TIN

Annual Survey Covering the Year 1973

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Contents:

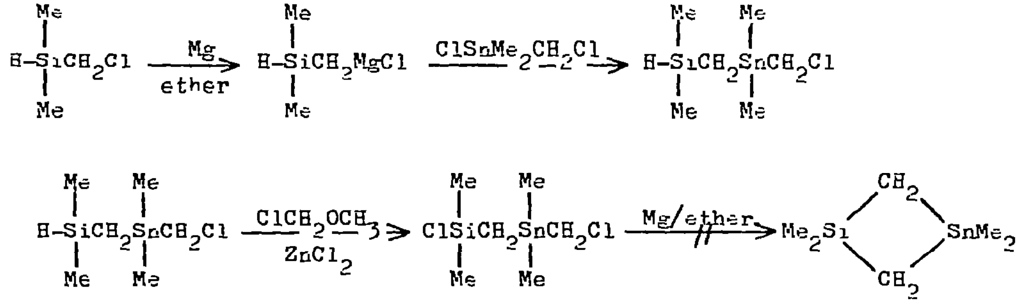
1. Review Articles

Several Articles of major importance have been published during the past year. Ho and Zuckerman have produced an excellent treatise covering structural organotin chemistry, which is not only comprehensive in the title material, but also includes much other associated data.[1] Smith and Smith have similarly comprehensively reviewed ^{119}Sn nmr chemical shift data. Besides being a lucid account of available techniques of measurement and applications to structure elucidation in solution, the review contains a tabular survey of known data.[2] The importance of penta-coordination in the physical and chemical properties of organotin compounds has been discussed by Nasielski,[3] whilst Gielen has reviewed the synthesis and properties of tetraorganotin compounds[4] and much of his own work on the kinetics of cleavage of the tin-carbon bond.[5] The use of organotin compounds as stabilizers for poly(vinyl chloride) has been reviewed.[6] Several other reviews which contain sections of interest have also appeared. A Russian monograph deals partly with organotin monomers and polymers.[7] Rudiments organotin chemistry has been described.[8] All aspects of the chemistry of cyclopentadienyltin compounds have been critically reviewed by Abel and his coworker whilst the report of Ustynyuk's plenary lecture at the 6th. International Confe ence on Organometallic Chemistry summarises his own studies (by ^{1}H, ^{2}H, and ^{13}C nmr) on the metallotropism of stannyl-cyclopentadienyl compounds, including mas spectral, structural (electron diffraction), and thermodynamic data.[10] The stability of organotin complexes with anionic and neutral ligands has been reviewed by Reutov and his coworkers.[11] Some aspects of organotin electrochemistry have been mentioned by Dessy.[12] The characterisation of organotin radicals by esr[13] and homolytic substitution of organotin compounds are reported in articles of much wider scope.[14,15]

2. Compounds with Four Tin-Carbon Bonds

Tetramethyltin has been obtained in 90% yield by refluxing tin(IV) chloride and tetramethyllead in toluene.[16] Treatment of finely divided tin (from tin(IV) chloride and magnesium in acetone) with ethyl bromide at 40° using Bu_4NI, tetraiodothiophene, or $(EtOCH_2CH_2)_2O$ as catalysts affords tetraethyltin.[17] Tetrakistrifluoromethyltin, $Sn(CF_3)_4$, is obtained by the reaction of tin(IV) iodide with trifluoromethyl radicals (from a hexafluoroethane discharge).[18] The mixed ethylbutylstannanes, $Et_nBu_{4-n}Sn$ ($n = 1-3$), may be prepared in high yields without alkyl group migration by the reaction of bis(tributyltin) oxide, dibutyltin oxide or butylstannonic acid with Et_2AlCl or $EtAlCl_2$ in the presence of sodium or potassium chloride. Without added alkali metal chloride, some alkyl group redistribution does take place.[19] The molecular structure of tetramethyltin has been redetermined by electron diffraction. Assuming the SnC_4 framework and the methyl group to have T_d and C_{3v} symmetry respectively, the relevant bond parameters were determined to be: $r(Sn\text{-}C) = 2.143_6(3_0)$A, $r(C\text{-}H) = 1.117_9(9_0)$A. The methyl groups rotate freely, or very nearly so.[20]

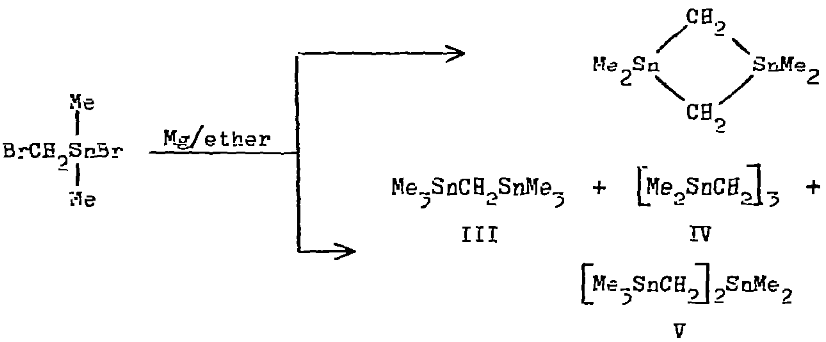
Mironov *et al.* have attempted to synthesise four-membered heterocyclic tin compounds *via* the following route:



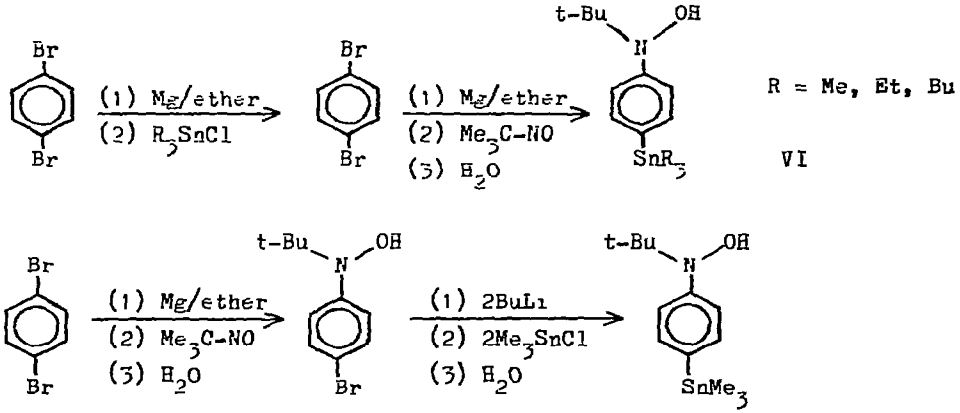
I II

The reaction of I with magnesium however, although quantitative, does not yield

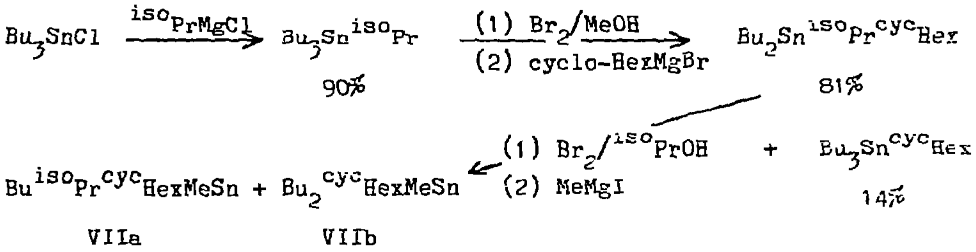
II. Instead mainly polymer is produced, together with a distillable fraction containing at least six compounds including $ClMe_2SiCH_2SnMe_3$ (16%) and traces of $Me_3SiCH_2SnMe_3$. Similarly, $BrCH_2SnMe_2Br$ ($ClCH_2SnMe_2Cl$ is inert) reacts with magnesium to afford again mostly polymer together with small amounts (3-6%) of III, IV, and V, but no four-membered heterocycle:



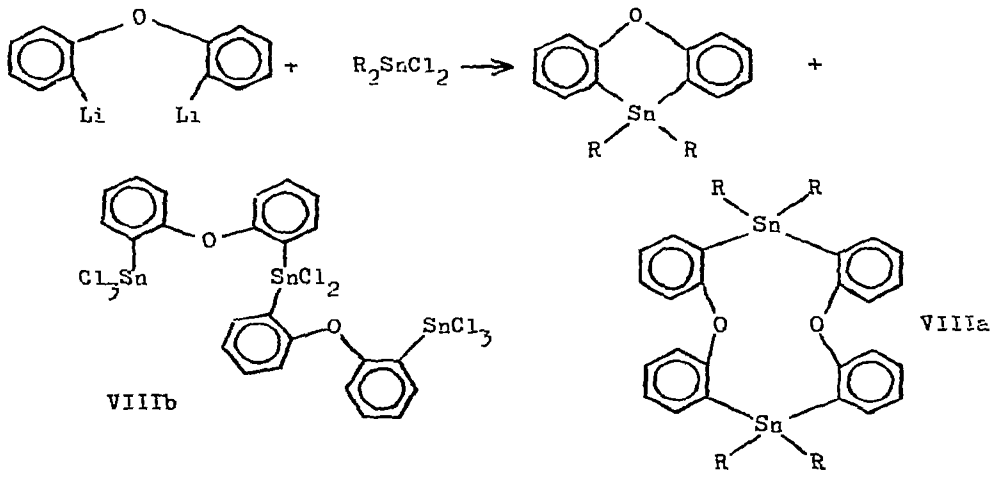
III is also synthesised in 35% yield from Me_3SnCH_2Cl, Me_3SnCl and magnesium.[21] The Grignard method has been used to synthesise several ω-substituted alkyl- and alkenylstannanes, RR'_3Sn (R' = Ph; R = ω-undecenyl, 4-pentenyl, 3-butenyl, 3-phenylpropyl, 4-phenoxybutyl. R' = Me; R = 3-butenyl, cyclohexylmethyl, 2-phenethyl, 3-phenylpropyl, 3-phenoxybutyl).[22] *N*-*tert*-Butyl-*N*-(*p*-trialkylstanny arylhydroxylamines VI have been prepared by the routes:[349]



Racemic tetraalkyltin compounds have been obtained by successive alkylations by Grignard reagents and bromodemetallations:



The final products VIIa and VIIb are formed in a 2:1 ratio.[23] Holloway has prepared several *t*-butyl and *t*-pentyl substituted dissymetric stannanes and distannanes by a similar series of reactions starting from tetraphenyltin. Reaction of di-*t*-butyl(phenyl)tin chloride with *t*-butyllithium or -magnesium halide results in the formation of the coupled product $({}^{t}Bu)_3PhSn-SnPh({}^{t}Bu)_3$, but the same reagents reacted with diphenylneophyltin iodide to yield $Ph_2(PhMe_2CCH_2){}^{t}BuSn$. Coupled products were also obtained by the reaction of *t*-pentylmagnesium chloride with Ph_3SnI, $Ph_2{}^{t}BuSnI$, $Ph_2(PhMe_2CCH_2)SnI$, and $Ph(PhCH_2){}^{t}BuSnI$. Only $Ph_2(PhCH_2)SnI$ could be successfully converted to the desired monostannane, $Ph_2(PhCH_2)(MeCH_2CMe_2)Sn$.[24] *o*- and *p*-Biphenyltriorganotin derivatives have been obtained in moderate to good yield from the corresponding lithium or Grignard reagents and the appropriate triorganotin chloride. All exhibited high thermostability having decomposition points well in excess of 200°.[25] 10,10-Dimethyl- and 10,10-diethylphenoxastannins have been prepared

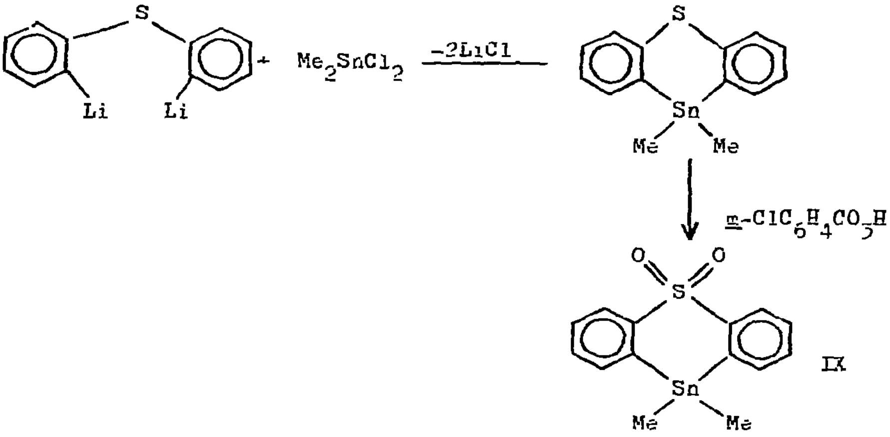


VIIIb

VIIIa

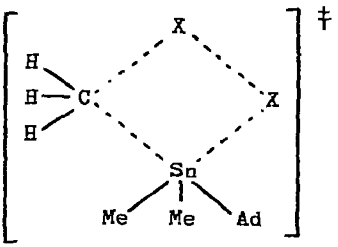
from the reaction of oxy-2,2'-bis(phenyllithium) with R_2SnCl_2 (R = Me, Et). Small amounts of the 12-membered heterocycles VIIIa were also obtained.

Pmr data showed that VIIIa (R = Me) exists in solution as a mixture of conformational isomers. The trimetallic species VIIIb is obtained by reaction of 10,10-dimethylphenoxastannin with $SnCl_4$. 10,10-Dimethylphenothiastannin is the only product obtained from the reaction of thio-2,2'-bis(phenyllithium) with Me_2SnCl_2. Oxidation with excess m-chloroperbenzoic acid affords IX.[332]

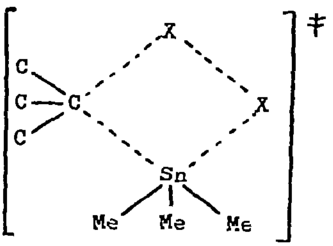


IX

1-Adamantyltin derivatives have been synthesised by the reaction of triorganotin sodium compounds and 1-halogenoadamantane in liquid ammonia (R = Me) or by the Wurtz-Fittig reaction (R = Ph). Tetrakis(adamantyl)tin was also obtained by the latter method. Bromodemetallation in $CDCl_3$ occurred with 48% Me-Sn bond fission, whilst iododemetallation resulted in 66% Me-Sn bond fission (compared with the statistical value of 75%) in accord with the four-centre transition states Xa and Xb,



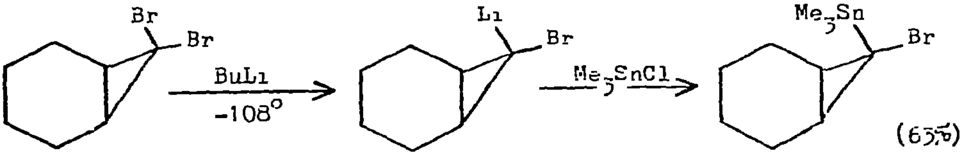
Xa



Xb

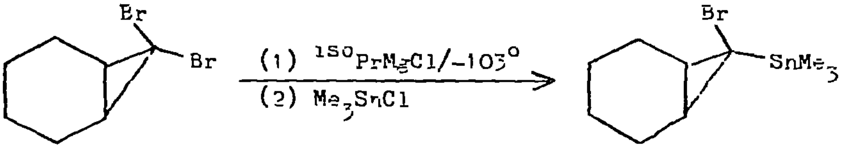
the former being favoured as the size of X increases. With $HgCl_2$ in DMSO-d_6, exclusive Me–Sn bond fission occurred, presumably via a more open ionic transition state. Triphenyladamantyltin reacts instantaneously with bromine in $CDCl_3$ with exclusive Sn–Ph bond cleavage. Tetrakis(adamantyl)tin is, not unexpectedly, very inert to both reagents.[26]

anti-7-Bromo-syn-7-lithionorcarane, prepared stereospecifically by the reaction of BuLi with 7,7-dibromonorane in THF at low temperature, reacts



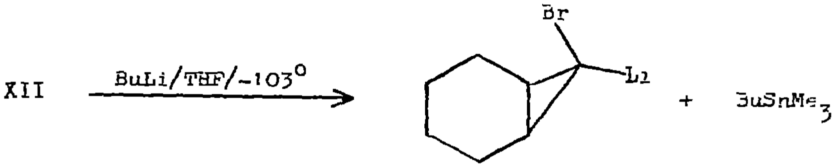
XI

with Me_3SnCl to give XI. The isomeric product, syn-7-anti-7-trimethylstannyl norcarane XII is obtained by the sequence:



XII

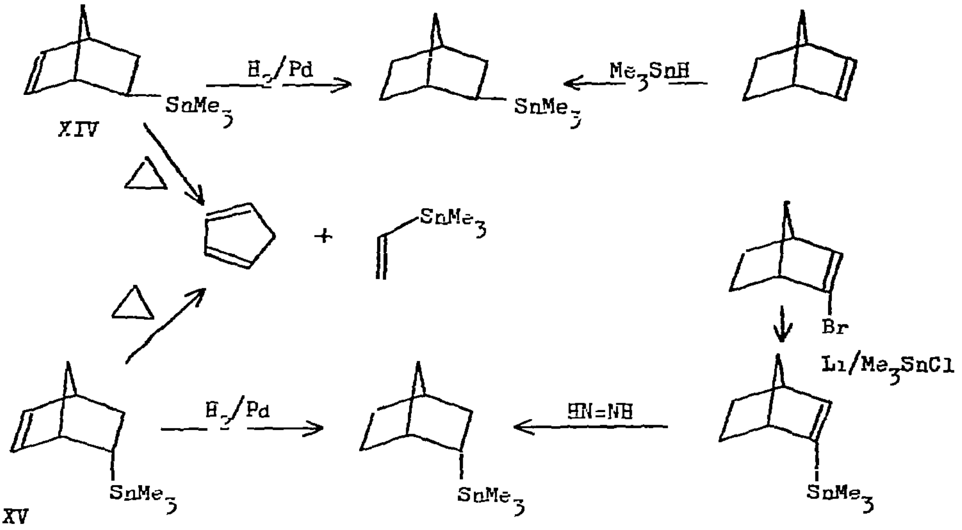
XII is cleaved by BuLi to afford the isomeric lithium reagent, syn-7-bromo-anti-7-lithionorcarane XIII.[27]



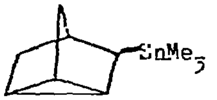
XIII

Kuivila and his coworkers have reported further data on the structures of the four products isolated from the free-radical addition of Me_3SnH to norbornadiene. The structures and configurations of exo- and endo-norborn-2-en-

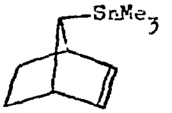
5-yltrimethyltin, XIV and XV respectively, were assigned from the series of reactions:



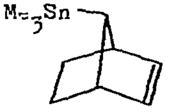
3-Nortricyclotrimethyltin XVI comprises ~11% of the Me_3SnH-norbornadiene adduct mixture, whilst the fourth product is *syn*-norborn-2-en-7-yltrimethyltin XVII. The structure of XVII, and the absence of the *anti*-isomer XVIII,



XVI



XVII

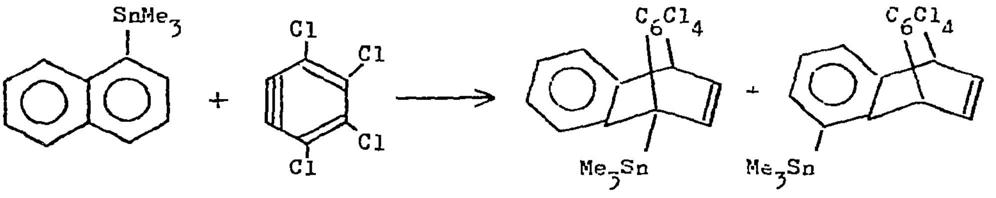


XVIII

was established by separate syntheses. Reaction of the lithium reagent of 7-bromonorcarane with Me_3SnCl afforded 30–45% yields of mixtures of both isomers. The use of sodium naphthalene to prepare the corresponding Grignard reagent, followed by reaction with Me_3SnCl gave only a 9% yield of the desired product, but a 31% yield was obtained using the procedure:[28]

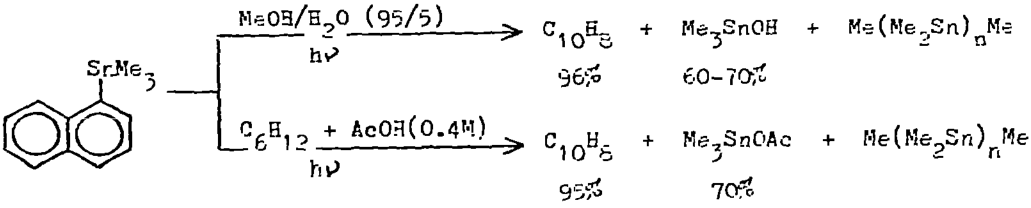
$$2Na^+C_{10}H_8^{\overline{\cdot}} + RBr + Me_3SnCl \longrightarrow 2C_{10}H_8 + RSnMe_3 + NaCl + NaBr$$

Both [1,4] XIX and [5,8] XX adducts are obtained from the reaction of trimethylnaphthyltin and tetrachlorobenzyne:



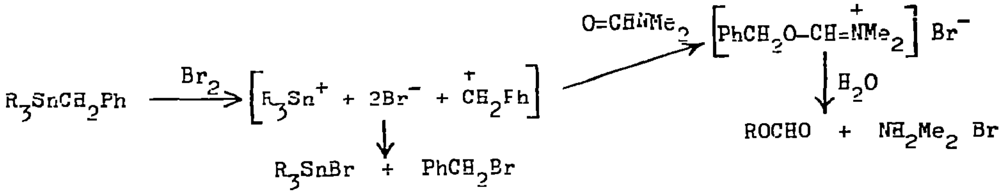
XIX XX

The barrier to rotation in XIX was deduced to be 11.7±0.4 kcal. mol^{-1}.[29] Photolysis of trimethylnaphthyltin in methanol/water or cyclohexane/acetic acid yields naphthalene:



The use of MeOD or AcOD results in the formation of more 1-deuterionaphthalene than 1-protonaphthalene, in agreement with a mechanism involving a competition between a bimolecular photosubstitution and a free-radical dissociation.[30] γ-Irradiation of tetrabutyltin gives traces of tributyltin and dibutyltin compounds. Similarly tributyltin chloride gives traces of tetrabutyltin and a dibutyltin compound. Irradiation of dibutyltin dichloride produces traces of tetrabutyltin and a tributyltin compound, together with stannous chloride (6.6%). BuSnCl$_3$ afforded a tar, whilst (Bu$_3$Sn)$_2$O yielded a precipitate of Bu$_2$SnO (16.4%). Irradiation of Bu$_4$Sn and pentafluorobenzene in hexane gives tributyltin flouride (7.8%) and Bu$_2$SnF$_2$ (0.1%). Hexabutylditin and pentafluorobenzene yielded Bu$_3$SnF (10.6%) and Bu$_2$SnO (4.1%) from traces of water or oxygen. Bu$_3$SnCl and pentafluorobenzene gave only Bu$_2$SnF$_2$ (5.8%) and no Bu$_3$SnF, whilst Bu$_2$SnCl$_2$ and pentafluorobenzene in hexane produced a precipitate of $SnCl_2$ (3.0%) and no Bu_3SnF or Bu_2Sn Irradiation of $BuSnCl_3$ or $(Bu_3Sn)_2O$ in the presence of pentafluorobenzene gave similar results as before. Bu_4Sn and perfluoro(dimethylcyclohexane) afforded Bu_3SnF (3.6%) and Bu_2SnF_2 (0.4%).[31] Trityl bromide is reduced by β-H abstracti from tetraalkyltins R_4Sn (R = Et, Me_2CH, Pr, Me_2CHCH_2) yielding Ph_3CH, R_3SnBr, and olefin.[32]

Demetallation of tetrabenzyltin and benzyltrimethyltin by bromine in DMF i accompanied by the formation of benzyl formate in addition to benzyl bromide via attack of benzyl cations on the solvent:[33]



Abraham has shown that the increases in $\Delta G^{\ddagger}$ on change of solvent from methanol to tert-butyl alcohol-methanol for the reaction

$$Et_4Sn \ + \ HgX_2 \longrightarrow EtHgX \ + \ Et_3SnX$$

$$X = Cl,\ I,\ OAc$$

are largely due to increases in the free energy of the transition states. It is suggested that the $[Et_4Sn\text{-}HgCl_2]^{\ddagger}$ transition state possesses a very high dipole moment of ca. 14 D.[34] In addition, Abraham and his coworkers have reported rate constants for the substitution of tetraalkyltins R_4Sn by mercury(II) carboxylates $(R'CO_2)_2Hg$ varying both R and R'.[35,36] Rate constants for the S_E2 substitution of tetraethyl- and tetrabutyltin by $(R'CO_2)_2Hg$ in methanol increases along the series tert-Bu < Et < Me < Ph < $ClCH_2CH_2$ < $MeOCH_2$ < $ClCH_2$, suggesting an 'open' transition state.[35] Rate constants for the substitution of R_4Sn by mercury(II) acetate in methanol follow the order expected on steric grounds (Me > Et > ^{n}Pr > ^{n}Bu > ^{iso}Bu > $^{neo}C_5H_{11}$ > ^{iso}Pr)

also suggesting a S_E2(open) mechanism with retention of configuration at the site of substitution. The substitutions in tert-butyl alcohol is suggested to take place through a transition state intermediate between an 'open' and a fully (cyclic) one.[36]

Seyferth has reported more syntheses of halomethylstannanes. Diiodomethyltrimethyltin XXI has been prepared via both lithium and Grignard reagents:

$$CHI_3 \;+\; {}^{iso}PrMgCl \xrightarrow[-PrI]{THF/-80^{\circ}} CHI_2MgCl \xrightarrow{Me_3SnCl} \underset{XXI}{Me_3SnCHI_2} \quad (72\%)$$

$$CHI_3 \;+\; BuLi \xrightarrow[-BuI]{THF/-95^{\circ}/20\ mins.} CHI_2Li \xrightarrow{Me_3SnCl} \underset{XXI}{Me_3SnCHI_2} \quad (66\%)$$

Although it was not possible to obtain Me_3SnCI_2Li, the analogous Grignard reagent, Me_3SnCI_2MgCl XXII, is sufficiently stable to be used as a preparative reagent:

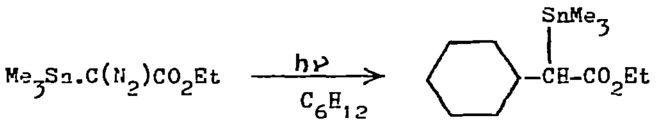
$$\begin{tikzcd}
Me_3SnNEt_2 \arrow[r, "CHI_3", "-HNEt_2"'] & \left[Me_3SnCI_3\right] \arrow[r, "{}^{iso}PrMgCl", "THF/-100^{\circ}"'] & \underset{XXII}{Me_3SnCI_2MgCl} \arrow[d, "Me_3SnCl"] & + \;{}^{iso}PrI \\
 & & \underset{(32\%)}{(Me_3Sn)_2CI_2} &
\end{tikzcd}$$

All the iodo-substituted compounds are light and air-sensitive, and colourise to dark red or red-purple even on careful storage.[37]

$$\begin{tikzcd}
Me_3SnNR_2 \;+\; N_2{:}CHCO_2Et \quad R = Et,\ SiMe_3 \arrow[dr] & \\
 & \underset{XXIII}{Me_3Sn.C(:N_2)CO_2Et} \arrow[d, "h\nu\ ,\ -N_2"] \\
(Me_3Sn)_2S \;+\; Hg\left[C(N_2)CO_2Et\right] \arrow[ur] & \underset{XXIV}{Me_3Sn(EtO_2C)C:}
\end{tikzcd}$$

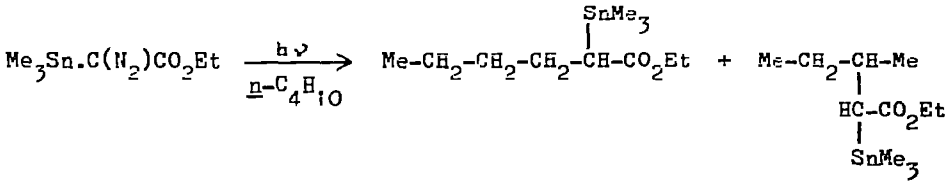
Ethyl diazoacetate reacts with trimethylstannylamines to afford ethyl (trimethylstannyl)diazoacetate XXIII. The same compound is also obtained from the mercury diazoacetate and $(Me_3Sn)_2S$.

XXIII may be cleaved photolytically to give the tin-substituted carbene XXIV, which can insert into C-H bonds and add to olefinic double bonds. *Ca.* 50% insertion into the C-H bonds of cyclohexane takes place to give XXV:



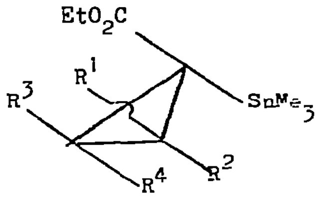
XXV

With *n*-butane, a 60% yield of a mixture of terminal and non-terminal insertion products in a 30:70 ratio is obtained:



$$Me_3Sn.C(N_2)CO_2Et \xrightarrow[n\text{-}C_4H_{10}]{h\nu} Me\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\underset{}{\overset{SnMe_3}{CH}}\text{-}CO_2Et + Me\text{-}CH_2\text{-}\underset{\underset{SnMe_3}{HC\text{-}CO_2Et}}{CH}\text{-}Me$$

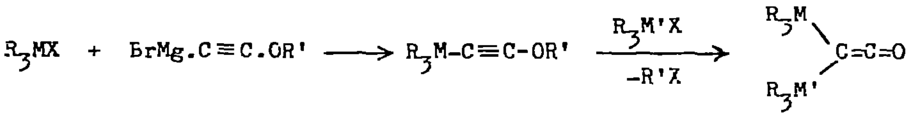
With *iso*-butene, and *cis*- and *trans*-2-butene, addition to the C=C double bond occurs completely *cis*-stereospecifically to yield the stannylcyclopropyl derivatives XXVI. The carbenes react in their singlet state.[38]



$R^1 - R^4$ = H, Me

XXVI

Bis(trimethylstannyl)ketene is formed on the pyrolysis of ethoxy(trimethylstannyl)acetylene. Bis(metallated)ketenes XXVII are also available by treating (alkoxyethynyl)magnesium bromides with two successive moles of triorganometallic halide:

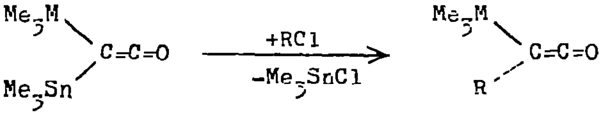


XXVII

M = M' = Ge, Sn; M = Si, M' = Ge, Sn;

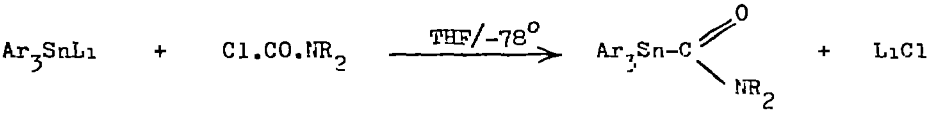
R = Me, Et, Pr; R' = Et, Bu

The stannylgermyl- or stannylsilylketenes are readily cleaved by germyl or boryl halides:[39]



M = Si, Ge; R = Cl_3Ge, Bu_2B

Stable (dialkylcarbamoyl)triaryltin derivatives XXVIII have been synthesis from the carbamoyl chloride and the appropriate triaryltin lithium in THF:[40]



XXVIII

The reaction of ketene with trialkylstannylamines or -amides yields the C-stannylated amides XXIXa and XXIXb:

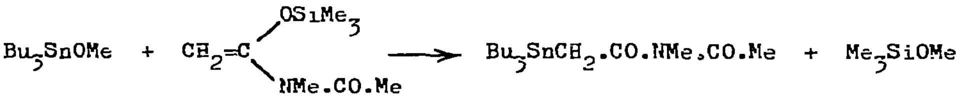
$$R_3SnNR'_2 \quad + \quad CH_2{=}C{=}O \longrightarrow R_3SnCH_2.CO.NR'_2$$

XXIXa

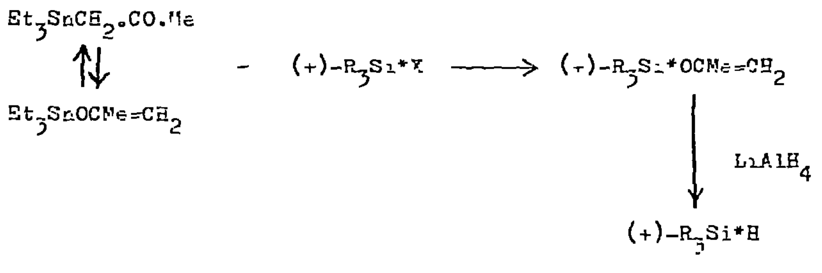
$$R_3Sn.NMe.CO.Me \quad + \quad CH_2{=}C{=}O \longrightarrow R_3SnCH_2.CO.NMe.CO.Me$$

XXIXb

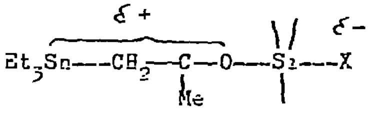
XXIXb (R = Bu) may also be obtained by group exchange between Bu_3SnOMe and the O-silylacetal XXX:



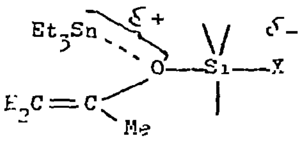
Group exchange also occurs between XXIXb and Me_3GeBr forming $Me_3GeCH_2.CO.NMeCOMe$. Triethylstannylacetone (equilibrium mixture of O-(10%) and C-(90%) isomers) reacts with enantiomeric chloro- and bromo-methyl-1-naphthylphenylsilane to give the triethyltin halide and optically active (isopropenoxy)silane:



The transformation takes place with a very high degree of stereospecificity (inversion of configuration at Si*; $\geqslant 81\%$. X = Cl; $\geqslant 84\%$, X = Br) via a S_N2-S_i mechanism. The transition states XXXI and XXXII were proposed for the keto and enol isomers, respectively.[42]

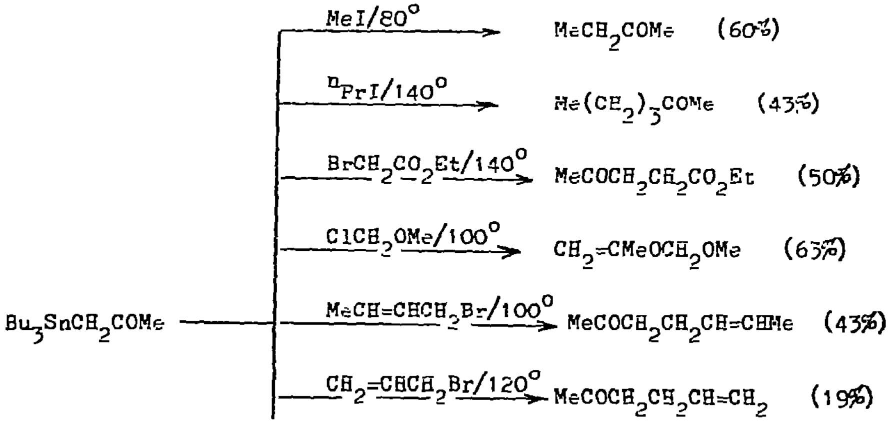


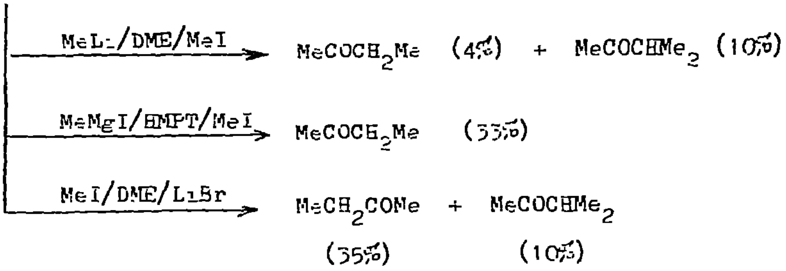
XXXI



XXXII

The reaction of Bu_3CH_2COMe with alkylating agents affords moderate yields of the corresponding alkylated ketones:



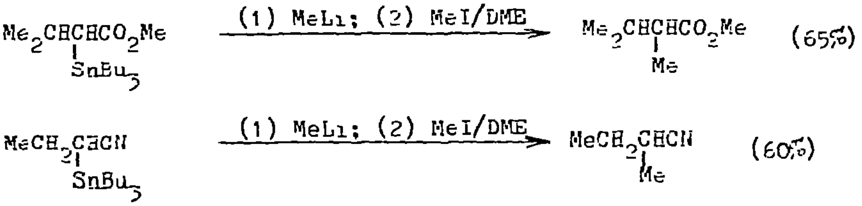


$$\xrightarrow{\text{MeLi/DME/MeI}} \text{MeCOCH}_2\text{Me}\ (4\%) + \text{MeCOCHMe}_2\ (10\%)$$

$$\xrightarrow{\text{MeMgI/HMPT/MeI}} \text{MeCOCH}_2\text{Me}\ (33\%)$$

$$\xrightarrow{\text{MeI/DME/LiBr}} \underset{(35\%)}{\text{MeCH}_2\text{COMe}} + \underset{(10\%)}{\text{MeCOCHMe}_2}$$

Direct alkylation does not occur with α-organotin substituted nitriles and esters, but good results are obtained by initial metal exchange with Grignard or lithium reagents, eg:



$$\underset{\text{SnBu}_3}{\text{Me}_2\text{CHCHCO}_2\text{Me}} \xrightarrow{\text{(1) MeLi; (2) MeI/DME}} \underset{\text{Me}}{\text{Me}_2\text{CHCHCO}_2\text{Me}}\quad (65\%)$$

$$\underset{\text{SnBu}_3}{\text{MeCH}_2\text{CHCN}} \xrightarrow{\text{(1) MeLi; (2) MeI/DME}} \underset{\text{Me}}{\text{MeCH}_2\text{CHCN}}\quad (60\%)$$

or by the presence of either magnesium or lithium bromide:

$$\text{Me}_2\text{CHCH(CO}_2\text{Me)SnBu}_3 \xrightarrow{\text{MeI/DME/LiBr}} \text{Me}_2\text{CHCH(CO}_2\text{Me)Me}\quad (66\%)$$

$$\text{Me}_2\text{CHCH(CO}_2\text{Et)SnBu}_3 \xrightarrow{\text{MeI/DME/LiBr}} \text{Me}_2\text{CHCH(CO}_2\text{Et)Me}\quad (52\%)$$

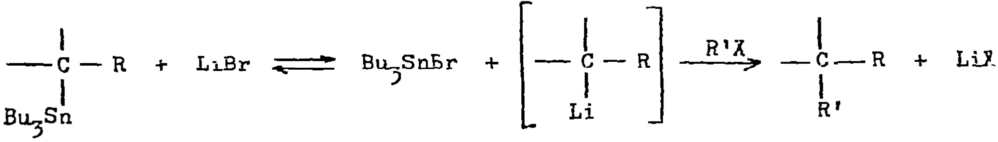
$$\text{MeCH}_2\text{CH(CN)SnBu}_3 \xrightarrow{\text{MeI/DME/LiBr}} \text{MeCH}_2\text{CH(CN)Me}\quad (50\%)$$

$$\text{MeCH}_2\text{CH(CN)SnBu}_3 \xrightarrow{\text{MeI/DME/MgBr}_2} \text{MeCH}_2\text{CH(CN)Me}\quad (72\%)$$

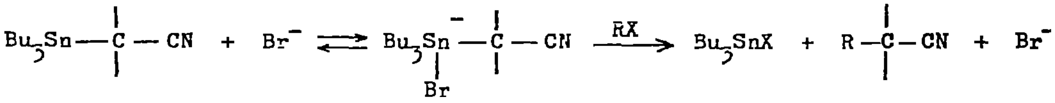
$$\text{Me}_2\text{CHCH(CN)SnBu}_3 \xrightarrow{\text{MeI/DME/LiBr}} \text{Me}_2\text{CHCH(CN)Me}\quad (78\%)$$

Two rationalisations were advanced for the role of added halide in these reactions:

(i) Metal exchange:



and (ii) nucleophilic assistance at tin which facilitates electrophilic attack by the alkylating agent:[43]



$$Bu_3Sn-\overset{|}{\underset{|}{C}}-CN + Br^- \rightleftharpoons Bu_3\underset{\overset{|}{Br}}{Sn}-\overset{-\,|}{\underset{|}{C}}-CN \xrightarrow{RX} Bu_3SnX + R-\overset{|}{\underset{|}{C}}-CN + Br^-$$

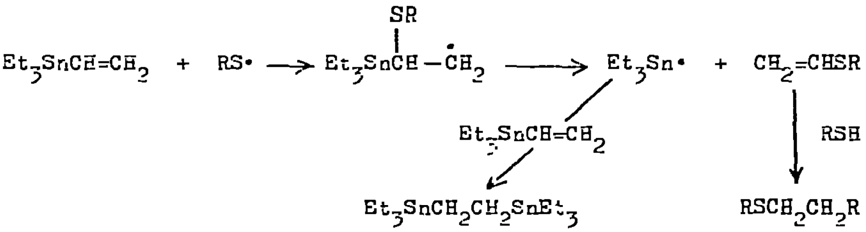
Irradiation of mixtures of triethylvinyltin and thiols result in free radical addition to the double bond:

$$RSH \xrightarrow{h\nu} RS\bullet + H\bullet$$

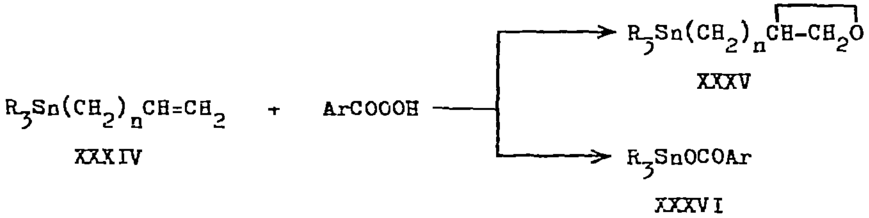
$$Et_3SnCH{=}CH_2 + RS\bullet \longrightarrow Et_3Sn\dot{C}HCH_2SR \xrightarrow{RSH} \underset{XXXIII}{Et_3SnCH_2CH_2SR} + RS$$

$$R = {}^{iso}Pr,\ {}^{n}Bu,\ {}^{tert}Bu$$

The β-thio substituted stannanes XXXIII are formed in > 60% yield. In addition $Et_3SnCH_2CH_2SnEt_3$ and $RSCH_2CH_2SR$ are formed in appreciable quantities. The formation of these products may be rationalised by initial attack of RS• at the α-carbon atom, followed by dissociation of the intermediate radicals:

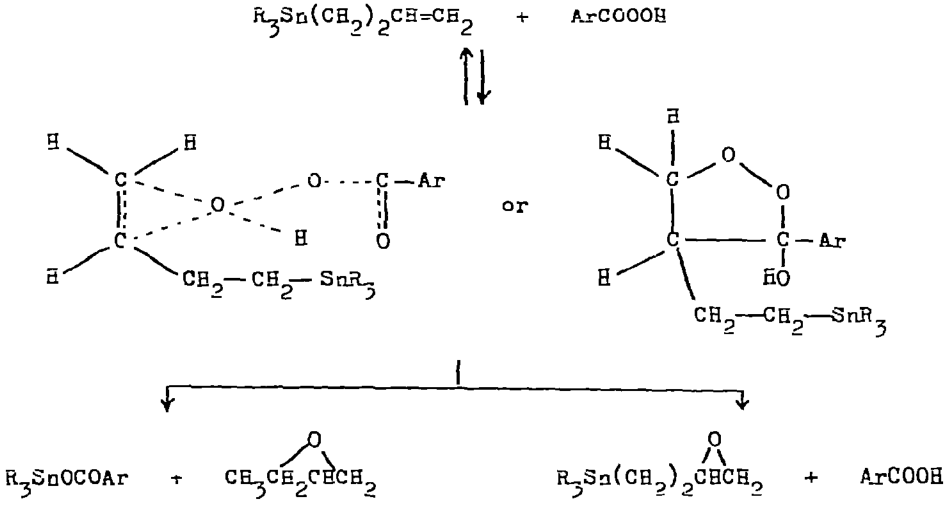


Corroboration of this proposal comes from the reaction of $Bu_3SnCH{=}CH_2$ with ${}^{iso}PrSH$, from which only $Bu_3SnCH_2CH_2SCHMe_2$, unaccompanied by any by-products, was isolated. In this case the bulkier alkyl groups attached to the metal prevent attack of the thiyl radicals at the α-carbon.[44] Diethyl malonate and ethyl acetoacetate react with $Et_3SnCH{=}CH_2$ in the presence of di-tert-butyl peroxide to give only the β-addition products, diethyl triethylstannylethylmalonate (37%) and 3-ethoxycarbonyl-5-triethylstannyl-2-pentanone (44%), respectively.[45] Treatment of alkenyltriorganostannanes XXXIV with perbenzoic acids affords mixtures of the corresponding (epoxyalkyl)triorganostannanes XXXV and triorganotin carboxylates XXXVI when n = 0 or 2, but only the latter are formed when n = 1.



