ with iodine is rather complex. C_5H_5SnI, $(C_5H_5)_3SnI$, and $C_5H_5SnI_3$, formed by exchange and oxidative-addition, have all been identified in the reaction mixture:

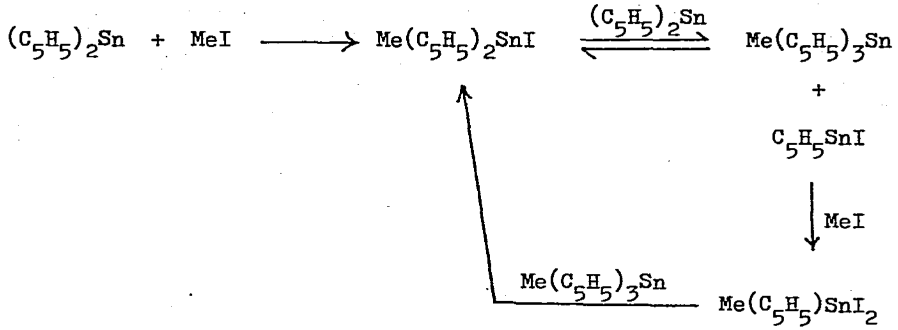
$$\begin{tikzcd}
(C_5H_5)_2Sn \arrow[r, "I_2"] & (C_5H_5)_2SnI_2 \arrow[r, "(C_5H_5)_2Sn"] & (C_5H_5)_3SnI + C_5H_5SnI \arrow[d, "I_2"] \\
 & & C_5H_5SnI_3 \arrow[ul, "(C_5H_5)_3SnI"']
\end{tikzcd}$$

Dicyclopentadienyltin also undergoes exchange with methyltin(IV) halides:

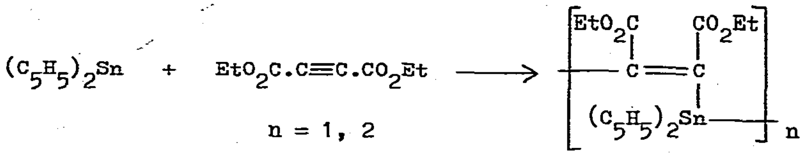
$$(C_5H_5)_2Sn + Me_2SnCl_2 \longrightarrow Me_2(C_5H_5)SnCl + C_5H_5SnCl$$

$$(C_5H_5)_2Sn \ + \ 2MeSnCl_3 \longrightarrow 2Me(C_5H_5)SnCl_2 \ + \ C_5H_5SnCl$$

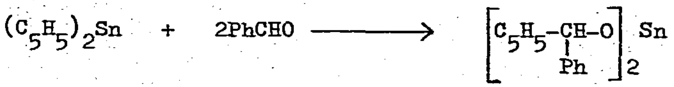
The reaction of $(C_5H_5)_2Sn$ with methyl iodide in benzene at room temperature in daylight initially gives rise to a precipitate of C_5H_5SnI, but ultimately only $Me(C_5H_5)_2SnI$ (> 90%) was prseent, suggesting the reaction scheme:



$(C_5H_5)_2Sn$ also undergoes oxidative-addition with diethylacetylene dicarboxylate to give a mixture of six- and nine-membered ring products.



With benzaldehyde, addition of the Sn-C bond across the C=O bond occurs:[226]



$$(C_5H_5)_2Sn \ + \ 2PhCHO \longrightarrow \left[C_5H_5\text{-}\underset{\displaystyle Ph}{\underset{|}{C}}H\text{-}O\right]_2 Sn$$

The cleavage of $(MeC_5H_4)_2Sn$ by β-diketones affords tin(II) bis(β-keto-enolates):[227]

$$(MeC_5H_4)_2Sn + R.CO.CH_2.CO.R' \longrightarrow Sn(OCR{:}CH.CO.R')_2$$

$$R, R' = Me, CF_3$$

Pentacarbonylmanganese hydride also cleaves cyclopentadienyl groups $(C_5H_5)_2Sn$ affording the unusual tin hydride $H_2Sn_2\left[Mn(CO)_5\right]_4$, the structure of which was confirmed by an X-ray diffraction study[228].

13. PHYSICAL AND SPECTROSCOPIC DATA.

In this Section are collected references to spectroscopic and physical data for compounds not previously referred to in the text.