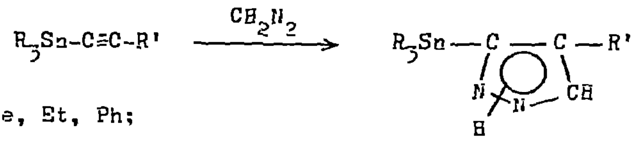
XXXIV XXXV XXXVI

The formation of the products can be rationalised by either 3-centre or 5-centre transition states, in which competition for a proton occurs between the incipient carboxylate anion and the α-carbon atom of the alkenyl groups eg:



The sensitivity to electrophilic attack of the α-carbon atom in allyltin compounds readily accounts therefore for specificity of reaction in that case. No bis-(epoxyalkyl)tin compounds could be formed. Reaction of $Bu_2Sn(CH=CH_2)_2$ with 3-chloroperbenzoic acid yielded dibutyl(epoxyethyl)vinyltin and dibutyltin bis(3-chlorobenzoate). whilst di-3-butenyldiphenyltin similarly afforded 3-butenyl(3,4-epoxybutyl)diphenyltin. Epoxyethyltin compounds decompose within a few days, but the epoxybutyl analogues are unchanged on prolonged storage. Reduction of tributyltin(3,4-epoxybutyl)tin with $LiAlH_4$ gave $Bu_3Sn(CH_2)_3CH_2OH$.[46]

Alkynyltin compounds undergo 1,3-dipolar cycloaddition reactions with diazoalkanes to afford the stannylpyrazole derivatives XXXVII:

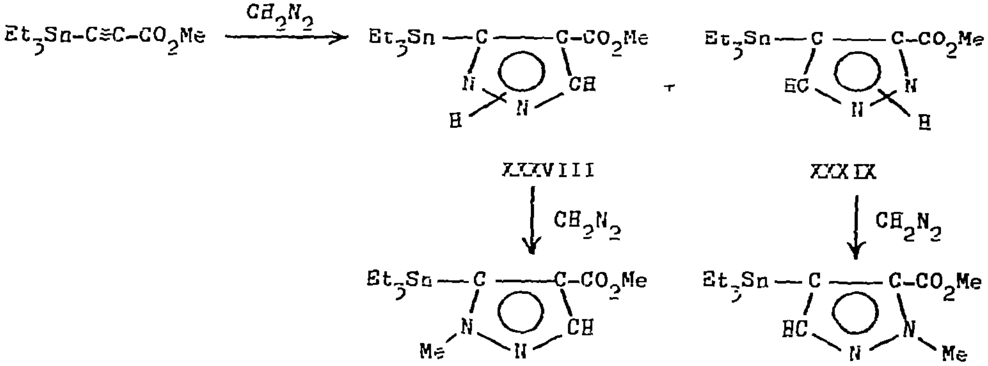


R = Me, Et, Ph;

R' = H, Ph, Ph_3Sn, CO_2Me

XXXVII

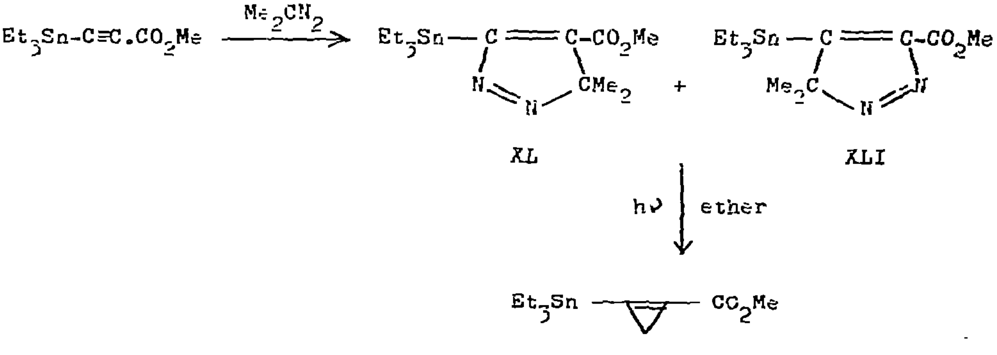
With dimethylacetylene dicarboxylate, both possible isomeric pyrazoles XXXVIII and XXXIX are formed in an 80:20 ratio which can be converted quantitatively to the N-methylated analogues by further diazomethane. Dimethyldiazomethane



XXXVIII

XXXIX

also reacts with $Et_3Sn.C{\equiv}C.CO_2Me$ to afford a mixture of isomeric pyrazolenines, XL and XLI, which undergo ring contraction under irradiation to give quantitatively the stannylcyclopropenyl derivative XLII:[47]



XL

XLI

XLII

Attempts to form the distannyldiacetylene XLIII by oxidative coupling using copper(I) chloride were unsuccessful, but the desired product is obtained by the reaction of Me_3SnNMe_2 and diacetylene.[48]

$$2Me_3SnNMe_2 \quad + \quad HC{\equiv}C{-}C{\equiv}CH \longrightarrow \underset{\text{XLIII}}{Me_3.C{\equiv}C.C{\equiv}C.SnMe_3} \qquad (16\%)$$

Acetyl chloride cleaves the alkynyl-tin bond of stannyl acetylenes to afford alkynyl-ketenes. Et_3SnCl catalyses the reactions by forming complexes with the acid chloride thus promoting electrophilic attack on the acetylene.[49]

$$Et_3Sn.C{\equiv}C.Ph \quad + \quad Me.CO.Cl \xrightarrow{120-150^{\circ}} \underset{100\%}{Et_3SnCl} \quad + \quad \underset{45\%}{Me.CO.C{\equiv}C.Ph} \quad + \quad Ph.C{\equiv}C.H$$

$$Et_3Sn.C{\equiv}C.Ph \quad + \quad Ph.CO.Cl \xrightarrow{Et_3SnCl/150^{\circ}} Ph.C{\equiv}C.CO.Ph \qquad (59\%)$$

$$Et_3Sn.C{\equiv}C.Bu \quad + \quad Me.CO.Cl \xrightarrow{Et_3SnCl} Bu.C{\equiv}C.CO.Me \qquad (30\%)$$

$$Et_3Sn.C{\equiv}C.Bu \quad + \quad Ph.CO.Cl \xrightarrow{Et_3SnCl} Bu.C{\equiv}C.CO.Ph \qquad (26\%)$$

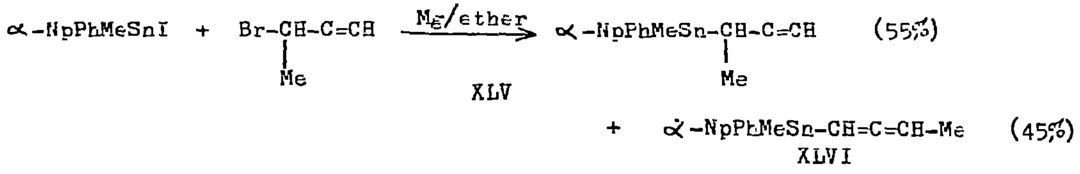
$$Et_3Sn.C{\equiv}C.CH_2Cl \quad + \quad Me.CO.Cl \longrightarrow ClCH_2.C{\equiv}C.CO.Me \qquad (83\%)$$

Bromotrichloromethane readily undergoes free radical addition to triorganoalkynyltin compounds to give triorgano(1-bromo-3,3,3-trichloropropenyl)stannane XLIV.[50]

$$R_3Sn.C{\equiv}CH \quad + \quad BrCCl_3 \xrightarrow[h\nu]{40-50^{\circ}} \underset{\text{XLIV}}{R_3SnCBr{=}CH.CCl_3} \qquad (70-80\%)$$

$$R = Et,\ Pr,\ Bu$$

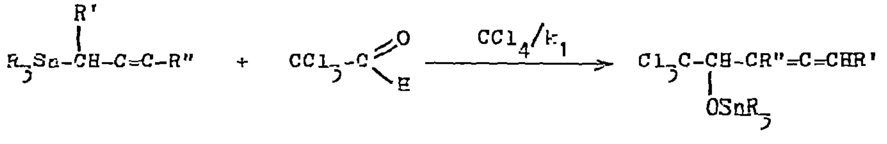
Reaction of α-NpPhMeSnI with the Grignard reagent prepared from 3-bromobutyne produces a mixture of the corresponding propargyl- (XLV) and allenyl-tin (XLVI) derivatives:

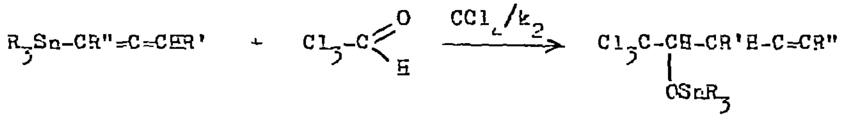


$$\alpha\text{-}NpPhMeSnI \quad + \quad Br{-}\underset{\displaystyle Me}{CH}{-}C{\equiv}CH \xrightarrow{Mg/ether} \underset{\text{XLV}}{\alpha\text{-}NpPhMeSn{-}\underset{\displaystyle Me}{CH}{-}C{\equiv}CH} \qquad (55\%)$$

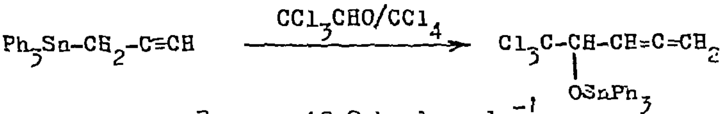
$$+ \quad \underset{\text{XLVI}}{\alpha\text{-}NpPhMeSn{-}CH{=}C{=}CH{-}Me} \qquad (45\%)$$

The kinetic product (XLV) is readily converted to the more thermodynamically stable allenyl isomer by donor solvents or Lewis acids. Both isomers exist in two diastereotopic *erythro* and *threo* forms.[51] Propargyl- and allenyl-tin compounds react with chloral to form isolable organotin alkoxides, from which the parent alcohol may be obtained by protolysis with malonic acid. The condensations are accompanied by respective interconversion of propargyl and allenyl functions:


$$R_3Sn{-}\overset{R'}{\overset{|}{C}}H{-}C{\equiv}C{-}R'' + CCl_3{-}C{\lessgtr}^{O}_{H} \xrightarrow{CCl_4/k_1} Cl_3C{-}\underset{OSnR_3}{\underset{|}{C}H}{-}CR''{=}C{=}CHR'$$


$$R_3Sn{-}CR''{=}C{=}CHR' + Cl_3{-}C{\lessgtr}^{O}_{H} \xrightarrow{CCl_4/k_2} Cl_3C{-}\underset{OSnR_3}{\underset{|}{C}H}{-}CR'H{-}C{\equiv}CR''$$

The reactivity varied with the group R in the order Me > Et > Bu > Ph. A comprehensive kinetic study of the triaryltin derivatives showed that the reactions are second order, and first order in each reactant, up to 90% of reaction. The rate of reaction is largely a function of unsaturation in the carbon chain, for example $Ph_3Sn.CH_2C{\equiv}CH$ reacts 6.5 times faster than its allenyl isomer. In addition, the rates are greatly influenced by substitution along the chain and by substitution on the phenyl groups attached to tin. Thus, whilst methyl substitution increases the rate of reaction in the propargyl case ($Ph_3Sn.CH_2C{\equiv}CH$ $k_{rel} = 1$; $Ph_3SnCHMe.C{\equiv}CH$, $k_{rel} = 2.4$), methyl substitution of the allenyl isomer severely decreases the rate. $Ph_3Sn.CH_2C{\equiv}CMe$ also exhibits a severe decrease in rate due to the donor effect of the methyl group. Ortho-methyl substitution of the phenyl groups attached to tin greatly reduces the rate due to steric hindrance; para-substitution, however, increases the rate of reaction (ortho-tolyl, $k_{rel} = 1$; phenyl, $k_{rel} = 26$; para-tolyl, $k_{rel} = 35$). Activation parameters have been determined for the reactions:



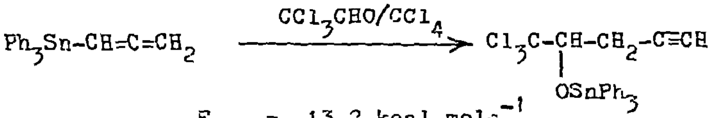
$$Ph_3Sn\text{-}CH_2\text{-}C{\equiv}CH \xrightarrow{CCl_3CHO/CCl_4} Cl_3C\text{-}\underset{\displaystyle OSnPh_3}{CH}\text{-}CH{=}C{=}CH_2$$

E_a = 12.8 kcal. mole^{-1}

ΔG^* = 23.6 kcal. mole^{-1}

ΔH^* = 12.3 kcal. mole^{-1}

ΔS^* = −38 e.u.



$$Ph_3Sn\text{-}CH{=}C{=}CH_2 \xrightarrow{CCl_3CHO/CCl_4} Cl_3C\text{-}\underset{\displaystyle OSnPh_3}{CH}\text{-}CH_2\text{-}C{\equiv}CH$$

E_a = 13.2 kcal.mole^{-1}

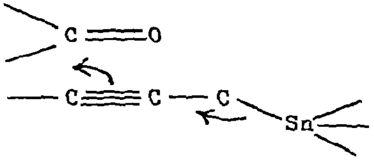
ΔG^* = 24.8 kcal. mole^{-1}

ΔH^* = 12.7 kcal. mole^{-1}

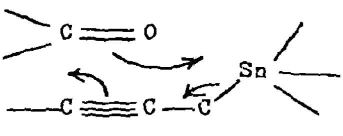
ΔS^* = −41 e.u.

Of the possible mechanisms operating (S_E2, S_E2', S_Ei') an S_E2 mechanism may be discounted since this would not account for the observed propargyl-allenyl transformations. A reasonable choice between the two remaining possibilities may be made on the basis of the high value of ΔS^*, which is comparable with the cyclic transition state XLVII of an S_Ei' mechanism, rather than that (XLVIII) of an S_E2' mechanism.

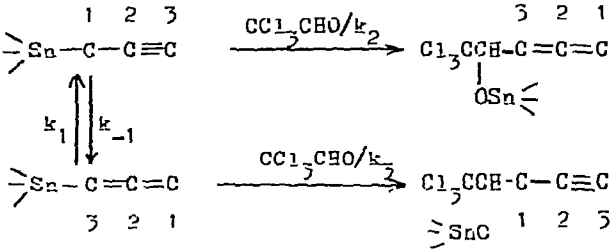
High concentrations of certain aldehydes (CCl_3CHO, p-$NO_2C_6H_4CHO \gg ClC_6H_4CHO$) promote the propargyl→allenyl transformation, but PhCHO, MeCHO, MeCOMe, or $C_6H_{11}O$ are inactive. Reaction of equilibrium mixtures of propargyl- and allenylstannanes with chloral, followed by hydrolysis of the alkoxytin products affords high yields of the transformed alcohols. The ratio of isomeric alcohols differed from the starting propargyl/allenyl ratio, and depends on the rate of equilibration of the isomers (k_1 and k_{-1}) and the rates of additon of the two isomers to chloral.[52]



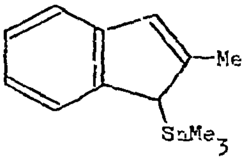
XLVIII



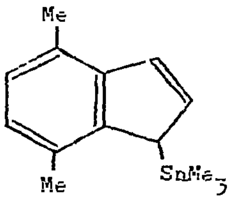
XLVII



Rakita has measured the variable temperature ^{1}H nmr spectra of 2-methyl- and 4,7-dimethyl-substituted trimethylstannylindenes IL and L, in a continuatio of his studies of the fluxional rearrangements of these compounds. Activation parameters for the rearrangement of IL and L were deduced to be 18.6 and 14.0 kcal. mole^{-1} (cf. 15.0 kcal. mole^{-1} for trimethylstannylindene). The effect of methyl substitution in these positions on $\Delta G^{\ddagger}$ were in a manner parallel to that predicted from a consideration of π-electron densities in the indenyl moiety.[53] The molecular ionisation potentials of trimethylstannylindene and -indane have both been determined to be 7.29 eV.[54] Kocheskov *et al.* have repor the synthesis of functionally substituted cyclopentadienyltin derivatives.[55]

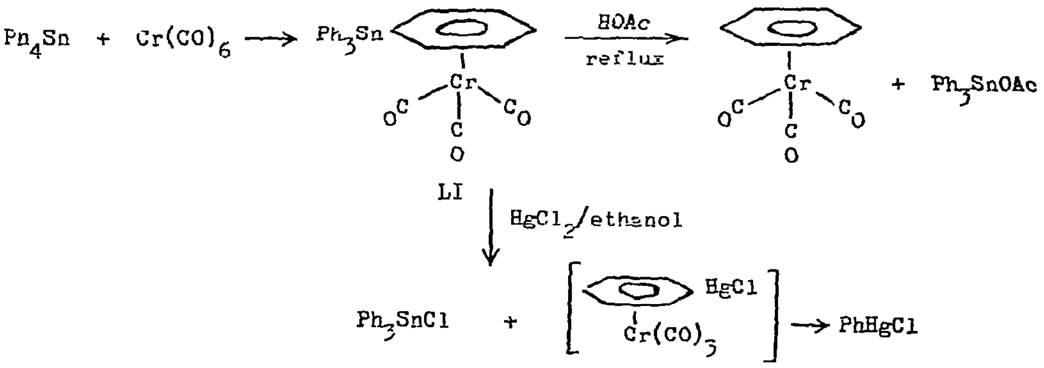


IL

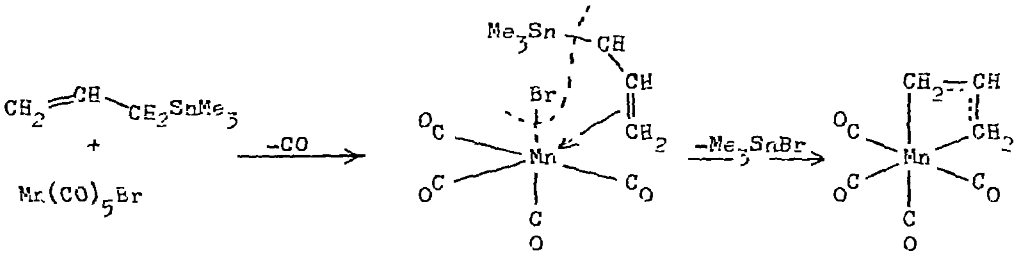


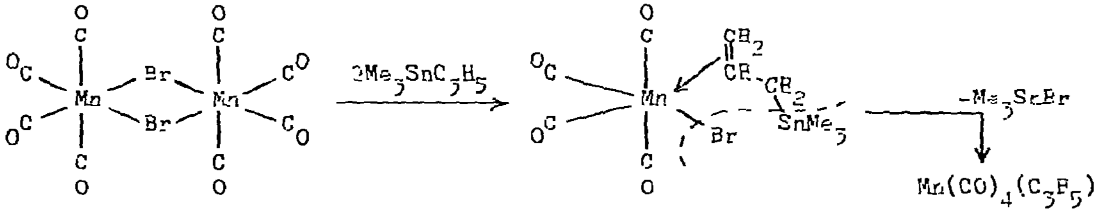
L

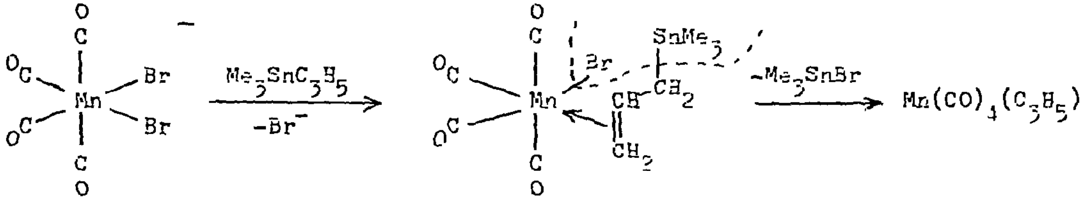
Heating Ph$_4$Sn with Cr(CO)$_6$ in diglyme afforded 44% of Ph$_3$SnC$_6$H$_5$.Cr(CO)$_3$ LI, which is cleaved by HgCl$_2$ and acetic acid:[56]



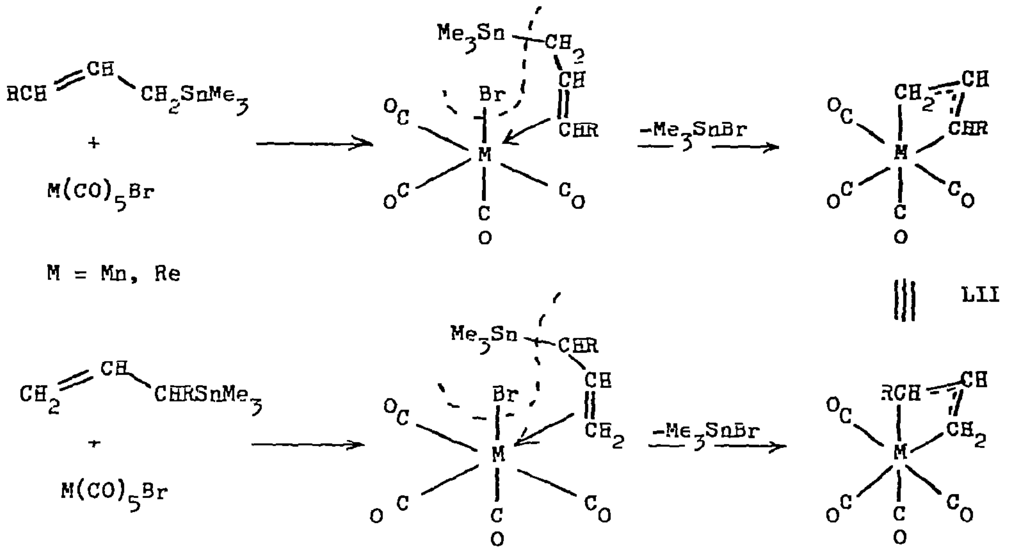
Abel *et al*. have reported the use of allyl-, cyclopentadienyl-, indenyl-, and related unsaturated trimethylstannanes in the synthesis of π-enyl metal carbonyl derivatives. Allyltrimethyltin reacts with $Mn(CO)_5Br$, dibromo-octacarbonylmanganese, and the dibromotetracarbonylmanganese anion to give high yields of allyltetracarbonyl manganese:





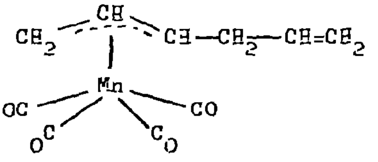


Interaction of $Mn(CO)_5Br$ and a wide range of allyltriorganostannanes $R_3SnCH_2CH{=}CH_2$ (R = Me, Et, Pr, Bu, Ph) and $Me_2Sn(CH_2CH{=}CH_2)_2$ also produced high yields of $Mn(CO)_4(C_3H_5)$. 1-, 2-, or 3-Substituted allyltrimethylstannanes produced the corresponding π-allyltetracarbonyls of manganese and rhenium. In the case of 1- and 3-substituted allylic systems, the Grignard method produced a mixture of isomeric 1- and 3-substituted allyltins. Reaction of both isomers, nevertheless, leads to the formation of identical products LII, *viz*.:

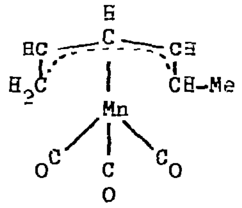


LII

Similarly, starting from 3-bromohexa-1,5-diene, a Grignard synthesis afforded a mixture of 3-trimethylstannylhexa-1,5-diene and 1-trimethylstannylhexa-2,5-diene, both of which, when treated with BrMn(CO)$_5$, afforded the same product LIIIa. A further product, identified as LIIIb, was also formed in this reactio

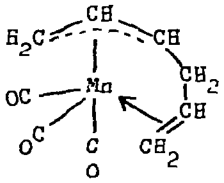


LIIIa



LIIIb

presumably *via* displacement of CO by the terminal olefin LIV, followed by a 1,3-proton shift to form the methylpentadienyl ligand system.



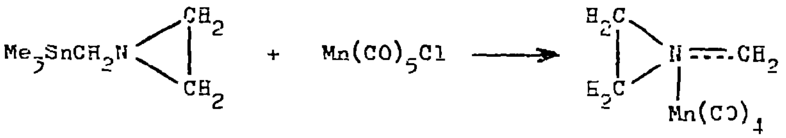
LIV

Trimethylstannylcyclopentadiene, -indene, and -fluorene are also very useful precursors for transition metal π-enyl derivatives. The mechanism is probably similar to that for the allyl systems, although the low Sn-C bond strength of these compounds does not preclude initial Sn-C bond fission followed by CO displacement. The $[Rh(CO)_2Cl]_2$ dimer is particularly reactive, undergoing reaction with $Me_3SnC_3H_5$ and $Me_3SnC_5H_5$ instantly at room temperature to produce quantitatively π-$C_3H_5Rh(CO)_2$ and π-$(C_5H_5)Rh(CO)_2$, respectively. Allylstannanes react with $Co_2(CO)_8$ and $Re_2(CO)_{10}$ to form high yields of π-allyl and stannyl-metal products:[57]

$$Ph_3SnCH_2CH{=}CH_2 \quad + \quad Co_2(CO)_8 \longrightarrow \pi\text{-}C_3H_5Co(CO)_3 \quad + \quad Ph_3SnCo(CO)_4$$

$$Me_3SnCH_2CH{=}CH_2 \quad + \quad Re_2(CO)_{10} \longrightarrow \pi\text{-}C_3H_5Re(CO)_4 \quad + \quad Me_3SnRe(CO)_5$$

Trimethylstannylmethylaziridine reacts similarly with $Mn(CO)_5Cl$ to form LV:[58]



LV

Lappert and his coworkers have investigated reactions of the alkynyltin compounds $R_3Sn.C{\equiv}C.Ph$ (R = Me, Et) with low oxidation state complexes of Mo^0, Mo^{II}. Co^0, Rh^I, Ir^I, and Pt^0. Four classes of reaction were observed:[58a]

(i) metathesis:

$$RhCl(CO)(PPh_3)_2 \xrightarrow{Me_3SnC\equiv CPh} Rh(C{\equiv}CPh)(CO)(PPh_3)_2$$

(ii) oxidative addition, with or without neutral ligand elimination:

$$RhCl(PPh_3)_3 + Me_3SnC{\equiv}CPh \longrightarrow Rh(C{\equiv}CPh)_2(SnMe_3)(PPh_3)_2$$

$$IrCl(CO)(PRPh_2) \quad + \quad R'_3SnC{\equiv}CPh \longrightarrow Ir(C{\equiv}CPh)_2(SnR'_3)(CO)(PRPh_2)_2$$

R = Ph, Me; R' = Me, Et

(iii) Metathesis and oxidative addition:

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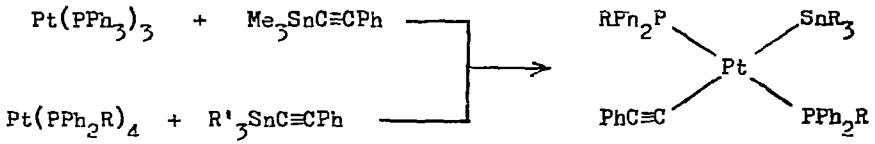


R = Me, Ph; R = Me, Et

$$Rh(C\equiv CPh)(PPh_3)_3 + Me_3SnC\equiv CPh \longrightarrow Rh(C\equiv CPh)_2(SnMe_3)(PPh_3)_2$$

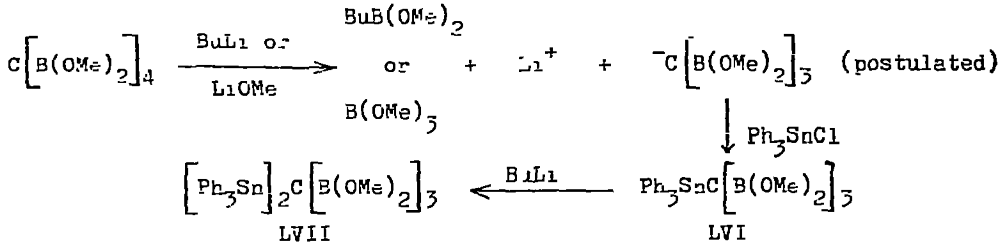
$$Ir(C\equiv CPh)(CO)(PPh_3)_2 + Me_3SnC\equiv CPh \longrightarrow Ir(C\equiv CPh)_2(SnMe_3)(CO)(PPh_3)$$

(iv) oxidative cleavage:

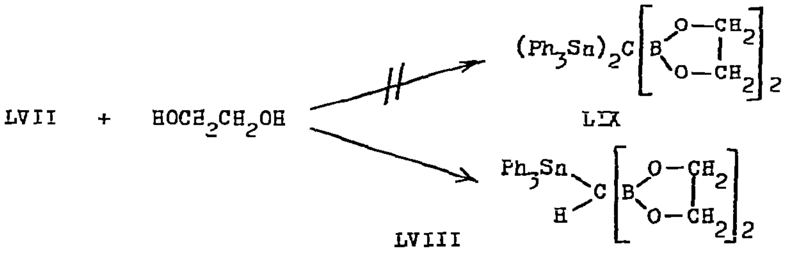
$$(\pi\text{-}C_5H_5)Mo(CO)_{3\ 2} + Me_3SnC\equiv CPh \longrightarrow (\pi\text{-}C_5H_5)Mo(SnMe_3)(CO)_3$$

$$Co_2(CO)_8 + Me_3SnC\equiv CPh \longrightarrow Co(SnMe_3)(CO)_4 + Co_2(C\equiv CPh)(CO)_6 \quad (?)$$

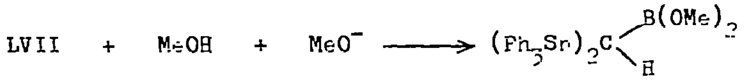
Matteson has described some of his results on tin derivatives of boronyl-substituted methanes. Treatment of tetrakis(dimethoxyboryl)methane with BuLi or LiOMe followed by Ph_3SnCl gives the monotin derivative LVI. LVI readily disproportionates on further treatment with BuLi to produce the ditin derivativ LVII:



LVI and LVII are readily hydrolysed at the boronic ester functions. Reaction of LVII with ethylene glycol resulted in cleavage of one of the boronyl groups from carbon to give LVIII, rather than the expected formation of LIX:

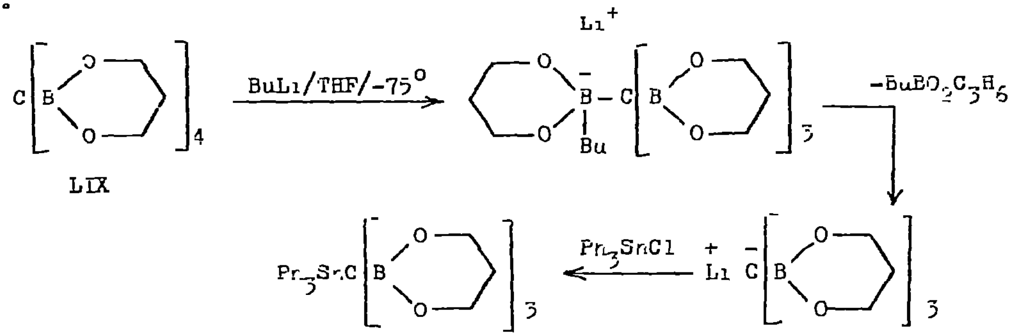


A similar cleavage occurs when LVII is treated with sodium methoxide in methanol:[59]



$$LVII + MeOH + MeO^- \longrightarrow (Ph_3Sn)_2C(B(OMe)_2)H$$

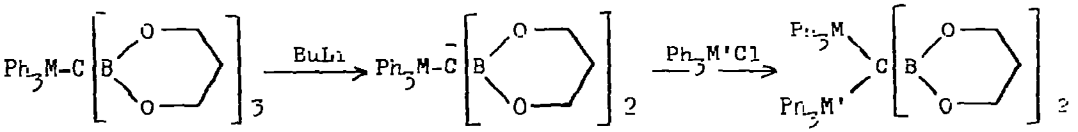
The propanediol methane tetraboronic ester LIX is much better behaved, and leads to the synthesis of a much wider range of stannyl-borylmethanes. Treatment of LIX with BuLi and Ph_3SnCl as before gives the monotin substituted product LX.[60,61]



LIX

LX (70%)

Unlike LVI, LX does not undergo base catalysed disproportionation, but further reaction with BuLi and triphenylgermanium, -tin, or -lead chlorides produced the simple LXIa and mixed LXIb and LXIc disubstituted products.



LXII

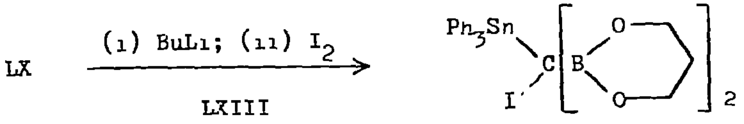
LXI

(a) M = M' = Sn

(b) M = Sn, M' = Pb

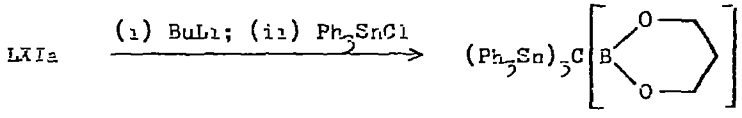
(c) M = Sn, M' = Ge or M = Ge, M' = Sn

Attempted bromination of LXII was not successful, but reaction with iodine produced the iodide LXIII as a stable crystalline solid.



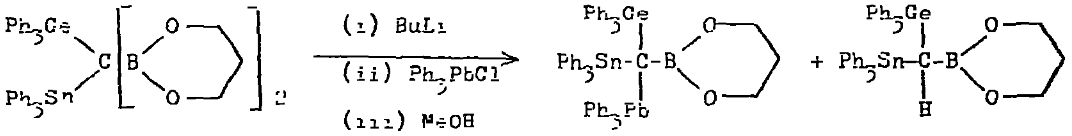
LXIII

The conversion of the ditin compound LXIa to the tritin compound LXIV proceeded smoothly:



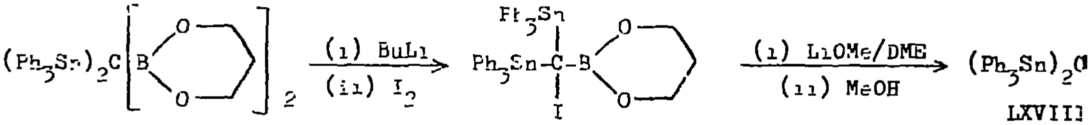
LXIV

The analogous reaction to form the mixed germanium-tin-lead compound LXV gave the desired product in only very small yield; the major product appeared to be the protodeboronation product LXVI, though both were not fully characterised.



LXV LXVI

Iodination of the carbanion from LXIa proceeded readily to give LXVII; which undergoes protodeboronation to afford LXVIII on treatment with LiOMe in DME followed by methanol. Attempted trapping of the $(Ph_3Sn)_2C$ grouping by cyclohexe in this reaction was unsuccessful. Attempts to react $Li^+ (Ph_3Sn)_2\bar{C}(BO_2C_3H_6)$ wit



LXVIII

LXVII

acetone or cyclopentane produced only the protodeboronation product $(Ph_3Sn)_2CHBO_2C_3H_6$. Attempts to replace the last boronic ester group of LXIV were also unsuccessful, the tritin derivative being extremely resistant to base attack.[61]

Organotin-substituted carboranes $R_n(X-1,2-C_2-B_{10}H_{10}X)_{4-n}SnP_n$ (R = alkyl, ar $X = C_{2-8}$ alkylene; n = 1, 2, 3) have been prepared by treating R_nSnH_{4-n} with the corresponding alkenylcarborane in the presence of benzoyl peroxide as catalyst.[62] A thesis describes the reactions of Group IV halides with decaborane anions.[63]

The alkaline cleavage of o-, m- and p-carboranyltrimethylstannanes by KOH in MeOH, and by KOD in MeOD, has been studied. The rate constants were the same within experimental error for both media and varied in the order ortho≫meta>para ($k^{20^\circ}_{rel}$ = 1020, 17, and 1, respectively). Corresponding thermodynamic parameters were also deduced. Since no kinetic isotope effect operates, the following mechanism was proposed:[63a]

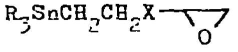
$$\begin{tikzcd}
\text{o,m,p-}HCB_{10}H_{10}C\text{-}SnMe_3 + B^- \arrow[r, shift left, "k_1"] & \text{o,m,p-}HCB_{10}H_{10}C^-(Me_3SnB) \arrow[l, shift left, "k_{-1}"] \arrow[d, "k_2"', "MeOH"] \\
 & \text{o,m,p-}HCB_{10}H_{10}CH + Me_3SnB
\end{tikzcd}$$

If $k_2 \gg k_{-1}$, the overall rate is expressed by the equation:

$$\text{Rate} = k_1 [Me_3SnR].[OH^-]$$

3. Hydrides

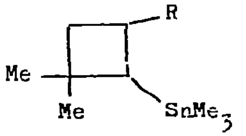
The hydrostannation of olefins and acetylenes has been used widely to synthesise a wide range of derivatives. A Russian patent reports the preparation of a variety of tetraorganostannanes $R_nR'_{4-n}Sn$ (R = alkyl, aryl; R' = alkenyl, residue of functionally substituted unsaturated compound; n = 2, 3) by γ-irradiation of mixtures of R_nSnH_{4-n} and olefins or functionally substituted unsaturated compounds.[64] Trimethyltin hydride adds to butadiene in the presence of a phosphinopalladium complex catalyst.[65] Organotin epoxides LXIX are produced in 49-85% yields by the addition of R_3SnH to vinyl glycidyl ethers.[66]



$R_3SnCH_2CH_2X$ X = $-CH_2O-$, $-CH_2OCH_2-$

LXIX

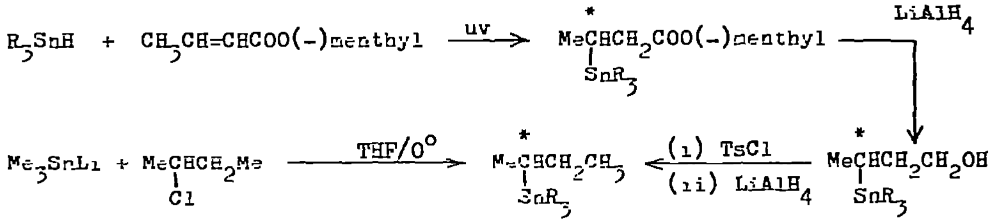
The addition of Me_3SnH to methyl 3,3-dimethyl-1-cyclobutenecarboxylate or 3,3-dimethyl-1-cyclobutenecarbonitrile in the presence of AIBN gives the adducts LXX as mixtures of cis- (24%) and trans- (76%) isomers. Analogous dimethylbromotin derivatives were also prepared.[67]



R = MeO_2C, NC

LXX

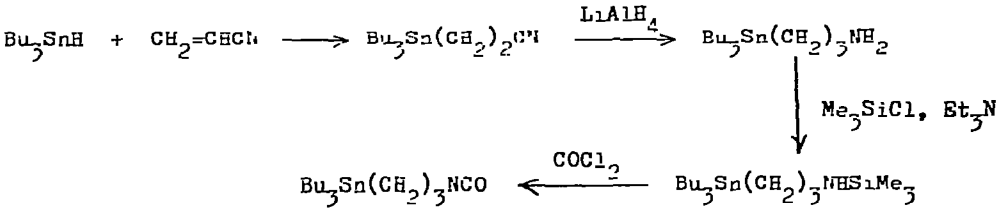
Chiral organotin compounds LXXI have been synthesised by the asymmetric hydrostannation of a C=C double bond:



LXXI

The same compounds are also obtained from Me_3SnLi and $MeC^{*}HClCH_2Me$. The asymmetry synthesis yield and optical purity of LXXI was determined by nmr using lanthanid shift reagents.[68,69]

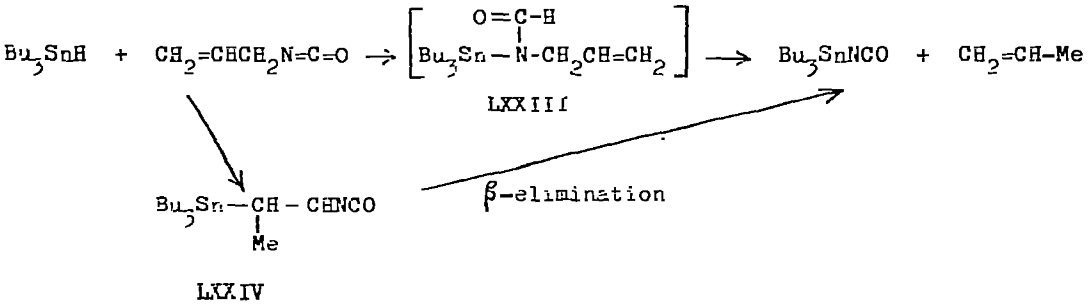
Trialkyltin acetates are produced from the treatment of trialkyltin hydride with ketene in a stream of inert gas.[70] 3-(Tributylstannyl)propyl isocyanate LXXII has been synthesised <u>via</u> the route:

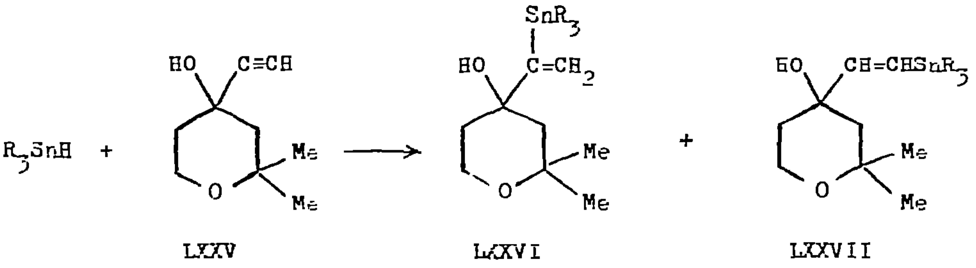


LXXII

LXXII could not be prepared by the addition of Bu_3SnH to $CH_2=CHCH_2NCO$. Instead, Bu_3NCO (66%) and propene (20%) were obtained, together with an unidentified visc substance. This behaviour is rationalised by the breakdown of the initial -N=C= and C=C hydrostannation products LXXIII and LXXIV:[70]

Triorganotin hydrides add to EtOC≡CH and BuOC≡CH by a free-radical process to give β-cis adducts,[71] and to the pyranol-acetylenes LXXV to give a mixture of





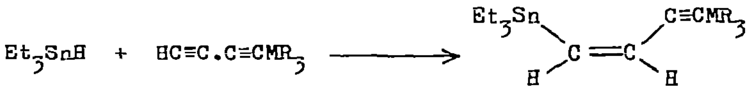
the adducts LXXVI and LXXVII.[72] The main product of the reaction of $\mathrm{Et_3SnH}$ with $\mathrm{Et_3SnC{\equiv}C.C{\equiv}CH}$ in a 1:1 molar ratio was 1,4-bis(triethylstannyl)-1-butene-3-yne LXXVIII. Bis(triethylstannyl)butadiyne was formed as a by-product.

$$\mathrm{Et_3SnH} + \mathrm{Et_3SnC{\equiv}C.C{\equiv}CH} \longrightarrow \underset{\mathrm{LXXVIII}\ (\sim 30\%)}{\mathrm{Et_3SnC{\equiv}C.CH{=}CHSnEt_3}} + \mathrm{Et_3SnC{\equiv}C.C{\equiv}CSnEt_3};$$

LXXVIII is cleaved by acetic acid at the alkynyl-tin bond:

$$\mathrm{Et_3SnC{\equiv}C.CH{=}CHSnEt_3} + \mathrm{CH_3CO_2H} \longrightarrow \mathrm{Et_3SnO_2CMe} + \mathrm{HC{\equiv}C.CH{=}CHSnEt_3}$$

The silyl- and germyl-diynes also underwent addition to afford cis products:



$\mathrm{MR_3 = Me_3Si,\ Et_3Ge}$

A free-radical chain mechanism was proposed.[73] Organotin hydrides undergo 1,2-addition to 1-butyne to give the corresponding 1-butenyltin compounds:

$$R_3SnH + HC{\equiv}CEt \longrightarrow R_3SnCH{=}CHEt$$

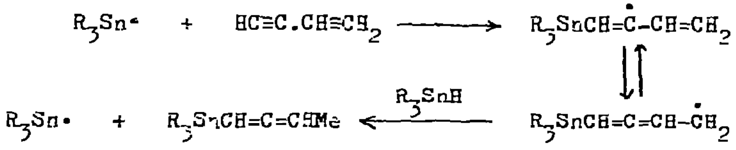
$$R_2SnH_2 + 2HC{\equiv}CEt \longrightarrow R_2Sn(CH{=}CHEt)_2$$

With vinyl acetylene, 1,4-addition takes place and allenyltin derivatives result

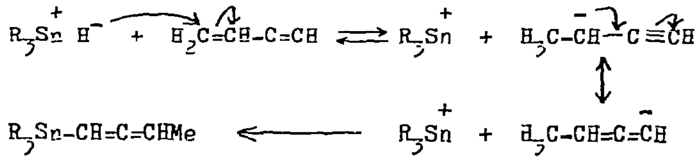
$$R_3SnH + HC{\equiv}C.CH{=}CH_2 \longrightarrow R_3Sn{-}CH{=}C{=}CHMe$$

Both radical and ionic mechanisms were proposed.[74]

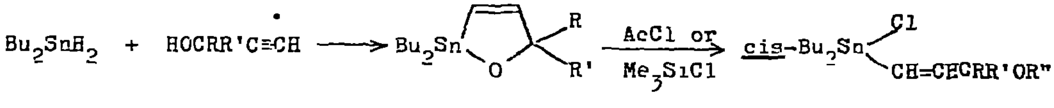
Radical:



Ionic:



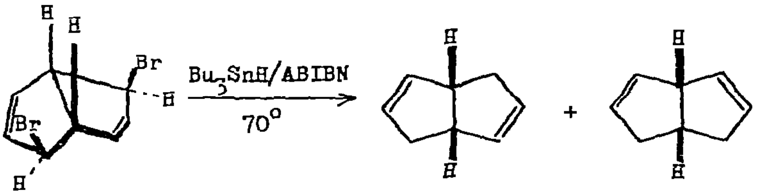
The heterocyclic products LXXIX are obtained from the cycloaddition reaction of Bu_2SnH_2 with $HOCRR'C{\equiv}CH$. LXXIX are cleaved stereospecifically by acetyl chloride and Me_3SiCl:[75]



LXXIX

R" = AC, Me_3Si

Organotin hydrides have been further used as reducing agents. The product of stereoselective cis,exo-1,4-bromination of semibullvalene LXXX is reduced by Bu_3SnH to form the dienes LXXXI and LXXXII in a 3:1 ratio.[76]

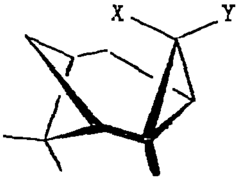


LXXX

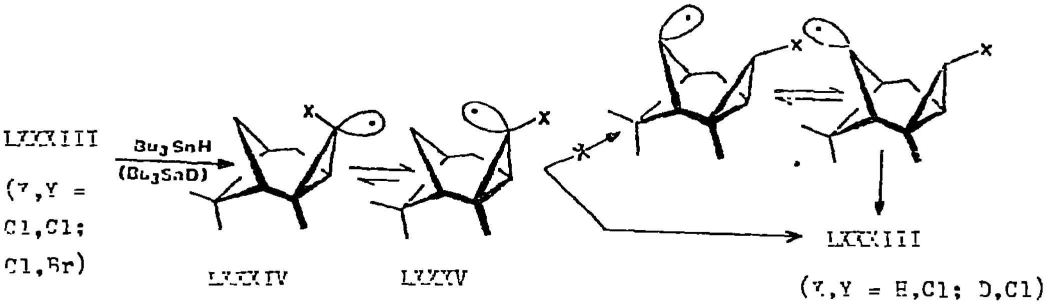
LXXXI LXXXII

78%

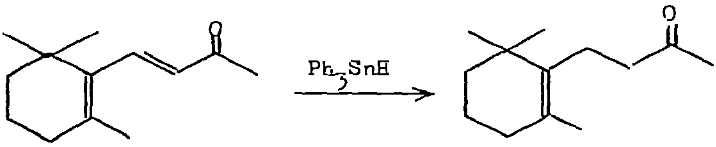
The reduction of both *gem*-cyclopropanyl compounds LXXXIII (X,Y = Cl,Cl; Cl,Br) by Bu_3SnH under free-radical conditions gives LXXXIII (X,Y = H,Cl). Reduction of LXXXIII (X,Y = Cl,Cl) by Bu_3SnD affords LXXXIII (X,Y = D,Cl). The following mechanism was proposed, in which the radical LXXXIV rapidly inverts to the less sterically hindered radical LXXXV. The Bu_3SnD reduction demonstrates that the radical LXXXV preferentially abstracts H(D) from the tin hydride rather than from the adjacent bridging methylene group:[77]



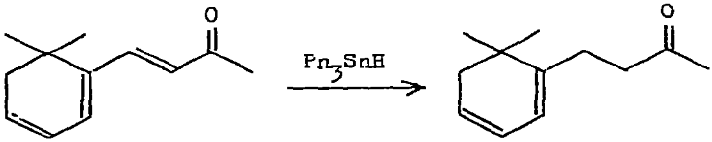
LXXXIII



β-Jonone and dehydro-β-jonone are reduced by Ph_3SnH to dihydro-β-jonone LXXXVI and dihydrodehydro-β-jonone LXXXVII.

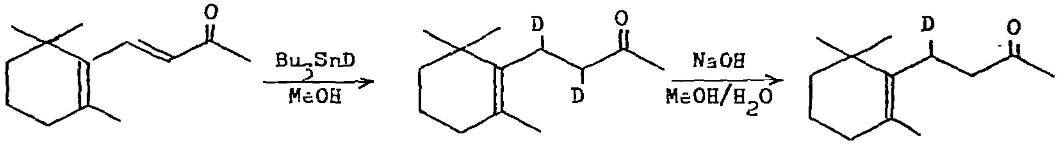


LXXXVI



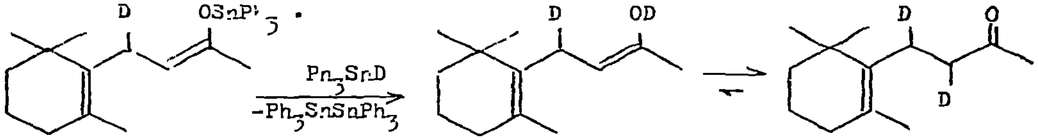
LXXXVII

Ph_3SnD in methanol reduces β-jonone to dihydro-β-jonone-d_2 IXC, which undergo H/D exchange with aqueous methanolic NaOH to afford dihydro-β-jonone-d_1 XC:



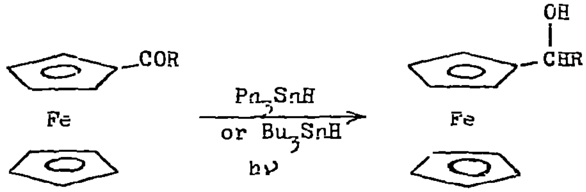
IXC (85%) XC (80%)

The mechanism of the reduction probably involves initial addition of tin deuter to give the alkoxystannane XCI, which reacts with a second molecule of Ph_3SnD:[78]



XCI

The reduction of ketones, especially ferrocenyl ketones, has been extensive studied. Ultra-violet irradiation of 1-formyl-, 1-acetyl-, and 1-benzoyl-ferroc in the presence of triphenyltin or tributyltin hydride gave the corresponding alcohols XCII as the major product:



XCII

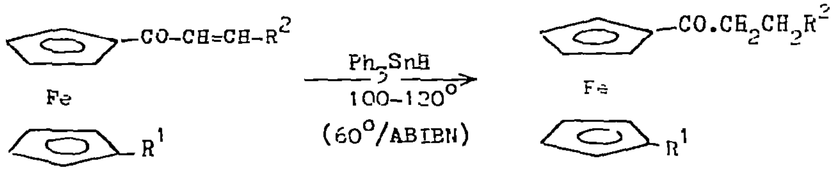
Quantum yields for the reactions are very low (≈0.002), and estimates of enthal changes in the primary reaction step:

$$\left[\underline{Fc}C(O)R\right]^* + R'_3SnH \longrightarrow \underline{Fc}\dot{C}R(OH) + R'_3Sn^\bullet \qquad \Delta H \approx +15 \text{ kJ mole}^{-1}$$

suggest that the inefficiency of the photoreduction arises because the initial step is relatively slow and physical decay of the excited state competes effectively with chemical reaction.[79] Ph_3SnH reduces 1-vinylferrocene at 70° with or without ABIBN to give high yields of XCIII:

$$\underline{Fc}\text{-CH=CH}_2 \xrightarrow{Ph_3SnH/ABIBN/70^\circ} \underset{XCIII}{\underline{Fc}\text{-CH}_2\text{-CH}_2\text{-SnPh}_3} \quad (53\text{-}68\%)$$

With α,β-ethylenic ketones XCIV, selective reduction of the C=C bond occurs:



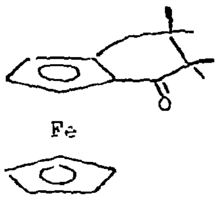
XCIV

57-96%

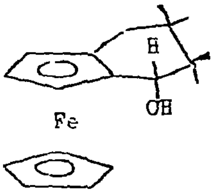
When R^1 = COPh, only the conjugated system is reduced. The presence of ABIBN notably accelerates the reaction. In contrast, the products obtained in reduction of acylferrocenes by Ph_3SnH in the absence of solvent depends on the presence or otherwise of radical generators. At 70°, in the presence of ABIBN, 1-acylferrocenes XCIV are rapidly reduced to the corresponding alcohols XCV. Without radical catalysts the reaction is very complex, and the reduction products XCV, XCVI, XCVII, and XCIII are obtained in quantities which vary with the group R and the conditions.

$$\underset{XCIV}{\underline{Fc}\text{-CO-R}} \longrightarrow \underset{XCV}{\underline{Fc}\text{-CHOH.R}} + \underset{XCVI}{\underline{Fc}\text{-CH}_2\text{R}} + \underset{XCVII}{\underline{Fc}\text{-CHR-O-CHR-}\underline{Fc}}$$

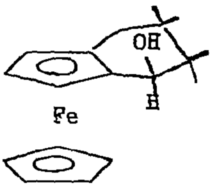
The use of $AlCl_3$ introduces more specificity; Fc-CO.Ph is converted to Fc-CH_2Ph at 85°, 2 hrs in a 65% yield as the only isolated product. The reduction of (α-oxotetramethylene)-1,2-ferrocene XCVIII is stereospecific without added ABIBN leading to 10-39% yields of the corresponding endo alcohol IC, whilst with ABIBN both endo and exo (C) isomers are formed in a ~70:30 ratio.



XCVIII

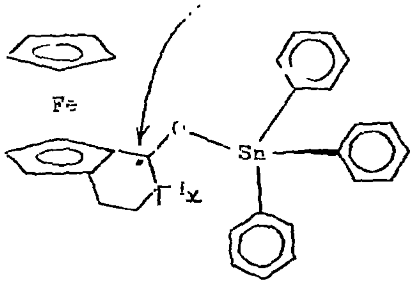


IC (*endo*)

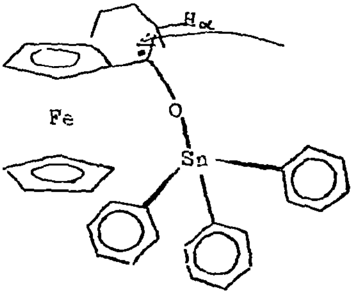


C (*exo*)

IC and C are stable at the reaction temperature employed ($\leqslant 100^{\circ}$), but slowly dehydrate at 120° to the corresponding olefin. In the absence of radical initiators, an ionic mechanism involving nucleophilic attack of the tin hydride, approaching *via* the less sterically hindered face would lead to the observed exclusive formation of the *endo* alcohol. With ABIBN, $Ph_3Sn\cdot$ radicals are formed which attack XCVIII to give an intermediate radical which can exist in the possible conformations CI and CII (leading to *exo* and *endo* alcohols respectively)



CI



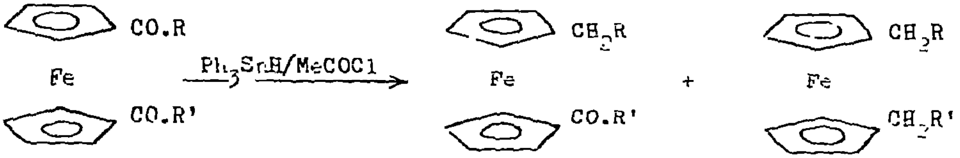
CII

Although the conformer CI is expected to be more stable on steric grounds , it appears that reaction at CII is preferred. Apparently the energy difference between the two conformers is small compared with the energy requirements of hydride attack on CI.[80]

The combined action of Ph_3SnH and acetyl chloride efficiently reduces acylferrocenes to alkylferrocenes:

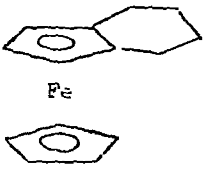
$$\underline{\underline{Fc}}\text{-CO-R} + 2Ph_3SnH + 2Me.CO.Cl \longrightarrow \underline{\underline{Fc}}\text{-CH}_2\text{-R} + 2Ph_3SnCl + (MeCO)_2O$$

The best results are obtained when a 1:2:4 ratio of $\underline{\underline{Fc}}$.CO.R, Ph_3SnH and Me.CO.Cl is used. Yields varying from 40–90% are obtained depending on the group R. Bu_3SnH is less reactive, but the yields are less dependent on R (55–66%); by-products such as **Fc**-C(OAc)=CHPh and **Fc**-CCl=CHPh are also formed. With 1,1'-diacylferrocenes, the reactivity of the functions depends on the substituents, and leads to the formation in some cases of 1'-alkylacylferrocenes. Thus, 1-acetyl 1'-benzoylferrocene CIII (R = Me, R' = Ph) is reduced to give 1'-benzoyl ethylferrocene CIV (R = Me, R' = Ph) (46%) and ethylbenzylferrocene CV (R = Me, R' = Ph) (13%). A large excess of reducing agent causes complete reduction to CV (R = Me, R' = Ph).

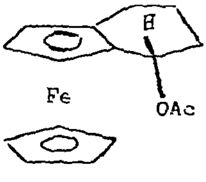


CIII CIV CV

Similar results are obtained for a variety of groups R and R'. Reduction of the ketones Ph.CO.R (R = Me, Ph) by Ph_3SnH and Me.CO.Cl gave mixtures of $PhCH_2R$ and PhCH(OAc)R depending on R and the reaction temperature. At 55°, reduction of Ph.CO.Ph gives only $PhCH_2Ph$, whilst at 25°, PhCH(OAc)Me is the major reduction product (80–85%) of Ph.CO.Me. (α-Oxotetramethylene)-1,2-ferrocene XCVIII is reduced under the same conditions to give CVI and small yields of the acetate CVII. Increased yields of CVII are obtained by using less Me.CO.Cl. No *exo*-acetate was detected.[81] Aliphatic and aromatic acetates and the acetates of ferrocenyl alcohols do not undergo reaction with Ph_3SnH in benzene, but addition of Me.CO.Cl results in reduction to the corresponding hydrocarbon, save for $PhCH_2CH(OAc)Me$



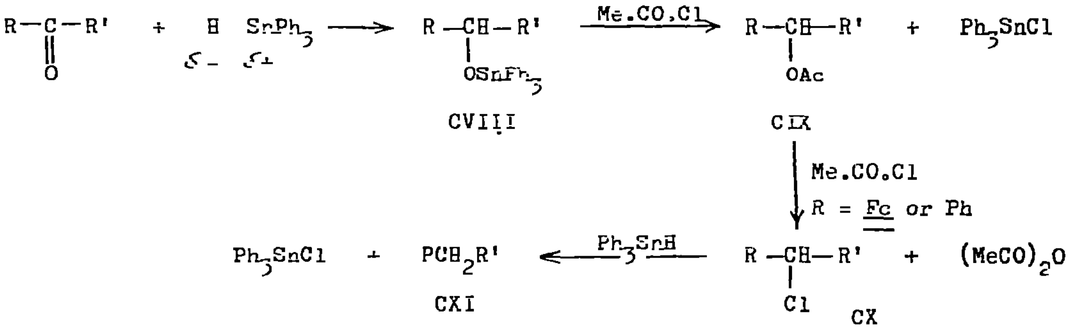
CVI



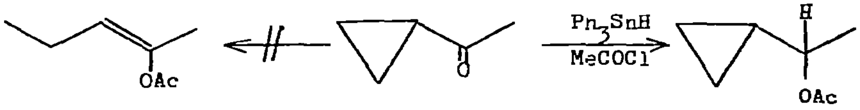
CVII

which is inert. This latter observation is hardly surprising since $PhCH_2CH(OAc$ is produced exclusively from the $Ph_3SnH/Me.CO.Cl$ reduction of $PhCH_2.CO.Me$. On the other hand, the reactivity of the ferrocenyl acetates rationalises their absence in the products of the similar reduction of acylferrocenes.

The mechanism of the $Ph_3SnH/Me.CO.Cl$ reduction of ketones has been studied in detail. The data suggest an ionic mechanism involving initial nucleophilic attack of the tin hydride on the ketone to afford the tin alkoxide CVIII. This is then cleaved by Me.CO.Cl to form the acetate CIX, which, if R = ferrocenyl or Ph, reacts with more Me.CO.Cl to give the chloride CX. Reduction of CX by Ph_3S yields the final hydrocarbon product CXI:

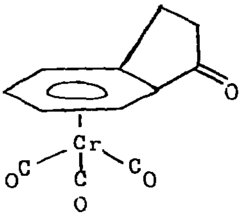


A radical mechanism for the reduction was eliminated since radical generators (ABIBN) or inhibitors (hydroquinone, galvanoxyl) did not affect the rate of reaction or the nature of the products. Further corroboration is available fro the reduction of cyclopropylmethylketone CXII, which is known to undergo reduct by both ionic and free radical mechanisms. $Ph_3SnH/Me.CO.Cl$ reduction of CXII produces only CXIII, expected for an ionic mechanism, and no ring-opened produc CXIV which is obtained when a radical mechanism operates.

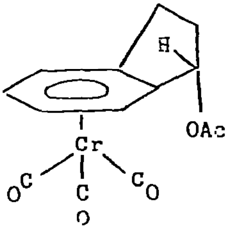


CXIV CXII CXIII

The reduction of 1-indanone chromium tricarbonyl CXV by $Ph_3SnH/MeCOCl$ in benzene gives exclusively the endo-acetate CXVI in 87% yield, again supporting an ionic,



CXV



CXVI

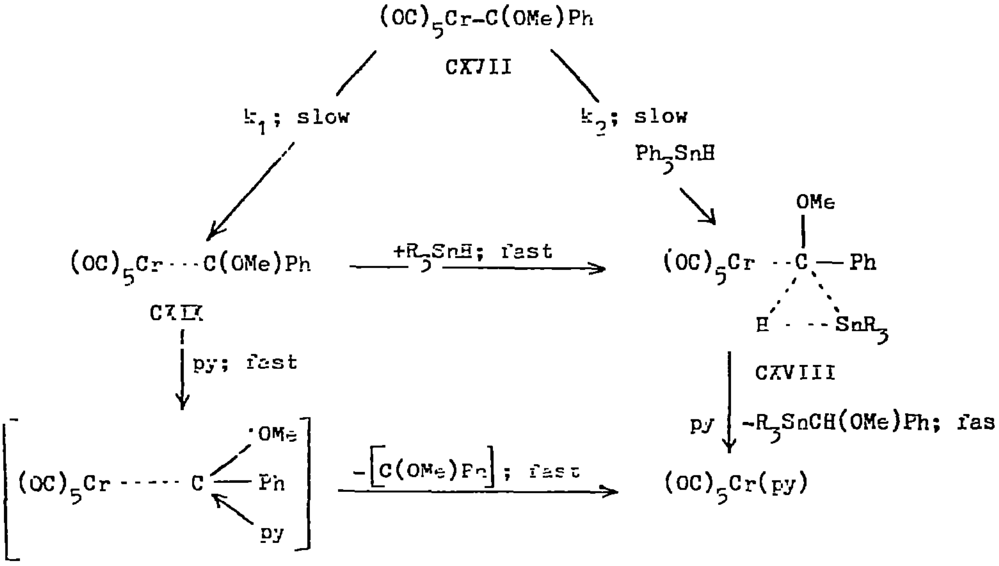
rather than a radical mechanism, which would be expected to give a mixture of endo and exo acetate isomers.[82]

Carbene complexes of chromium and molybdenum $(OC)_5MC(X)C_6H_4Y$ (X = OMe, NC_nH_n (n = 2, 4); Y = p-OMe, p-Me, H, p-Cl) react with triorganotin hydrides in the presence of coordinating base (pyridine, acetonitrile) in hexane to give the insertion products $R_3SnCHXC_6H_4Y$. The Group VI metal is recovered as the base complexes $B_nM(CO)_{6-n}$. Competition experiments show that the susceptibility of silicon, germanium, and tin hydrides to insertion of $[PhCOMe]$ vary in the order $Et_3SiH > Ph_3SiH < Ph_3GeH < Ph_3SnH$, Pr_3SnH.[83] A detailed kinetic study of the reaction of $Cr(CO)_5[C(OMe)Ph]$ CXVII with R_3SnH (R = Pr, Ph) shows that the rate of reaction is given by

$$-\frac{d}{dt}[Cr] = k_{obs}[Cr] = k_1[Cr] + k_2[Cr][R_3SnH] + k_3[Cr][py]$$

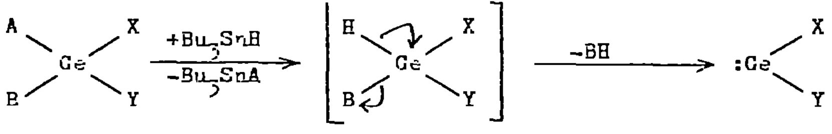
$$Cr = CXVII$$

From the data the following mechanism was proposed:



The dominant reaction path under the conditions used was the second-order proces (k_2). Derived activation parameters were consistent with the direct formation of CXVIII by nucleophilic attack on the carbocation centre in a concerted proces CXVIII is also formed from CXIX in which the Cr–C bond is stretched, and therefo more susceptible to nucleophilic attack by R_3SnH. The other second-order proces (k_3) is not kinetically significant under normal conditions.[84]

Et_3SnH reacts rapidly with Et_3GeK in benzene to afford $Et_3Ge.SnEt_3$ (20%) an KH (50%).[85] Me_3SnH slowly reacts with germylcyclopentadiene $H_3GeC_5H_5$ at 60° to give monogermane and $Me_3SnC_5H_5$. Reaction in the opposite sense, ie, to give Me_3SnGeH_3 and C_5H_6, was thought also to take place.[86] Satge *et al*, have used th reduction of a wide variety of germanium(IV) compounds by Bu_3SnH to produce germanium(II) intermediate species:

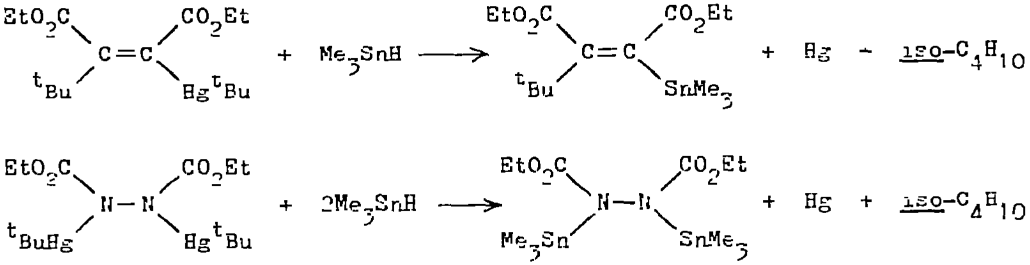


A = Cl, Br; B = OR, NR_2

X,Y = OR,OR; Cl,OR; Br,OR; NR_2,NR_2; O O; O S; S S; RN NR

tert-Butylmercury compounds undergo reaction with Me_3SnH to give the corresponding trimethyltin derivative in essentially quantitative yield:[89]

$$ {}^{t}\text{BuHgCl} + \text{Me}_3\text{SnH} \longrightarrow \text{Me}_3\text{SnCl} + \text{Hg} + \underline{\text{iso}}\text{-C}_4\text{H}_{10} $$

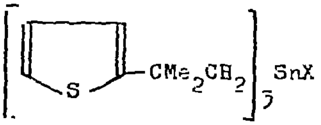


4. Halides

The 'direct' synthesis and other methods of preparation of organotin halides continues to be the subject of much interest, mostly in the patent literature. Organotin trifluorides $RSnF_3$ (R = alkyl, alkenyl, aryl) are prepared by treating the respective organotin carboxylates with concentrated HF in benzene.[90] Me_2SnCl_2 has been prepared in 75-80% yield by heating tin with MeCl in HMPA at 140-50°.[91] Benzyl- and octyltin chlorides and bromides have been obtained by refluxing at 170° mixtures of tin granules, alkyl halide, the corresponding alcohol in the presence of $BuNH_2$, cyclohexylamine or $PhNH_2$, and phenol.[333] Arsenic compounds of the types R_nAsX_{3-n}, R_mAsX_{5-m}, $R_nH_{3-n}AsO_4$ or $R_nH_{3-n}AsO_3$ (R = alkyl or aryl; n = 1-3; m = 1-5; x = Br, Cl) are catalysts for the manufacture of organotin chlorides and bromides. Thus heating tin foil, BuCl, Ph_3As, and iodine 32 hrs at 170-80° resulted in 95% tin conversion to $BuSnCl_3$ (16%), Bu_2SnCl_2 (78%), and Bu_3SnCl (6%).[92] α-Chloromethylethers $ROCH_2Cl$ (R = Me, Et, Bu) react with powdered tin at 20-80° to give small (~17%) yields of $(ROCH_2)_2SnCl_2$.[93] Bis(alkylsilyl)tin dihalides have been prepared by treating tin with 2-5 equivalents of alkylsilyl halide at 100-200° in the presence of an amine or phosphine catalyst.[94] Diallyltin dibromide is formed in 52% yield after 7-8 days from allyl bromide and tin (70% conversion) in the absence of oxygen. Raising the reaction temperature increased the conversion of tin to 80%, but lowered the yield of product to < 20%. No reaction takes place in the absence of oxygen.[95] Diallyltin dibromid is also obtained by irradiation of tin and allyl bromide in an inert atmosphere. Heating a mixture of tin leaves, magnesium, BuI and butanol at 220-5° under nitrogen results in the formation of Bu_2SnI_2.[97] High yields (~90%) of dialkylt diiodides are obtained by the reaction of alkyl iodides with tin using a *N*-containing heterocyclic or quaternary ammonium compound as catalyst.[98] The optimum conditions for 'direct' synthesis of dialkyltin diiodides have been investigated 'Spongy' tin metal (from solutions of $SnCl_2$ with zinc) was found to react best. *n*-BuI afforded the highest yield of dialkyltin diiodide (80%); other iodides (*n*-amyl, *n*-hexyl, 2-ethylhexyl, and *n*-octyl) gave only 16-30% yields. The addit of amine or amine hydrochloride catalysts was necessary, otherwise the reactions are slow.[99] The activation energy of the reaction $Sn + BuBr \longrightarrow Bu_2SnBr_2$ has been deduced to be 9 ± 2 kcal. mole^{-1}; the enthalpy of formation is 11 kcal. mole^{-1}.[100] Reduction of alkyl halides at a tin cathode in tetraethylammonium halide - methyl cyanide media results in mixed degrees of alkylation at tin. Th primary products are polymers derived from $[RSn]$ and $[R_2Sn]$ species. The final products depend on the environment and tend to be complex mixtures. Electrolysi under aerobic conditions leads to a 'direct' synthesis of Bu_2SnO and Oct_2SnO. A mixture of alkyltin halides is formed in an undivided cell by the interaction of anode and cathode products, other products include complex alkylhalogenostannate(IV) anions.[122]

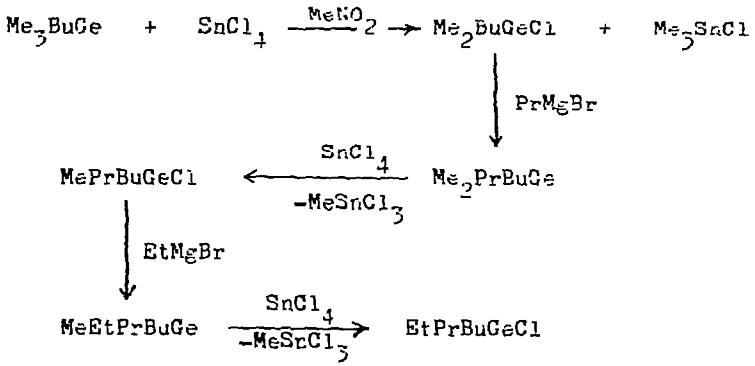
Diorganotin dichlorides have been prepared in moderate yields (35-55%) by reacting anhydrous tin(II) chloride with Grignard reagents in ether. The intermediate diorganotin species is then oxidised by sodium hypochlorite to the diorganotin oxide, which is converted to the dichloride by dilute hydrochloric acid.[101] Bis(ferrocenyl)tin and bis(cymantrenyl)tin dichlorides CXX and CXXI respectively, are obtained in 70-80% yield by oxidation of tin(II) chloride with the corresponding diorganomercurial in DME or THF. CXXI forms a 1:1 comple with DMF, and is readily hydrolysed by dilute aqueous alcoholic ammonia or sodium carbonate to bis(cymantrenyl)tin oxide monohydrate. Halide exchange occurs with CXXI and sodium iodide to afford bis(cymantrenyl)tin diiodide.[102]

Reaction of R_3SnCl or R_2SnCl_2 with R'MgCl gives $R_3R'Sn$ or $R_2SnR'_2$ respectively which, treated with $SnCl_4$, give $R_2R'SnCl$ (R, R' = Me, Bu, Pr, cyclohexyl, octyl, hexyl).[103] Thienylalkyltin compounds CXXII are obtained from thienylalkyl



CXXII

Grignard reagents and $SnCl_4$.[104] Wurtz reaction of $SnCl_4$ and BuCl gives Bu_4Sn, which undergoes ligand redistribution with $SnCl_4$ to give Bu_3SnCl and Bu_2SnCl_2.[105] Ligand redistribution reactions of this type in the $R_4Ge/SnCl_4$, $R_4Sn/GeCl_4$, $R_6Ge_2/SnCl_4$, $R_3SiGeR_3/SnCl_4$, and $R_8Ge_3/SnCl_4$ systems have been extensively studied by Bulter and Drenth. Solvent effects are important; the rates of alkyl/chlorine exchange increase with increasing dielectric constant of the solvent. Thus, in nitromethane the reaction rate in the $R_4Ge/SnCl_4$ system is at least 100 times faster than in benzene. In the $R_4Ge/SnCl_4$ & $SnR_4/GeCl_4$ systems, only the transfer of one alkyl group could be accomplished. The reaction rates as expected decreased with increasing bulkiness of the alkyl group; eg. for $R_4Ge/SnCl_4$/nitromethane, rate = Me $>$ Et $>$ Pr $\gg$ Bu $\gg$ pentyl. Dealkylation of mixed tetraalkylgermanes is very selective; the rate of dealkylation decreasing in the order Me $>$ Et $>$ Pr $>$ Bu. Thus, reaction of $Et_2PrBuGe$ with $SnCl_4$ gave exclusively $EtSnCl_3$ and EtPrBuGeCl. This specificity allows the synthesis of the mixed tetraalkylgermane MeEtPrBuGe CXXIII by the route:

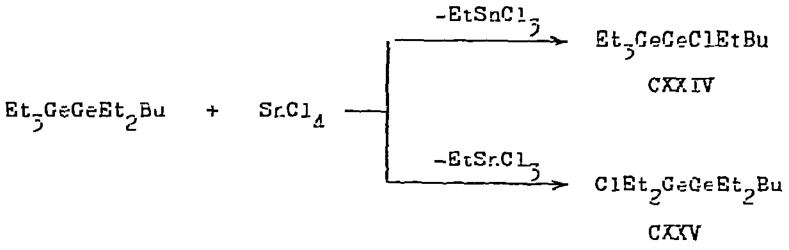


CXXIII

Reaction of $SnCl_4$ with digermanes proceeded similarly. Hexaethyldigermane and $SnCl_4$ in acetyl chloride react to give $Et_3GeGeClEt_2$ and $EtSnCl_3$, the reaction proceeding faster than Et_4Ge and $SnCl_4$ under the same conditions. Kinetic studies show that the reaction is first order in each reactant and second order overall. Addition of ABIBN has no effect, but the size of the alkyl group markedly affected the rate. Relative rate constants for the system $R_6Ge_2/SnCl_4$ were found to be: R = Me, k_{rel} = 125; R = Et, k_{rel} = 1; R = Bu, k_{rel} = 0.25. High selectivity in dealkylation was again observed. Thus reaction of Me_3GeGeE with $SnCl_4$ gave exclusively $MeSnCl_3$:

$$Me_3GeGeEt_3 \quad + \quad SnCl_4 \xrightarrow{MeNO_2} Me_2ClGeGeEt_3 \quad + \quad MeSnCl_3$$

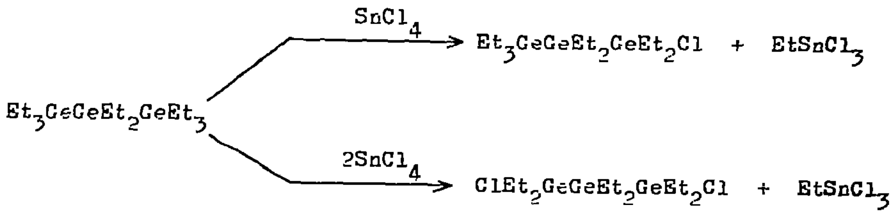
With $Et_3GeGeEt_2Bu$, statistical dealkylation takes place forming CXXIV and CXXV in a 2:3 ratio:



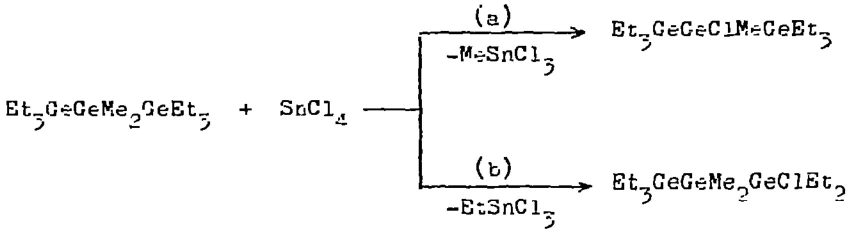
Exclusive dealkylation at germanium takes place with $Me_3SiGeEt_3$:

$$Me_3SiGeEt_3 \quad + \quad SnCl_4 \xrightarrow{MeNO_2} Me_3SiGeClEt_2 \quad + \quad EtSnCl_3$$

Reaction of octaethyltrigermane with one or two moles of $SnCl_4$ in nitromethane resulted in exclusive terminal substitution:



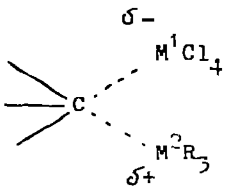
However, 2,2-dimethylhexaethyltrigermane with $SnCl_4$ gave predominantly methyl substitution in acetyl chloride, but ethyl substitution in nitromethane:



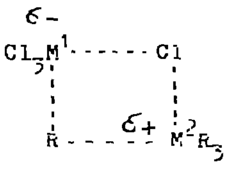
MeCOCl: 90% (a), 10% (b)

$MeNO_2$: 5% (a), 95% (b)

An S_E2(open) CXXVI rather than an S_E2(cyclic) CXXVII mechanism was preferred for these reactions.[106]



CXXVI



CXXVII

GeX_4 (X = Br, I) react with tetraalkylstannanes R_4Sn (R = Et, Bu, Ph) at 250° to form R_2SnX_2 and R_2GeX_2.[107] Butylvinyltin dichloride has been prepared by heating $SnCl_4$ with Bu_4Sn, treating the resulting $BuSnCl_3$ with excess vinylmagnesium bromide, and allowing the butyltrivinyltin to disproportionate with $BuSnCl_3$.[108] Other unsymmetrical triorganotin halides such as dicyclohexylbutyltin chloride and dimethylcyclohexyltin chloride have been obtained by similar methods.[109] Dialkyltin dichlorides have also been prepared by group exchange between $SnCl_4$ and tetraalkylleads. Thus, stirring Et_4Pb and $SnCl_4$ in toluene gave Et_2SnCl_2 in solution and a precipitate of Et_2PbCl_2. A 2:1 ratio of Et_4Pb and $SnCl_4$ gave Et_2SnCl_2 and Et_3PbCl.[110]

Bis(chloromethyl)tin dichloride consists of infinite chains of weakly chlorine-bridged $(ClCH_2)_2SnCl_2$ molecules in the solid (cf. the structure of Me_2SnCl_2) (Fig. 1), thus distorting the geometry at tin from tetrahedral towards

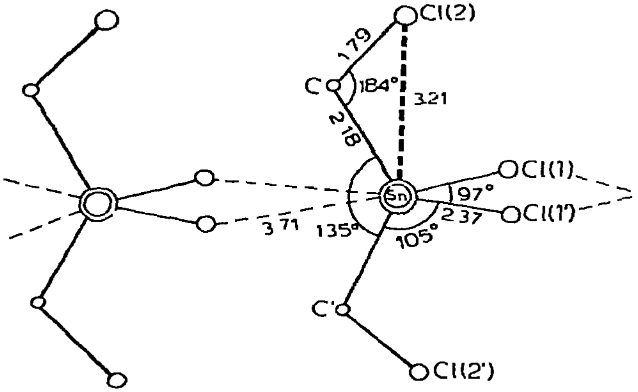
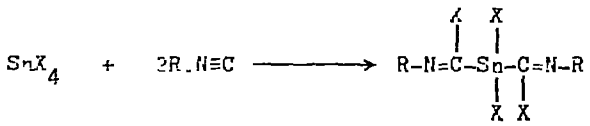


Fig. 1. Crystal Structure of $(ClCH_2)_2SnCl_2$. (Reproduced by permission of the Consultants Bureau).

octahedral. The Sn-C and Sn-Cl bond distances are 2.18 A and 2.37 A, respective Sn....Cl = 3.71 A. The Cl-Sn-Cl and C-Sn-C bond angles are 97° and 135°, respectively.[111]

The reaction of isonitriles with tin(IV) halides yields halogenocarbiminotin halides CXXVII and CXXIX by insertion into tin-halogen bonds.

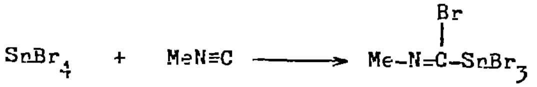


$$SnX_4 + 2R.N{\equiv}C \longrightarrow R{-}N{=}\overset{X}{C}{-}\underset{X}{\overset{X}{Sn}}{-}\underset{X}{C}{=}N{-}R$$

R = Me, X = Cl

R = Ph, X = Cl, Br

CXXVIII



$$SnBr_4 + MeN{\equiv}C \longrightarrow Me{-}N{=}\overset{Br}{C}{-}SnBr_3$$

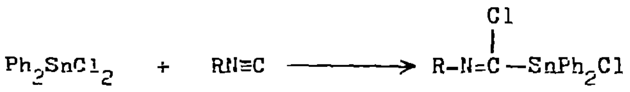
CXXIX

Phenyl isocyanide inserts into both Sn-Cl and Sn-C bonds of Me_3SnCl to form CXXX:

$$Me_3SnCl + 3PhN{\equiv}C \longrightarrow \left[Ph{-}N{=}\overset{Me}{C}\right]_3 Sn{-}\overset{Cl}{C}{=}N{-}Ph$$

CXXX

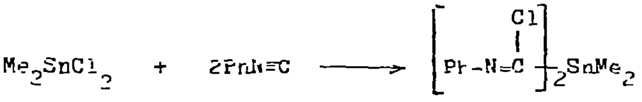
but methyl and phenyl isocyanides insert into only one of the Sn-Cl bonds of Ph_2SnCl_2:



$$Ph_2SnCl_2 + RN{\equiv}C \longrightarrow R{-}N{=}\overset{Cl}{\overset{|}{C}}{-}SnPh_2Cl$$

CXXXI

When R = Ph, CXXXI exists as a dimer. Both Sn-Cl bonds of Me_2SnCl_2 are reactive towards PhN≡C affording CXXXII also as a dimer.[112]

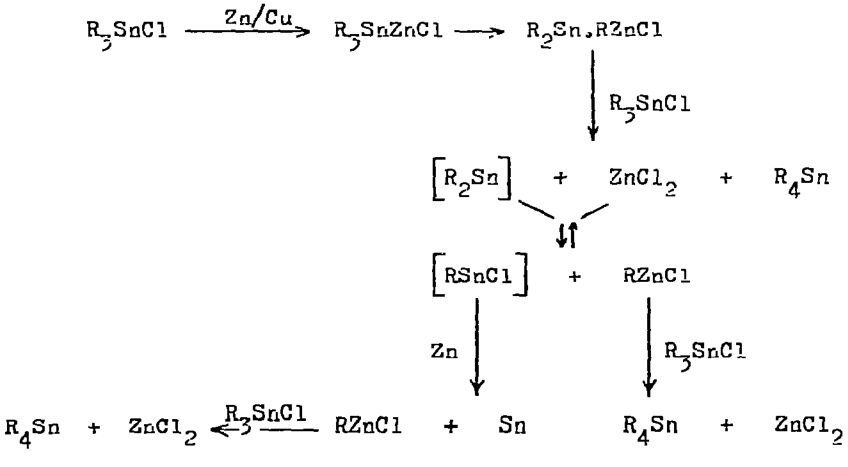


$$Me_2SnCl_2 + 2PhN{\equiv}C \longrightarrow \left[Ph{-}N{=}\overset{Cl}{\overset{|}{C}}\right]_2SnMe_2$$

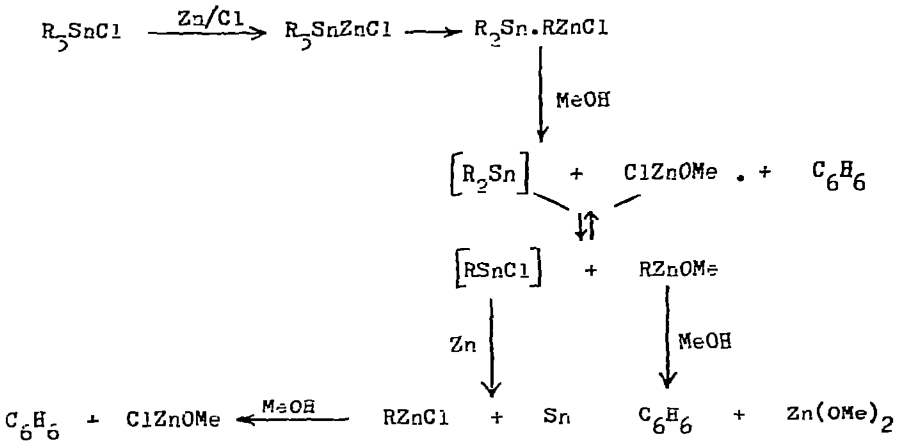
CXXXII

Noltes and van der Kerk have published more of their work on the interaction of organotin halides with zinc metal. The reactions proceed with the initial formation of reactive organozinc compounds, but the final products vary with the reaction conditions. Whereas Ph_3SnCl does not react with zinc in aprotic solvents such as ether, THF or toluene, with a zinc-copper couple (Zn/Cu) in THF, quantitative formation of Ph_4Sn, tin metal and zinc chloride occurs over two-three weeks. Hexaphenylditin does not react with Zn/Cu under these conditions, and hence may be excluded as a reaction intermediate. In the presence of protic reagents (H_2O, MeOH) the reaction products are benzene, tin metal, ClZnOMe and $Zn(OMe)_2$. The presence of strongly coordinating ligands such as TMED or bipyridyl results in the formation of hexaphenylditin as the major product. Me_3SnCl reacts similarly. These observations are accounted for by the reaction schemes:

Aprotic conditions:



Protic conditions:



The formation of hexphenylditin is easily rationalised on the basis of the know chemistry of $Ph_3SnZnCl.TMED$:

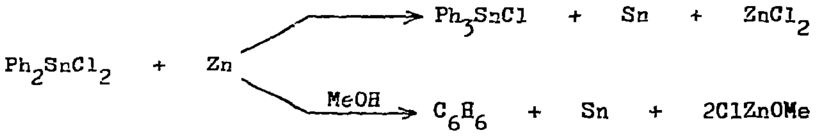
$$Ph_3SnCl \xrightarrow[TMED]{Zn/Cu} Ph_3SnZnCl.TMED \xrightarrow{Ph_3SnCl} Ph_6Sn_2 + ZnCl_2.TMED$$

The reactions of $Me_2PhSnCl$ and $MePh_2SnCl$ with Zn/Cu in THF give mixtures of products:

$$4Me_2PhSnCl + 2Zn/Cu \longrightarrow 0.42Me_4Sn + 0.57Me_3PhSn + 1.35Me_2Ph_2Sn$$
$$+ 0.99Sn$$

$$4MePh_2SnCl + 2Zn/Cu \longrightarrow 0.02Me_4Sn + 0.07Me_3PhSn + 0.47Me_2Ph_2Sn$$
$$+ 1.81MePh_3Sn + 0.78Sn$$

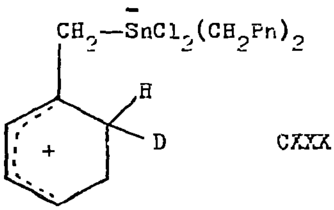
In the presence of MeOH, both compounds give methane, benzene and tin metal in the expected quantities. Ph_2SnCl_2 and $PhSnCl_3$ will react with unactivated zinc metal at room temperature:



$$3PhSnCl_3 + 4Zn \longrightarrow Ph_3SnCl + 2Sn + 4ZnCl_2$$

The reactions of both Ph_2SnCl_2 and $PhSnCl_3$ with Zn/Cu yield Ph_4Sn and tin metal.[113]

Tribenzyltin chloride and DCl undergo D-H exchange exclusively at the *ortho*-position of the C_6H_5 ring. No isotope exchange occurs with toluene under the same conditions. The intermediate CXXXIV was proposed.[114]



CXXXIV

$PhSnCl_3$ catalyses the racemisation of α-methylbenzyl chloride in ether. The reaction is first-order in alkyl halide, but a mixture of first and third for $PhSnCl_3$.[115] *o*- and *p*-Tritolyltin iodides react with the appropriate silver salts in benzene to afford the corresponding tritolyltin oxalate, isothiocyanate, nitrate, phosphate and sulphate.[116] A polarographic study of *tert*-Bu_2SnCl_2 in aqueous solution shows that the bulky *tert*-butyl group stabilises four-coordination at tin, enhances the acidity of complexing water molecules, and favours the addition of the first electron, but opposes the addition of the second.[117]

The interaction of phosphorus-oxygen compounds with organotin halides has been studied by Pudovik and his coworkers. Reaction of *n*-butyl diethylphosphinite with Et_3SnCl at 160° or 220° yields the phosphoryl complex CXXXV, together with butyl chloride and metallic tin:

$$Et_2PO^nBu + Et_3SnCl \longrightarrow Et_2{}^nBuP{=}O.SnClEt_3 + Sn + BuCl$$

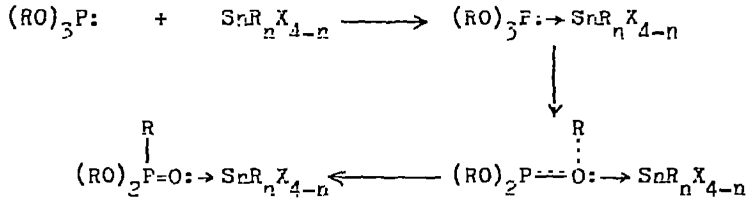
CXXXV

At 160°, Et_4Sn, tin and the complex CXXXVa were isolated:

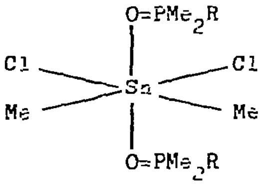
$$\begin{tikzcd}
Et_2PO^nBu + Et_3SnCl \arrow[r] & Et_2P(Cl){=}O \arrow[d] & + BuCl + Sn + Et_4Sn \\
 & Et_2P(Cl){=}O.SnClEt_3 &
\end{tikzcd}$$

CXXXVa

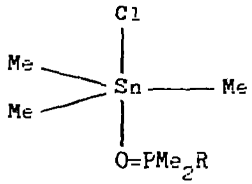
The analogous complex $Et_2{}^{sec}BuP{=}O.SnClEt_3$ was also obtained from the reaction of $Et_2PO^{sec}Bu$ with Et_3SnCl.[118] The reaction of trialkylphosphites $P(OR)_3$ (R = Et, Pr, Bu) with ethyltin halides Et_nSnX_{4-n} (X = Cl, Br, I; n = 1-3) yields the 1:1 or 1:2 phosphonate complexes $[(RO)_2PR{=}O]_2.Et_nSnX_{4-n}$ (n = 1, 2) and $[(RO)_2PR{=}O]Et_3SnX$ usually as liquids. Infra-red and DTA data suggested that the isomerisation of the phosphite is not catalytic, but an intracomplex process:[119]



Complexes of Me_3SnCl (1:1), Me_2SnCl_2(1:2), and $RSnCl_3$ (R = Me, Et, Bu) (1:2) with $Me_2P(O)OMe$ and $Me_2P(O)Cl$ are obtained by mixing the components in pentane. The complexes are generally stable in solution, but the tendency towards dissociation increases with increasing number of alkyl groups attached to tin. Struct CXXXVI and CXXXVII were proposed for the Me_2SnCl_2 and Me_3SnCl complexes, respectively, since only a single Sn-C stretching band was observed in the infra-red in each case.[120]



CXXXVI

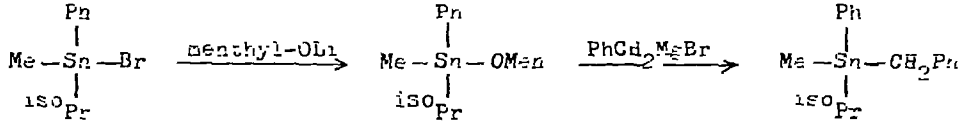


CXXXVII

R = OMe, Cl

Analogous complexes with phosphorus(V) mono- and dithioesters have similarly been prepared.[331]

Halogen exchange phenomena between organotin halides have been investigated by several groups. Taddei et al. have examined chemical shift non-equivalence of diastereotopic groups for the series of organotin monohalides $MePh^{iso}PrSnX$ (X = Cl, Br, I). In CCl_4 or CS_2 these compounds do not show magnetic non-equivalence for the diastereotopic methyl group even at -100°, but a small (0.01-0.03 ppm) chemical shift difference is observed in dilute benzene. Coalescence is observed in more concentrated solution for the chloride. Replacement of a methyl by a mesityl group slows down the rate of inversion at the asymmetric centre and magnetic non-equivalence of the methyl groups of the *iso*-propyl group is observed even in CCl_4, which is maintained above 100°. Coalescence is observed at concentrations of *ca.* in benzene. The optically active tetraorganotin compound CXXXVIII has been synthesised *via* the asymmetric synthesis:[121]



CXXXVIII

$[\alpha]_D = 44.6°$

Exchange of electronegative groups between Me_3Sn moieties has been studied by Russian and Canadian authors, both using nmr techniques. Reeves and Chan using pseudo-first-order rate constants in a complete line shape analysis have deduced that exchange in the Me_3SnX-Me_3SnY (X,Y = Cl,Br,I) system in toluene takes place *via* the dissociative mechanism involving small equilibrium concentrations of Me_3Sn^+ and halide ions:[123]

$$Me_3SnX \rightleftharpoons Me_3Sn^+ + X^-$$

$$Me_3SnY \rightleftharpoons Me_3Sn^+ + Y^-$$

$$Me_3SnX + Y^- \rightleftharpoons Me_3SnY + X^-$$

Me_3SnCl/Me_3SnI exchange in toluene and pyridine has also been studied by Peregudov *et al.* The reaction was deduced to be third order in toluene with an activation energy of 2.6±0.2 kcal. mole^{-1}. A marked increase in rate of exchange was noted in the more polar solvent. Other systems studied by these authors are: Me_3SnX (X = Cl, Br)/Me_3SnOPh in CCl_4 (fast at room temperature), Me_3SnX (X = Cl, Br, I, OPh)/Me$_3$SnSPh in CCl$_4$ (slow at room temperature), and Me$_3$SnI/Me$_3$SnX (X = SPh, (in toluene (slow at 80^o). Spectra of the mixtures Me$_3$SnCl/Ph$_3$SnSPh and Me$_3$SnC Ph$_3$SnCl contain signals belonging to both possible trimethyltin species. An associative mechanism with a cyclic four-centre transition state was preferred The presence of *tert*-butyl groups on tin very strongly decreases the electrophilicity of trialkyltin halides towards iodide ions and nucleophilic solvents.

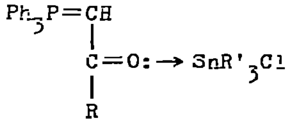
Reeves and Chan have also studied halogen exchange in binary mixtures of dimethyltin dihalides. The data are interpreted in terms of a scheme similar that proposed above for Me$_3$SnX exchange involving four ionization steps and tw halogen transfer steps, possibly *via* a pentacoordinate tin intermediate. Mole iodine inhibits exchange due to the formation of complex trihalide anions I$_2$X$^-$.