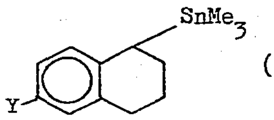
(i) Vibrational Spectra:

Data have been obtained for the following compounds: $Sn(C_3H_5)_4$ (IR and R)[232]; $Bu_{4-n}SnX_n$ (n = 1-3; X = F, Cl, Br, I) (IR)[233]; $Me_2SnCl_2.2DMSO$ (single crystal and solution Raman study)[234]; 1-oxa-2-stannacyclopentanes and 1-oxa-2-stannacyclopentenes (IR and R)[235,236]; Me_3SnS_2CMe (IR and R)[237]; $Me_3SnC{\equiv}CH$ (IR)[238]; meta- and para-substituted $ArCH_2SnMe_3$ derivatives (IR)[239]; $Me_2Sn(acac)_2$ (R)[258]; divinyltin compounds[260].

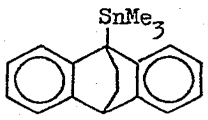
(ii) Nmr Data:

Reeves has used nmr to study the behaviour of the dimethyltin ion in lyotropic nematic phases[240]. Gielen has shown that methylneophylphenyltin hydride, (Methylneophylphenylstannyl)cyclopentadienyl molybdenum tin tricarbonyl, and $Me_2PhSnGeMePh\alpha$-Np are configurationally stable within the nmr time scale even in the presence of strong nucleophiles[254]. A theoretical interpretation of the ^{119}Sn nmr chemical shifts of methyltin amines, chlorides, methylthiolates, alkoxides, and hydrides, and hexamethylditin, has been presented[256].

Other data which is available includes the following: $Me_3SnC_9H_7$ (^{1}H and ^{13}C)[241]; *meta*- and *para*-substituted phenyltrimethylstannanes (^{1}H and ^{13}C)[242]; stannacycloalkanes (^{1}H)[243]; $PhSnCl_3$ and $MeC_6H_4SnCl_3$ (^{1}H and ^{13}C)[244]; neophyltin compounds (^{13}C)[245]; organotin cyclopentadienyl derivatives (^{119}Sn)[246]; trifluoromethylphenyltin compounds (^{119}Sn and ^{19}F)[247]; substituted phenyl-, benzyltrimethylstannanes (^{13}C)[248]; Me_3SnCH_2Ph, 4-fluoroindenyl and indenyltrimethyltin,



(Y = H, F) and



(^{13}C)[249]; oxirane-tin derivatives (^{1}H)[250]; methyltin alkane- and benzenethiolates (^{119}Sn)[251]; trimethylstannylphosphines and their pentacarbonylchromium, and tungsten complexes (^{119}Sn)[252]; hexaorganoditins (^{119}Sn)[253]; Me_3SnS_2CMe (^{1}H)[237]; $Me_3SnC\equiv CH$ (^{1}H)[238]; exo- and endo-2-norbornyl, 1- and 2-adamantyl and 3-nortricyclotrimethylstannanes (^{13}C)[255]; and organotin acetylacetonates (^{1}H)[263].

(iii) Mass Spectral Data.

Ionization and appearance potentials have been measured for $Me_3SnC\equiv CH$[238] and Me_3SnSPh[270]. Mass spectral data have been listed for $Bu_{4-n}SnX_n$ (n = 1-3, X = F, Cl, Br, I)[233]; stannacyclopentanes, -hexanes, and -heptanes[268]; 10,10-dimethyl- and 10,10-diethylphenoxastannin, 10,10-dimethylphenothiastannin, 10,10-dimethylphenothiastannin 5,5-dioxide, 5,5-dimethyl-5,10-dihydrodibenzo[b,e]stannin, and 10,10'-*spiro*-biphenoxastannin[269]; and $Ph_{3-n}(C_6F_5)_nSnMn(CO)_5$ (n = 0-3)[271].

(iv) Mössbauer Spectra.

The three isomers of trigonal bipyramidal R_3SnL_2 derivatives have been distinguished by linear regression analysis of quadrupole splitting data for five-coordinate R_3SnL_2 and six-coordinate R_2SnL_4 species. Splittings fall in the ranges ca. 1.7–2.3 mm/sec for cis-R_3SnL_2, ca. 3.0–3.9 mm/sec for equatorial-R_3SnL_2, and ca. 3.5–4.0 mm/sec for mer-R_3SnL_2[257]. $Me_2Sn(acac)_2$ has been subjected to a detailed temperature study in the range $4.2 \leqslant T \leqslant 120^{o}K$[258]. Other systems which have been studied include six-coordinate complexes of the types $\left[R_2SnL_4\right]\left[X\right]_2$, $R_2SnCl_2L_2$, R_3SnClL_2 (R = Me, Ph; L = oxygen donor; X = BPh_4^-, ClO_4^- or PF_6^-)[259]; divinyltin compounds[260]; 3-stanna-1,2-dicarba-closo-dodecaborane[261]; diorganotin dihalides[262]; organotin acetylacetonates[263]; organotin dialkyldithiocarbamates[264]; triorganotin and diorganotin arylmercaptides[265]; organotin derivatives of succinimide, phthalimide and hexahydrophthalimide[266]; and tin-cobalt bonded derivatives[267].