Adducts of Me$_2$SnCl$_2$ with picolinaldehydes C$_5$H$_4$NCH=NR (R = Me, *p*-MeOC$_6$H$_4$, *p*-MeC$_6$H$_4$, *p*-ClC$_6$H$_4$) have been synthesised and examined by nmr. Equilibrium constants for the reaction:

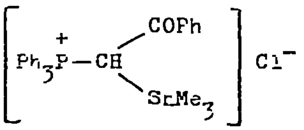
$$Me_2SnCl_2 \quad + \quad L \rightleftharpoons Me_2SnCl_2.L$$

in acetonitrile were obtained. Heats of complex formation were obtained by calorimetry.[127] The ^{1}H nmr of phenyltin trihalides and their complexes with oxygen and sulphur donors have been measured. Small increases in Sn...H coupli constants were noted.[128]

The interaction of carbonyl-stabilized phosphorus ylids with organotin hal form 1:1 adducts *via* *O*- rather than *C*-coordination of the ylid to tin CIXL (cf. AS 1972).[129]

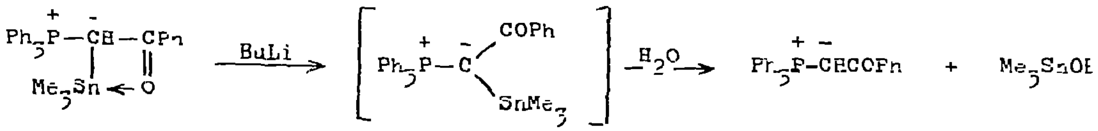


CIXL



CXL

Ishii has proposed the ionic structure CXL involving covalent Sn-C bonds. Treatment of CXL with BuLi, followed by hydrolysis yielded the free ylid and Me$_3$SnOH



Phenyl isocyanate is trimerised by CXL to the isocyanurate.[130]

Reaction of $BuSnCl_3$ with 2,4-pentanedione in the presence of pyridine leads to the isolation of the pyridine adduct of $BuCl_2Sn(O_2C_5H_7)$ CXLI:

$$\begin{tikzcd}
2BuSnCl_3 + 2C_5H_8O_2 \arrow[r] & \left[2BuSnCl_3 \cdot C_5H_8O_2\right] \arrow[r, "2py"] & \left\{2pyH\ BuCl_3Sn(C_5H_7O_2)\right\} \arrow[d, "-2Cl"] \\
 & 2BuCl_2Sn(O_2C_5H_7)py & 2BuCl_2Sn(C_5H_7O_2) + 2pyHCl \arrow[l, "py"']
\end{tikzcd}$$

CXLI

In solution CXLI exists as a mixture of at least two geometric isomers.[131]

Randaccio has determined the crystal structure of the Schiff base complex bis(salicylaldehyde)ethylenediimino-dimethyltin dichloride, $Me_2SnCl_2.salenH_2$. The structure consists of polymeric chains in which $salenH_2$ molecules bridge Me_2SnCl_2 units (Fig. 2). The coordination at tin is almost regular octahedral with a trans,trans,trans arrangement of methyl groups, and chlorine and oxygen atoms. The Sn-Cl bond distances are very long (2.59, 2.64 A); r(Sn-O) = 2.22 A; r(Sn-C) = 2.19, 2.10 A.[132]

Data for several other complexes of organotin halides with Lewis bases is available: R_nSnCl_{4-n} (R = Et, Pr, Bu, Ph; n = 1 - 4) with 1-vinyl azoles,[133] $RPhSnCl_2$ (R = alkyl, aryl) with bipyridyl and phenanthroline,[134] diaryltin dichlorides with oxine,[135] Ph_3SnCl, Me_2SnCl_2 with 2,2'-bipyridine N,N'-dioxide,[136] diaryltin dihalides with DPSO,[137] methyltin halides with pyridine, DMSO, DMF, HMPT, dioxane, TMED.[138]

5. Pseudohalides

Crystals of $Me_2Sn(NCS)_2$.terpyridyl contain seven-coordinate tin atoms with a pentagonal-bipyramidal configuration (Fig. 3). The two methyl groups occupy

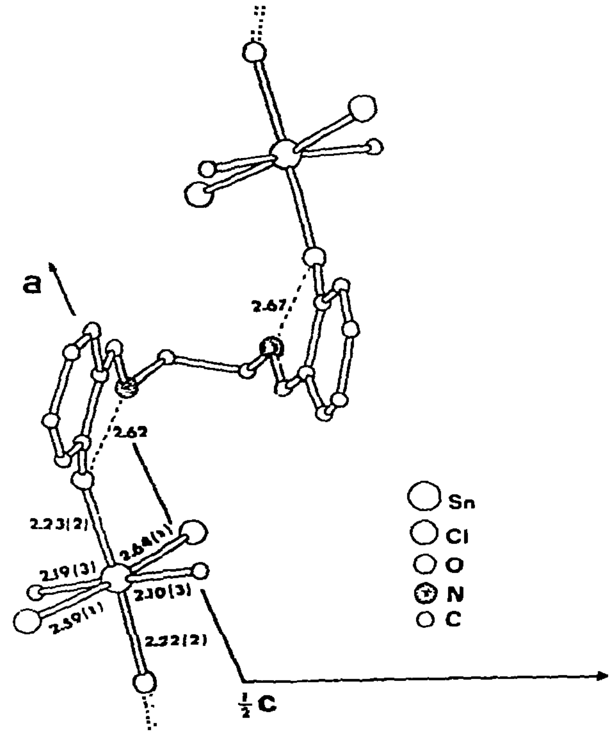


Fig. 2. Crystal Structure of the bis(salicylaldehyde)ethylenediimine complex of Me_2SnCl_2.

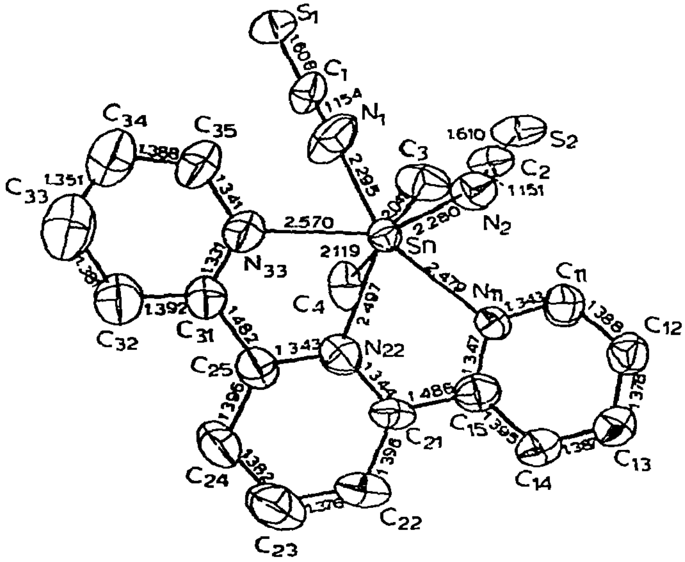
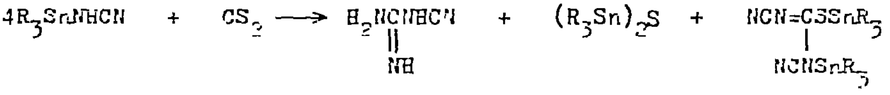


Fig. 3. Crystal Structure of $Me_2Sn(NCS)_2$.ter. (Reproduced by permission of th

American Chemical Society).

mutually trans axial positions; r(Sn-C) = 2.105 A, C-Sn-C = 173.7°. The NCS groups are bonded to tin via the nitrogen atoms. These with the nitrogen donors of the terpyridyl ligand occupy the equatorial sites; r(Sn-NCS) = 2.283 A, r(Sn-N(ter)) = 2.515 A. The equatorial atoms are essentially coplanar.[139] Dergunov et al. have determined the heats of combustion and formation of Bu_3SnNCO and $Bu_3N{=}C{=}NSnBu_3$. The thermochemical bond energies were deduced to be 102±5 and 100±5 kcal. mole^{-1}, respectively.[140]

Triorganotin cyanamides react with CS_2 at reflux temperature to give dicyanamide, the corresponding bis(triorganotin) sulphide, and the N,N'-dicyano-N'-(triorganostannyl)-S-(triorganostannyl)isothiourea CXLII.

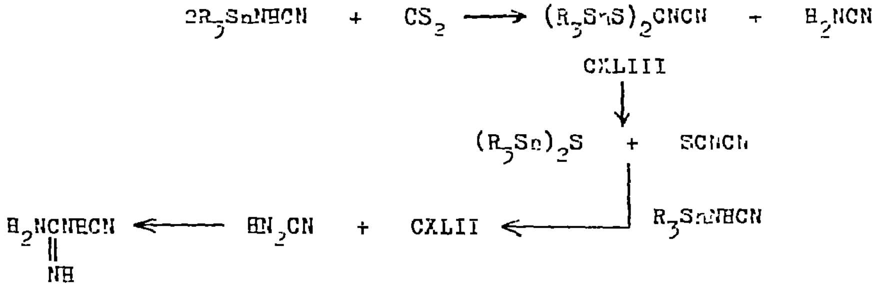


$$4R_3SnNHCN + CS_2 \longrightarrow \underset{\displaystyle NH}{\overset{}{H_2NC\overset{\|}{}NHCN}} + (R_3Sn)_2S + \underset{\displaystyle NCNSnR_3}{NCN{=}CSSnR_3}$$

R = Me, Ph, $PhCH_2$

CXLII

The reactions were thought to proceed via the intermediate formation of a bis-(triorganotin)cyanodithioimidocarbonate CXLII:[141]



$$2R_3SnNHCN + CS_2 \longrightarrow (R_3SnS)_2CNCN + H_2NCN$$

CXLIII

$$\text{CXLIII} \longrightarrow (R_3Sn)_2S + SCNCN$$

$$SCNCN + R_3SnNHCN \longrightarrow \text{CXLII} + HN_2CN$$

$$HN_2CN \longrightarrow H_2NC(=NH)NHCN$$

A thesis describes the synthesis and some reactions of triphenyltin carbodiimides and cyanamides.[142] Triaryltin cyanides are obtained from R_3SnI and AgCN. They are readily hydrolysed to the corresponding tin hydroxide.[143]

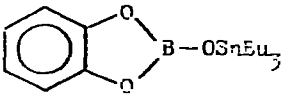
6. Oxides, Hydroxides, Peroxides, and Alkoxides.

Two patents relate to the 'direct' synthesis of dialkyltin oxides. Treating 'mossy' tin with dimethyl sulphate in the presence of Bu_3N or Ph_3P gives Me_2SnSO_4

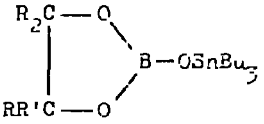
in 75-80% yields, which may then be hydrolysed by aqueous KOH to Me_2SnO.[144] Didodecyl-, dioctyl- and dihexadecyltin oxides of high purity are obtained by the interaction of the alkyl iodides and tin metal in the presence of NaOH.[145] Dioctyltin oxide has also been prepared by the hydrolysis of Oct_2SnCl_2 by aqueo NaOH in the presence of hydrocarbons such as toluene.[146]

Bis(trialkyltin) oxides $(R_3Sn)_2O$ (R = Pr, Bu) form 1:1 and 2:1 adducts wit tin(IV) and titanium(IV) chlorides and 1:1 adducts with antimony(V) chloride, involving $(R_3Sn)_2O{:}\rightarrow MX_n$ coordination. They are insoluble in most organic solvents and decompose on heating. The six-coordinate 1:2 adducts were considered to possess a *trans* arrangement of oxide donor molecules.[147] Stannylphosph carbamates are prepared by treating phosphorus isocyanates with bis(triorganoti oxides in CCl_4.[148]

Stannaboroxanes of the types CXLIV - CXLVI have been synthesised by Mehrot *et al.* by the azeotropic removal of water from mixtures of $(Bu_3Sn)_2O$, boric acid and the appropriate glycol in boiling benzene.



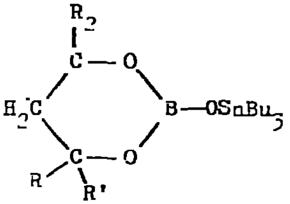
CXLIV



R = R' = H, Me

R = H, R' = Me

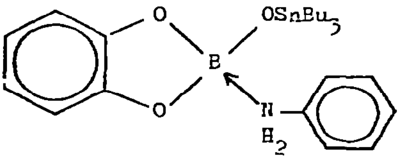
CXLV



R = R' = H; R = Me, R' = H

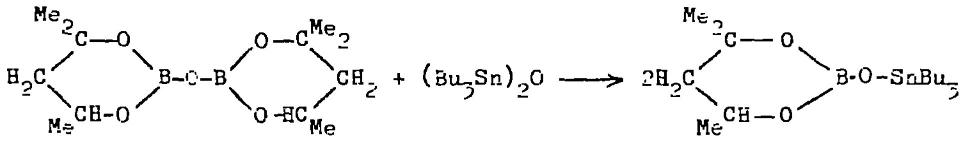
CXLVI

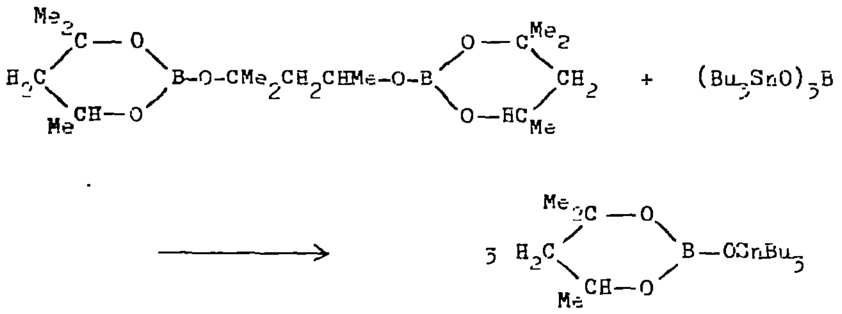
Tris(trialkylstannyl)borates $(R_3SnO)_3B$ (R = Me. Et, Pr, ^{n}Bu, ^{iso}Bu, Ph) are obtained similarly. CXLIV forms a 1:1 complex CXVIII with aniline.



CXLVII

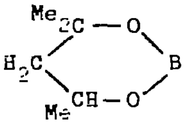
Stannoxy and boroxy groups readily exchange:





$$2(Bu_3SnO)_3B + (^{iso}PrO)_3B \longrightarrow 3(Bu_3SnO)_2BO^{iso}Pr$$

$$(Bu_3SnO)_3B + 2(^{iso}PrO)_3B \longrightarrow 3Bu_3SnOSn(O^{iso}Pr)_2$$

CXLVI (R = Me, R' = H) was also synthesised by transalcoholysis between  B—OH and Bu_3SnOEt, and from metathesis between Bu_3SnCl and the sodium salt of the borate.[149,150] The Sn-O bond of the stannaboroxanes is cleaved in preference to the B-O bond by HCl, MeCOCl, Me_3SiCl, Me_3GeCl, RCOOH, ROH and RSH, the more electronegative group becoming attached to the tin. Similarly reaction with phenyl isocyanate takes place at the Sn-O bond:[150]

$$>B\text{-}O\text{-}Sn< \; + \; PhNCO \longrightarrow \; >B\text{-}O\text{-}CO\text{-}NPh\text{-}Sn<$$

Trimethyltin pentafluoro-ortho-tellurate CXLVIII is obtained by the reacti of $HOTeF_5$ with Me_4Sn or Me_3SnCl:

$$Me_4Sn + HOTeF_5 \xrightarrow{-CH_4} \underset{\text{CXLVIII}}{Me_3SnOTeF_5} \xleftarrow{-HCl} Me_3SnCl + HOTeF_5$$

Infra-red and nmr data indicate the presence of four-coordinate tin in CXLVIII, but interaction with methyl cyanide results in the formation of the adduct $\underset{\overset{\uparrow}{N\equiv CMe}}{Me_3SnOTeF_5}$, whilst with DMSO, complete dissociation occurs to give $[Me_3Sn(DMSO)_2$ $[F_5TeO]^-$.[151]

Reaction of Et_3SnOMe or $(Et_3Sn)_2O$ with the appropriate acetylenic glycol affords high yields of the corresponding stannylated compounds. At 270° they decomposed to give $Et_3SnC\equiv CSnEt_3$ and the corresponding ketone.[177]

$$\begin{array}{c} 2Et_3SnOMe \\ \text{or} \\ (Et_3Sn)_2O \end{array} \quad + \quad HOCRR^1.C\equiv C.R^2R^3COH \longrightarrow Et_3SnOCRR^1.C\equiv C.R^2R^3COSnEt_3$$

$$R = R^1 = R^2 = R^3 = H, \; Me$$

$$R = R^2 = Me; \; R^1 = R^3 = H, \; Et$$

$$R = H; \; R^1 = R^2 = Me; \; R^3 = Et$$

Satisfactory routes to alkyltin trialkoxides have been devised. Metathesis between alkyltin trichlorides and sodium alkoxides in refluxing benzene,[152] and alcoholysis of tris(diethylamino)butyltin[153] afford high yields of pure materia

$$RSnCl_3 \quad + \quad 3NaOR' \xrightarrow[\text{reflux}]{\text{benzene}} RSn(OR')_3$$

$$R = Et, \; {}^{n}Bu; \; R' = Me, \; Et, \; {}^{iso}Pr, \; {}^{n}Bu, \; {}^{t}Bu$$

$$BuSn(NEt_2)_3 \quad + \quad 3ROH \xrightarrow{\text{benzene}} BuSn(OR)_3$$

$$R = Et, \; {}^{n}Pr, \; {}^{iso}Pr, \; {}^{n}Bu, \; {}^{iso}Bu, \; {}^{sec}Bu, \; {}^{t}Bu, \; {}^{neo}pentyl$$

Attempts to prepare trialkoxytin compounds by alcoholysis of $BuSnO_{1.5}$, usually resulted in the recovery of unreacted stannonic acid, although with ${}^{t}BuOH$ $BuSnO(O^{t}Bu)$ was obtained. $BuSn(O^{iso}Pr)_3$ undergoes group exchange with $BuSnCl_3$ & $BuSn(O_2CR)_3$ to yield mixed chloride and carboxylate alkoxides:

$$2BuSn(O^{iso}Pr)_3 + BuSnX_3 \xrightarrow{exothermic} 3BuSn(O^{iso}Pr)_2X$$

$$BuSn(O^{iso}Pr)_3 + 2BuSnX_3 \xrightarrow{exothermic} 3BuSn(O^{iso}Pr)X_2$$

$X = Cl, O_2CMe, O_2CEt$

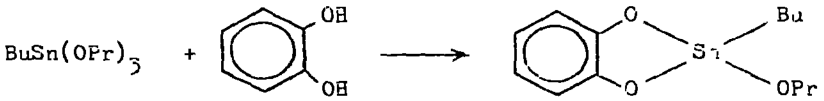
and with protic reagents to yield similar mixed products:

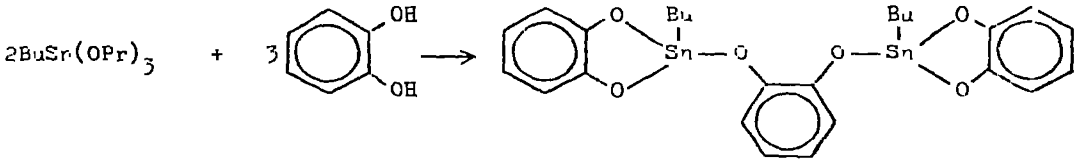
$$2RSn(OPr)_3 + 3H_2O \longrightarrow 2RSnO_{1.5}$$

$R = Et, Bu$

$$BuSn(OPr)_3 + nMe_2C{=}NOH \longrightarrow BuSn(OPr)_{3-n}(ON{=}CMe_2)_n$$

$n = 1 - 3$





$$BuSn(OPr)_3 + H_2NCH_2Ph \longrightarrow BuSn(OPr)_2(NHCH_2Ph$$

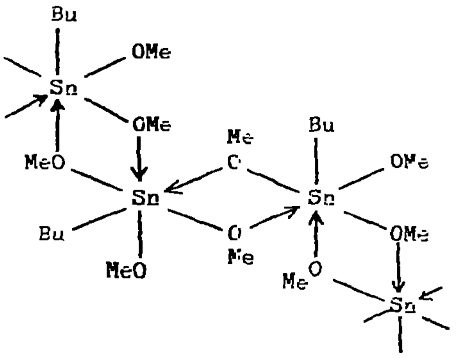
$$BuSn(OPr)_3 + H_2NCH_2CH_2NH_2 \longrightarrow BuSn(OPr)(NHCH_2CH_2NH)$$

$$BuSn(OPr)_3 + nRNH.CO.Me \longrightarrow BuSn(OPr)_{3-n}(NR.CO.Me)_n$$

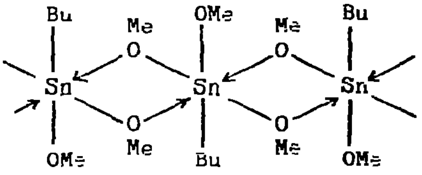
$n = 1,2;\ R = {}^{iso}Pr,\ {}^{n}Bu$

The reaction of $BuSn(OPr)_3$ with amides $R.CO.NH_2$ (R = H, Me) in refluxing benzene results in the replacement of both amido hydrogen atoms yielding $BuSn(OPr)(NCOR)$, $BuSn(NCOR)(HNCOR)$, and $(BuSn)_2(NCOR)_3$, respectively from 1:1, 1:2, and 2:3 molar ratios of reactants. Similar dialkyltin bis(amido) derivatives are obtained by reaction of $R_2Sn(OEt)_2$ (R = Et, Pr, Bu) and acetamide after prolonged heating.[152]

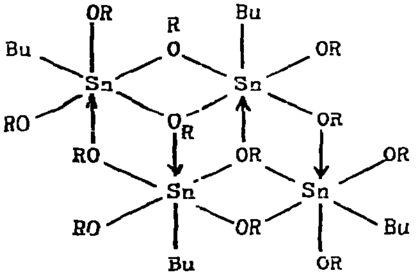
The autoassociation of butyltin trialkoxides BuSn(OR)$_3$ has been studied by ^{119}Sn nmr. Four types of behaviour were distinguished depending on the nature of the group R. When R is a linear alkyl chain (Et, ^{n}Pr, ^{n}Bu), the tin trialkoxides are essentially six-coordinate at room temperature, presumably involving both bridging and non-bridging alkoxy groups. In BuSn(OMe)$_3$, association is at a maximum, and polymeric structures such as CIL or CL are proposed. The triethoxide, -*n*-propoxide, and -*n*-butoxide are less associated due to the bulkier alkyl groups, and the tetrameric structure CLI seems likely. BuSn(^{iso}Bu)$_3$ is also essentially six coordinate at room temperature, but dissociates to a five-coordin species as the temperature is increased. Increasing alkyl substitution (R = *neo*-pentyl. *iso*-Pr, *sec*-Bu) results in the complete inhibition of six-coordinatio at low temperatures, and these alkoxides are thought to be five coordinate in the neat state. Increase in temperature leads to a dramatic decrease in autoassociation leading to a four-coordinate monomeric species. BuSn(O^{t}Bu)$_3$



CIL



CL



CLI

exhibits only four-coordinate behaviour at all temperatures. ΔH values of ca. 12 kcal. mole^{-1} were derived for the coordinate Sn-O bonds.[153] Taddei et al. have studied intermolecular exchange and configurational stability of methylneophylphenyltin alkoxides and phenoxide, for which chemical non-equivalence of the diastereotopic methyl groups is observed in benzene. Intermolecular exchange of alkoxy or phenoxy groups is much faster than configurational inversion at the tin atom. The rate of exchange decreases as the bulkiness of R increases, but the rate of inversion is only marginally affected. A mechanism involving intermolecular association and non-dissociative positional exchange of groups bonded to tin was proposed. Addition of free alcohols, which exchange with the alkoxy groups, increases the rate of inversion.[154]

Exchange between organotin alkoxides and silicon compounds has been studied by Armitage and Pereyre. Halogenosilanes and -germanes convert butyltin methoxides, oxides, and acetates to the corresponding butyltin halides:[155]

$$Bu_3SnOMe \quad + \quad Me_3MX \longrightarrow Bu_3SnX \quad + \quad Me_3MOMe$$

M = Si; X = F, Cl, Br, I

M = Ge; X = Br

$$(Bu_3Sn)_2O \quad + \quad 2Me_3MX \longrightarrow 2Bu_3SnX \quad + \quad (Me_3M)_2O$$

M = Si, Ge; X = Cl, Br

$$Bu_3SnO_2CMe \quad + \quad Me_3SiX \longrightarrow Bu_3SnX \quad + \quad Me_3SnO_2CMe$$

X = Cl, Br

$$Me_2SiCl_2 \quad + \quad Bu_3SnY \longrightarrow Bu_3SnCl \quad + \quad Me_2SiClY$$

Y = OMe, O$_2$CMe

$$R_3SiX \quad + \quad Bu_2Sn(OMe)_2 \longrightarrow Bu_2Sn(OMe)X \quad + \quad R_3SiOMe$$

R = Et; X = F

R = Me; X = Cl, Br, I

$$Me_3SiX + Bu_2Sn(O_2CMe)_2 \longrightarrow Bu_2(O_2CMe)X + Me_3SiO_2CMe$$

X = Cl, Br, I

$$Bu_2SnY_2 + Me_2SiCl_2 \longrightarrow Bu_2SnCl_2 + Me_2SiY_2$$

$$Bu_2SnY_2 + 2Me_3SiCl \longrightarrow Bu_2SnCl_2 + 2Me_3SiY$$

Y = OMe, O_2CMe

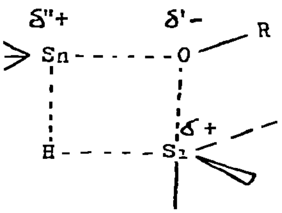
$$Bu_2Sn(O_2CMe)Cl + Me_3SiCl \longrightarrow Bu_2SnCl_2 + Me_3SiO_2CMe$$

Reaction of SnI_4 and $Bu_2Sn(OMe)_2$ gives $Sn(OMe)_4$ and Bu_2SnI_2.[184] Pereyre has systematically and comprehensively investigated the exchange reaction between silanes and alkoxytin compounds:

$$R_3SiH + R'_3SnOR'' \longrightarrow R_3SiOR'' + R'_3SnH$$

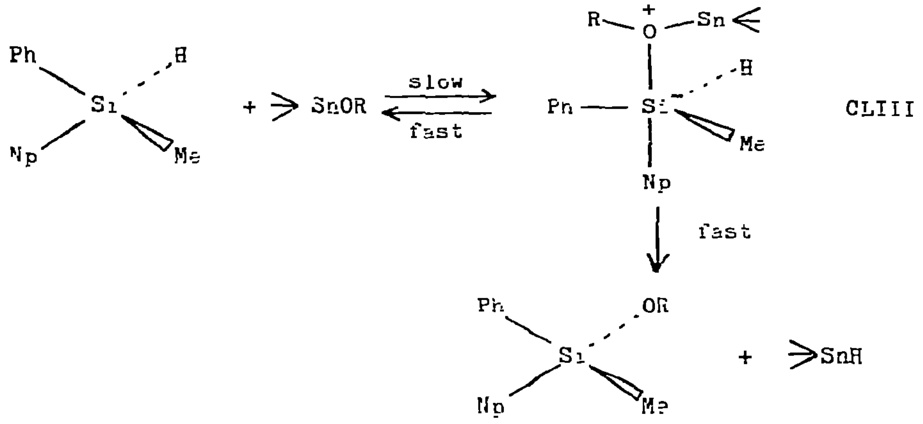
The use of optically-active methylphenyl-α-naphthylsilane MePhα-NpSi*H in the reaction results in a very high degree of retention of configuration at the asymmetric silicon atom. Kinetic data indicate second-order kinetics (first or in each reactant) with a high activation energy and a primary isotope effect $k(SiH)/k(SiD)$. The reaction rate is enhanced by electron-withdrawing groups on the silane and electron-releasing groups on the organotin alkoxide. Increas bulkiness of the alkoxy group decreases the rate in the order: $Me > Et > {}^{n}Pr > {}^{n}Bu > {}^{iso}Pr$. A correlation between the basicity of the organotin alkoxide and i reactivity is also apparent. The data supported two possible mechanisms:

(i) a S_Ni-Si mechanism with a transition state involving a trigonal-bipyramida silicon atom CLII:



CLII

(ii) a two-step mechanism *via* an unstable pentacovalent silicon intermediat
CLIII:



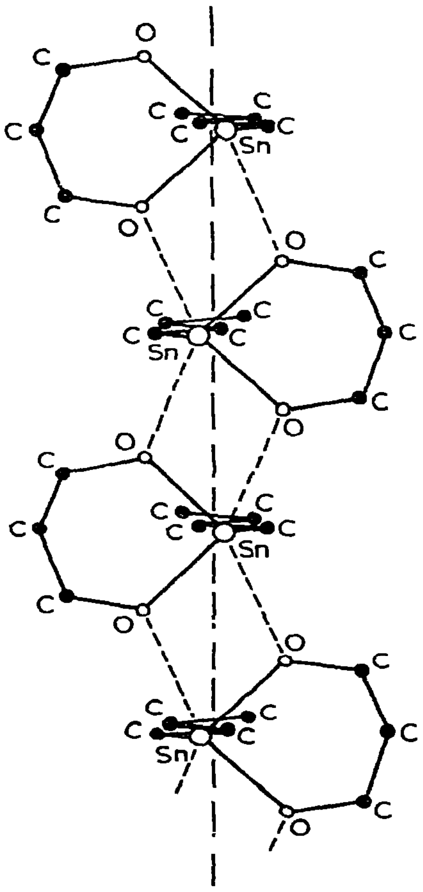
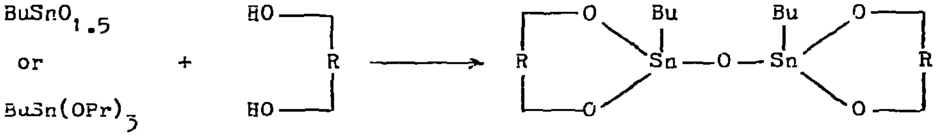


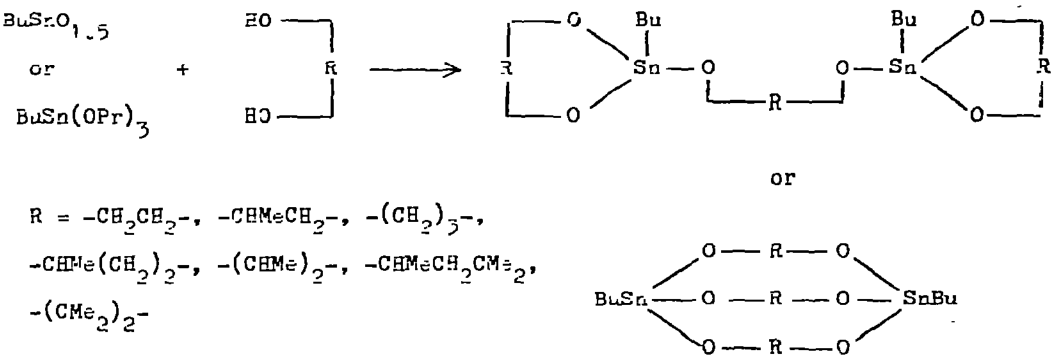
Fig. 4. The structure of dibutylstannadioxa-2,6-cyclohexane.

which can dissociate to give the products or reactants at similar rates.[156]

The crystal structure of dibutylstannadioxa-2,6-cyclohexane has been determined, and consists of chains of $Bu_2Sn(O_2C_3H_6)$ units linked by coordinate O→S bonds forming distannoxane Sn_2O_2 rings with tetragonal bipyramidal coordination for the tin (Fig. 4). The four oxygen atoms form a plane [r(Sn-O) = 2.05 A; r(Sn←O) = 2.57 A]. The intermolecular association is broken down by basic solvents. In apolar solvents or in the vapour state, a monomer-dimer equlibriu is proposed.[157] Several monobutyltin glycolates have been synthesised by the reaction of $BuSnO_{1.5}$ or $BuSn(OPr)_3$ with glycols, the water or propanol being removed azeotropically:



CLIV

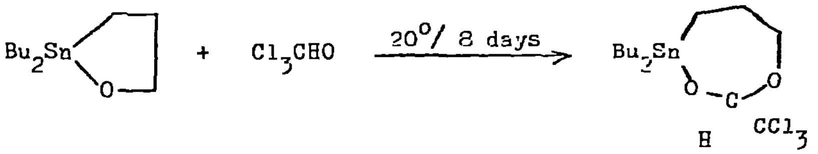


R = $-CH_2CH_2-$, $-CHMeCH_2-$, $-(CH_2)_3-$, $-CHMe(CH_2)_2-$, $-(CHMe)_2-$, $-CHMeCH_2CMe_2$, $-(CMe_2)_2-$

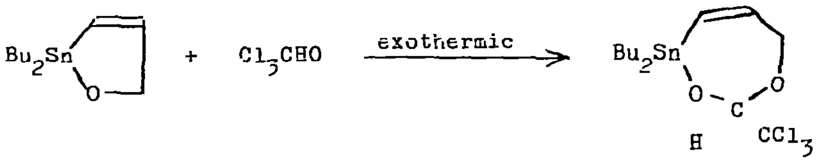
CLV

CLIV and CLV exhibit varying degrees of association. CLIV are dimeric save for R = $-CH_2CH_2-$ which has an average molecular association of five, and R = -CHMeC and $-CMe_2CMe_2-$ (monomeric). CLV are all monomeric except for R = $-CH_2CH_2-$ which trimeric.[158]

Cyclic acetals CLVI and CLVII are obtained by the reaction of chloral with dibutylstannaoxa-cyclopentane and -cyclopentene:



CLVI



CLVII

The products are thermally unstable; attempted distillation regenerates the reactants.[159]

The Bordeaux group has investigated the synthesis and thermal decomposition of halogeno-substituted tributyltin alkoxides. Polyhalogeno-substituted alkoxide CLVIII are obtained by the transalcoholysis of Bu_3SnOMe using the corresponding perhalogeno-alcohol:

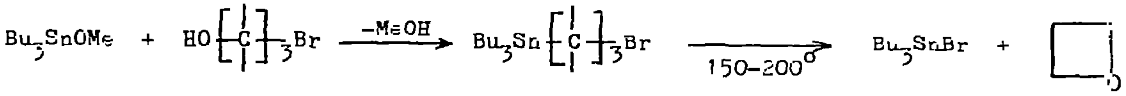
$$Bu_3SnOMe \quad + \quad RR'COH \longrightarrow \underset{\text{CLVIII}}{Bu_3SnOCRR'} \quad + \quad MeOH$$

$$R = Me,\ Cl;\ R' = H,\ Cl,\ CHCl_2,\ CHBr_2,\ CHClBr$$

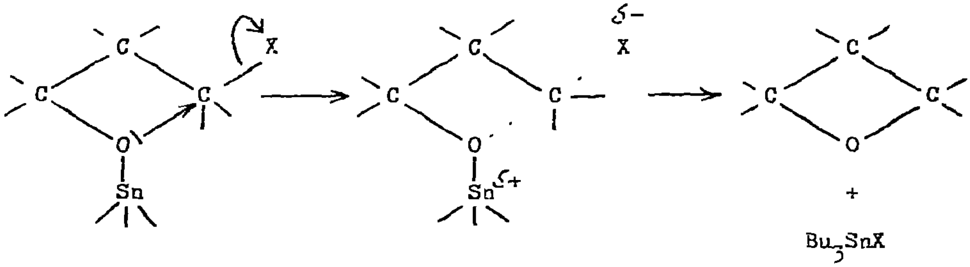
The compounds $Bu_3SnOCMe_2CHX_2$ (R = Cl, Br) thus obtained could be thermally decomposed to afford the aldehydes Me_2XCCHO.[160]

$$Bu_3SnOCMe_2CHX_2 \longrightarrow Bu_3SnX \quad + \quad OHCCXMe_2$$

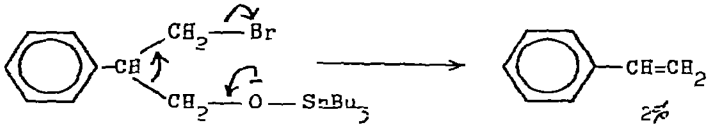
Thermal decomposition of tributyltin 3-bromoalkoxides, derived from Bu_3SnOMe and 1,3-halogenohydrins, decompose at 150–200° to give oxetanes in high yield (usually > 80%):



The corresponding 3-chloroalkoxides behave similarly, but a higher temperature is needed for the decomposition. A mechanism involving intramolecular nucleophilic attack at C-3 is proposed:

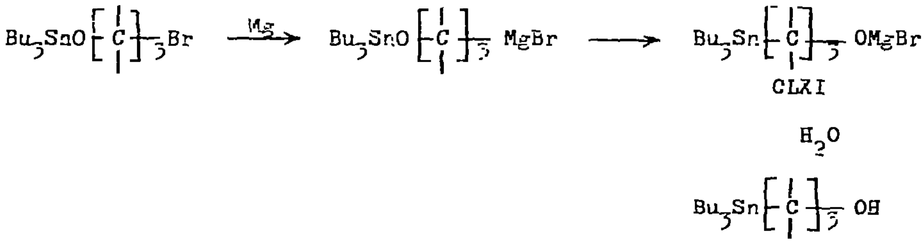


A small quantity of styrene is also formed in the thermal decomposition of CLIX, indicating that the alternative mechanism:



CLIX

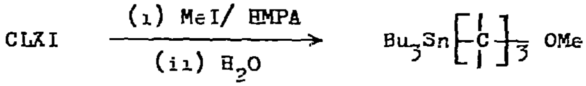
also operates in this case. Treatment of tributyltin 3-bromoalkoxides with magnesium metal in ether, followed by hydrolysis results in their conversion to the corresponding 3-hydroxypropyltributylstannanes CLX. An intramolecular re-arrangement of the initially formed Grignard reagent was proposed



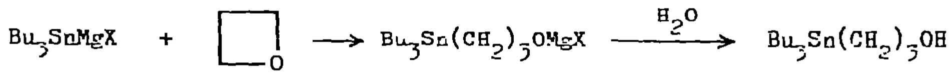
CLXI

CLX

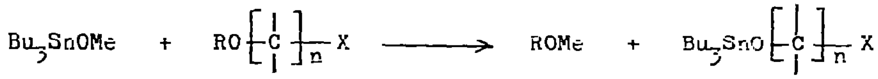
The intermediacy of the alkoxy-magnesium species CLXI was confirmed by methylati with methyl iodide:



$Bu_3Sn(CH_2)_3OH$ could also be obtained by reaction of the stannyl Grignard Bu_3SnMgX with oxetane, followed by hydrolysis:[161]



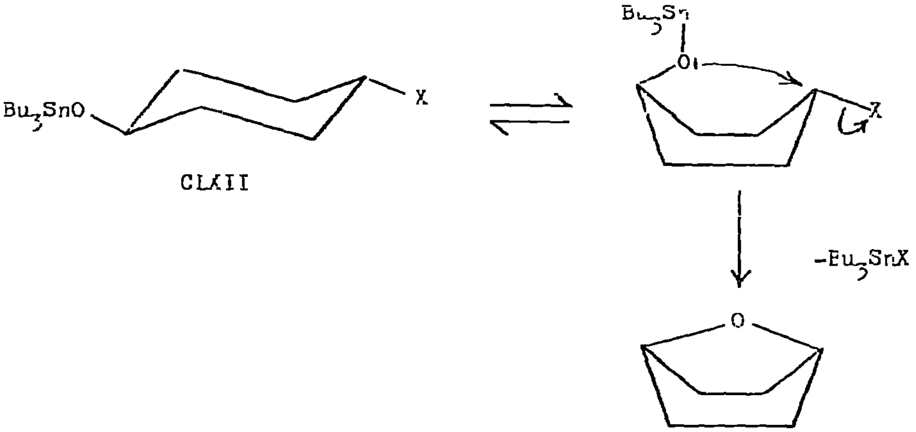
Tributyltin 4- and 5-halogenoalkoxides may be prepared either by transalcoholysis (n = 4, R =H) or by transesterification (n = 4, 5; R = Ac):



$$Bu_3SnOMe + RO\left[-\overset{|}{\underset{|}{C}}-\right]_n X \longrightarrow ROMe + Bu_3SnO\left[-\overset{|}{\underset{|}{C}}-\right]_n X$$

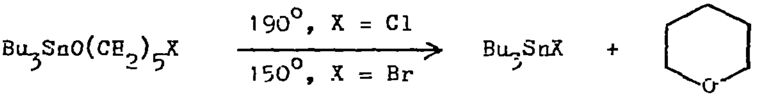
X = Cl, Br

Thermal decomposition of the 4-halogenoalkoxides takes place at a relatively low temperature (80-100°) to yield tetrahydrofurans by intramolecular nucleophilic attack of oxygen at C-4. Cyclic 4-halogenoalkoxides CLXII require much higher temperatures for decomposition (150°, X = Br; 200°, X = Cl), due to the necessity for initial boat→chair isomerism:



CLXII

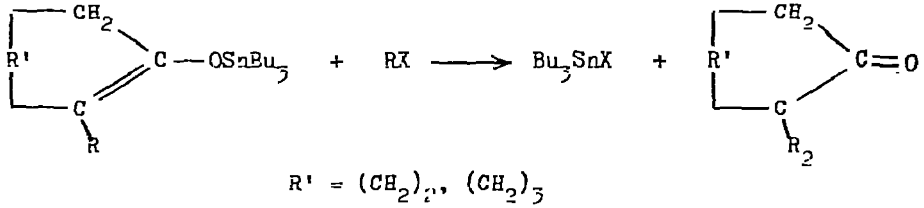
5-Halogenoalkoxides thermolise at 150-190° to afford tetrahydropyran compounds:[162]



Polymeric diorganotin alkoxides have been obtained by metathesis. The average degree of polymerisation varies from 78 to 1400.[163]

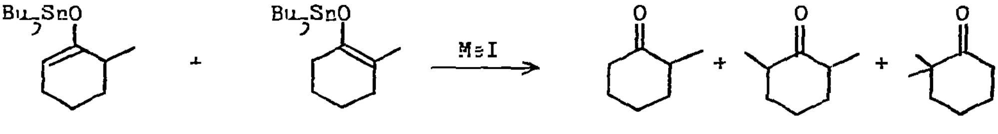
$$R_2SnCl_2 + Na^+\ {}^-O-R'-O^-\ {}^+Na \xrightarrow{-NaCl} -\!\!\left[SnR_2-O-R'-O\right]_n\!\!-$$

Enol acetates of acetophenones react with Et_3SnOR (R = Me, Et) to form equilibrium mixtures of the *O*- and *C*-isomers $CH_2{=}C(OSnEt_3)Ar$ and Et_3SnCH_2COAr (Ar = *p*-ClC_6H_4, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, 2,4,6-$Me_3C_6H_2$). Treatment with Me_3GeBr gave similar mixtures of *O*- and *C*-germyl isomers.[164] Organotin enolates may be alkylated by alkyl halides to give the corresponding ketone in usually very high yield:



$R' = (CH_2)_2, (CH_2)_3$

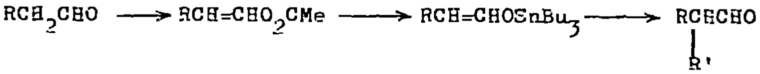
No polyalkylation or *O*-alkylation is observed. Alkyl iodides react more easily than bromides, and methyl halides faster than ethyl halides. Unsaturated halid such as $MeCH{=}CHCH_2Br$ react similarly. Alkylation of the isomeric mixtures CLXI



CLXIII

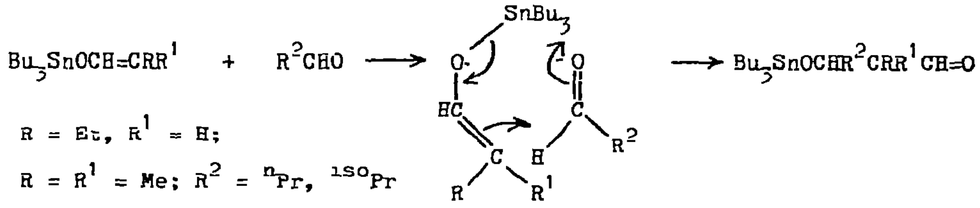
(i)	85%	15%	4%	79%	17%
(ii)	45%	55%	6%	44%	50%

Aldehydes may be alkylated by initial conversion to the enol acetate, then to the organotin enolate, which is treated with alkyl halide:



$$RCH_2CHO \longrightarrow RCH{=}CHO_2CMe \longrightarrow RCH{=}CHOSnBu_3 \longrightarrow \underset{R'}{RCH}CHO$$

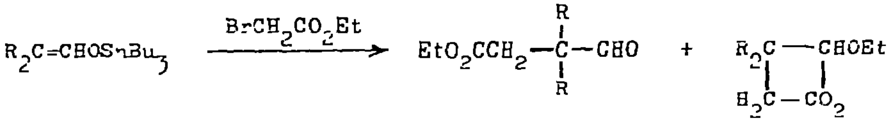
Organotin enolates react with aldehydes:



R = Et, R^1 = H;

R = R^1 = Me; R^2 = ^{n}Pr, ^{iso}Pr

No reaction could be observed with ^{t}BuCHO. With functionally-substituted halides, both *O*- and *C*-alkylation is observed, and mixtures are sometimes produced:



29% (R = Me)   71% (R = Me)

20% (R = Et)   80% (R = Et)

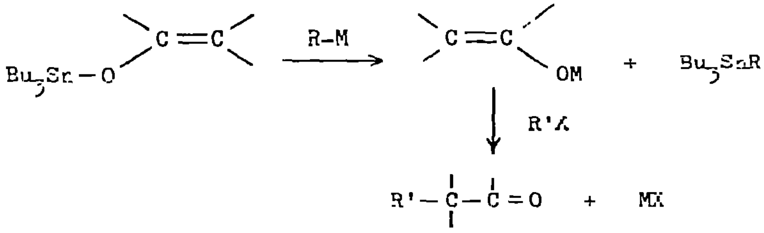
$$RR'C{=}CHOSnBu_3 \xrightarrow{ClCO_2Et} RR'C{=}CHOCO_2Et$$

R = R' = Me; R = Et, R' = H

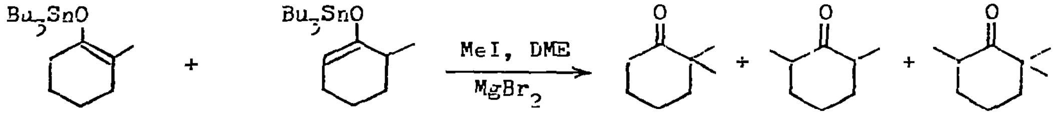
$$Me_2C{=}CHOSnBu_3 \xrightarrow{ClCH_2OMe} MeOCH_2CMe_2CHO$$

$$Et_2C{=}CHOSnBu_3 \xrightarrow{ClCH_2OMe} \underset{40\%}{MeOCH_2CEt_2CHO} + \underset{60\%}{Et_2C{=}CHOCH_2OMe}$$

Alkylation may be achieved by initial exchange between the stannyl enolate and organolithium or Grignard reagent, followed by addition of alkyl halide, methyl sulphate or tosylate as alkylating agents:



Some dialkylation is observed. Addition of lithium or magnesium halides also promotes alkylation by exchange to form the corresponding lithium or magnesium enolate, eg:



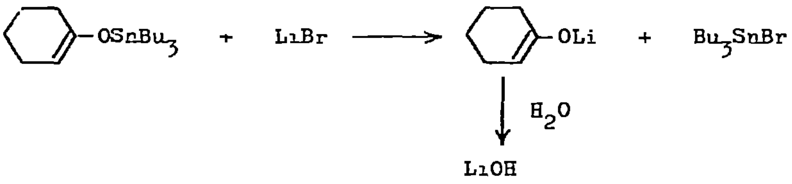
(i)   15%   85%   63%   20%

(25 : 75)

(ii)   55%   45%   76%   13%

(62 : 38)

The formation of lithium or magnesium enolate intermediates is demonstrated by the isolation of LiOH from the reaction:[43]

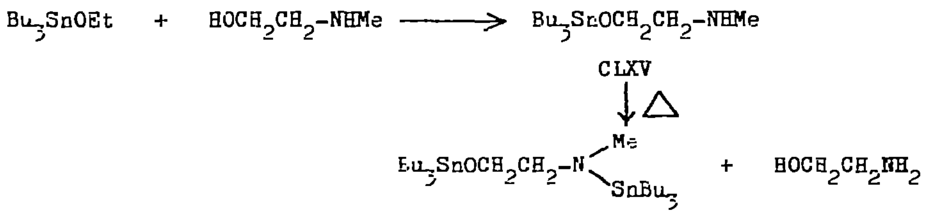


Mehrotra has synthesised a variety of mono-, di-, and trialkyltin derivati of alkanolamines by transalcoholysis. Bu_3SnOEt with N,N'-dialkylalkanolamines yield the tributyltin derivatives CLXIV:

$$Bu_3SnOEt \quad + \quad HO\text{-}R\text{-}NR'_2 \xrightarrow[\text{reflux}]{\text{benzene}} Bu_3SnO\text{-}R\text{-}NR'_2 \quad + \quad EtOH$$

$$R = -CH_2CH_2-,\quad -CH_2CH_2CH_2-,\quad -CH_2CHMe-;\ R' = Me,\ Et$$

With monoalkylalkanolamines, the monostannylated product CLXV is formed initiall but disproportionates to the distannylated compound CLXVI on distillation:



$$Bu_3SnOEt \quad + \quad HOCH_2CH_2\text{-}NHMe \longrightarrow Bu_3SnOCH_2CH_2\text{-}NHMe$$

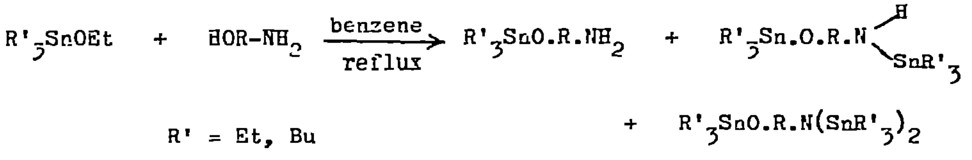
CLXV

$$\downarrow \Delta$$

$$Bu_3SnOCH_2CH_2\text{-}N\begin{matrix} Me \\ SnBu_3 \end{matrix} \quad + \quad HOCH_2CH_2NH_2$$

CLXVI

Similar behaviour is observed with unsubstituted alkanolamines $HO\text{-}R\text{-}NH_2$, and on distillation mono-, di-, and tristannylated products are obtained. When the reaction is carried out in m-dichlorobenzene (bp. 170°), CLXVII (R = Bu) is formed in 90% yield.