(v) Miscellaneous Data.

He(I) photoelectron data have been measured for $Sn(CH_2SiMe_3)_4$[272]; Me_3SnPh and Me_3SnCH_2Ph[273]; cyclopropylcarbinyltrimethyltin, allyltrimethyltin and isobutyltrimethyltin[274]; trialkylallylstannanes and benzyltrimethylstannane[275]; and Me_3SnSMe[276]. ESCA core electron binding energies have been obtained for dialkyltin dihalides[262]. The electron spin resonance spectra of organotin radicals produced by ^{60}Co γ-irradiation of R_4Sn (R = Me, Et, Bu), R_3SnCl (R = Me, Bu), R_6Sn_2 (R = Me, Ph) and Ph_3SnH[277], and also of the stable tin-centred radical $\left[(Me_3Si)_2CH\right]_3Sn\cdot$[278] have been measured. Analysis of esr spectral data has been used to derive the following order of Lewis acid acceptor strength $SnCl_4 > SnBr_4 > SiF_4 \gtrsim {}^{t}Bu_2SnCr(CO)_5 \approx SiCl_4 \gtrsim GeCl_4$[279]. United atom theory has been applied to trisubstituted radicals and anions of the type SnX_3 (X = H, Me, F, Cl)[280].

Dipole moments have been determined for Me_3SnSPh, $Me_3SnSC_6H_4Cl$-p, $Me_3SnSSnMe_3$[281], Me_3SnNCO and Me_3NCS[282], and $Sn(C_3H_5)_4$[232]. Dielectric data for benzene solutions of R_4Sn, R_2SnCl_2 and $R_2Sn\left[O_2C(CH_2)_6Me\right]_2$ are available[283].

The uv spectrum of Me_3SnS_2CMe has been measured[237]. The heats of mixing of tetraalkyltin compounds with normal and branched alkanes have been determined[284]. Extended Hückel calculations of allyltin compounds have provided evidence for $\sigma-\pi$ conjugation[285].

A method for the determination of tin in organotin monomers and polymers by radioisotopic X-ray fluorescence analysis has been described[286].

14. APPLICATIONS.

$R_3SnOC_6H_2X_2CN$ (X = halogen) compounds are selective herbicides for clover, sugar beet and soya bean[288]. Tris(cyclohexylmethyl)tin derivatives show miticide activity and fungicide activity against bean flour mildew, apple mildew and scab[289,290]. $Bu_3SnCH_2O_2SPh$ shows pesticide activity and is a seed antifungal agent[24]. The related Bu_3SnCH_2SOR compounds are acaricides, insecticides, and herbicides[25]. $R_3SnS(CH_2)_nCOR$ (n = 1,2,6) exhibit hydrophilic biocidal activity[291]. Organotin thiophencarboxylates[151], substituted aryltin trichlorides[92], perfluorodistannacyclohexadiene derivatives[21], and $R_2Sn(X\text{-}C_5H_3N\text{-}E)_2$ (E = O, S)[292] show bacteriocidal and fungicidal activity. Mixed triorganotin chloride derivatives, $R_2R'SnCl$, show wide insecticidal, herbicidal and fungicidal activity[89]. Tri-2-norbornyltin compounds are fungicides and miticides[293], and triorganotin triazoles are acaricides and insecticides[189]. Some $R_3SnOC(NR)NHCN$ derivatives show antifungal activity[192]. Cyclic diorganotin dialkoxides[120] and diacetatodistannoxanes[294] are catalysts for the polymerisation of polyisocyanates. Organotin systems such as $Me_3SnOH\text{-}MoO_2(acac)$, $Bu_3SnCl(OH)\text{-}H_2WO_4$, and $Me_3SnOH\text{-}VO(acac)$ catalyse the epoxidation of alkenes[295].

Organophosphatostannanes have been used as catalysts for hardening organopolysiloxanes[163]. Several types of thiolato-tin derivatives have been used as polymer stabilizing agents[166,168,169,172,296-299]. $R_2Sn(OR')(OSnR_2)_n(OR')$ derivatives are useful as curing agents in adhesion-resistant organopolysiloxane compounds for vegetable parchment[300].

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