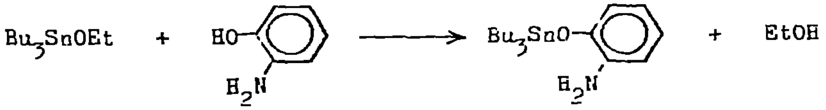


$$R'_3SnOEt \quad + \quad HOR\text{-}NH_2 \xrightarrow[\text{reflux}]{\text{benzene}} R'_3SnO.R.NH_2 \quad + \quad R'_3Sn.O.R.N\begin{matrix} H \\ SnR'_3 \end{matrix}$$

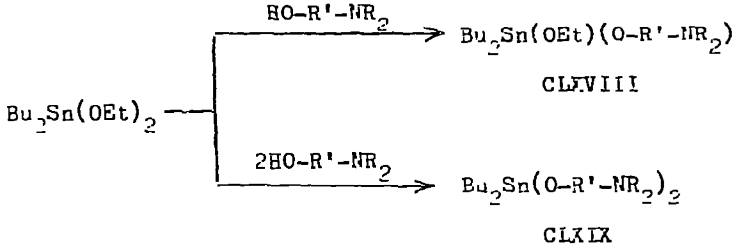
$$R' = Et,\ Bu \qquad\qquad + \quad R'_3SnO.R.N(SnR'_3)_2$$

CLXVII

Only the hysroxyl group of o-aminophenol reacts with Bu_3SnOEt, even at high temperatures.[165,166]



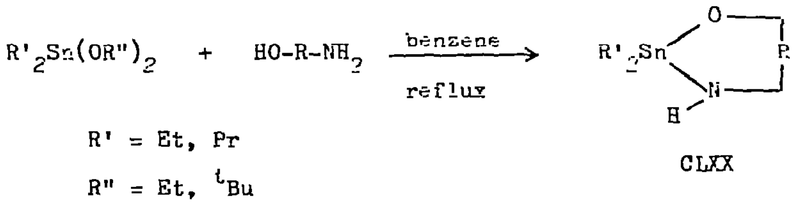
Dibutyltin diethoxide reacts with N,N-dialkylalkanolamines in 1:1 and 1:2 ratios boiling benzene to form the derivatives CLXVIII and CLXIX:



CLXVIII

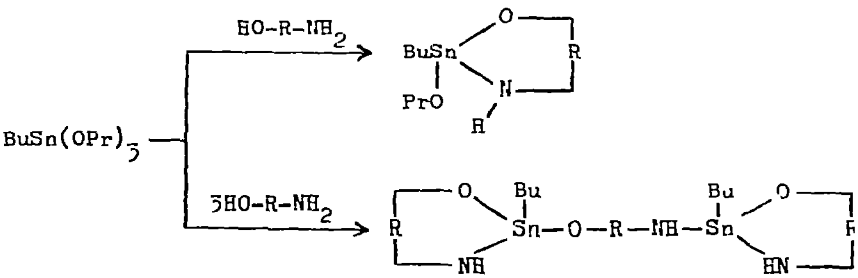
CLXIX

With unsubstituted alkanolamines the heterocycles CLXX are formed:[166,167]



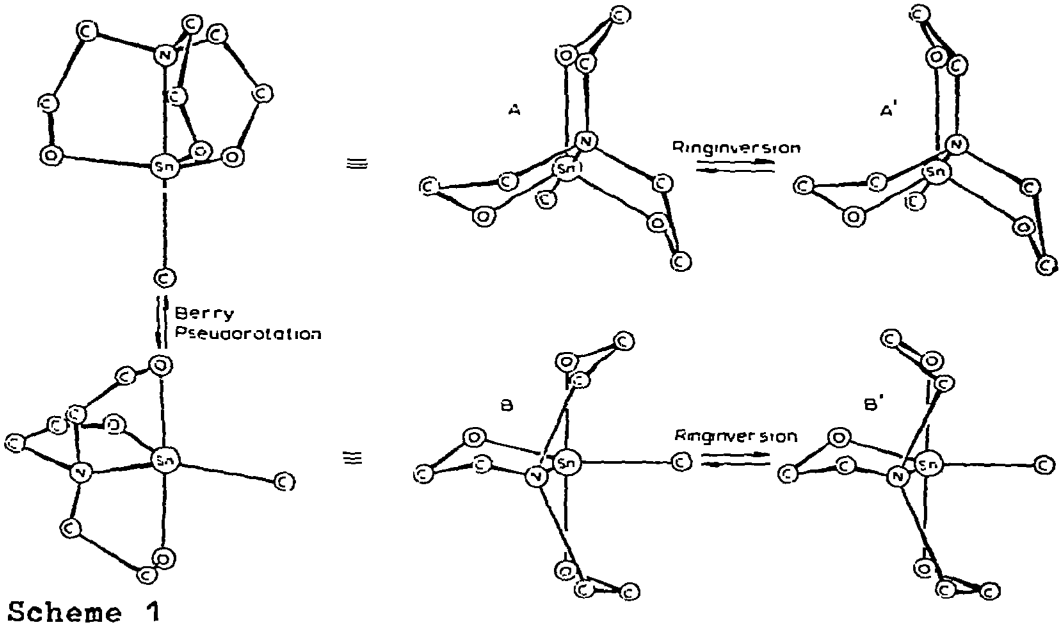
CLXX

$BuSn(OPr)_3$ reacts to give cyclic products even at room temperature:[166]



Nmr and molecular weight data have been used to demonstrate pentacoordination at tin for the stannatranes $R_2Sn(OCH_2CH_2)_2NR$ and $RSn(OCH_2CH_2)_3N$.[168] Variable temperature ^1H nmr spectra for the latter class of compounds show that both a

Berry-pseudorotation $\left[\Delta G^*_{25} = 18.3 \text{ kcal. mole}^{-1}\right]$ and a ring-inversion $\left[\Delta G^*_{25} = 14.1 \text{ kcal. mole}^{-1}\right]$ between four different conformations take place, viz.:[169]



Scheme 1

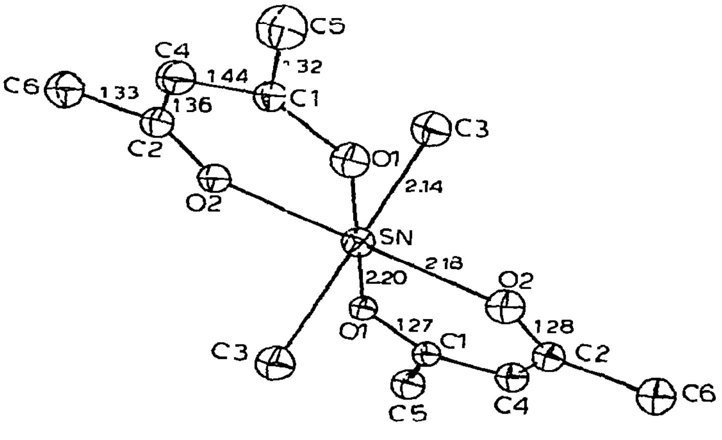
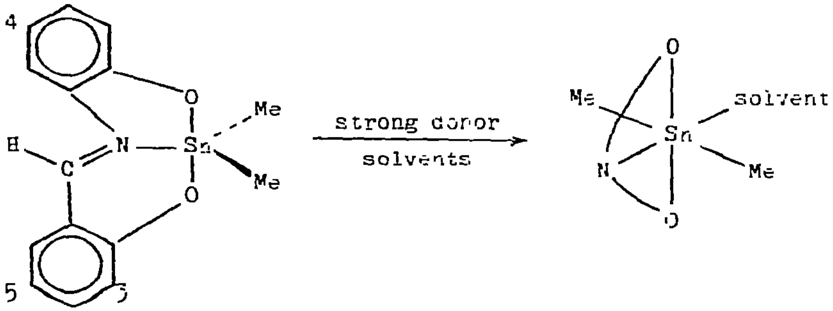


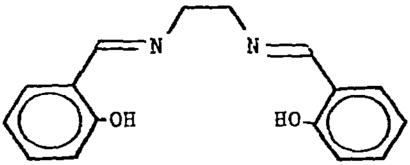
Fig. 5. The structure of bis(2,4-pentanedionato)dimethyltin. (Reproduced by permission of the American Chemical Society).

The structure of bis(2,4-pentanedionato)dimethyltin has been investigated both in the solid and in solution. In the crystal, the space group demands the molecule to be centrosymmetric and therefore the methyl groups must be mutually *trans* about octahedrally coordinated tin (Fig. 5); r(Sn-C) = 2.14 A, r(Sn-O) = 2.18, 2.20 A.[170] Raman spectra of single crystals and benzene solutions demonstrate that this configuration is preserved in solution,[171] in contrast to the *cis* structure assigned on the basis of dipole moment measurements.[172]

Tanaka and Kawakami have synthesised the Schiff base - dimethyltin complexes CLXXI, with various substituents in the 3, 4, and 5 positions indicated. Nmr data indicate a bent C-Sn-C moiety in less donating solvents. In strong donor solvents, the tin atom becomes six-coordinate:[173]

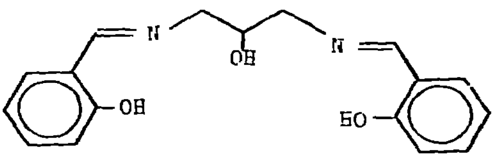


Infra-red and Mössbauer measurements of organotin derivatives of the quadri- and terdentate Schiff bases CLXXII - CLXXIV:



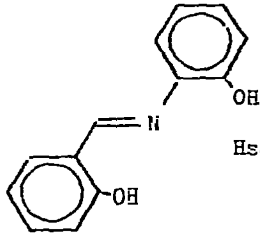
salenH$_2$

CLXXII



H$_2$saldap-2-OH

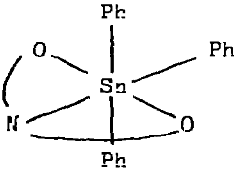
CLXXIII



Hsal-N-2-HOC$_6$H$_4$

CLXXIV

suggest distorted *trans*-octahedral structures for R$_2$Sn(salen) (R = Me, Et, Ph) and Me$_2$Sn(saldap-2-OH). In Ph$_2$Sn(Hsaldap-2-O) the ligand appears to be only terdentate with a similar structure as the R$_2$Sn(sal-N-2-OC$_6$H$_4$) (R = Me, Ph) complexes (distorted trigonal bipyramidal with R groups occupying equatorial positions). The complex Ph$_3$Sn(sal-N-2-OC$_6$H$_4$) appears to have the *mer*-octahedral structure CLXXV.[174,175]

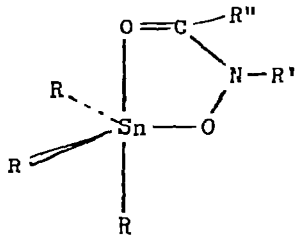


CLXXV

Several diaryltin bis(oximates) have been synthesised.[135]

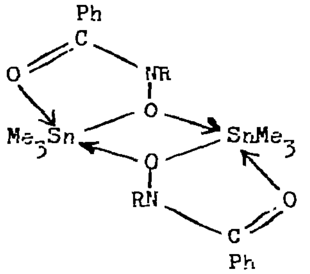
The thermal decomposition of the organotin peroxide Ph$_3$SnOOCMe$_2$Ph in anisol does not follow first-order kinetics. The rate of the process increases with increase in the initial concentration of the peroxide, but the reaction products do not affect the kinetics. Addition of α,α-dimethylperoxide as initiator causes a considerable increase in rate. The decomposition products were Ph$_3$SnOH (0.48 mole), Ph$_2$SnO (0.54 mole), CH$_4$ (0.16 mole), PhCOMe (0.5 mole), α,α-dimeth benzyl alcohol (0.42 mole) and MeOC$_6$H$_4$Me (0.2 mole).[176]

Full synthetic and spectroscopic details for *O*-triorganotin hydroxylamine derivatives R$_3$SnONR^{1}R^2 (R = Me, Pr, Ph; R^1 = R^2 = Et; R^1 = H, Ph; R^2 = COPh) have been published (cf. AS 1972). In chloroform solution, the derivatives are monomeric, with four-coordination proposed for Me$_3$SnONEt$_2$, but five-coordination with intramolecular carbonyl tin coordination, viz. CLXXVI, for the *N*-acy substituted derivatives.



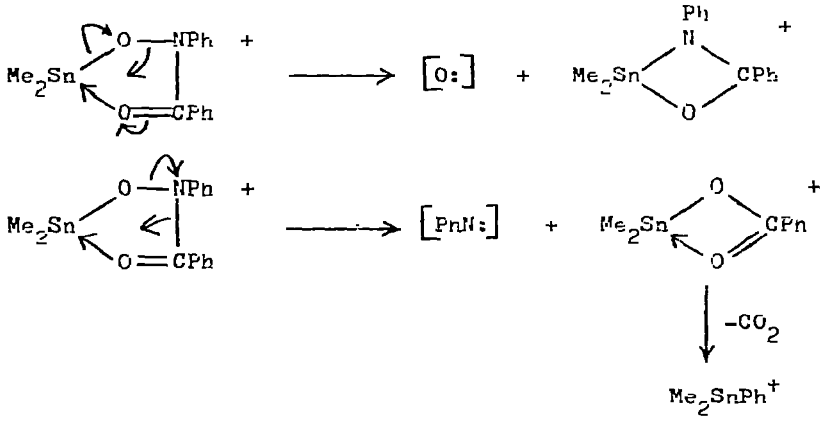
CLXXVI

Infra-red dilution studies demonstrate the presence of additional hydrogen-bonding in the *N*-proto derivatives. The mass spectra for the two trimethyltin derivatives $Me_3SnONR.CO.Ph$ (R = H, Ph) suggest dimerisation *via* Sn_2O_2 ring formation CLXXVII occurs in the solid phase.



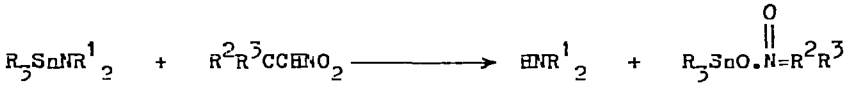
CLXXVII

The ring contraction processes:



also featured strongly in the spectra.[178]

Lorberth and Lange have undertaken a similar investigation of the triorgano-tin esters of nitronic acids $R_3SnON(O){=}CR^1R^2$ CLXXVIII. These are readily synthesised by the reaction of aminostannanes with α-nitroalkanes:

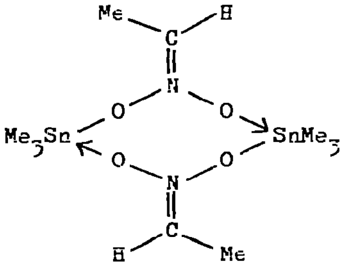


$$R_3SnNR^1_2 + R^2R^3CCHNO_2 \longrightarrow HNR^1_2 + R_3SnO.\overset{\overset{O}{\|}}{N}{=}R^2R^3$$

CLXXVIII

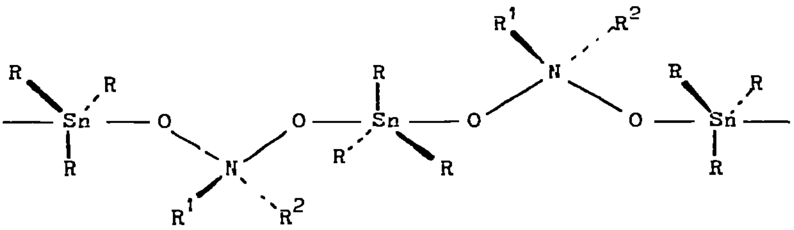
R = Me, Et; R^1 = Me, Et, $SiMe_3$; R^2 = R^3 = H, Me
R^2 = H, R^3 = Me

The products were obtained as stable crystalline solids, which were monomeric in solution. Nmr spectra excluded the alternative α-stannyl nitroalkane structu $R_3Sn\text{-}CR^2R^3NO_2$. Mass spectra indicate that $Me_3SnO_2N{=}CHMe$ also exists as a dimer CLXXIX in the solid (cf. $Me_3SnONR.CO.Ph$ <u>vide supra</u>).[179] Infra-red and Raman



CLXXIX

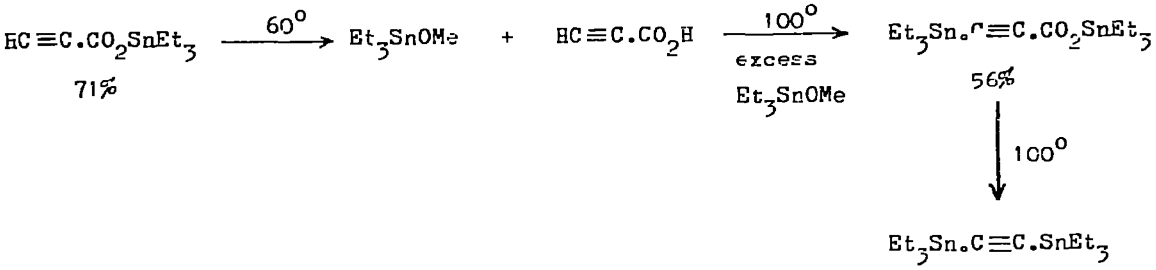
spectra for the derivatives $R_3SnON(O)R^1_2$ (R^1 = H, Me) indicate 'local' D_{3h} symmetr for the R_3Sn groups and C_{2v} symmetry for the $-ON(O)R^1_2$ ligands. These data, together with Mössbauer data indicate the presence of trigonal pyramidally coordinated tin with bridging ligands CLXXX:[180]



CLXXX

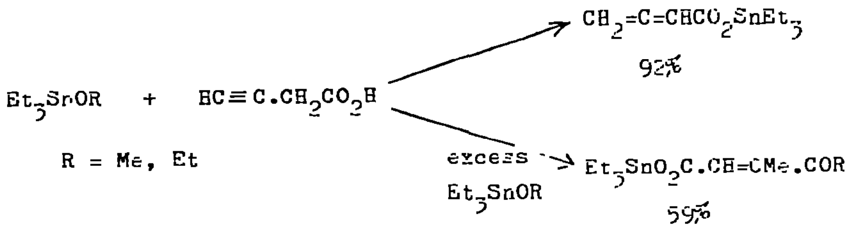
7 Carboxylates.

Triethylstannyl derivatives of alkynoic acids have been obtained from Et_3SnOMe and the acid:



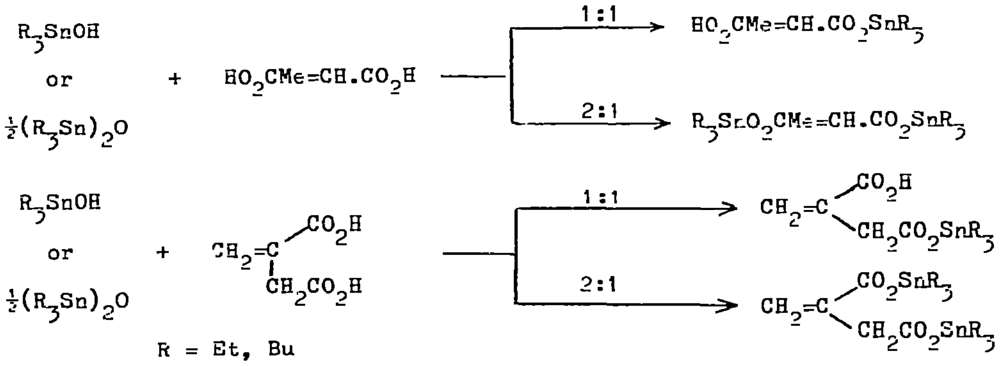
$$Et_3SnOMe + MeC{\equiv}C.CO_2H \longrightarrow \underset{70\%}{Et_3SnO_2C.C{\equiv}CMe}$$

Isomerisation occurred with $HC{\equiv}C.CH_2CO_2H$:



Treatment of $Et_3Sn.C{\equiv}C.CO_2SnEt_3$ with halogens afforded ~68% yields of $X.C{\equiv}C.CO_2SnEt_3$ (X = Cl, Br).[181]

Mono- and distannyl derivatives of bifunctional alkenoic acids are similarly obtained from the triorganotin oxide or hydroxide:[182]



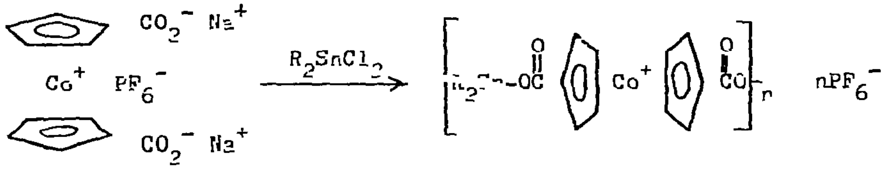
Silyl-substituted organotin carboxylates have been prepared by transesterification:[183]

$$Et_3SiO_2CCHR^1CH_2SiR_3 + EOSnR^2_3 \longrightarrow Et_3SiOE + R^2_3SnO_2CHR^1CH_2SiR_3$$

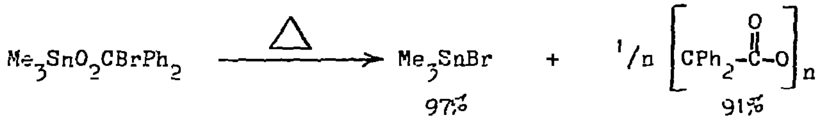
E = H, Me, SnR_3; R^1 = H, Me; R_3Si = Et_3Si, $(EtO)_2MeSi$; R^2 = Et, Bu

Heating $R_2Sn(O_2CR')_2$ (R = Me, Bu; R' = Me, Et, isoPr) and SnX_4 in hexane and be affords $Sn(O_2CR')_4$ and R_2SnX_2 (X = Cl, Br, I).[184] Dialkyltin derivatives of p-(arylamino)phenoxyacetic acids have been prepared by heating p-ArNH-C_6H_4-CH_2CO and R_2SnO or the corresponding salt and R_2SnCl_2.[185]

Low molecular weight metallopolymers have been prepared by rapid stirring of the disodium salt of cobalticinium-1,1'-dicarboxylic acid with diorganotin dichlorides in aqueous nitrobenzene:[186]



The infra-red spectra of trivinyltin carboxylates $(CH_2{=}CH)_3SnO_2CR$ (R = Me, CH_2Cl, $CHCl_2$, CF_3) suggest monomeric character when R = $CHCl_2$ and CF_3, but polymeric bridged structures when R = Me, CH_2Cl. Depolymerisation occurs in solution.[187] A similar polymeric nature for dimethyltin chloride carboxylates is proposed from mass spectroscopic studies. Tetramethyl-1,3-bis(carboxy)distanoxanes and tetramethyl-1-carboxy-3-hydroxydistannoxanes are dimeric in the solid. Halogeno-substituted tin carboxylates $Me_3SnO_2CBrRR^1$ (R = R^1 = Me, Ph; R = H, R^1 = Pr) may be pyrolysed to give Me_3SnBr and the corresponding polyester, eg:



$$Me_3SnO_2CBrPh_2 \xrightarrow{\Delta} \underset{97\%}{Me_3SnBr} + \tfrac{1}{n}\underset{91\%}{\left[CPh_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O\right]_n}$$

When the pyrolysis is carried out in the presence of CX_3CO_2H (X = Cl, Br) or MeOH the corresponding α-functionally substituted diphenylacetic acid is produced, suggesting that $^-O{-}CO{-}\overset{+}{C}Ph_2$, or its precursor, is the reactive species. The

$$Me_3SnO_2CBrPh_2 \xrightarrow[CX_3CO_2H]{} Me_3SnBr + CX_3CO.OCPh_2CO_2H$$

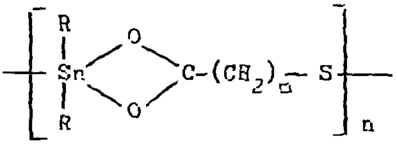
reaction of $CX_3CO_2CPh_2CO_2H$ (X = Cl, Br) with $(Me_3Sn)_2S$ gives benzilic acid polyester and $Me_3SnO_2CCX_3$, presumably <u>via</u> a similar elimination.[189]

Reaction of $BuSnO_{1.5}$ with thioglycolic acid yields polymeric CLXXXI in whi one of the ligands retains a free SH group:

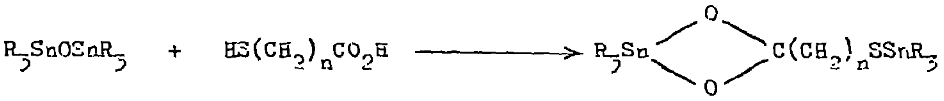
$$BuSnO_{1.5} + 2HSCH_2CO_2H \longrightarrow [BuSn(O_2CCH_2SH)(O_2CCH_2S)]_n + H_2O$$

CLXXXI

Diorganotin derivatives $[R_2SnS(CH_2)_mCO_2]_n$ (R = Me, Bu, Ph; M = 1, 2, 3) prepared similarly are also polymeric, with both oxygen atoms of each carboxylate group attached to the same tin atom, viz:

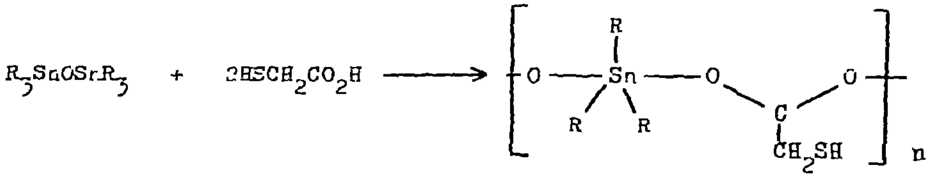


Two types of derivative are obtained from bistriorganotin oxides and mercapto-carboxylic acids depending on the ratio of reactants employed. A 1:1 ratio produces monomeric, binuclear derivatives CLXXXII. The presence of two different tin environments is confirmed by the Mössbauer spectra.

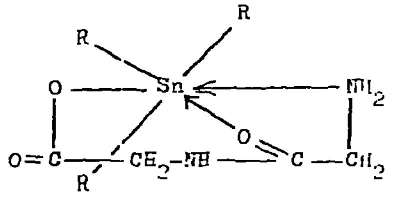


CLXXXII

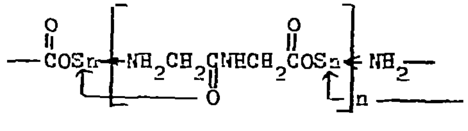
A 1:2 ratio of reactants produces polymeric carboxylates CLXXXIII, in which all tin atoms are equivalent:[190]



Trialkyltin derivatives of amino acids and dipeptides R_3SnAA [R = Me, C_6H_{11}; AA = glycine (gly), DL-α-alanine (ala), DL-α-amino-n-butyric acid (but), DL-α-valine (val), DL-α-leucine (leu), L-α-isoleucine (isoleu), β-alanine (β-ala), and glycylglycine (glygly)] and Bu$_3$Sn(gly) have been systematically investigated by Ho and Zuckerman. The syntheses were achieved by azeotropic removal of water from mixtures of the triorganotin oxide or hydroxide and the amino acid in boiling benzene; catalytic quantities of DMF are sometimes necessary. The structure adopted by the derivatives depends on the nature of the groups attached to tin and the amino acid. A one-dimensional associated lattice involving five-coordinate non-planar R$_3$Sn groups bridged by amino carboxylate residues is inferred for twelve of the derivatives all Me$_3$Sn derivatives, Bu$_3$Sn(gly), (C$_6$H$_{11}$)$_3$Sn(gly), (β-ala), (glygly) . Infra-red data indic es that bridging takes place *via* amino-N→Sn rather than C=O→Sn coordination. Confirmation of polymeric lattices for Me$_3$Sn(gly), (ala), (glygly) and Bu$_3$Sn(gl results from the observation of ambient temperature Mössbauer spectra in thos cases. (C$_6$H$_{11}$)$_3$Sn(but) and (C$_6$H$_{11}$)$_3$Sn(val) are four-coordinate monomers, but high coordination numbers are indicated for (C$_6$H$_{11}$)$_3$Sn(ala), (leu), (isoleu). (C$_6$H$_{11}$)$_3$Sn(glygly) appears to possess six-coordinate tin with monomeric or polymeric *mer*-octahedral structures CLXXXIII or CLXXXIV.[191,192]



CLXXXIII



CLXXXIV

8. Oxyacid Derivatives.

Bis(trialkyltin) carbonates (R$_3$Sn)$_2$CO$_3$ (R = Me, C$_6$H$_{11}$) have been prepared by bubbling CO$_2$ gas through benzene solutions of the corresponding hydroxides.[19

Interaction of N$_2$O$_4$ with Me$_4$Sn produces Me$_2$Sn(NO$_3$)$_2$ and the dimer of nitros methane:[193]

$$Me_4Sn \quad + \quad 2N_2O_4 \longrightarrow Me_2Sn(NO_3)_2 \quad + \quad (MeNO)_2$$

In the crystal, dimethyltin dinitrate contains inequivalent unsymmetrically bidentate nitrate ligands: r(Sn-O^1) = 2.15, 2.17 A; r(Sn-O^2) = 2.42, 2.70 A. The two methyl groups subtend an angle of 143.6° at tin, and hence the molecule is a further example of a dimethyltin derivative whose structure is best described as intermediate between four-coordinate tetrahedral and six-coordinate trans octahedral.[194]

The addition of di-n-propyl sulphoxide to an acetone-chloroform solution of diphenyltin dinitrate results in the formation of μ-oxalato-bis(di-n-propyl sulphoxide)nitratodiphenyltin. The structure of this unexpected product is shown in Fig. 6. The coordination about the tin is pentagonal bipyramidal, with the two phenyl groups occupying apical sites; r(Sn-C) = 2.116 A. Equatorial positions are occupied by oxygen atoms from bidentate nitrate [r(Sn-O) = 2.588, 2.408 A] and oxalate [r(Sn-O) = 2.282, 2.248 A] groups, and the sulphoxide ligand [r(Sn-O) = 2.178 A] in a planar arrangement. The C-Sn-C group is almost

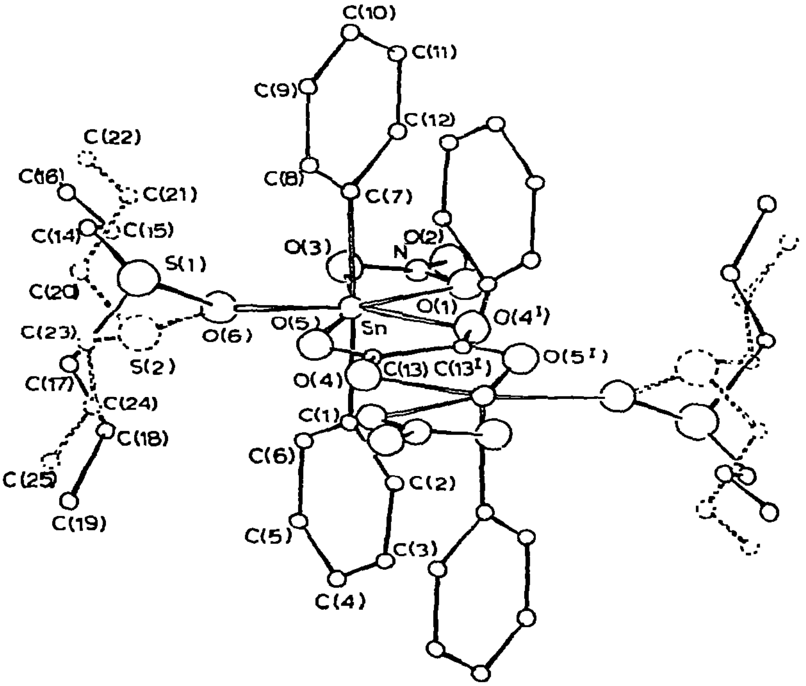


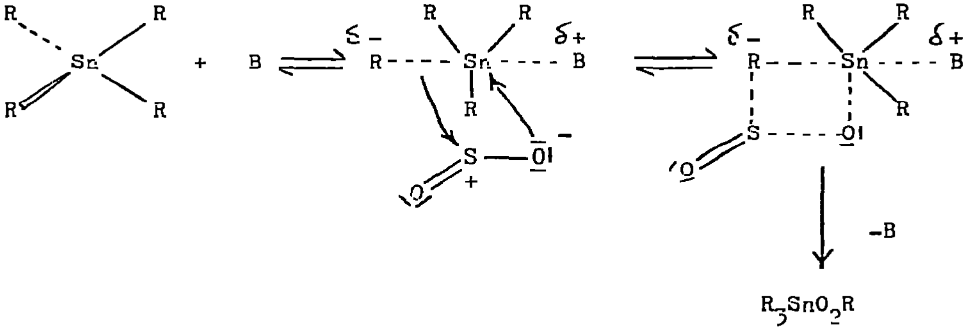
Fig. 6. The structure of μ-oxalato-bis(di-n-propyl sulphoxide)nitratodiphenyltin. (Reproduced by permission of the Chemical Society).

linear ($\widehat{C-Sn-C}$ = 176.8°). Some disorder occurs in the sulphoxide ligand, which occupies two positions around the Sn-O bond.[195]

The presence of 2,2'-bipyridyl facilitates the insertion of liquid SO_2 into two Sn-C bonds of R_4Sn (R = Me, Et) producing dialkyltin bis(alkylsulphinates),

$$3Me_4Sn \quad + \quad 4SO_2 \quad \xrightarrow[\text{bipyridyl}]{-30^{\circ}/60\ \text{hrs}} \quad \underset{66\%}{2Me_3SnO_2SMe} \quad + \quad \underset{33\%}{Me_2Sn(O_2SMe)_2}$$

The insertion is stepwise; the trialkyltin monosulphinates undergo further insertion under the same conditions to afford the identical bis(sulphinates). The following base-assisted mechanism was proposed:[196]



Reaction of R_4Sn (R = Me, Et) with liquid SO_2 at 60° results in disproportionati of sulphur and the formation of the corresponding bis(trialkyltin) sulphates $(R_3Sn)_2SO_4$ and alkanethiosulphonis S-alkyl esters RSO_2SR.[197]

$$2R_4Sn \quad + \quad 3SO_2 \quad \xrightarrow{60^{\circ}} \quad (R_3Sn)_2SO_4 \quad + \quad RSO_2SR$$

Tetravinyltin gives a monosulphinate at low temperatures and a disuphinate at or above room temperature;

$$(CH_2{=}CH)_2Sn(O_2SCH{=}CH_2)_2 \quad \xleftarrow[\text{liq. } SO_2]{20^{\circ}/\ 2\ \text{d.}} \quad Sn(CH{=}CH_2)_4 \quad \xrightarrow[\text{liq. } SO_2]{-30^{\circ}/\ 1\ \text{d.}} \quad (CH_2{=}CH)_3SnO_2$$

tetraallyltin always forms an unstable disulphinate which slowly decomposes into a polymeric product of composition $(C_3H_5)_2Sn.1{\cdot}5SO_2$:

$$\begin{array}{lr} (CH_2{=}CH{-}CH_2)_4Sn \quad + \quad 2SO_2 \xrightarrow{-30^{\circ}/\ 1\ d.} & (CH_2{=}CH{-}CH_2)_2Sn(O_2SCH_2{-}CH{=}CH_2) \\ & {\scriptstyle 25^{\circ}}\Big\downarrow{\scriptstyle -SO_2} \\ & (C_3H_5)_2Sn.1.5SO_2 \end{array}$$

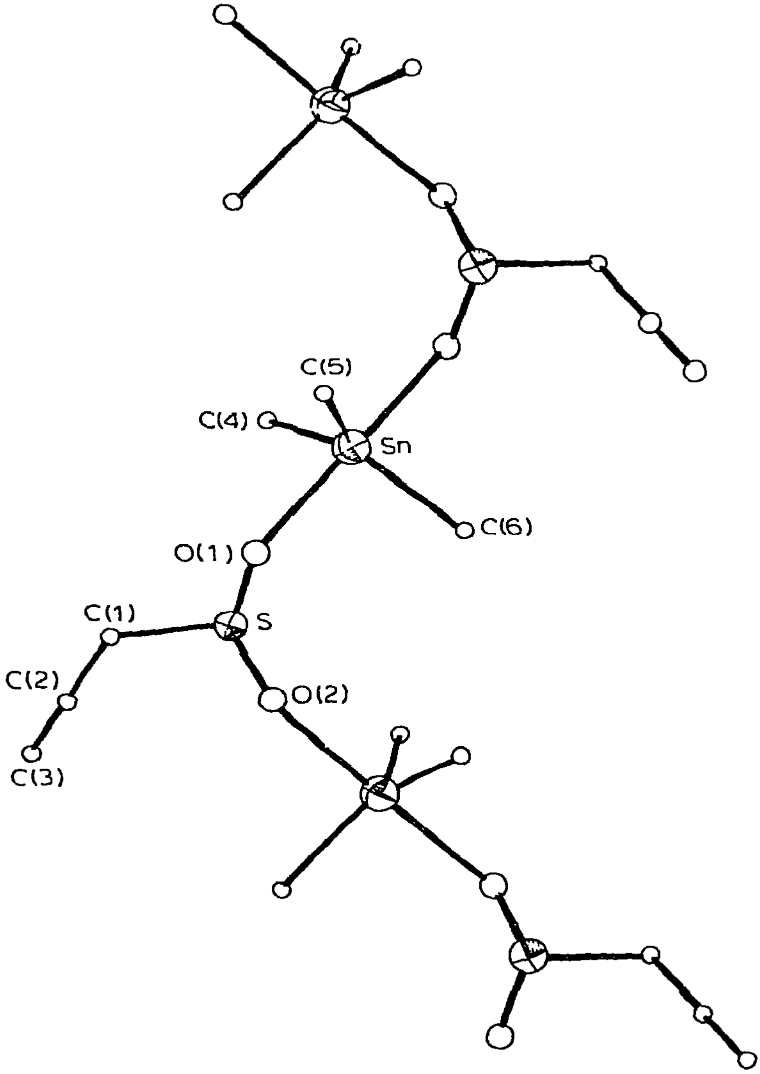


Fig. 7. The structure of $Me_3SnO_2CH_2C{\equiv}CH$. (Reproduced by permission from Acta Cryst., 29B (1973) 560).

The trialkenyltin chlorides R_3SnCl ($R = CH{=}CH_2$, $CH_2{-}CH{=}CH_2$) take up one and two moles of SO_2, respectively, at room temperature forming CLXXXV and CLXXXVI:

$$(CH_2{=}CH)_3SnCl \quad + \quad SO_2 \quad \xrightarrow{20^\circ} \quad (CH_2{=}CH)_2Sn(Cl)(O_2SCH{=}CH_2)$$

CLXXXV

$$(CH_2{=}CHCH_2)_3SnCl \quad + \quad 2SO_2 \quad \xrightarrow{20^\circ} \quad (CH_2{=}CHCH_2)Sn(Cl)(O_2SCH_2CH{=}CH_2)_2$$

CLXXXVI

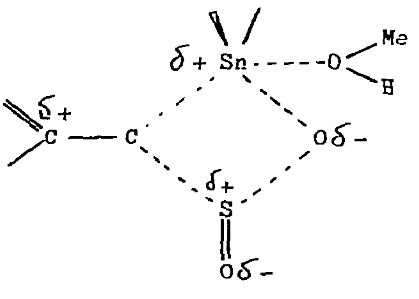
Divinyltin dichloride does not react even at 70°. Alkenyltin sulphinates are also available by metathesis between the tin chlorides and sodium sulphinates:[19]

$$(CH_2{=}CH)_{4-n}SnCl_n \quad + \quad nNaO_2SR \quad \xrightarrow[THF]{20^\circ} \quad (CH_2{=}CH)_{4-n}Sn(O_2SR)_n \quad + nNaCl$$

R = Ph, p-tol; n = 1, 2

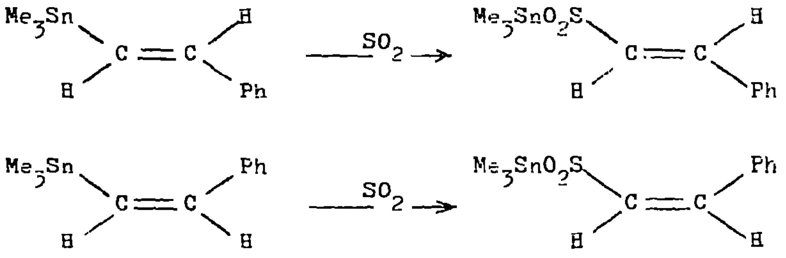
Ginderow and Huber have publised full details of the structure of the product of SO_2 insertion into trimethylpropargyltin. The compound consists of propargylsulphinate-bridged planar trimethyltin groups (Fig. 7); r(Sn-C) = 2.156 2.171 A, r(Sn-O) = 2.301A.[199]

Kitching has extended his mechanistic studies of the SO_2-insertion reaction to aryl- and benzyltrimethylstannanes. For a series of 3- and 4-substituted phenyltin compounds in methanol, the reaction is cleanly second-order (first-order in each reactant). The kinetic data suggest a four-centred S_Ei transition state with some polar character, viz.:



The kinetics in benzene are more complex, k_2(obs) increasing with $[SO_2]$.

Insertion into the vinyl-tin bond of β-styryltrimethyltin takes place with essentially complete retention of configuration at carbon as expected for an S_E1 process:[200]



Second-order kinetics have also been demonstrated for the SO_2 insertion into the benzyl-tin bond of *meta*- and *para*-substituted benzyltrimethylstannanes. The rate of reaction is relatively insensitive to substitution, suggesting that the mechanism changes with substituent, with charge developing as to be best dispersed by the substituent.[201]

Diorganotin bis(arylsulphonates) CLXXXVII have been prepared by the reaction of the trimethylsilylarylsulphonate with R_2SnO:[202]

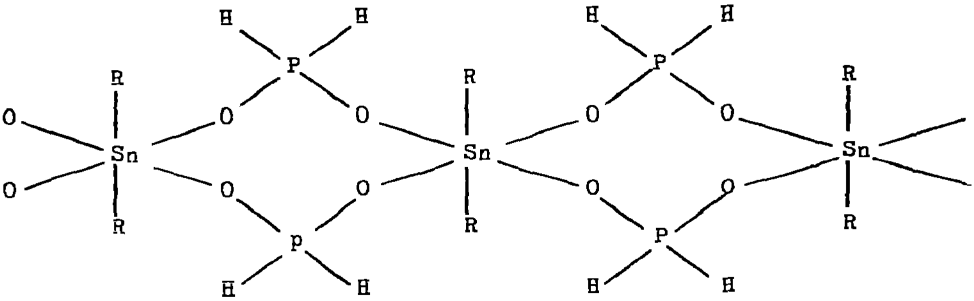
$$2\underline{p}\text{-}CFX{=}CFC_6H_4SO_2OSiMe_3 \quad + \quad R_2SnO \xrightarrow{\text{hexane}} (Me_3Si)_2O \quad + \quad R_2Sn(OSO_2C_6H_4CF{=}CFX\text{-}\underline{p})_2$$

X = Cl, F; R = alkyl, aryl

CLXXXVII

Methyl fluorosulphonate cleaves a Me-Sn bond of Me_4Sn forming trimethyltin fluorosulphonate.[203] Ph_4Sn, Ph_3SnCl and Ph_2SnCl_2 are completely solvolysed by disulphuric acid. Alkyltin compounds, R_4Sn, R_3SnCl, R_2SnCl_2 and R_2SnO, generally afford alkyltin cations.[204]

Dialkyltin salt of phosphorus oxyacids $R_2Sn(PO_2H_2)_2$ (R = Me, Et, Bu), R_2SnPO_3X (R = Me, Et, Bu; X = H: R = Me, X = F, OH) and $(Me_2Sn)_3(PO_4)_2$ have been prepared in aqueous solution from the appropriate R_2SnCl_2 and the sodium salts of phosphorus oxyacids. Infra-red and Mössbauer data for $R_2Sn(PO_2H_2)_2$ indicate six-coordinate tin atoms with *trans* alkyl groups and bidentate bridging hypophosphite groups CLXXXVIII. For the phosphites R_2SnPO_3X, polymeric structures are proposed which contain non-linear R_2Sn arrangements in a distorted *trans*

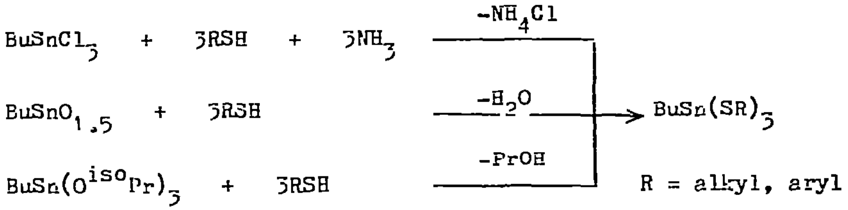


CLXXXVIII

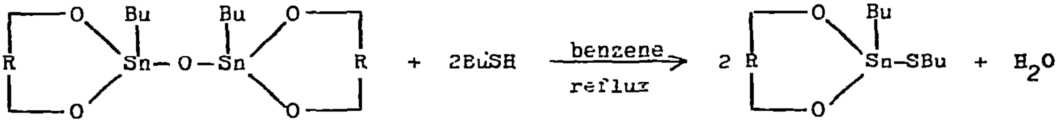
octahedral or trigonal bipyramidal configuration. Penta- rather than hexacoordination at tin is preferred for $(Me_3Sn)_3(PO_4)_2$.[205]

9. Sulphur, Selenium, and Tellurium Derivatives.

Mehrotra has synthesised tris(thiolato)butylstannanes by three different routes:



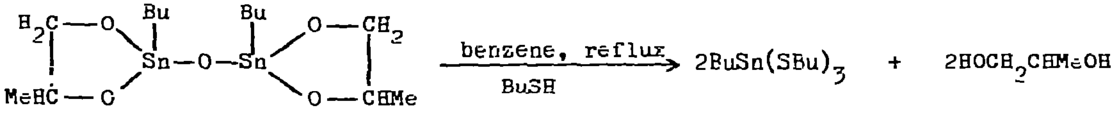
Refluxing the butyltin glycolate CIXC with BuSH resulted in reaction at the Sn-O-Sn bridge:



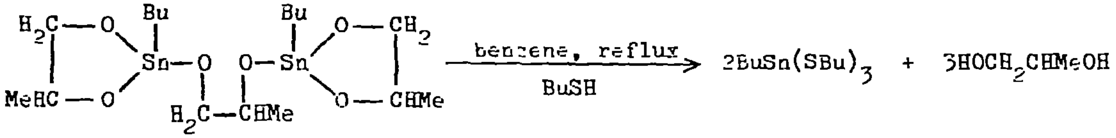
CIXC

R = $-CHMe.CHMe-$, $-CHMe.CH_2.CMe_2-$

but all Sn-O bonds of the glycolates CXC and CXCI are cleaved under the same conditions:

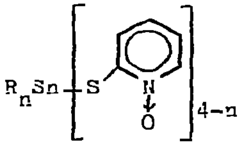


CXC



CXCI

All the tris(thiolato) derivatives are monomeric; $BuSn(OCHMe)_2(SBu)$ is dimeric.[206] The preparation of several new tin-sulphur compounds is reported in the patent literature. Organotin derivatives of 2-mercaptopyridine *N*-oxide CXCII have been prepared from the organotin oxide and the mercaptide.[207]



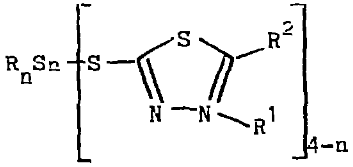
CXCII

n = 2; R = Me, Bu, oct

n = 1; R = Bu

n = 3; R = Bu

(2-Thiazolythio)tin derivatives CXCIII are similarly obtained from the free thiol



CXCIII

$n = 2, 3$; R = Et, Bu, oct, Ph; R^1 = H, Me, CH_2CO_2Me; R^2 = H, Me, CO_2Et

and the organotin chloride or oxide.[208] Ethylenebis(dithiocarbamato)bis(chlorodiorgano)stannanes, $R_2ClSnS_2CNH.CH_2.CH_2.NHCS_2SnClR_2$ (R = Me, Bu, oct, Ph), have been prepared from the R_2SnCl_2 and the sodium salt.[209] Thiophosphorylstannanes $(C_6H_{11})_3SnSP(S)R^1R^2$ ($R^1 = R^2$ = Me_2CHO, Me_2CHCH_2O, PrO, EtO, $C_6H_{11}O$; R = Et, $R^1 = R^2$ = EtO, Me_2CHO) have been obtained by treating $(C_6H_{11})_3SnCl$ with $KSP(S)R^1R^2$.[210]

The structures of three triphenyltin thiolates have been determined.

Ph$_3$SnSC$_6$H$_4$-^{t}Bu-*p*[211] and Ph$_3$SnSC$_6$H$_2$Me$_3$-2,4,6[212] both contain tetrahedrally coordinated tin (Figs. 8 and 9, respectively). The metal-ligand bond distances, not

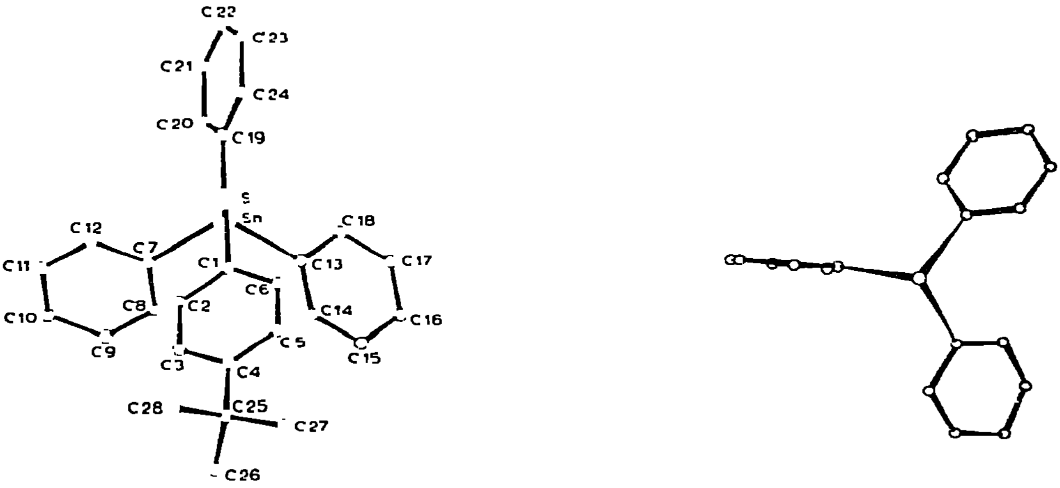


Fig. 8. The structure of Ph$_3$SnSC$_6$H$_4$-^{t}Bu-*p*.

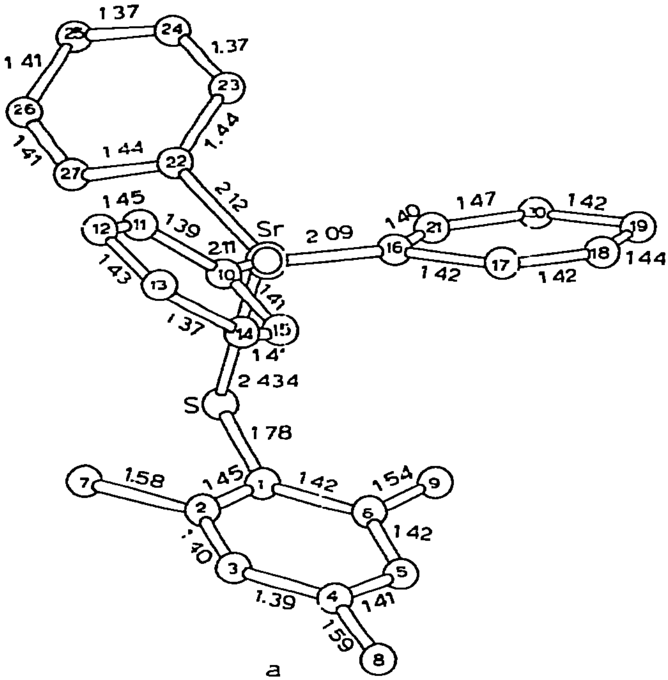


Fig. 9. The structure of Ph$_3$SnSC$_6$H$_2$Me$_3$-2,4,6. (Reproduced by permission of the Consultants Bureau).

unexpectedly are similar in the two compounds: $Ph_3SnSC_6H_4$-^{t}Bu-p, r(Sn-C) = 2.126 A; r(Sn-S) = 2.413 A. $Ph_3SnSC_6H_2Me_3$-2,4,6, r(Sn-C) = 2.13 A; r(Sn-S) = 2.434 A. The triphenyltin derivative of 4-thiopyridone has a structure in the solid made up of chains of molecules connected by intermolecular N→Sn coordination (Fig. 10),

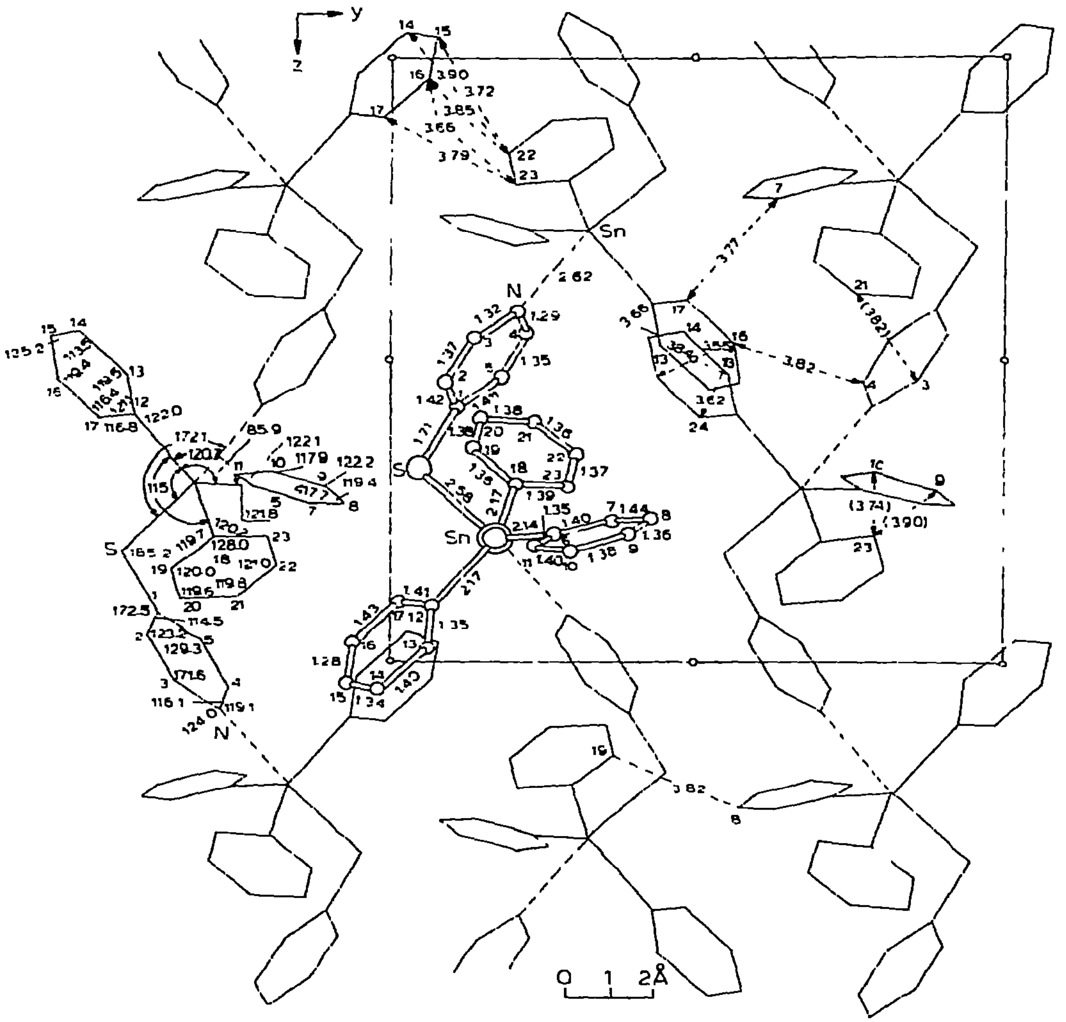


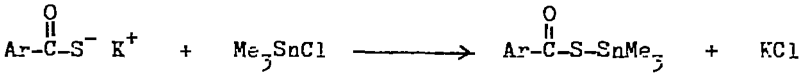
Fig. 10. The structure of $Ph_3SnSC_5H_4N$. (Reproduced by permission of the Consultants Bureau).

raising the coordination number of the tin to five in a trigonal bipyramidal arrangement. The Sn-S and Sn-C bonds are longer (2.58 and 2.16 A, respectively than in the four-coordinate compounds; r(Sn-N) = 2.62 A.[213]

Et_3SnSR (R = Et, Ph) convert alkyl and aryl isocyanates to the correspondi isocyanurates.[214] Exchange equilibria between triphenyltin, triphenyllead and phenylmercuric thiophenolates and the free thiophenol are qualitatively reporte in a conference abstract. Substitution of the 3- or 4-positions of the thiophen group only slightly affects the equilibrium constants, but 2-substitution has a significant effect due to steric hindrance and intramolecular coordination and hydrogen bonding.[215]

Neutral diorganotin *cis*-1,2-dicyanoethylenedithiolate compounds $R_2Sn(mnt)$ (R = Me, Ph) have been prepared from R_2SnCl_2 and Na_2mnt in a 1:1 ratio. They appear to be polymeric with a coordination number greater than four. Anionic derivatives, $\left[R_2Sn(mnt)_2\right]_2^{2-}$, $R_2Sn(mnt)X^-$ (R = Me, Ph; X = Cl, Br, I) may also be obtained as Ph_4M (M = P, As) or R_4N (R = Me, Ph) salts by judicious choice of reagents and molar ratios.[216]

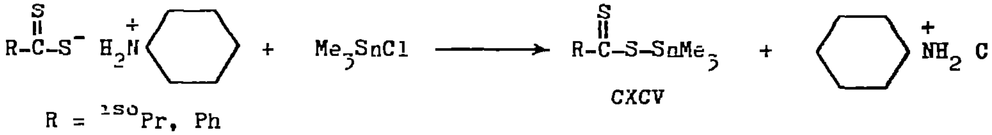
Ishii has investigated organotin derivatives of mono- and dithio-carboxylic acids. Interaction of potassium monothiobenzoate with Me_3SnCl results in the exclusive formation of the Sn-S bonded isomer CXCIV:[217]



$$Ar-\overset{O}{\overset{\parallel}{C}}-S^- K^+ + Me_3SnCl \longrightarrow Ar-\overset{O}{\overset{\parallel}{C}}-S-SnMe_3 + KCl$$

CXCIV

Trimethyltin dithiocarboxylates CXCV are prepared similarly using the piperidini salt of the dithiocarboxylic acid:[218]



CXCV

$Me_3SnS(CH_2)_2CO_2SnMe_3$, from Me_3SnCl, NEt_3, and 3-mercaptopropionic acid in cold water, disproportionates at 130-40° to Me_4Sn and $Me_2\overline{Sn-SCH_2CH_2CO_2}$.[219]

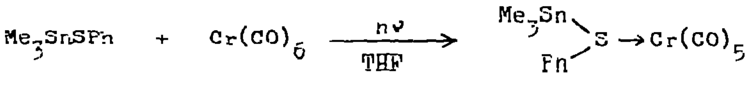
Irradiation of 1:1 mixtures of bis(trimethyltin) sulphide,[220] selenide,[221] or telluride[222] and a Group VI hexacarbonyl in THF results in the formation of the stannylchalcogenide metal pentacarbonyl complexes CXCVI:

$$M(CO)_6 \quad + \quad (Me_3Sn)_2E \quad \xrightarrow[THF]{h\nu} \quad (Me_3Sn)_2E \rightarrow M(CO)_5$$

CXCVI

M = Cr, Mo, W; E = S, Se, Te

Me_3SnSPh and $Cr(CO)_6$ afforded CXCVII under similar conditions:[220]



$$Me_3SnSPh \quad + \quad Cr(CO)_6 \quad \xrightarrow[THF]{h\nu} \quad (Me_3Sn)(Ph)S \rightarrow Cr(CO)_5$$

CXCVII

$(Me_3Sn)_2Te$ was obtained by the reaction of Me_3SnCl with sodium telluride Na_2Te in dry benzene.[222]

Methane- and benzeneseleno- derivatives of tin have been synthesised by various methods. Routes to methaneseleno- derivatives include protolysis of aminotin compounds by MeSeH, and the reaction of methyltin halides with $LiAl(SeMe)_4$ or $Me_3SiSeMe$:

$$Me_3SnNMe_2 \quad + \quad MeSeH \quad \longrightarrow \quad Me_3SnSeMe \quad + \quad Me_2NH$$

$$4Me_3SnX \quad + \quad LiAl(SeMe)_4 \quad \longrightarrow \quad 4Me_3SnSeMe \quad + \quad LiX \quad + \quad AlX_3$$

X = Cl, Br

$$Me_{4-n}SnX_n \quad + \quad nMe_3SiSeMe \quad \longrightarrow \quad Me_{4-n}Sn(SeMe)_n \quad + \quad nMe_3SiX$$

X = F, Cl, Br; n = 1 - 4

The Sn-SeMe bond is quantitatively cleaved by HCl, but is unaffected by MeSH or H_2S.[223] Benzeneseleno- derivatives have been prepared from the organotin oxide or chloride:

$$R_2SnO \quad + \quad 2PhSeH \quad \longrightarrow \quad R_2Sn(SePh)_2 \quad + \quad H_2O$$

R = Me, Bu

$$(Bu_3Sn)_2O \quad + \quad 2PhSeH \longrightarrow 2Bu_3SnSePh \quad + \quad H_2O$$

$$Et_2SnCl_2 \quad + \quad 2PhSeH \quad + \quad 2Et_3N \longrightarrow Et_2Sn(SePh)_2 \quad + \quad 2Et_3NHCl$$

$$Ph_3SnCl \quad + \quad PhSeH \quad + \quad Et_3N \longrightarrow Ph_3SnSePh \quad + \quad Et_3NHCl$$

Iodine quantitatively cleaves the Sn-Se bond:

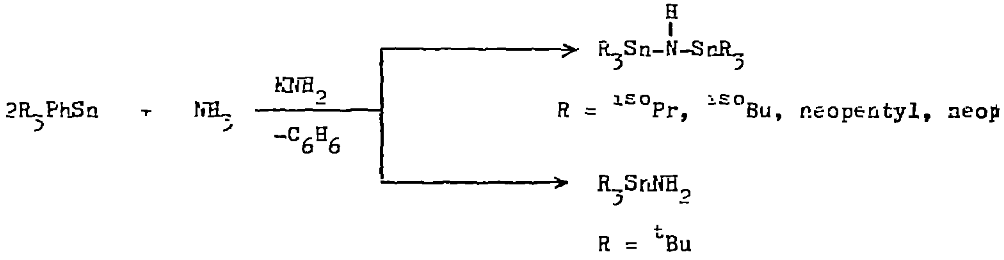
$$Bu_2Sn(SePh)_2 \quad + \quad I_2 \longrightarrow Bu_2SnI_2 \quad + \quad PhSeSePh$$

No adduct formation could be observed with $Bu_2Sn(SePh)_2$ and various oxygen and nitrogen donors, but addition of water produces a hydrated oxide.[224]

The N,N-dialkylselenocarbamato-tin derivatives $Me_2Sn(Se.CO.NR_2)_2$, $Me_2ClSnSe.CO.CR_2$ (R = Me, Et) and $Me_3Se.CO.NMe_2$ have been prepared from the organotin chloride and an alkylammonium salt of the selenocarbamate. Infra-red and nmr data indicate weak carbonyl ->tin interactions in the dimethyltin derivatives. In $Me_3SnSe.CO.NMe_2$, the carbonyl group is 'free' and the tin four-coordinate.[225]

10. Group V Derivatives.

Trialkylphenyltin compounds with sterically hindered alkyl substituents rea with KNH_2 in liquid ammonia to give N-protostannylamine:[226]

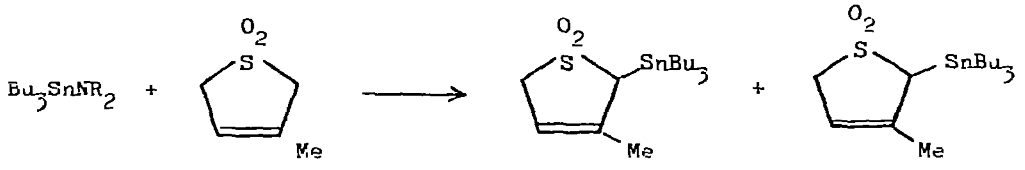


$$2R_3PhSn \quad + \quad NH_3 \xrightarrow[-C_6H_6]{KNH_2} \begin{cases} R_3Sn\overset{H}{\overset{|}{N}}SnR_3 & R = {}^{iso}Pr,\ {}^{iso}Bu,\ \text{neopentyl, neop} \\ R_3SnNH_2 & R = {}^{t}Bu \end{cases}$$

The ease of protolysis of the Sn-N bond has been used in the synthesis of $Bu_3SnCH_2SO_2Ph$ CXCVIII[227] and sulpholene and sulpholane derivatives ICC-CCI:[228]

$$Bu_3SnNR_2 \quad + \quad PhSO_2Me \xrightarrow{75^{o}/\ 1\ hr.} Bu_3SnCH_2SO_2Ph \quad (80\%)$$

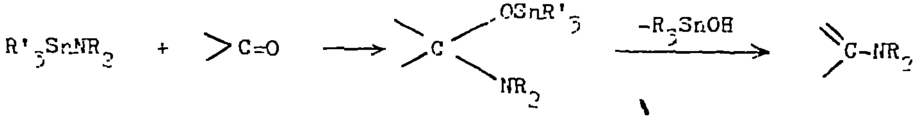
CXCVIII



ICC CC

CCI

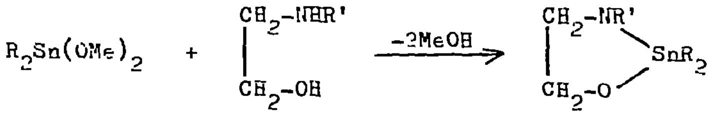
Aminostannanes, Bu_3SnNR_2 (R = alkyl, aryl), react with aldehydes in two different ways to produce either an enamine or an enoxytin compound (or the corresponding α-keto tin compound). The nature of the product formed is determined by steric and electronic factors. With less bulky groups attached to nitrogen and on the aldehyde or ketone and high nitrogen basicity, the reaction proceeds *via* initial addition of the Sn–N bond to the >C=O double bond to produce an intermediate CCII detectable by nmr. These adducts are unstable, and subsequently decompose giving the enamine.



CCII

With bulky groups and less nucleophilic nitrogen, a second mechanism operates. This is proposed to involve nucleophilic attack not at carbon but at the α-hydrogen producing α-stannylketones or enoxytin compounds.[229]

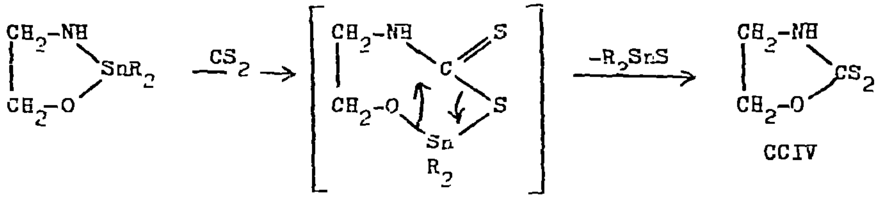
1-Oxa-3-aza-2-stannacyclopentanes CCIII, prepared from $R_2Sn(OMe)_2$ and the appropriate 2-aminoethanol,



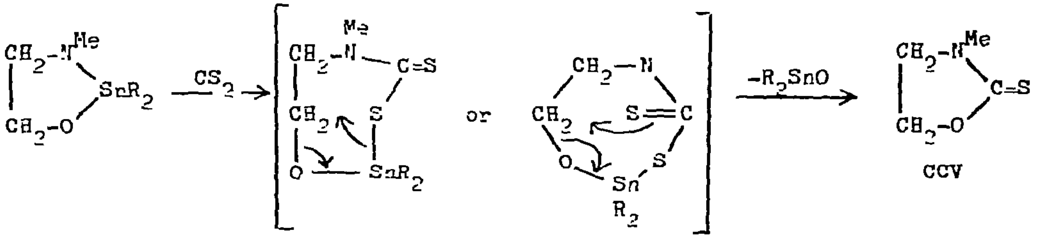
R = Et, Bu; R' = H, Me

CCIII

react with CS_2 to afford 1,3-oxazolidine-2-thione CCIV or 3-methyl-1,3-oxazolid. 2-thione CCV by an addition-eliminatin process:



CCIV

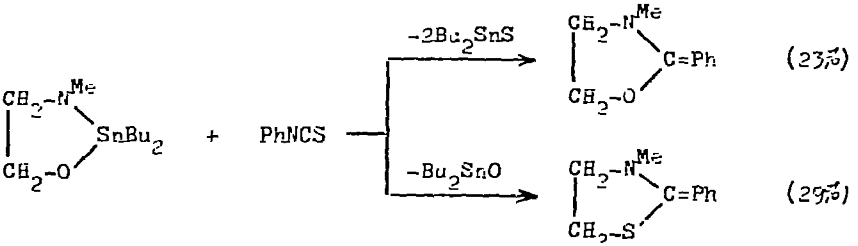


CCVI

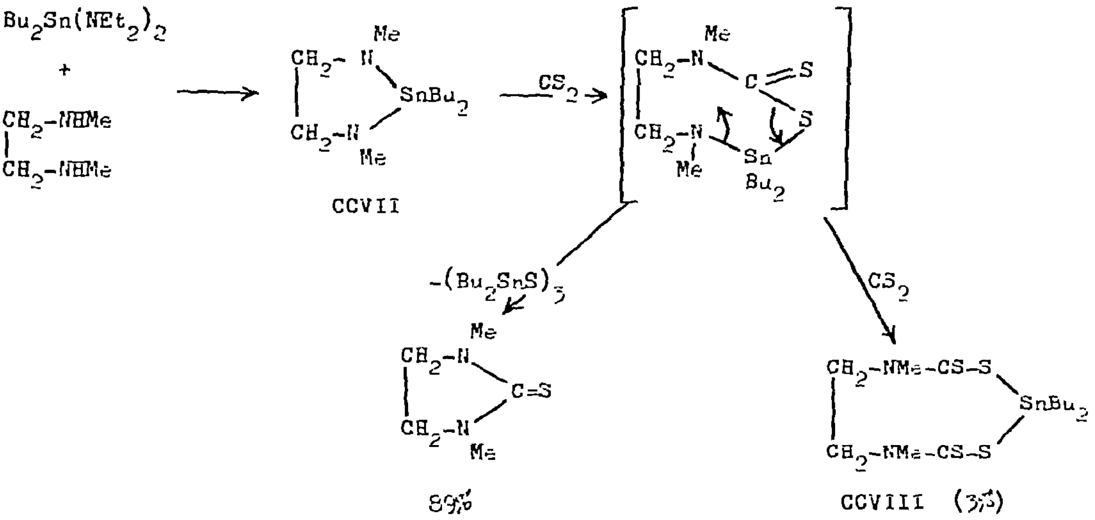
CCV

small amounts of CCIV

When the latter reaction was performed at low temperaturem stable insertion products CCVI (R =Et) could be isolated. Elimination of both Bu_2SnS and Bu_2SnO was observed in the reaction with PhNCS:



The diazastannacyclopentane CCVII, prepared *in situ*, reacts violently with CS_2 at 0° to give the 1:2 adduct CCVIII, ethylene thiourea and $(Bu_2SnS)_3$:[230]

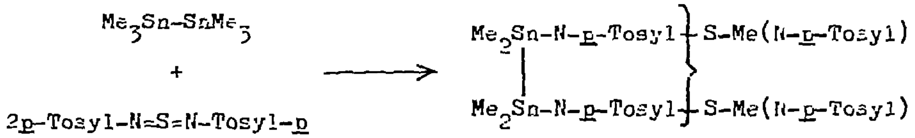


Trimethyltin compounds Me_3SnX (X = Me, NMe_2, OMe) react with di-*p*-tosyl-sulphodiimide to give *S*-substituted *S*-*p*-tosylimido-*S*--(trimethylstannyl)-*p*-tosylamido Sulphuranes CCIX in good yields:

$$Me_3SnX + p\text{-}Tosyl\text{-}N{=}S{=}N\text{-}Tosyl\text{-}p \longrightarrow (Me_3Sn\text{-}N\text{-}p\text{-}Tosyl)SX(N\text{-}p\text{-}Tosyl)$$

CCIX

CCIX (R = NMe_2) reacts with further Me_3SnNMe_2 to give $(Me_3Sn\text{-}N\text{-}p\text{-}Tosyl)_2S(NMe_2)_2$ and hydrolyses to $O{=}S(NMe_2)_2$, Me_3SnOH and *p*-Tosyl-NH_2. CCIX (X = Me) is also obtained by the reaction of Me_4Sn with *p*-Tosyl-sulphinylamine, *p*-Tosyl-NSO. Hexamethylditin reacts with two moles of di-*p*-Tosylsulphodiimide to give CCX:[231]



CCX

The reaction of tetrasulphurtetranitride S_4N_4 with Me_3SnNMe_2 produces bis-(trimethylstannyl)sulphodiimide CCXI. Treatment of CCXI with Me_3SiCl results in the formation of the corresponding silylsulphodiimide CCXII is formed.[232]

$$S_4N_4 \quad + \quad 4Me_3SnNMe_2 \longrightarrow 2(Me_2N)_2S \quad + \quad 2Me_3Sn{-}N{=}S{=}N{-}SnMe_3$$

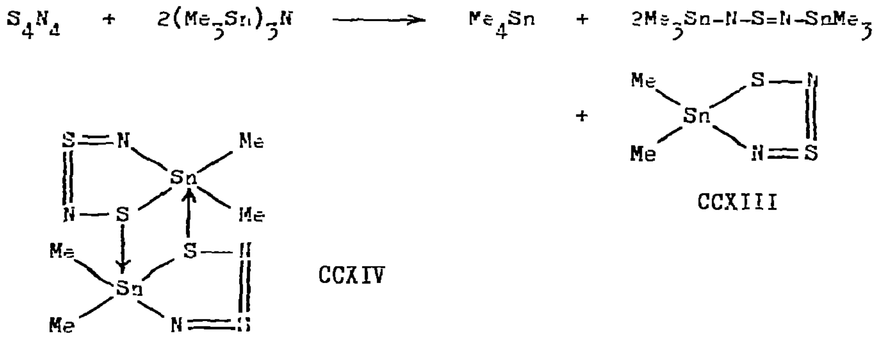
$$\text{CCXI}$$

$$\Big\downarrow Me_3SiCl$$

$$Me_3Si{-}N{=}S{=}N{-}SiMe_3$$

$$\text{CCXII}$$

S_4N_4 also reacts with $(Me_3Sn)_3N$ to afford CCXI, Me_4Sn and the dimethyltin heterocycle CCXIII, which is monomeric in the gas phase but dimeric with structu CCXIV in the solid:[233]



CCXIII

CCXIV

Exchange between Et_3SnOMe and N-trimethylsilylacetamide affords the corresponding stannylamide, which itself undergoes exchange with Me_3GeBr:

$$Me_3SiNMe.CO.Me \quad + \quad Et_3SnOMe \xrightarrow{-Me_3SiOMe} Et_3SnNMe.CO.Me$$

$$\Big\downarrow Me_3GeBr$$

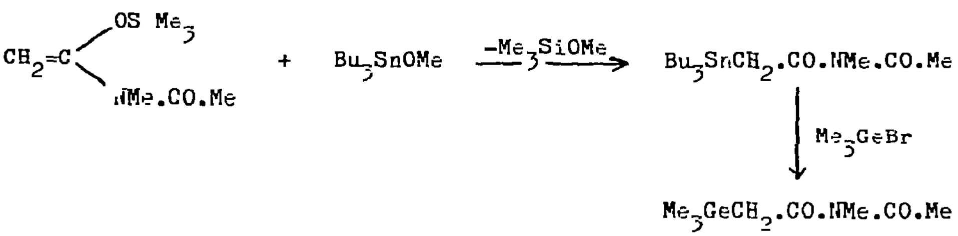
$$Me_3GeNMe.CO.Me \quad + \quad Et_3SnBr$$

Stannylamides react with ketene to give C-stannylated addition products:

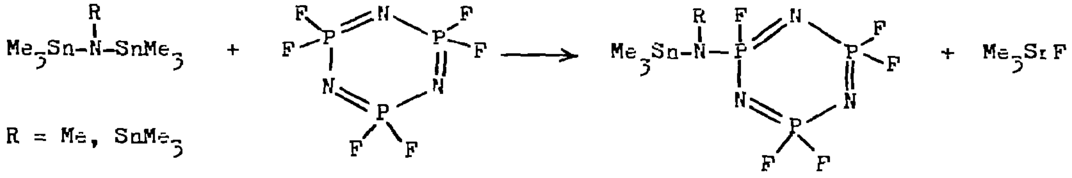
$$R_3SnNMe.CO.Me \quad + \quad CH_2{=}C{=}O \longrightarrow R_3SnCH_2.CO.NMe.CO.Me$$

$$R = Me,\ Et$$

The tributyltin homologue is produced by exchange between Bu_3SnOMe and the O-trimethylsilyl isomer:[234]

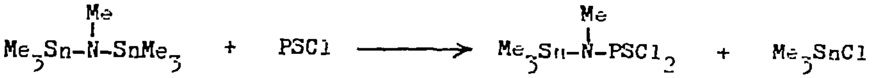


$(Me_3Sn)_2NMe$ and $(Me_3Sn)_3N$ react with phosphorus- and sulphur-halogen bonded compounds to yield the Sn-N-P(S) bonded compounds CCXV - CCXVIII:



R = Me, SnMe$_3$

CCXV

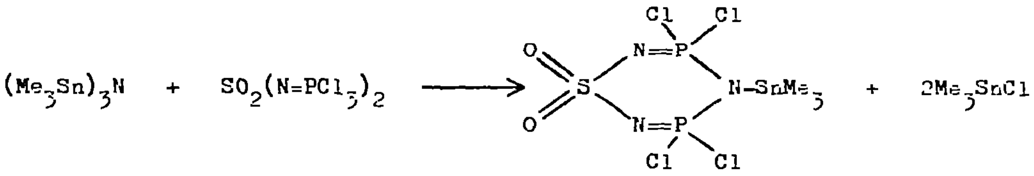


$$Me_3Sn-\overset{Me}{N}-SnMe_3 + PSCl \longrightarrow Me_3Sn-\overset{Me}{N}-PSCl_2 + Me_3SnCl$$

CCXVI

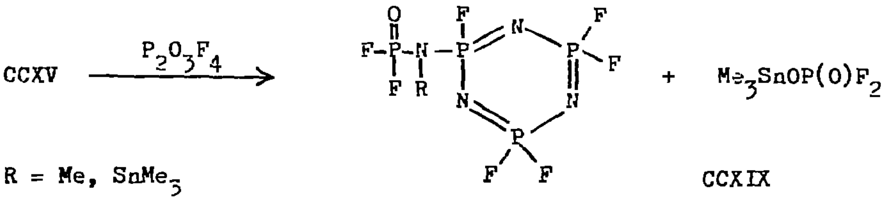
$$Me_3Sn-\overset{Me}{N}-SnMe_3 + C_4F_9SOCl \longrightarrow Me_3Sn-\overset{Me}{N}-SOC_4F_9 + Me_3SnCl$$

CCXVII



CCXVIII

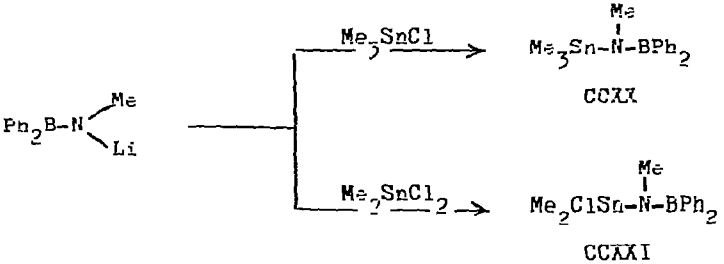
CCXV react with $P_2O_3F_4$ to produce the compounds CCXIX:[235]



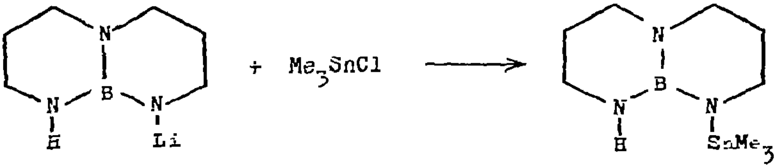
R = Me, SnMe$_3$

CCXIX

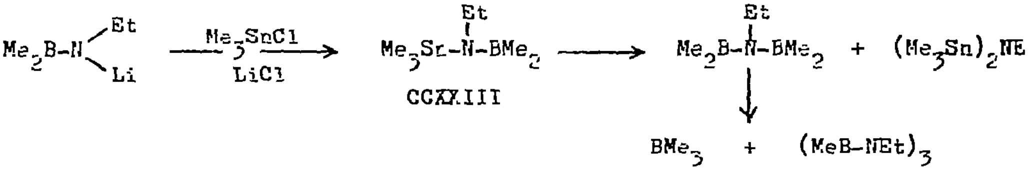
Stannylaminoboranes have been synthesised by Wells and Neilson and by Nöth and Geisler. The former authors have prepared the compounds $(Me_3Sn)_2N.BR.NMe_2$ (R = Ph, NMe_2) by the cleavage of $(Me_3Sn)_3N$ by the appropriate chloroborane.[236] Geisler and Nöth have used the lithium salt method to obtain the compounds CCXX-CCXXII:


CCXX

CCXXI


CCXXII

From the attempted synthesis of $Me_3Sn.NEt.BMe_2$ CCXXIII, only the decomposition products BMe_3, $(MeB-NEt)_3$ and $(Me_3Sn)_2NEt$ were identified, although B^{11} nmr evidence was obtained from the formation of CCXXIII:


CCXXIII

Trimethylstannylimidosulphuryl fluoride CCXXIV has been prepared by the reaction of NSF_3 with $(Me_3Sn)_2O$ or from $Hg[N{=}S(O)F_2]_2$ and Me_3SnCl in ether at -70°. CCXXIV decomposed at room temperature to give Me_3SnF and $[N{=}S(O)F]_3$, and reacted with $[F_2P(O)]_2O$ to give $F_2(O)PN{=}S(O)F_2$ and $Me_3SnOP(O)F_2$.[238]

Lappert *et al*. have synthesised several alkylideneaminotin derivatives $Me_{4-n}Sn[N{=}C(CF_3)_2]_n$ (n = 1 - 4)[239] and $Me_3SnN{=}CR_2$ (R = CF_3, ^tBu, Ph, *p*-Tol)[240] by the lithium salt method (Me_3SnCl + $LiN{=}CR_2$), and by transamination (Me_3SnNMe_2

+ HN=CR$_2$). The trimethylstannyl compounds are protolysed by water, alcohols, PhC≡CH, C_6F_5H and cpMo(CO)$_3$H to afford the expected products. Reaction with *trans*-(Ph$_3$P)$_2$Pt(Cl)H gives Pt-Sn bonded compounds:

$$\mathrm{Me_3Sn{=}C(CF_3)_2} \quad + \quad \textit{trans}\text{-}\mathrm{(Ph_3P)_2Pt(Cl)H} \longrightarrow \textit{trans}\text{-}\mathrm{(Ph_3P)_2Pt(SnMe_3)N{=}C(CF_3)_2}$$

67%

$$\mathrm{Me_3SnN{=}C^tBu_2} \quad + \quad \textit{trans}\text{-}\mathrm{(Ph_3P)_2Pt(Cl)H} \longrightarrow \textit{trans}\text{-}\mathrm{(Ph_3P)_2Pt(SnMe_3)Cl}$$

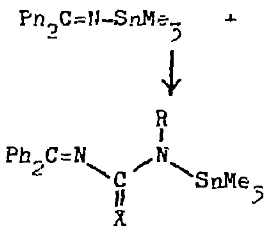
70%

Reaction with metal chlorides cp$_2$TiCl$_2$, *cis*-(Ph$_3$P)$_2$PtCl$_2$ gives Me$_3$SnCl and the alkylideneamino-metal derivative. 1:1 Addition products are obtained with unsaturated reagents such as PhN=C=O or acrylonitrile:[240]

$$\mathrm{Me_3SnCH(CN)CH_2.N{=}CPh_2} \xleftarrow[\mathrm{R\,=\,Ph}]{\mathrm{CH_2{=}CHCN}} \mathrm{Me_3SnN{=}CR_2} \xrightarrow[\mathrm{R\,=\,CF_3,Ph}]{\mathrm{PhN{=}C{=}O}} \mathrm{Me_3Sn.NPh.CO.N{=}CR_2}$$

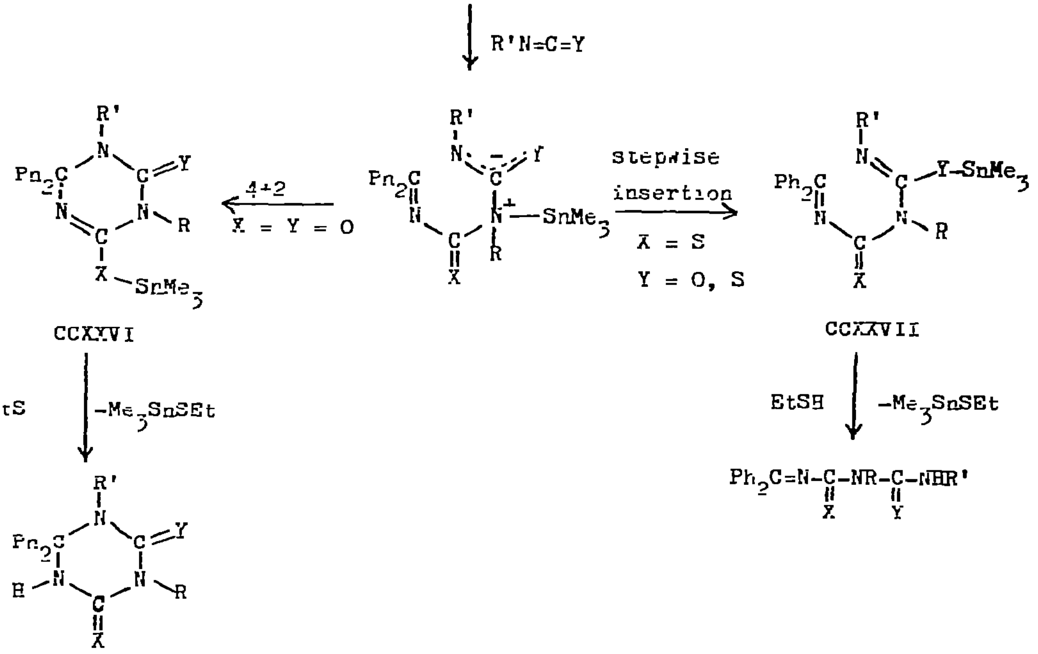
trans-Pt[N=C(CF$_3$)$_2$](SnMe$_3$)(PPh$_3$)$_2$ is obtained by oxidative-addition of Me$_3$SnN=C(CF$_3$)$_2$ to *trans*-Pt(Ph$_3$P)$_2$(stilbene).[241]

Addition of isocyanates or isothiocyanates RN=C=X (R = Me, Ph; X = O, S) to Me$_3$SnN=CPh$_2$ produces 1:1 addition products CCXXV. Treatment of the adducts CCXXV (X = O) with a second mole of isocyanate results in cyclisation to afford the triazine derivatives CCXXVI, which may be destannylated by EtSH. In contrast addition of a further mole of isocyanate or isothiocyanate to the 1:1 isothio-



R = Me, Ph; X = O, S

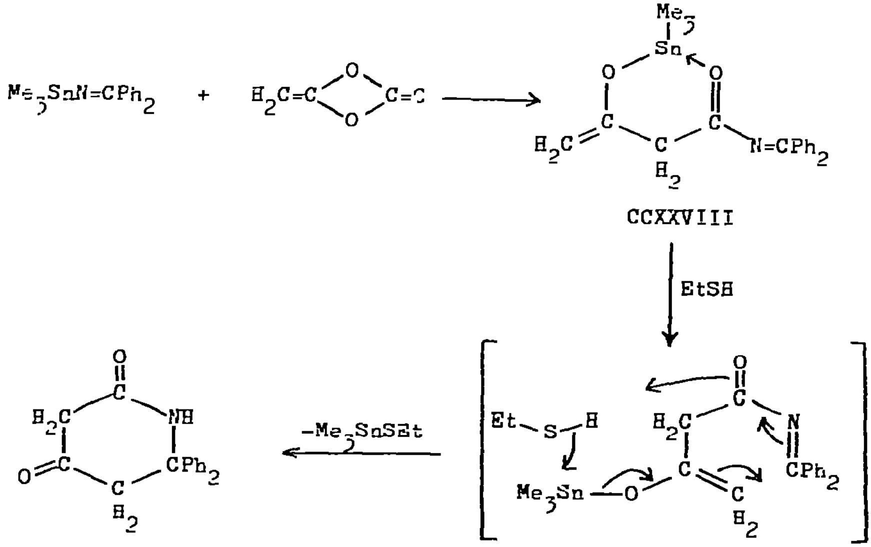
CCXXV



CCXXVI

CCXXVII

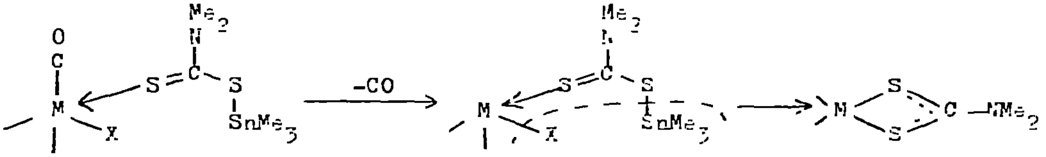
cyanate adducts CCXXV (X = S) results in the production of linear isomers CCXXVII, which are also destannylated by EtSH. Treatment of $Me_3SnN{=}CPh_2$ with diketene at room temperature gave the chelated derivative CCXXVIII. Addition of EtSH to CCXXVIII causes a rapid cyclisation to occur:[242]



CCXXVIII

The structure of several classes of organotin-nitrogen bonded compounds has been investigated by Mössbauer spectroscopy. *N*-Stannylamines and -imines possess four-coordinate tin. Higher coordination numbers occur in *N*-stannylamides and -carbamates *via* $R_3Sn{-}NR{-}C(X){=}O \rightarrow SnR_3{-}$ coordination (X = H, OR, $OSnR_3$). *N*,*O*-Bis(trialkylstannyl)carbamates, $R_3Sn^1{-}NR{-}CO{-}OSn^2R_3$ contain both four (Sn^2) and five (Sn^1) coordinate tin atoms, except for R = Me, when the coordination number of all tin atoms is raised to five.[213]

The addition products of Me_3SnNMe_2 with CS_2, COS, PhNCO, and PhNCS are useful reagents for the synthesis of transition metal carbonyl dithiocarbamate, monothiocarbamate, ureido, and thioureido complexes. In this way the dithiocarbamate complexes $Mn(CO)_4S_2CNMe_2$, $Fe(CO)_3IS_2CNMe_2$, π-$cpFe(CO)S_2CNMe_2$, π-$cpW(CO)_2S_2CNMe_2$, π-$C_3H_5Fe(CO)_2S_2CNMe_2$ and $Rh(CO)_2S_2CNMe_2$ have been obtained. The following mechanism was favoured:

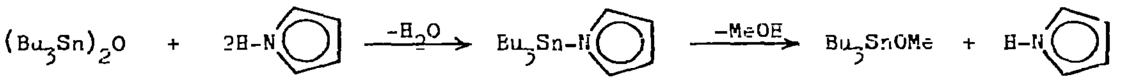


$Me_3SnS.CO.NMe_2$ and $Me_3Sn.NPh.CX.NMe_2$ (X = O, S) react similarly with $Mn(CO)_5Br$:[214]

$$2Mn(CO)_5Br \;+\; 2Me_3SnS.CO.NMe_2 \longrightarrow \left[Mn(CO)_3OSCNMe_2\right]_2 \;+\; 2Me_3SnBr \;+\; 4CO$$

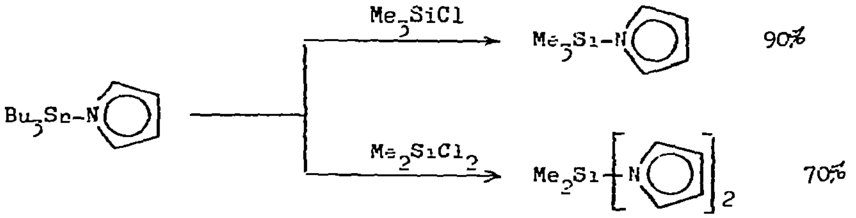
$$2Mn(CO)_5Br \;+\; 2Me_3Sn.NPh.CO.NMe_2 \longrightarrow \left[Mn(CO)_4PhN.CS.NMe_2\right]_2 \;+\; 2Me_3SnBr \;+\; 4CO$$

N-Tributylstannylpyrrole CCXXIX is obtained by either of the routes:

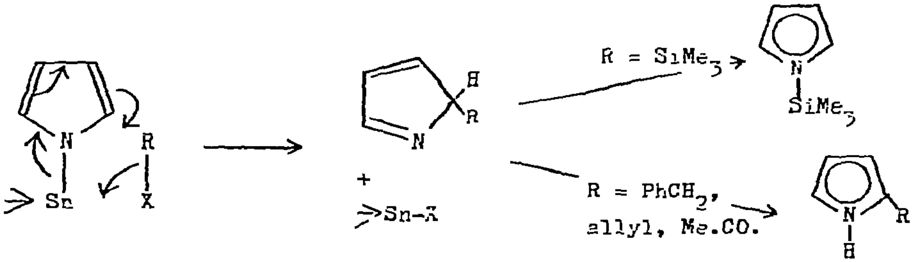


CCXXIX

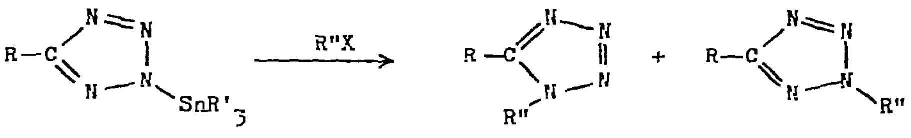
The Sn-N bond is cleaved by chlorosilanes to give *N*-substituted products:



Reaction with hexyne after heating (60 hrs at 100°, then 24 hrs at 150°) affords tributylstannylhexyne in 55% yield. Acetyl chloride affords small quantities o *N*-acetylpyrrole (2-6%), but much larger amounts of 2-acetylpyrrole (20-45%). 2- and 3-Substituted pyrroles are obtained with benzyl and allyl bromides. These results are rationalised by the scheme:



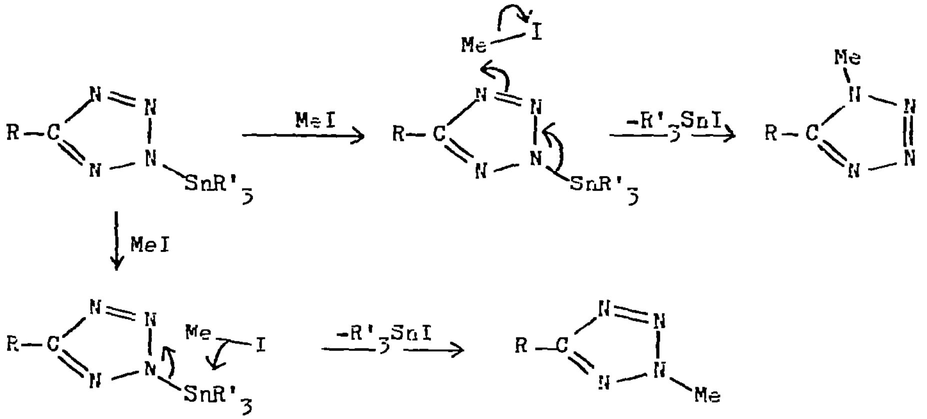
In which silyl migration takes place more readily than hydrogen migration.[245] Triphenyltin imidazole may be prepared from Ph_3SnCl and imidazole in MeCN.[246] Selective 1-substitution of 5-substituted tetrazoles by methyl iodide, methyl *p*-toluenesulphonate, dimethyl sulphate or ethyl bromoacetate is achieved by blocking the 2-nitrogen with the $^nBu_3Sn$ group. The ratio of [1,5] CCXXX to [2,5] CCXXXI isomer in the product is usually *ca.* 90:10.



CCXXX

CCXXXI

Much lower selectivity was observed when the Me_3Sn group was used as the blocking agent. The following mechanisms were proposed.[247]



Trimethylstannyl-di-*tert*-butylphosphine CCXXXII has been prepared by the reaction of Me_3SnCl, ${}^tBu_2PCl$ and magnesium in HMPA:[248]

$$Me_3SnCl \quad + \quad {}^tBu_2PCl \quad + \quad Mg \xrightarrow{HMPA} \underset{\text{CCXXXII}}{Me_3SnP^tBu_2} \quad + \quad MgCl_2$$

The chromium and molybdenum tricarbonyl complexes of $(Me_3Sn)_3P$ CCXXXIII have been obtained in ~80% yield by the reaction:[249]

$$(MeCN)_3M(CO)_3 \quad + \quad 3(Me_3Sn)_3P \longrightarrow \underset{\text{CCXXXIII}}{(Me_3Sn)_3P\ M(CO)_3} \quad + \quad 3MeCN$$

M = Cr, Mo

Treatment of Me_3SnPH_2 or $(Me_3Sn)_3P$ with H_2ECF_3 or $HE(CF_3)_2$ (E = P, As) produces stannyl trifluoromethylphosphines of the types $Me_3SnE(H)CF_3$, $(Me_3Sn)_2ECF_3$ and $Me_3SnE(CF_3)_2$. $(Me_3Sn)_2AsCF_3$ is also obtained by the reaction of $Me_3SnP(CF_3)_2$ with H_2AsCF_3.[250,251] Anderson and Drake have synthesised mixed germanium-tin-arsines by protolysis of stannylamines:

$$Me_3GeAsHR \quad + \quad Me_3SnNMe_2 \xrightarrow{-Me_2NH} \underset{\text{CCXXXIV}}{Me_3Ge.AsR.SnMe_3}$$

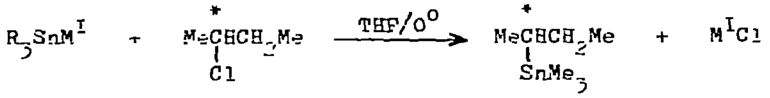
R = Me_3Ge, Me, Ph

$$Me_2Sn(NMe_2)_2 \quad + \quad 2(Me_3Ge)_2AsH \xrightarrow{-Me_2NH} (Me_3Ge)_2As\ SnMe_2$$

CCXXXIV undergoes redistribution to the symmetrical arsines $(Me_3M)_2AsR$.[252]

11. Tin-Main Group Metal Bonded Derivatives.

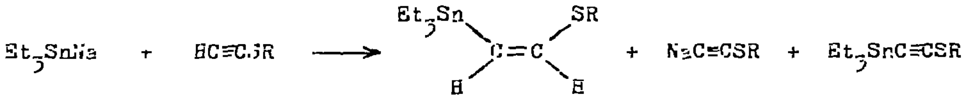
Optically-active sec-butyl chloride reacts with trialkyltin lithium or sodium in THF with nearly complete inversion of configuration:[68,69]

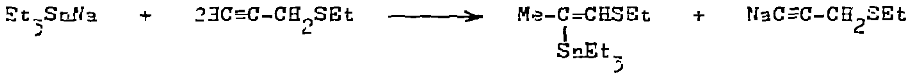


$$R_3SnM^I + Me\overset{*}{C}HCH_2Me\ (Cl) \xrightarrow{THF/0^o} Me\overset{*}{C}HCH_2Me\ (SnMe_3) + M^ICl$$

M^I = Na, Li

Triethylstannylsodium reacts with alkyl alkynyl sulphides[253,254] and ethers[254,255] in liquid ammonia. With the alkynyl sulphides HC≡CSR (R = Me, Et β-stannylation occurs:

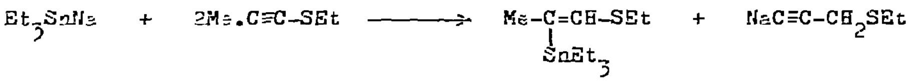




$$Et_3SnNa + 2HC{\equiv}C{-}CH_2SEt \longrightarrow Me{-}C(SnEt_3){=}CHSEt + NaC{\equiv}C{-}CH_2SEt$$

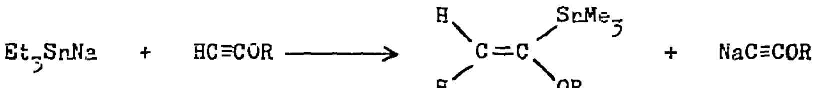
CCXXXV

CCXXXV is also obtained using Me.C≡CSEt:



$$Et_3SnNa + 2Me.C{\equiv}C{-}SEt \longrightarrow Me{-}C(SnEt_3){=}CH{-}SEt + NaC{\equiv}C{-}CH_2SEt$$

indicating that HC≡C.CH$_2$SEt isomerises to Me.C≡C.SEt under the reaction conditio employed. In contrast, alkynyl ethers undergo α-stannylation with Et$_3$SnNa:



R = Me, Et

Ethyl 2-propynyl ether is stannylated at the terminal carbon of the triple bond:

$$Et_3SnNa + HC{\equiv}C{-}CH_2OEt \longrightarrow Et_3SnCH{=}CH{-}CH_2OEt + NaC{\equiv}CCH_2OEt$$

Two new methods have been devised for the preparation of LiSn$_4$Me$_9$:[293]

$$3Me_6Sn_2 + 2LiSnMe_3 \xrightarrow{THF} 2LiSn_4Me_9 + 3C_2H_6$$

$$5LiSnMe_3 + 3Me_3SnCl \xrightarrow{THF} 2LiSn_4Me_9 + 3C_2H_6 + 3LiCl$$

The interaction of Ph_3SnM^I (M^I = Li, Na) with several transition metal complexes has been investigated. Ph_3SnLi and $(R_2PPh)_2NiCl$ (R = Et, Bu) in THF/ether gives crystalline $(R_2PPh)_2NiPhCl$ presumably via the formation of a $Ph_3Sn{-}Ni$ intermediate, which then eliminates $[Ph_2Sn]$. $(Ph_3P)_2CoCl_2$ and $LiSnPh_3$ in THF at −10° give $(Ph_3P)_2CoCl$, $Ph_3SnSnPh_3$, and elementary cobalt. Reaction of $(Ph_3P)_2NiCl_2$ with Ph_3SnNa in THF at −78° gives a red, crystalline material consisting of a mixture of compounds of the type $Na_x[(Ph_3P)_{4-x}Ni(SnPh_3)_x].yTHF$ (x = 1 - 4). Similar compounds are obtained from nickel-olefin complexes:

$$\begin{tikzcd}
(Ph_3P)_2Ni(C_2H_4) \arrow[r, "2LiSnPh_3/THF/0^{\circ}", "-C_2H_4"'] \arrow[d, "NaSnPh_3"', "-78^{\circ}/THF"] & Li_2\left[(Ph_3P)_2Ni(SnPh_3)_2\right].5THF \\
Na\left[(Ph_3P)NiSnPh_3\right]4THF &
\end{tikzcd}$$

$$\begin{tikzcd}
Ni(cyclooctadienyl\text{-}1,5)_2 \arrow[r, "4NaSnPh_3/THF/-70^{\circ}"] \arrow[d, "PPh_3/NaSnPh_3/THF"] & Na_4\left[Ni(SnPh_3)_4\right].4THF \\
Na_3\left[(Ph_3P)Ni(SnPh_3)_3\right].5THF &
\end{tikzcd}$$

A similar cobalt derivative has also been prepared:[256]

$$(Ph_3P)_3CoCl + 2NaSnPh_3 \xrightarrow{THF} Na\left[(Ph_3P)_2Co(SnPh_3)_2\right].7THF$$

Neuman and Blaukat have prepared bis(triorganostannyl)mercurials, $R_3Sn{-}Hg{-}SnR_3$ (R = Me, Et, Pr, ${}^tBu$, Ph) CCXXXVI from ${}^tBu_2Hg$ and $2R_3SnH$ at low temperature. In air they are immediately oxidised to the corresponding distannoxanes. Decomposition to the distannane and mercury occurs at −10°, save for the phenyl compound which decomposes at 20°, and the *tert*-butyl compound, which is surprisingly stable, and melts at 196°. Dialkyltin dihydrides usually afford the decomposition products of the diorganostannylmercurials CCXXXVII, although $({}^tBuSnHg)_n$ can be isolated.

$$nR_2SnH_2 + n\,{}^tBu_2Hg \xrightarrow{-30^\circ} (R_2Sn\text{-}Hg)_n \longrightarrow (R_2Sn)_n + nHg$$

CCXXXVII

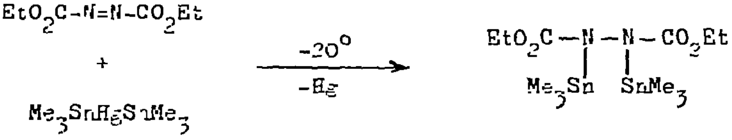
The trialkyltin residues attached to mercury exchange readily. Thus, mixing equimolecular quantities of CCXXXVI (R = Me and Et) at -30°, then allowing the mixture to warm to 25° results in the formation of all three distannanes:

$$(Me_3Sn)_2Hg + (Et_3Sn)_2Hg \longrightarrow \tfrac{1}{2}Me_6Sn_2 + Me_3SnSnEt_3 + \tfrac{1}{2}Et_6Sn_2$$

Addition of Me_3SnH to CCXXXVI (R = ${}^tBu$) results in the quantitative formation of Me_6Sn_2, Hg, and ${}^tBu_3SnH$:

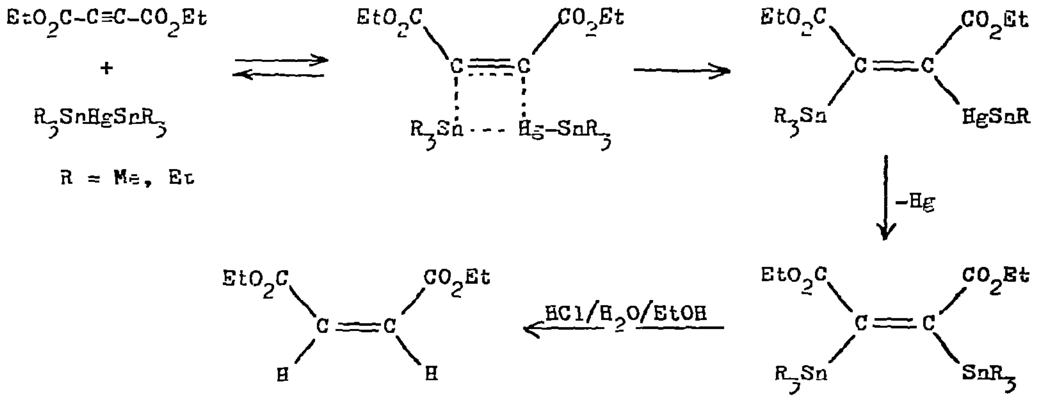
$$\begin{tikzcd}({}^tBu_3Sn)_2Hg + 2Me_3SnH \arrow[r, shift left, "20^\circ"] & (Me_3Sn)_2Hg \arrow[l, shift left] \arrow[d] + 2\,{}^tBu_3SnH \\ & Me_6Sn_2 + Hg\end{tikzcd}$$

CCXXXVI (R = Me) adds to the N=N bond of diethyl azodicarboxylate:



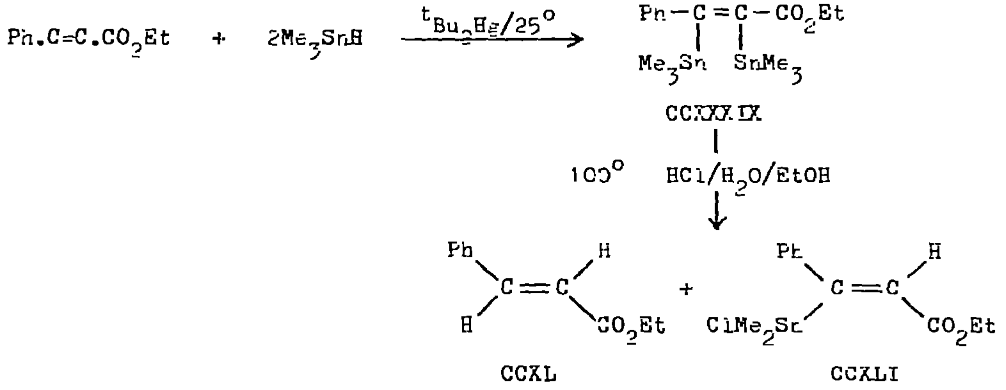
$$EtO_2C\text{-}N{=}N\text{-}CO_2Et + Me_3SnHgSnMe_3 \xrightarrow[-Hg]{-20^\circ} EtO_2C\text{-}N(SnMe_3)\text{-}N(SnMe_3)\text{-}CO_2Et$$

and to the C≡C bond of diethylacetylene dicarboxylate:



CCXXXVIII

The formation of solely the cis isomer CCXXXVIII is confirmed by acid cleavage to only diethyl maleate. Reaction of CCXXXVI (R = Me) with ethyl propiolate proceeds by initial formation of Me_3SnH and $Me_3SnHgC{\equiv}C.CO_2Et$. Several subsequent reactions are observed and $Me_3SnC{\equiv}C.CO_2Et$, $(Me_3Sn)_2CH\text{-}CH(SnMe_3)CO_2Et$, and $Me_3Sn\text{-}CH{=}C(SnMe_3)CO_2Et$ or $(Me_3Sn)_2C{=}CH.CO_2Et$ were identified in the product mixture. Addition to acetylenes may also be accomplished by the '<u>in situ</u>' generation of the distannylmercurial. Preferably the reactant is mixed with $^tBu_2Hg$ (or R_3SnH); R_3SnH (or $^tBu_2Hg$) is then added slowly at 0–20°. Using this technique, an 80% yield of CCXXXIX may be obtained. Acid hydrolysis of CCXXXIX



CCXXXIX

CCXL

CCXLI

produces CCXL and CCXLI. Alkynyl groups may be transferred from mercury to tin by a similar method:

$$(R\text{-}C{\equiv}C)_2Hg \; + \; {}^tBu_2Hg \xrightarrow{2Me_3SnH/0\text{-}20^o} 2Hg \; + \; 2\,{}^{iso}C_4H_{10} \; + \; 2R\text{-}C{\equiv}C\text{-}SnMe_3$$

$$R = Ph,\ CO_2Et$$

Diallylmercury and Me_3SnH give trimethylallyltin in 75% yield.[257] Silylmethylstannylmercurials abstract fluorine from perfluoroalkylmercurials:[258]

$$\left[(CF_3)_3C\right]_2Hg \; + \; \left[(Me_3SiCH_2)_3Sn\right]_2Hg \longrightarrow \underset{98\%}{Hg} \; + \; \underset{83\%}{FSn(CH_2SiMe_3)_3}$$

$$\left[(CF_3)_2CF\right]_2Hg \; + \; \left[(Me_3SiCH_2)_3Sn\right]_2Hg \xrightarrow[\text{catalyst}]{CsF} \underset{92\%}{Hg} \; + \; \underset{75\%}{CF_3CF{=}CF_2} \; + \; \text{some } (CF_3)_2C{=}CF_2 \; + \; \underset{83\%}{FSn(CH_2SiMe_3)_3}$$

Exchange between trispentafluorophenyltin bromide and the germyl mercurial CCXLI in toluene yields the mixed germylstannylmercurial CCXLIII:

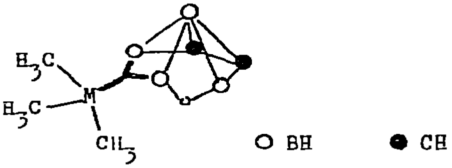
$$\underset{\text{CCXLII}}{Et_3GeHg(C_6F_5)_3} + (C_6F_5)_3SnBr \xrightarrow{uv} Et_3SnBr + \underset{\text{CCXLIII}}{(C_6H_5)_3GeHgSn(C_6F_5)_3}$$

Bis(triethylgermyl)mercury reacts under the same conditions to afford CCXLIV:[25]

$$Et_3GeHgGeEt_3 + 2(C_6F_5)_3SnBr \xrightarrow{uv} 2Et_3GeBr + \underset{\text{CCXLIV}}{(C_6F_5)_3SnHgSn(C_6F_5)_3}$$

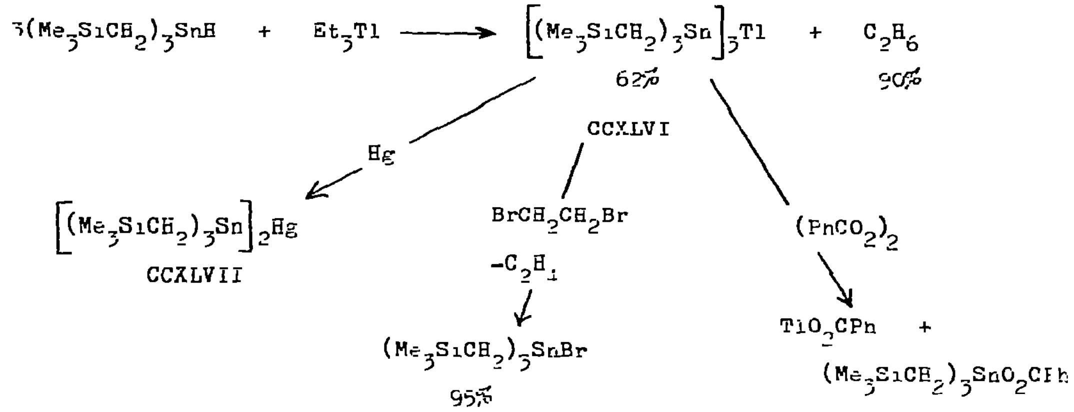
μ-Trimethylstannyldicarbahexaborane(8) CCXLV is obtained as a colourless liquid by the reaction of the sodium salt with Me_3SnBr in THF:

$$Na^+ \ C_2B_4H_7^- + Me_3SnBr \xrightarrow{25^o/THF/1\ hr.} \underset{\substack{65\text{-}70\% \\ \text{CCXLV}}}{\mu\text{-}Me_3SnC_2B_4H_7} + NaBr$$



CCXLV

CCXLV is stable indefinitely at 120°, but decomposes rapidly at 220° yielding Me_3 and the parent $C_2B_4H_8$, which is also produced by cleavage with HCl. The corresponding reaction with DCl produces μ-$DC_2B_4H_7$.[260] The interaction of Group III trimethylmetallates and $LiSnMe_3$ produce the metal-metal bonded derivatives $Li\left[Me_3SnMMe_3\right]$ (M = Al, Ga, In, Tl) except for Me_3B, which gave $LiBMe_4$, Me_4Sn and $Li\left[Sn(SnMe_3)_3\right]$. Some $LiTlMe_4$ was also formed along with other minor products in the reaction with Me_3Tl. The Al-Sn compound decomposed in 1 day at 0° to form $Li(AlMe_4)$, Me_4 and $Li\left[Sn(SnMe_3)_3\right]$. The gallium and indium derivatives decomposed similarly but over a longer period (75% over two days). The thallium derivatives showed less than 25% decomposition after 3 days at room temperature in the dark.[261] No reaction occurs between hexamethylditin and $LiBR_4$ (R = H, Me) in DME. LiMMe$_4$ (M = Al, Ga, Tl) react to give Me$_4$Sn and various Group III derivatives. LiAlH$_4$ gives Me$_3$SnH (49%) and LiSn(SnMe$_3$)$_3$ (51%).[262] The synthesis and characterisation of tin-Group III derivatives,[263] and of 1,3-dimethyl-2-trimethylstannyldiazaboracycloalkanes[264] have been reported in theses. Hydrostannolysis of Et$_3$Tl by (Me$_3$SiCH$_2$)$_3$SnH at -10 - -20° gives the tin-thallium compound CCXLVI, which reacts with mercury to give the mercurial CCXLVII, and with ethylene dibromide and dibenzoyl peroxide to give the corresponding organotin bromide and benzoate.[265]



A patent reports the synthesis of hexaalkyldistannanes R$_6$Sn$_2$ (R = ^{iso}Pr, hexyl, Bu) from R$_3$SnCl and sodium.[266] The crystal structure of hexaphenylditin has been determined (Fig. 11); r(Sn-Sn) = 2.770 A, r(Sn-C) = 2.180 A.[267] Treatment of Ph$_6$Sn$_2$ with HCl in dry benzene affords tetraphenylditin 1,2-dichloride, which may be converted to the corresponding 1,2-dibenzoate by sodium benzoate.[268,269] The composition of the crude (R$_2$Sn)$_n$ mixtures obtained from the reaction between R$_2$SnH$_2$ and ^{t}Bu$_2$Hg (*vide supra*) have been deduced by mass spectroscopy. When R = ^{cyclo}Hexyl, only the pentastannane is formed. When R = Et, ^{n}Bu, ^{iso}Bu, cyclohexastannanes predominate together with small amounts of five- and (R = Et) seven-membered ring compounds. Higher temperatures favour $n > 6$.[271] Charge transfer type interactions appear to occur between hexamethylditin and tetracyanoethylene.[272,273] Photolysis of vicinal dihalides in the presence of hexabutylditin results in dehalogenation to olefins. Thus 2,3-

dichlorobutane gives 40% of 2-butenes with a *cis/trans* ratio of 2:1.[274]

The stannyl-stibine-metal carbonyl complexes CCXLVIII have been prepared by the photolysis of $(Me_3Sn)_2Sb$ and the Group VI metal hexacarbonyl in THF at room temperature:

$$M(CO)_6 \quad + \quad Sb(SnMe_3)_3 \xrightarrow[-CO]{h\nu} (Me_3Sn)_3Sb\rightarrow M(CO)_5$$

CCXLVIII

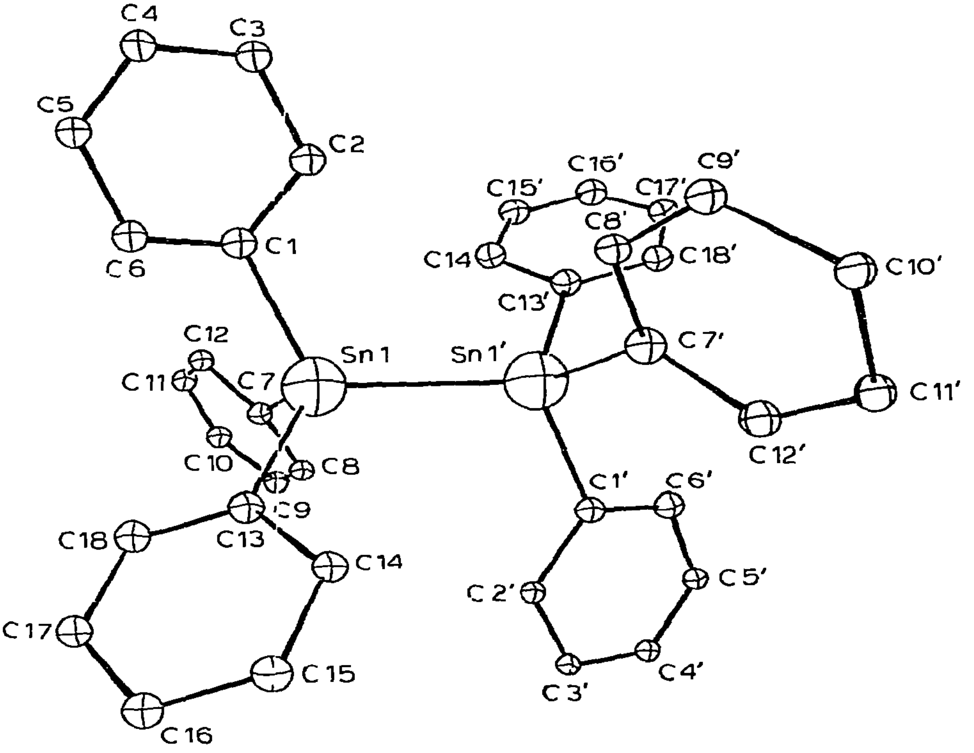
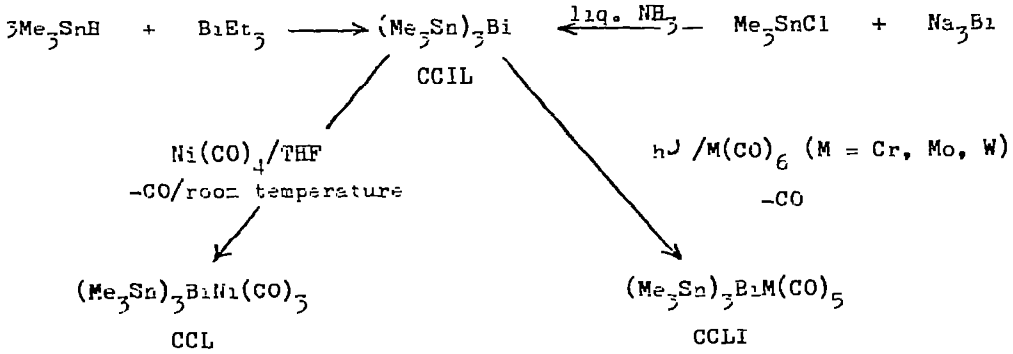


Fig. 11. The Structure of $Ph_3SnSnPh_3$. (Reproduced by permission from Z. anorg allg. Chem., 396 (1973) 81).

The complexes may be sublimed *in vacuo* to yield golden yellow prisms.[275] Tris(trimethylstannyl)bismuth CCIL has been synthesised by hydrostannolysis and also by reaction of Me_3SnCl with Na_3Bi in liquid ammonia:



CCL displaces CO from nickel tetracarbonyl and from Group VI metal hexacarbonyls under uv irradiation to give the complexes CCL and CCLI, respectively.[276]

12. Tin-Transition Metal Bonded Derivatives.

The crystal structures of the two molybdenum-tin compounds $(C_7H_7)Mo(CO)_2(SnPh_nCl_{3-n})$ (n = 1, 2) have been determined. Both contain tetrahedral tin (Figs. 12 and 13). The tin-ligand bond distances are very similar in

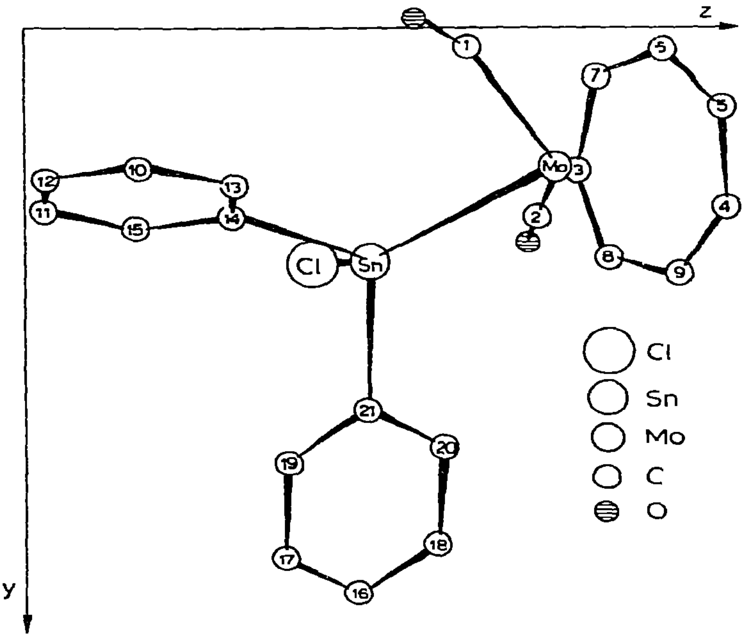


Fig. 12. The structure of $(C_7H_7)Mo(CO)_2SnPh_2Cl$. (Reproduced by permission from Z. anorg. allg. Chem., 402 (1973) 129).

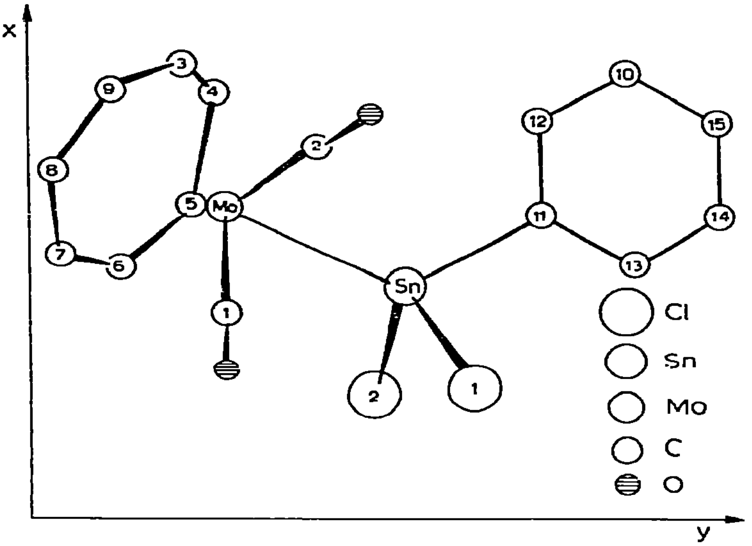


Fig. 13. The structure of $(C_7H_7)Mo(CO)_2SnPhCl_2$. (Reproduced by permission from Z. anorg. allg. Chem., <u>402</u> (1973) 129).

the two compounds: r(Sn-Mo) = 2.717 A (n = 1), 2.739 A (n = 1); r(Sn-Cl) = 2.400 (n = 1), 2.424 A, (n = 2); r(Sn-C) = 2.147 A (n = 1), 2.152 A, 2.167 A (n = 2).[27]

Amine elimination between Me_3SnNMe_2 and cp_2MH_2 (M = Mo, W) or cp_2TaH_3 occurs in boiling THF to produce, respectively $cp_2M(H)SnMe_3$ and $cp_2Ta(H)_2SnMe_3$. Hydroge chloride gas immediately cleaves the Sn-W bond of $cp_2W(H)SnMe_3$ to give $cp_2W(H)Cl$ which is converted gas to cp_2WCl_2. The hydrides may be converted to the corresponding chlorides $cp_2M(Cl)SnMe_3$ (M = Mo, W) by careful choice of reagent. Additi of CCl_4 rapidly produces cp_2MCl_2; but the same reagent in a 1:1 stoichiometric ratio with THF as solvent affords high yields of $cp_2M(Cl)SnMe_3$. Organic chloride (benzyl and allyl chloride) give the same products but in much lower yields. CBr with $cp_2W(H)SnMe_3$, even in a 1:1 ratio, yield cp_2WBr_2. However the bromo- and io molybdenum and tungsten compounds may be obtained by the reaction of the appropri hydride with benzyl bromide or iodide or allyl iodide. The M-H bonds of $cp_2M(H)S$ react with dimethylacetylene dicarboxylate to give insertion products CCLII:[278]

$$cp_2M(H)SnMe_3 \quad + \quad MeOC.C{\equiv}C.CO_2Me \longrightarrow cp_2W(SnMe_3)\ C(CO_2Me){=}CH.CO_2Me$$

CCLII

Triphenyltin pentacarbonylmanganese has been prepared from the reaction of Ph_3SnCl and the Grignard-like species CCLIII:[279]

$$Mn(CO)_5Br \quad + \quad Ln \xrightarrow{THF} \left\{ \left[Mn(CO)_5 \right]_2 LnBr \right\} \xrightarrow{Ph_3SnCl} Ph_3SnMn(CO)_5$$

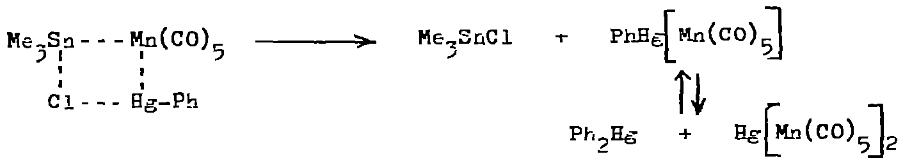
CCLIII

Ln = Y, Pr, Sm, Dy, Ho, Er, Yb

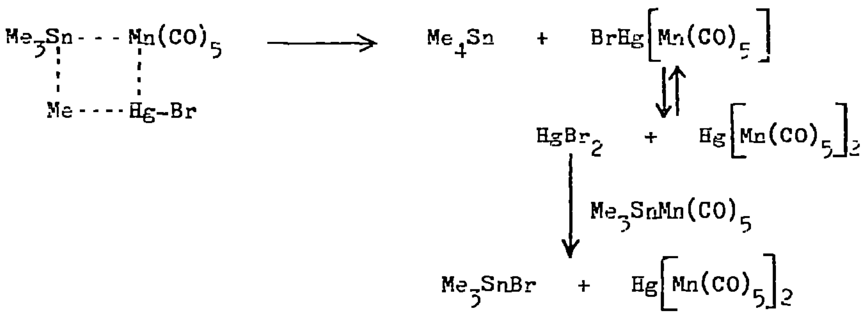
$Me_3SnMn(CO)_5$ CCLIV is obtained in poor yield from Me_3SnH and $Mn_2(CO)_{10}$. Several reactions of CCLIV and related compounds have been investigated. CCLIV is unaffected by water, methanol, or aqueous NaOH. But quantitative Sn-Mn bond cleavage occurs with 1,2-dibromoethane, $HgCl_2$, and RHgX (R = Me, Ph; X = Cl, Br). With the latter reagents, the products obtained are determined by the nature of R and X:

$$
\begin{array}{l}
\underset{\text{CCLIV}}{Me_3SnMn(CO)_5} \xrightarrow{BrCH_2CH_2Br} Me_3SnBr + C_2H_4 + BrMn(CO)_5 \\
Me_3SnMn(CO)_5 \xrightarrow{HgCl_2} 2Me_3SnCl + Hg\left[Mn(CO)_5\right]_2 \\
Me_3SnMn(CO)_5 \xrightarrow{MeHgBr} Hg\left[Mn(CO)_5\right]_2 + Me_4Sn + Me_3SnBr \\
Me_3SnMn(CO)_5 \xrightarrow{PhHgCl} Ph_2Hg + Hg\left[Mn(CO)_5\right]_2 + 2Me_3SnC \\
Me_3SnMn(CO)_5 \xrightarrow{MeHgCl} Hg\left[Mn(CO)_5\right]_2 + Me_4Sn + Me_3SnCl \\
\qquad + \text{ traces of } Me_2Hg
\end{array}
$$

Four-centre mechanisms were proposed for the metal-metal bond cleavage, followed by disproportionation of the mixed mercurial:



$$
\begin{array}{ccc}
Me_3Sn\text{---}Mn(CO)_5 & & \\
\vdots \qquad\quad \vdots & \longrightarrow & Me_3SnCl \; + \; PhHg\left[Mn(CO)_5\right] \\
Cl\text{---}Hg\text{-}Ph & & \qquad\qquad \upharpoonleft\!\downharpoonright \\
& & Ph_2Hg \; + \; Hg\left[Mn(CO)_5\right]_2
\end{array}
$$



Chlorination of tin was observed with CF_3COCl and $HSiCl_3$ to give $Me_2ClSnMn(CO)_5$, and with $SnCl_4$ successive replacement of all three methyl groups was observed.[28] Roberts has also investigated the reactivity of CCLIV, as well as $(CH_2{=}CHCH_2)_3SnMn(CO)_5$, $Me_3SnFe(CO)_2cp$ and $Me_2Sn[Fe(CO)_2cp]_2$. Reaction with iodine in $CDCl_3$, MeOD, or DMSO-d_6 proceeded with metal-metal bond fission, excep with the allyltin derivative where Sn-C fission was observed. MeHgCl reacted wi $Me_3SnFe(CO)_2cp$ in DMSO-d_6 to give $MeHgFe(CO)_2cp$ and Me_3SnCl as initial products, which subsequently afforded Me_4Sn, Me_2Hg, $Hg[Fe(CO)_2cp]_2$ and $ClHgFe(CO)_2cp$. The reaction of $Me_2Sn[Fe(CO)_2cp]_2$ is more complex, but appears to follow similar reaction paths. The reaction of $Me_3SnMn(CO)_5$ with MeHgCl in acetone-d_6 yielded Me_3SnCl, Me_2Hg and Me_4Sn (*vide supra*). The intermediate $MeHg(CO)_5$ could be isol by precipitation. $Me_3SnFe(CO)_2cp$ with a ten-fold excess of Me_3SiCl gave Me_3SnCl in 88% yield. The Sn-Mn bond of $Me_3SnMn(CO)_5$ is cleaved more readily; 52 and 80% yields of Me_3SnCl were obtained with equimolecular and ten-fold excess, respectively, of Me_3SiCl. Inorganic halides MCl_4 (M = Si, Sn, Ti) and MCl_2 (M = Zn, Hg) also reacted with $Me_3SnMn(CO)_5$ and $Me_3SnFe(CO)_2cp$ to give varying amount of Me_3SnCl. Reaction with $HgCl_2$ gave high yields of $ClHgMn(CO)_5$ and $ClHgFe(CO)_2$ Allylmercuric chloride is a major product from the reaction of $HgCl_2$ with the triallyltin derivative.[281]

The triphenyltin-chromium and molybdenum derivatives CCLV have been prepared by metathesis. The corresponding trimethyltin derivatives could not be isolated

$$\left[(Me_5C_5)M(CO)_2\right]_2 \xrightarrow[THF]{Na/Hg} \left[(Me_5C_5)M(CO)_2\right]^- \xrightarrow{Ph_3SnCl} Ph_3SnM(CO)_2(Me_5C_5)$$

CCLV

The same method has been used to synthesise Sn-W bonded species:

$$[Et_4N]^+[W(CO)_4(acac)]^- \quad + \quad Me_2SnCl_2 \quad \xrightarrow[THF]{-2CO} \quad [Et_4N]^+[W(CO)_3(Me_2SnCl)(acac)Cl]$$

(ref. 283)

$$Na^+[cpW(CO)_2L]^- \quad + \quad Me_3SnCl \quad \xrightarrow{THF} \quad Me_3SnW(CO)_2cp(L)$$

(refs. 284,285)

$L = PMe_3, PMe_2Ph, PMePh_2, PPh_3, P(OMe)_3, P(OPh)_3$

The Ph_3Sn and carbene ligands are mutually <u>trans</u> in the molybdenum and tungsten complexes $cpM(CO)_2(SnPh_3)[C(OR)R']$ (M = Mo, W; R = Me, Et; R' = Me, Ph). Infra-red indicates the presence of two conformers due to restricted rotation about the M-carbene bond. The ethoxy-carbene complexes react with $EtNH_2$ and Et_2NH to give the analogous ethylaminocarbene complexes.[286]

Abel and Dunster have formulated a simple versatile route to trimethyltin derivatives of Mn, Mo, Fe, Co, and Ni carbonyls by the reaction of metal-metal bonded dimeric transition metal carbonyls with $(Me_3Sn)_3N$ or $(Me_3Sn)_2O$:[287]

$$[cpM(CO)_n]_2 \quad \xrightarrow{(Me_3Sn)_3N \text{ or } (Me_3Sn)_2O} \quad Me_3SnM(CO)_ncp$$

M = Mo, n = 3; M = Fe, n = 2; M = Ni, n = 1

$$[M_2(CO)_{2n}]_2 \quad \xrightarrow{(Me_3Sn)_3N \text{ or } (Me_3Sn)_2O} \quad Me_3SnM(CO)_n$$

M = Mn, n = 5; M = Co, n = 4

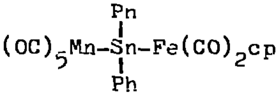
The transition metal-tin hydrides $(OC)_5MSnPh_2H$ (M = Mn, Re) have been obtained as oils by the ${}^{iso}Bu_2AlH$ reduction of the corresponding chloride. Attempted coupling with Ph_3SnEt_2 leads to complex mixtures:

$$(OC)_5MnSnPh_2H \quad + \quad Et_2NSnPh_3 \quad \longrightarrow \quad Et_2NH \quad + \quad Ph_3SnSnPh_3 \quad + \quad Ph_3SnMn(CO)_5$$

$$+ \text{ unidentified products}$$

But reaction occurs with $cpFe(CO)_2\ _2$ at 90° to form the trimetallic complex CCXVI:

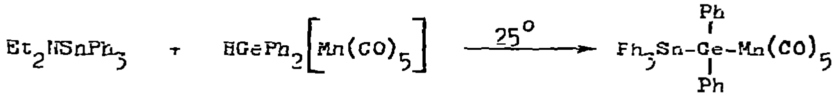
$$HSnPh_2[Mn(CO)_5] \quad + \quad [cpFe(CO)_2]_2 \quad \xrightarrow{90^\circ}$$



$$(OC)_5Mn\text{-}\overset{\displaystyle Ph}{\underset{\displaystyle Ph}{Sn}}\text{-}Fe(CO)_2cp$$

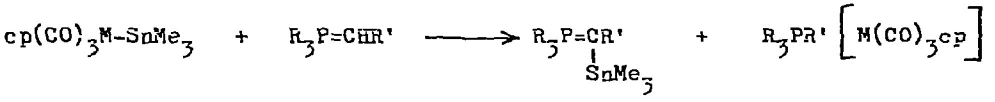
CCXVI

The germanium analogue, however, does couple with Ph_3SnNEt_2:[288]



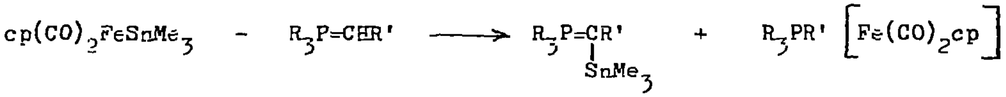
$$Et_2NSnPh_3 + HGePh_2[Mn(CO)_5] \xrightarrow{25^{\circ}} Ph_3Sn\text{-}Ge(Ph)_2\text{-}Mn(CO)_5$$

Phosphorus ylids react with methyltin derivatives of molybdenum, tungsten, cobalt and iron carbonyls with tin-metal bond cleavage and the formation of stannylated phosphorus ylids:[289,290]



$$cp(CO)_3M\text{-}SnMe_3 + R_3P{=}CHR' \longrightarrow R_3P{=}CR'(SnMe_3) + R_3PR'[M(CO)_3cp]$$

M = Mo, W; R = Me, Et; R' = H, Me, $SiMe_3$

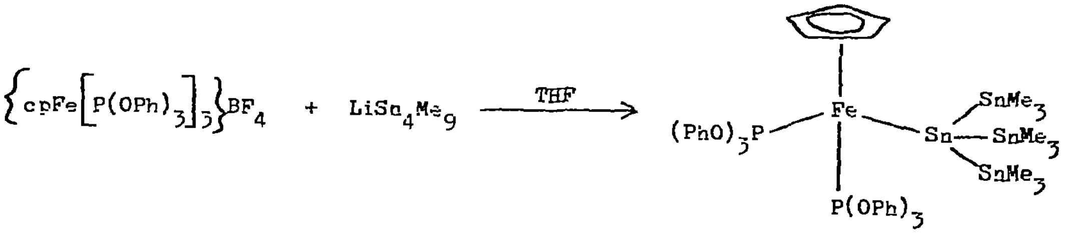


$$cp(CO)_2FeSnMe_3 - R_3P{=}CHR' \longrightarrow R_3P{=}CR'(SnMe_3) + R_3PR'[Fe(CO)_2cp]$$

$$Me_2Sn\ Mo(CO)_3cp + Me_3P{=}CH_2 \longrightarrow (Me_3P{=}CH)_2SnMe_3 + Me_3PH[Mo(CO)_3c$$

The crystal structure of the iron complex $Fe(CO)(cp)(SnPh_3)(PhC{\equiv}CPh)$ has been determined (to R = 17%); mean r(Sn-C) = 2.2 A, r(Sn-Fe) = 2.56 A.[291] Dipole moment measurements on the complexes $Ph_3SnFe(CO)_2(NO)L$ (L = Co, PPh_3, $AsPh_3$, P(O indicate L to occupy a cis position relative to the axial Ph_3Sn group, in contra to the analogous Co and Mn complexes, for which both ligands are in axial positi of the trigonal bipyramid.[292]

The reaction of $\{cpFe[P(OPh)_3]_3\}BF_4$ with $LiSn_4Me_9$ in THF affords the comple CCXVII containing the $Sn(SnMe_3)_3^-$ ligand:[293]



CCXVII

Iodine and bromine cleave the Sn–Sn bonds of CCXVII to form the corresponding $cpFe[P(OPh)_3]_2SnX_3$ (X = Br, I) complexes. With excess halogen, Fe–Sn cleavage occurs leading to the complexes $cpFe[P(OPh)_3]_2X$.[294]

Reduction of $Os_3(CO)_{12}$ with sodium in liquid ammonia produces a cream solid which reacts with R_3SnCl (R = Me, Ph) to afford the complexes $Os(CO)_4(SnR_3)_2$, together with low yields of $Os(CO)_4(SnR_3)(H)$ (R = Me). With Me_2SnCl_2, the Sn–Os heterocycle $[Os(CO)_4SnMe_2]_2$ is formed.[295] Bis(diorganohalotin)tetracarbonylosmium compounds have been discussed in a thesis.[296]

Tin and cobalt atoms alternate around a planar Sn_2Co_2 ring in $[cpCo(CO)SnMe_2]_2$ (Fig. 14). The tin has slightly distorted tetrahedral coordination; r(Sn–Co) =

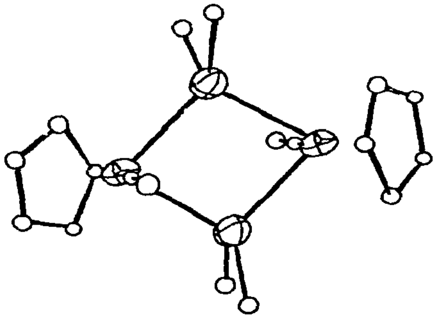


Fig. 14. The structure of $[cpCo(CO)SnMe_2]_2$. (Reproduced by permission of the Chemical Society).

2.542 A, r(Sn–C) = 2.20 A, $\widehat{Sn-Co-Sn}$ = 78°.[297] Reaction of the diene-cobalt carbonyl complexes $(\pi\text{-}L)Co_2(CO)_6$ (L = norbornadiene, isoprene, 2,3-dimethyl-1,3-butadiene) with Ph_3SnCl afforded only $Ph_3SnCo(CO)_4$.[298] The Sn–Ni complexes $cp(RCl_2Sn)(Ph_3P)Ni$ (R = Et, Bu) have been obtained by Grignard alkylation of the corresponding Cl_3Sn–Ni complex.[299] Me_3SnH displaces hydrocarbons from platinum alkyls and aryls:

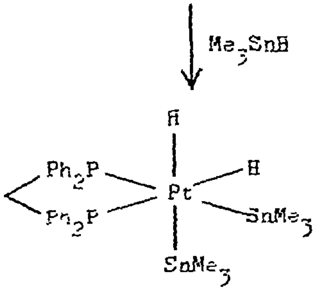
$$(Ph_2P)_2CH_2PtR_2 + 3Me_3SnH \longrightarrow (Ph_2P)CH_2Pt(H)(SnMe_3)_3 + 2RH$$

Reaction occurs at room temperature for R = Me, Et, but high temperatures are needed for R = Ph. Pt-Pb bonds are also cleaved by Me_3SnH:

$$(Ph_2P)_2CH_2Pt(PbPh_3)_2 \quad + \quad 3Me_3SnH \longrightarrow (Ph_2P)CH_2Pt(H)(SnMe_3) \quad + \quad H_2 \quad + \quad Pb_2Ph_6$$

Successive oxidative-addition of Me_3SnH to the Pt^0 complex CCLVIII produces a complex CCLIX which is considered to have two hydrogen atoms bonded to platinum

$$\left[(Ph_2P)_2CH_2\right]_2Pt \xrightarrow{Me_3SnH} \left[(Ph_2P)_2CH_2\right]PtH(SnMe_3) \quad + \quad (Ph_2P)_2CH_2$$



CCLIX

13. Systems Involving Organotin Radicals.

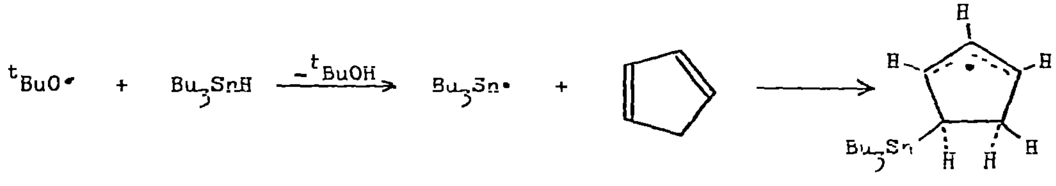
The extremely stable stannyl radical, $\left[(Me_3Si)_2CH\right]_3Sn\cdot$, has been generated by the photolysis of $\left[(Me_3Si)_2CH\right]_2Sn$ by visible light in benzene or hexane:

$$\left[(Me_3Si)_2CH\right]_2Sn \xrightarrow{h\nu} (Me_3Si)_2\dot{C}H \quad + \quad (Me_3Si)_2CHSn\cdot$$

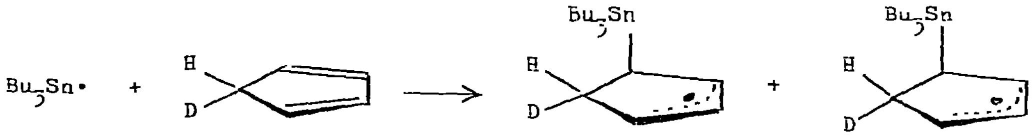
$$\left[(Me_3Si)_2CH\right]_2Sn \quad + \quad (Me_3Si)_2\dot{C}H \longrightarrow \left[(Me_3Si)_2CH\right]_3Sn\cdot$$

Its stability ($>$750 hrs. at room temperature in the dark) is attributed to the bulkiness of the bis(trimethylsilyl)methyl groups preventing dimerisation or hydrogen abstraction. The esr spectrum exhibits coupling with the methine proto and $^{117,119}Sn$ nuclei.[301] The radicals $Me_nCl_{3-n}Sn\cdot$ (n = 0, 1, 2, 3) have been generated in either an adamantane matrix or a self-matrix by γ-irradiation (^{60}Co of the corresponding $Me_{n+1}Cl_{3-n}Sn$. The esr spectra suggest that $Me_3Sn\cdot$ deviates from planarity, and that the deviation increases with increased chlorine substitution.[302]

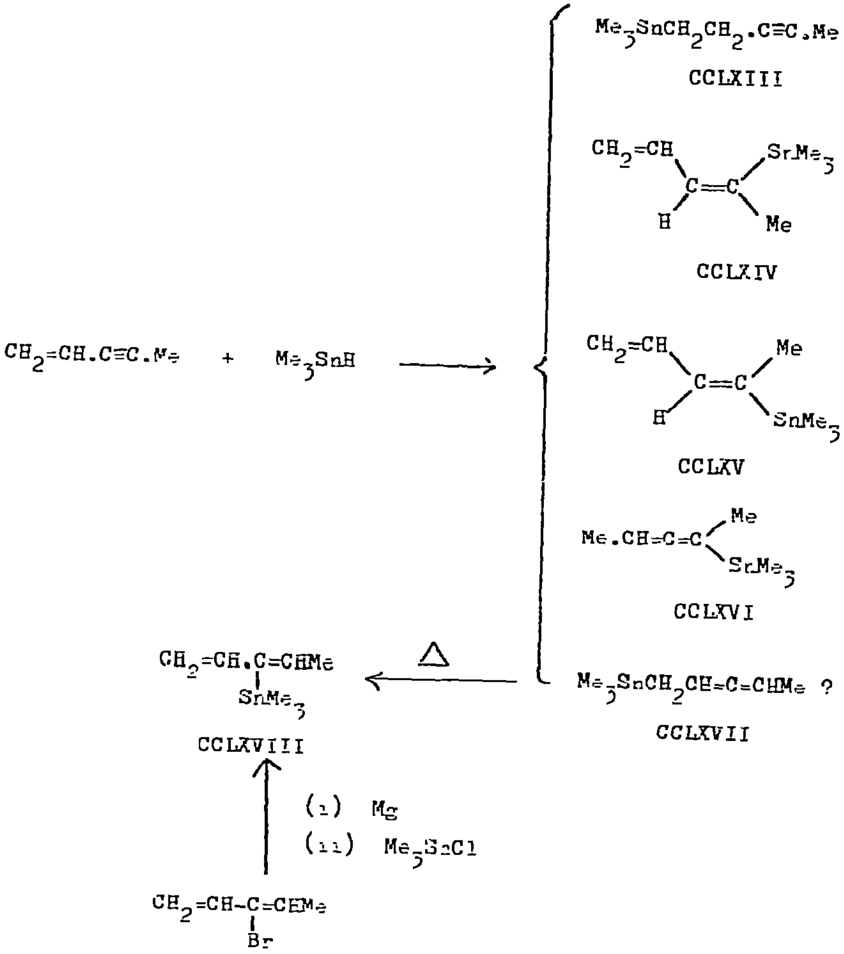
The addition of $Bu_3Sn^{\bullet}$ to cyclopentadiene yields only one paramagnetic product, the 4-(tributylstannyl)-cyclopent-1-en-3-yl radical CCLX:


CCLV

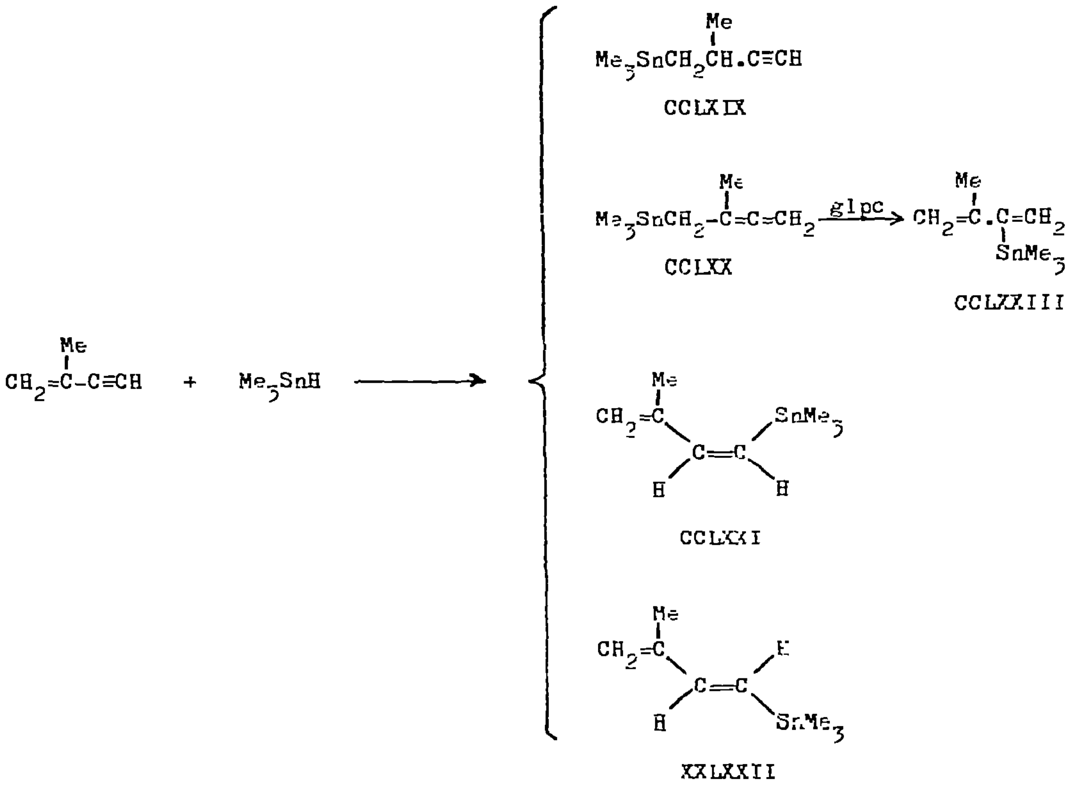
The two isomeric species CCLXI and CCLXII are produced in about the same concentration from deuteriocyclopentadiene:[303]


CCLXI CCLXII

Poutsma and Ibarbia have investigated in detail the ABIBN-catalysed addition of Me_3SnH to conjugated enynes. Addition to 1-penten-3-yne gives a mixture of the 1,2-adduct CCLXIII, the 4,3-adducts CCLXIV and CCLXV, the 4,1-adduct CCLXVI, and probably the 1,4-adduct CCLXVII. The independent preparation of the isomer CCLXVIII showed that the product CCLXII was definitely not CCLXVIII:



Addition to 2-methyl-1-buten-3-yne similarly gives the 1,2-adduct CCLXIX, the 1,4-adduct CCLXX, and the 4,3-adducts CCLXXI and CCLXXII:



$$CH_2=C(Me)-C\equiv CH + Me_3SnH \rightarrow$$

$Me_3SnCH_2CH(Me).C\equiv CH$ CCLXIX

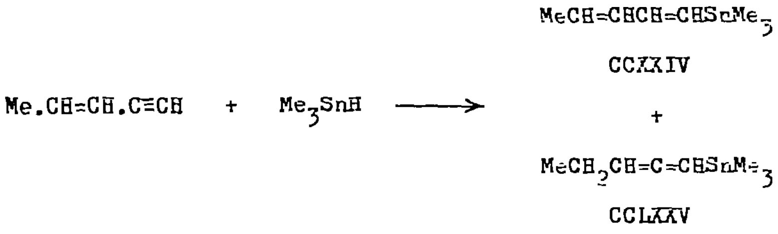
$Me_3SnCH_2-C(Me)=C=CH_2 \xrightarrow{glpc} CH_2=C(Me).C(SnMe_3)=CH_2$

CCLXX CCLXXIII

CCLXXI

XXLXXII

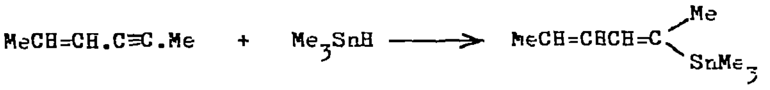
The 1,4-adduct CCLXX rearranges in the glpc to CCLXXIII. Hydrostannation of *cis*- and *trans*-3-penten-1-yne affords largely a mixture of 4,3-adducts CCLXXIV together with a small amount of CCLXXV:



$$Me.CH=CH.C\equiv CH + Me_3SnH \longrightarrow MeCH=CHCH=CHSnMe_3 + MeCH_2CH=C=CHSnMe_3$$

CCLXXIV CCLXXV

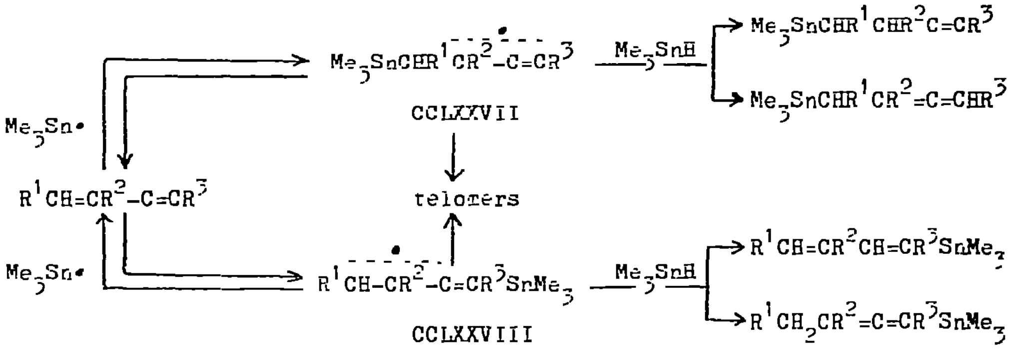
2-Hexen-4-ynes give largely the corresponding adducts CCLXXVI:



$$MeCH=CH.C\equiv C.Me + Me_3SnH \longrightarrow MeCH=CHCH=C(Me)SnMe_3$$

CCLXXVI

Telomerisation also accompanies the addition reactions. In the proposed mechanism, intermediate propargyl CCLXXVII and methyleneallylic CCLXXVIII radicals are formed by attack of Me_3Sn radicals on the enyne:[304]



Trialkylallylstannanes react with organic halides with exchange of allyl and halide functions:

$$Me_3Sn{-}CH_2{-}CH{=}CH_2 \quad + \quad Cl{-}R \longrightarrow Me_3SnCl \quad + \quad CH_2{=}CH{-}CH_2{-}R$$

$$R = CCl_3,\ CHCl_2,\ CH_2CO_2Me,\ CCl_2Me \qquad \text{(ref. 305)}$$

$$Bu_3SnCH_2CH{=}CHMe \quad + \quad CCl_4 \longrightarrow Bu_3SnCl \quad + \quad \underset{Me}{Cl_3CCH}CH{=}CH_2 \qquad \text{(ref.}$$

The reactions are promoted by ABIBN and benzoyl peroxide, and inhibited by p-quinone and galvinoxyl. The following free-radical chain mechanism was postulated:[305,306]

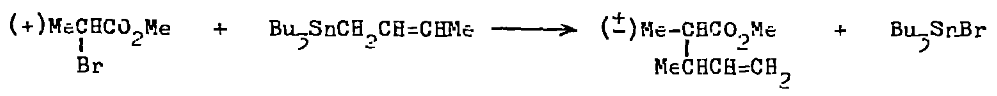
$$Q\bullet \quad + \quad R_3SnCH_2CH{=}CH_2 \longrightarrow QCH_2CH{=}CH_2 \quad + \quad R_3Sn\bullet$$

$$R_3Sn\bullet \quad + \quad R^1X \longrightarrow R_3SnX \quad + \quad R^1\bullet$$

$$R^1\bullet \quad + \quad R_3SnCH_2CH{=}CH_2 \longrightarrow R^1CH_2CH{=}CH_2 \quad + \quad R_3Sn\bullet$$

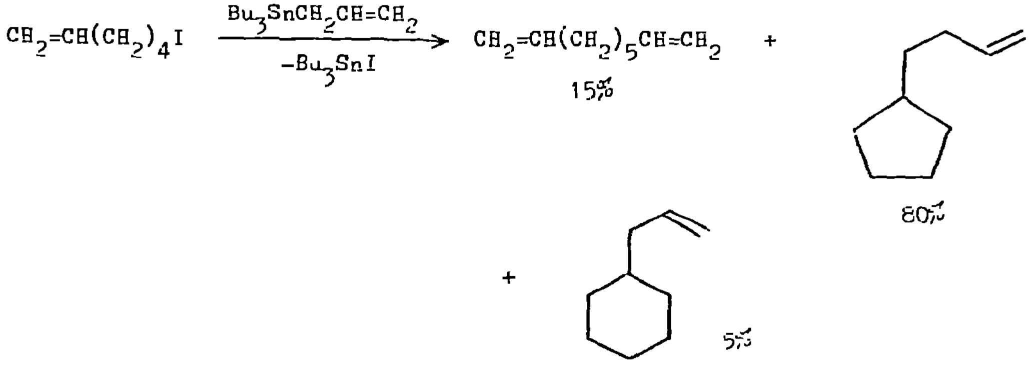
Elegant conclusive support for this mechanism is available from further work by Grignon and Pereyre,[306] who have demonstrated

(i) the formation of racemic products starting from an optically-active halide:

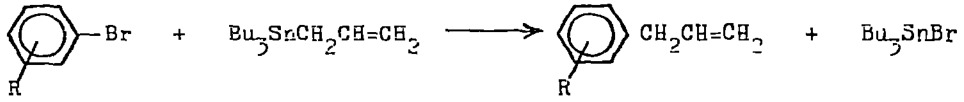


$$(+)\underset{\displaystyle Br}{MeCHCO_2Me} + Bu_3SnCH_2CH{=}CHMe \longrightarrow (\pm)Me\text{-}\underset{\displaystyle MeCHCH{=}CH_2}{CHCO_2Me} + Bu_3SnBr$$

(ii) the rearrangement of the unstable intermediate hexen-5-yl radical, which is known to readily cyclise:



(iii) the operation of polar effects. In the reactions



the reactivity follows the order R = *m*-CF_3 > *p*-F > H > *p*-Me > *p*-OMe, together with a good correlation with Hammett constants. Also, with $Me_3SnCH_2CH{=}CH_2$, the reactivity sequence $CCl_4 > HCCl_3 > H_2CCl_2 > MeCH_2CH_2Cl$ was observed.

(iv) the presence of a structure-reactivity relationship for the halides. Thus, the relative rate constants Me_3CBr ($k_{rel} = 8.6$) > Me_2CHBr ($k_{rel} = 2.1$) > $MeCH_2CH_2I$ r ($k_{rel} = 1$) follow the order of the stability of the radical R•. In addition, it was observed that the rate varied with the halogen in the order RI > RBr > RCl.[306] Halogen atom abstraction from alkyl halides by trialkyltin radicals has also been studied by Coates and Tedder[307] and by Jackson *et al.*[308] The former authors irradiated mixtures of Me_3SnH and alkyl halides in the gas phase, when rapid halogen displacement by hydrogen takes place.[307] The halogen abstraction by Bu_3Sn• radicals (generated in solution by photolysis of mixtures of *t*-butyl peroxide and $Bu_3SnSnBu_3$) is influenced both by polar and enthalpy effects.[308]

In both systems the rates of reaction increase in the order F<Cl<Br<I and primary< secondary< tertiary. Jackson also determined the activation energies for halogen abstraction by $Bu_3Sn\cdot$ radicals for a large number of organic halide

Organotin halides and carboxylates undergo homolytic substitution at the t centre by t-butoxy radicals (generated by photolysis of di-t-butyl peroxide):[30]

$$ {}^{t}BuO\cdot \quad + \quad R_nSnX_{4-n} \longrightarrow {}^{t}BuOSnR_{n-1}X_{4-n} \quad + \quad R\cdot \qquad (i) $$

(X = halide, carboxylate; n = 1 - 3)

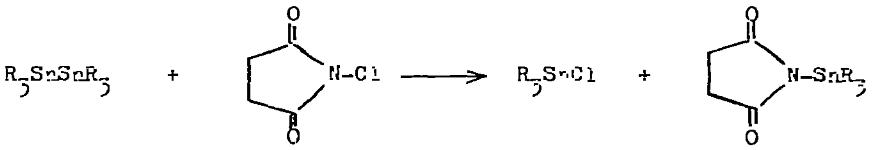
If the t-butoxy radical is derived from t-butyl hypochlorite, a chain reaction established in which the reactions (i) and (ii) are the propagating steps.

$$ R\cdot \quad + \quad {}^{t}BuOCl \longrightarrow RCl \quad + \quad {}^{t}BuO\cdot \qquad (ii) $$

Ketone triplets bring about an S_H2 reaction at the tin centre:[309]

$$ R^1{}_2CO^{\cdot} \quad + \quad R_nSnX_{4-n} \longrightarrow R^1{}_2COSnR_{n-1}X_{4-n} \quad + \quad R\cdot $$

Photolysis of a mixture of $Bu_3SnSnBu_3$ and acetone result in the formation of $Me_2\dot{C}OSnBu_3$ by an analogous process.[309,310] Tributyltin radicals react with α-diketones, oxalates, and quinones apparently to form radical anions.[310] The reaction of N-chlorosuccinimide with hexaalkylditins is catalysed by molecular oxygen and inhibited by galvinoxyl:



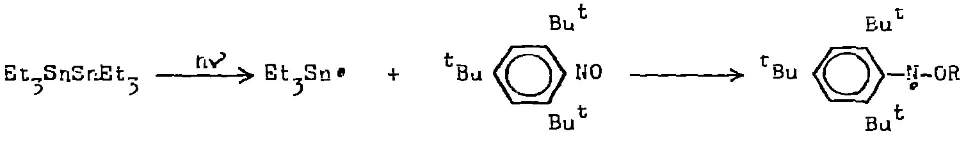
CCLXXIX

CCLXXIX is quantitatively cleaved by bromine to give R_3SnBr and N-bromosuccinimi
The chain mechanism involving the propagation steps

$$ R_3Sn\cdot \quad + \quad R'_2NX \longrightarrow R_3SnX \quad + \quad R'_2N\cdot $$

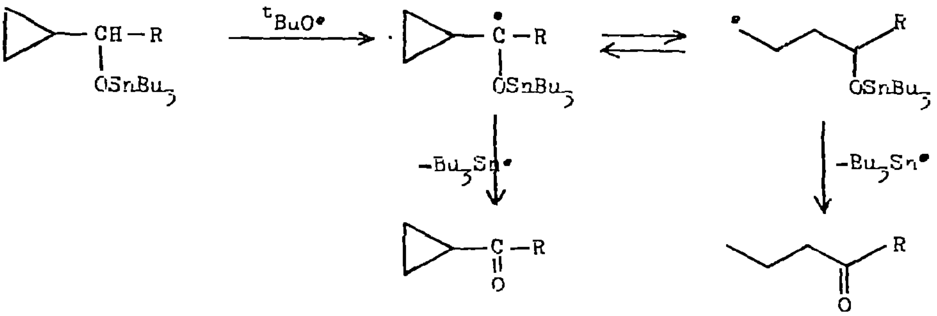
$$ R'_2N\cdot \quad + \quad R_3SnSnR_3 \longrightarrow R'_2NSnR_3 \quad + \quad R_3Sn\cdot $$

was proposed. Me$_2$N• radicals (from the decomposition of 1,1,4,4-tetramethyl-2-tetrazine) participate in S$_H$2 reactions with Me$_6$Sn$_2$, however Me$_3$Sn• radicals do not appear to attack the nitrogen of tetramethylhydrazine.[311] Et$_3$Sn• radicals add exclusively to the oxygen atom of 2,4,6-tri-_t_-butylnitrosobenzene to yield the anilino radical CCLXXX:[312]



CCLXXX

The oxidation of cyclopropyltin alkoxides with di-_t_-butyl peroxide yields cyclopropylketones and non-cyclic products:[313]



Generation of Me$_3$Sn• radicals in the presence of oxygen results in the formation of the stannylperoxy radical CCLXXXI:

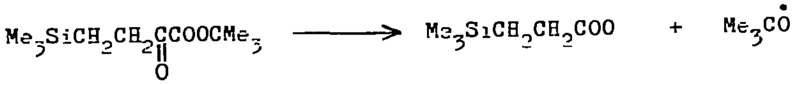
$$Me_3Sn\bullet + O_2 \longrightarrow Me_3SnOO\bullet$$

CCLXXXI

The rates of decay of the Me$_3$SnOO• radicals is second order in radical concentration.[314] Attempted radical-anionic coupling of triphenylvinyltin using a potassium mirror at -78° leads to tin-vinyl bond fission yielding Ph$_6$Sn$_2$ (91%).[315] ^{18}F atoms cleave the Me-Sn bond of Me$_3$SnH:[316]

$$^{18}F + Me_3SnH \longrightarrow Me^{18}F + Me_2\overset{\bullet}{Sn}H$$

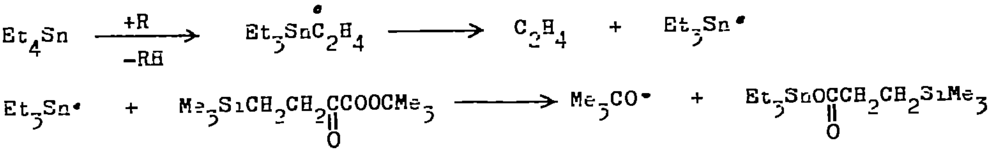
Vyazankin *et al.* have studied the decomposition of *tert*-butyl- 3-(trimethyl silyl)peroxypropionate CCLXXXII in a variety of solvents including Et_4Sn and Et_6Sn_2. In Et_4Sn, the initial step in the decomposition is the homolysis of the O–O bond of CCLXXXII:



$$Me_3SiCH_2CH_2\underset{\underset{O}{\|}}{C}OOCMe_3 \longrightarrow Me_3SiCH_2CH_2CO\dot{O} + Me_3C\dot{O}$$

CCLXXXII

which initiates the chain processes:



$$Et_4Sn \xrightarrow[-RH]{+R} Et_3Sn\dot{C}_2H_4 \longrightarrow C_2H_4 + Et_3Sn^\bullet$$

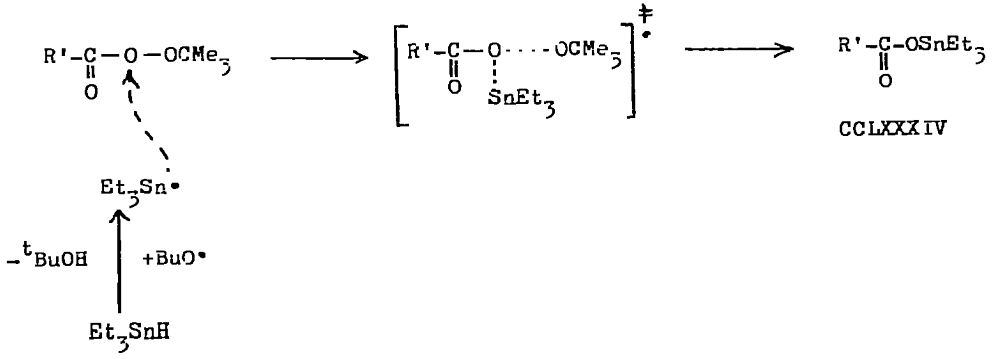
$$Et_3Sn^\bullet + Me_3SiCH_2CH_2\underset{\underset{O}{\|}}{C}OOCMe_3 \longrightarrow Me_3CO^\bullet + Et_3SnO\underset{\underset{O}{\|}}{C}CH_2CH_2SiMe_3$$

CCLXXXII

R = $Me_3SiCH_2CH_2CO_2$, $Me_3SiCH_2CH_2$, Me_3CO

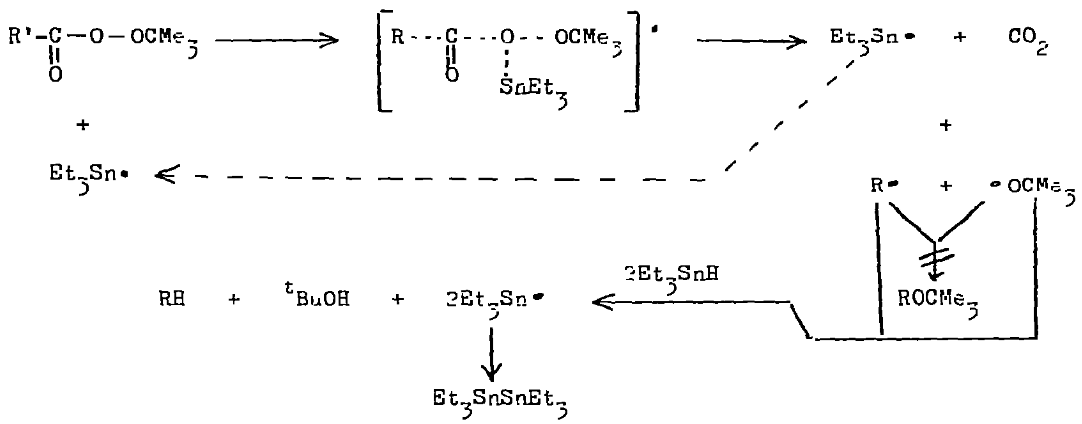
The main decomposition products are ${}^tBuOH$, C_2H_4, 3-(trimethylsilyl)propionic aci and CCLXXXIII. Decomposition in Et_6Sn_2 is not slowed down by radical inhibitors and proceeds *via* a four-centre mechanism.[317]

Stannyl radicals $R_3Sn^\bullet$ (generated from R_3SnH) strongly induce the radical decompositions of peresters,[318,319] peroxides,[319] and tetrazenes.[320] With the peresters R'C(O)-O-OCMe$_3$ (R' = Me, Ph, ${}^tBu$), two competing mechanisms are observ an S_H2 reaction and a radical-catalysed fragmentation. In both the stannyl radi is the attacking species. In the S_H2 process, O-O bond fission occurs with the formation of the stannyl esters CCLCCCIV:

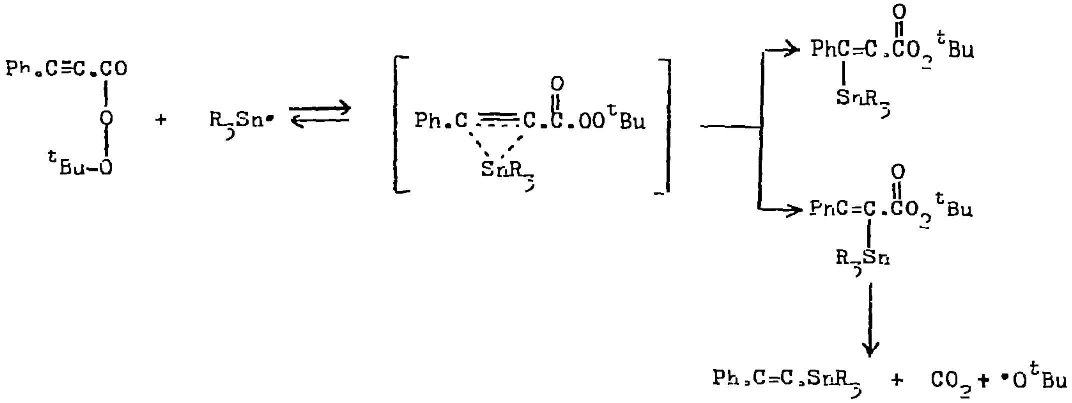


CCLXXXIV

whilst in the latter case, R'•, CO_2, and •O^tBu are formed and the stannyl radica regenerated:[318]



Competing mechanisms also operate in the stannyl-radical assisted degradation of the ^{t}butyl peresters of phenylperoxypropiolic and cinnamic acids; (i) a S_H2 reaction at a peroxidic oxygen as above yielding ${}^tBuOH$ and $Ph.C\equiv C.CO.OSnR_3$ or $PhCH=CH.CO.OSnR_3$, and (ii) attack on the α-carbon atom with sp- or sp^2-hybridisation, leading to fragmentation with the formation of CO_2, ${}^tBuO$, and stannyl-alkyne or -alkene, eg:



The free-radical degradation of phenylpropiolic and cinnamyl peroxides is also strongly induced by R_3Sn radicals:

$$\begin{array}{ccccccccccc}(PhC\equiv C.CO.O)_2 & + & 2Et_3SnH & \longrightarrow & PhC\equiv C.CO_2SnEt_3 & + & Et_6Sn_2 & + & CO_2 & + & H_2 \\ & & & & 1.81 & & 0.10 & & 0.21 & & 0.15\end{array}$$

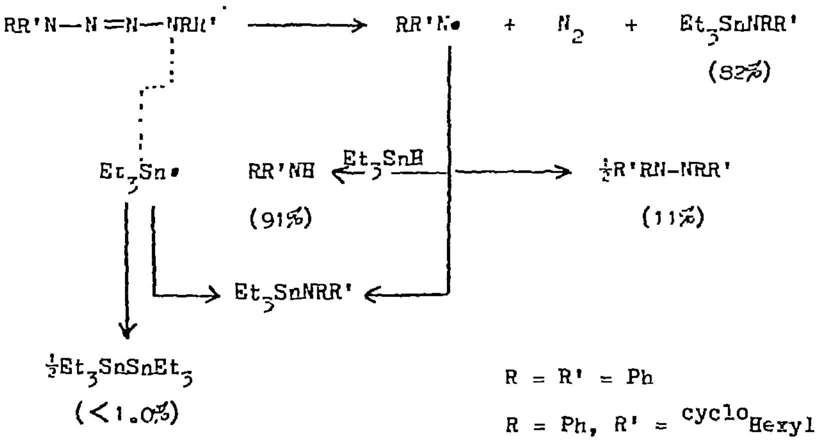
$$(PhCH{=}CH.CO.O)_2 + 2Et_3SnH \longrightarrow \underset{1.76}{PhCH{=}CH.CO_2SnEt_3} + \underset{0.14}{Et_6Sn_2} + \underset{0.12}{CO_2} + \underset{0}{H}$$

The stannyl mercurial CCLXXXV has a similar effect on the decomposition:[319]

$$(PhC{\equiv}C.CO.O)_2 + \underset{CCLXXXV}{Me_3SnHgSnMe_3} \longrightarrow \underset{0.48}{PhC{\equiv}CSnMe_3} + \underset{1.4}{PhC{\equiv}C.CO_2SnMe_3} + \underset{1.0}{Hg} + \underset{0.52}{CO_2}$$

$$PhC{\equiv}C.CO.O.O{}^tBu + \underset{CCLXXXV}{Me_3SnHgSnMe_3} \longrightarrow \underset{0.41}{PhC{\equiv}CSnMe_3} + \underset{0.59}{PhC{\equiv}C.CO_2SnMe_3} + \underset{0.41}{CO_2} + \underset{0.92}{Hg} + {}^tBuOSnMe_3$$

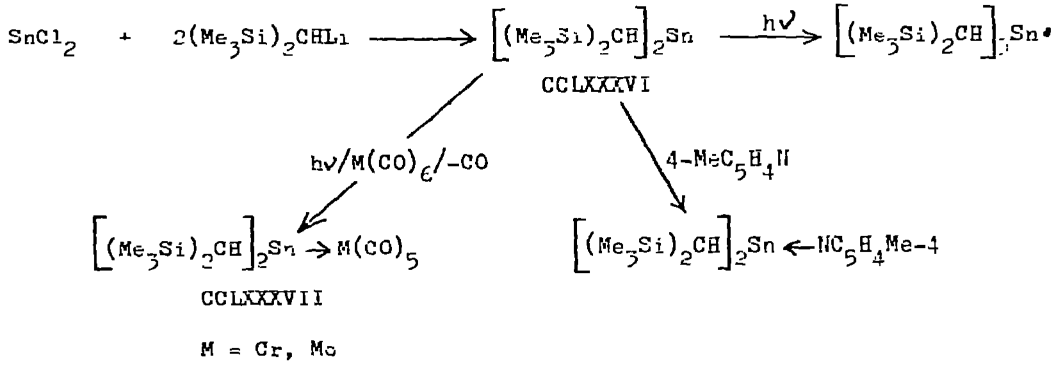
Stannyl radical attack takes place at N-1 or N-4 of tetraphenyl-2-tetrazene and 1,4-dicyclohexyl-1,4-diphenyl-2-tetrazene:



The yields in parentheses refer to R = R' = Ph. Dicarbazolyldiazene reacts in the same way, but not dipiperidinodiazene. Cleavage of tetraphenylhydrazine is also accelerated by stannyl radicals.[320]

14. Divalent Derivatives.

The novel stannylene $[(Me_3Si)_2CH]_2Sn$ CCLXXXVI has been synthesised from $SnCl_2$ and $(Me_3Si)_2CHLi$ in ether at 0°.[321] The photolysis of CCLXXXVI by visible light to produce the $[(Me_3Si)_2CH]_3Sn\bullet$ radical has already been mentioned (*vide supra*).[301] Monomeric, diamagnetic CCLXXXVI functions both as a Lewis base, displacing CO from Group VI metal carbonyls forming the complexes CCLXXXVII, and also as a Lewis acid towards γ-picoline:[321]



The crystal structure of (di-*tert*-butylstannylene)-pyridinopentacarbonylchromium has been determined by Brice and Cotton (Fig. 15). The $Cr(CO)_5$ group has, as

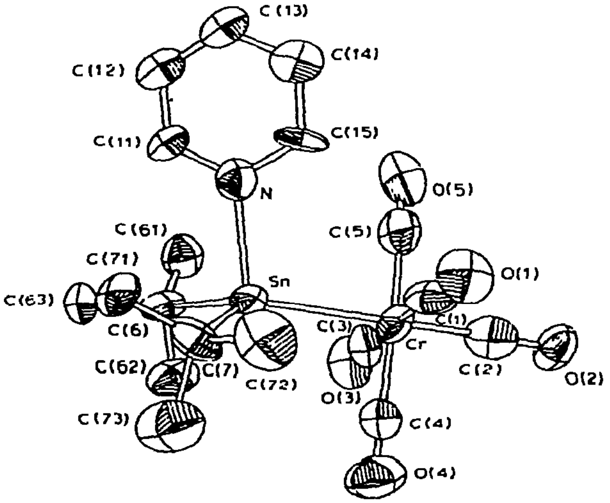
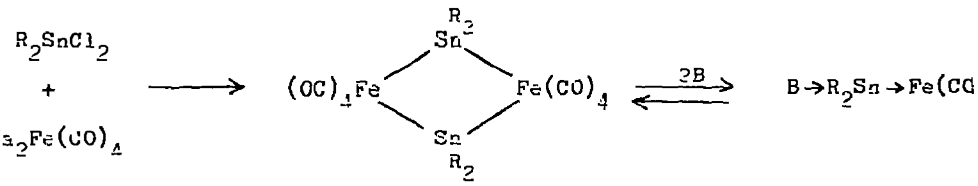


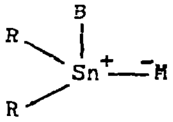
Fig. 15. The structure of $^tBu_2SnCr(CO)_5 \cdot py$. (Reproduced by permission of the American Chemical Society).

expected, virtual C_{4v} symmetry. The tin is four-coordinate, forming bonds to chromium [r(Sn-Cr) = 2,654 A], two *tert*-butyl groups [r(Sn-C) = 2.25 A], and the pyridine nitrogen atom [r(Sn-N) = 2.29 A]. The bond angles at tin show that the geometry is intermediate between tetrahedral and trigonal-bipyramidal with a vacant axial position.[322] Similar base-stabilised stannylene-iron tetracarbon complexes have been obtained by the base-induced homolytic fission of tin-iron bonded heterocycles:[323]

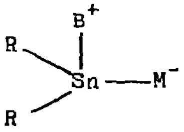


R = Me, ^tBu, Ph; B = THF, pyridine, acetone, MeCN, Et_2O, DMF, DMSO

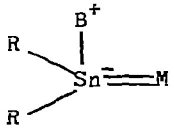
Marks, Zuckerman, *et al.* have proposed ylidic structures such as CCLXXXVIII – CCXC to rationalise Mössbauer and ESCA data for these types of complexes.[324]



CCLXXXVIII

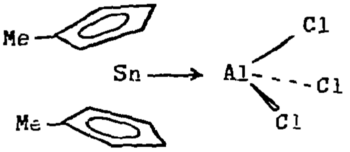


CCLXXXIX



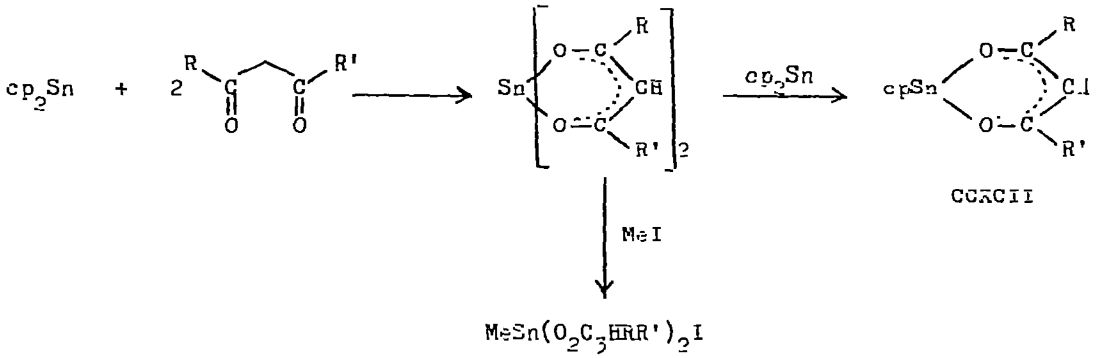
CCXC

The aluminium trichloride complex of $(MeC_5H_4)_2Sn$ has been prepared from its components. Its infra-red spectrum supported the preservation of penta*hapto* rings, and the structure CCXCI was proposed.[325]



CCXCI

Full details of the protolytic cleavage reactions of cyclopentadienyltin compounds to affords tin(II) oximes, hydroxylamines, cyanide, imidazole, 1,2,4-triazole, 1,2-diazole,[326] and thiolates[327] have appeared. Cyclopentadienyltricarbonyltungsten hydride also reacts to afford $\{[cp(OC)_3W]_2Sn^{IV}\}_n$;[326,328] whilst 1,3-diketones yield tin(II) bis(1,3-diketones), which rapidly equilibriate with cp_2Sn in benzene with the formation of cyclopentadienyltin 1,3-ketonates CCXCII and undergo oxidative-addition with methyl iodide:



CCXCII

Tetramethyltin methylates tin(II) chloride at room temperature yielding a dark red polymeric tin(IV) species.[329] Dicyclopentadienyltin is oxidised by elemental halogens to dicyclopentadienyltin(IV) dihalides:

$$cp_2Sn + X_2 \xrightarrow{\text{benzene}} cp_2SnX_2$$

X = Cl, Br, I

Cyclopentadienyltin(IV) halides have also been obtained by substitution of tin(IV) halides:

$$SnX_4 + ncpM \longrightarrow cp_nSnX_{4-n} + nMX$$

M = Na, MgBr; n = 1 - 3

Methyl iodide reacts with cp_2Sn at 50°:[330]

$$cp_2Sn + MeI \longrightarrow cp_2MeSnI$$

15. Applications.

The BF_3 complex of dibutyltin dilaurate is useful in the homopolymerisation of trioxane.[334] The trialkyltin compounds, $R_3SnS(CH_2)_nCO_2SnR_3$ (n = 1,2) or

$HOCH_2CO_2SnR_3$, are catalysts in polyurethane manufacture.[219] Organotin carboxylates are good photo- and thermal stabilisers for PVC.[335] The interaction of organotin stabilisers with chlorohydrocarbons does not involve free-radicals.[336]

Polymers with R_3Sn-substituents (R = Me, Pr, Bu, $PhCH_2$) have been developed as marine antifouling coatings.[337] Developments in anti-fouling paints have been discussed.[338] 1,4-Bis(S-tributyltincarbodithio)piperazine is an active constituent of stain resistant paints.[339] The biochemical mode of action of tricyclohexyltin hydroxide has been examined,[340] as has the efficacy of Ph_3SnOAc as a crop protectant for some Lepidopterous pests.[341] Tri(thienylalkyl)tin chloride, oxide and hydroxide have miticidal activity.[104] Tricyclohexyltin dithiophosphonates are active against house flies and two-spotted mites and their eggs.[210] (2-Thiazolylthio)tin compounds exhibit a total herbicide effect.[208] Ethylene bis(dithiocarbamato) bis(chlorostannanes) give 95% control of Phytophora investans on tomato seedlings and protect barley against Helminthosphorium.[209] $Bu_3SnCH_2SO_2Ph$ is a pesticide and a seed protecting agent.[227] Tin orthosulphites are fungicides for the control of mildew.[342] Various organotin compounds, including unsymmetrical triorganotin chlorides and acetates,[103,109] alkyl-(2-pyridylthio)tin N-oxides,[207] tributylstannylsulpholenes and sulpholanes,[228] organotin azolides,[246] tributyltin esters of 4-(2-hydroxyethoxy)benzoic acid and 4,4'-ethylenedioxy-bis(benzoic acid),[343] $R_2Sn(EC_5H_4N\text{-}o)_2$ (R = Bu, Oct; E = O, S),[344] R_3SnR' (R = Bu, Ph; R' = $MeOOC(CN)_2$, $C(CN)_2NO$, $N(CN)Ac$),[345] tributyltin (2-cyano-4,6-dichlorophenoxy)tin.[346] Tributyltin bis(polyoxyethylene)alkyl phosphates are surfactants, bacteriocides, and antistatic agents.[347] Alkyltin trihalides and alkylstannonic acids function as water repellent agents.[348]

16. Physical Measurements.

(i) Thermodynamic Data.

Spalding has described a general procedure for the derivation of thermochemical data from mass spectroscopic measurements. Using this method, the gas phase heats of formation ($\Delta_f H$) for the series Me_2SnCl_{4-n} (n = 0 - 4) were determined.[405] $\overline{D}(Sn\text{-}{}^nPr)$ has been deduced to be 46 kcal mole^{-1}.[406] The heats of

Me_2SnCl_2-picolinaldimine formation have been determined by calorimetry in MeCN.[127] From determined heats of formation, values of the Sn–N bond energy in Bu_3SnNCO and $Bu_3SnN{=}C{=}NSnBu_3$ were calculated to be 102±5 kcal. mole^{-1} and 100±5 kcal. mole^{-1}, respectively.[140] Appearance potential measurements lead to a value of ~2.5 eV for the bond dissociation energy in $Me_3SnMn(CO)_5$.[365]

(ii) <u>Infra-red and Raman Data</u>.

The following compounds have been investigated in varying degrees; (R) denotes Raman data:

Adamantyltin compounds;[26] trimethyltin derivatives of the norbornyl skeleton;[28] $Me_3SnC(N_2)CO_2Et$;[39] dialkylcarbamoyltin compounds;[40] trialkyltin derivatives of pyrazoles and pyrazolenines;[47] trimethylstannyl – Pt, Ir, Rh acetylides;[58] $Bu_3Sn(CH_2)_3NCO$;[70] the addition products of Et_3SnH with diynes,[73] and of R_3SnH (R = Et, Pr, Ph) with enynes;[74] (α-methoxybenzyl)triorganostannanes, (α-pyrrolidin-1-ylbenzyl)-tributyltin;[83] $^tBu(EtO_2C)C{=}C(CO_2Et)(SnMe_3)$, $[(EtO_2C)(Me_3Sn)N]_2$;[89] addition products of isonitriles with tin halides;[112] R_3SnCl complexes with carbonyl-stabilised phosphorus ylids;[130] $BuCl_2Sn(O_2C_5H_7)$;[131] complexes of $RPhSnCl_2$ with bipyridyl and phenanthroline;[134] diphenyltin oxinates and chloride oxinates,[135] $R_3SnSC{:}(NCN){-}N(CN)SnR_3$ (R = Me, Ph, $PhCH_2$), triorganotin cyanamides;[141] complexes of $(R_3Sn)_2O$ (R = Pr, Bu) with $SnCl_4$, $TiCl_4$, $SbCl_5$;[147] 2-(tributylstannoxy)-1,3,2-dioxaborolanes;[149] $Me_3SnOTeF_5$;[151] organotin trialkoxides and derivatives;[152] butyltin glycolates;[158] dialkyltin bis(aminoalkoxides);[167] $Me_2Sn(O_2C_5H_7)_2$ (single crystal and solution Raman);[171] di- and triorganotin derivatives of Schiff bases;[174] <u>O</u>-trialkyltin hydroxylamines;[178] triorganotin derivatives of nitronic acids (IR and R);[180] organotin mercaptocarboxylates;[190] triorganotin derivatives of amino acids (IR and R);[191,192] $Me_2Sn(NO_3)_2$;[193] μ-oxalato-bis(dipropyl sulphoxide)-nitrato diphenyltin;[195] $Me_2Sn(O_2SMe)_2$;[196] $(CH_2{=}CH)_nSnCl_{4-n}$ (n = 2, 3, 4), vinyltin sulphinates (IR and R);[198] $R_2Sn(PO_2H_2)_2$, R_2SnPO_3X (X = F, H, OH), $(Me_2Sn)_3(PO_4)_2$ 1,2-dicyanoethylenedithiolatodiorganotin derivatives;[216] substituted benzoylthiotrimethylstannanes;[217] trimethyltin derivatives of dithio acids;[218] $(Me_3Sn)_2E{:}M(CO)_5$ (E = S, Se, Te; M = Cr, Mo, W) (IR and R);[220-222] $Me_nSn(SeMe)_{4-n}$ (n = 0 – 3) (IR and R);[223] $R_2Sn(SePh)_2$, $R_3SnSePh$ (R = Me, Et, Bu, Ph);[224]

$Me_2Sn(OS{=}CNR_2)_2$, $Me_3SnOS{=}CNR_2$, $Me_2ClSnOS{=}CNR_2$;[225] $(R_3Sn)_2NH$ (R = ^{iso}Pr, ^{iso}Bu, ^{t}Bu, neopentyl, neophyl, ^{n}Pr, $^{cyclo}Hexyl$);[226] adducts of CS_2 and PhNCS with oxa-aza-stannacyclopentanes and diazastannacyclopentanes;[230] adducts of Me_3SnX (X = Me, NMe_2, OMe, $SnMe_3$) with sulphodiimides;[231] $Me_3Sn{-}N{=}S{=}N{-}SnMe_3$;[232] $Me_2SnS_2N_2$;[233] $(Me_3Sn)NMeR$ (R = $P_3N_3F_5$, $PSCl_2$, $SO_2C_4F_9$), $(Me_3Sn)_2NR$ (R = $P_3N_3F_5$, $SO_2C_4F_9$, $PCl_2{=}NSO_2F$), $Me_3SnPOF_2NP_3N_3F_5$, $Me_3SnN(PCl_2{=}N)_2SO_2$;[235] $Me_nSn[N{=}C(CF_3)_2]_2$ (n = 0 – 3);[239] adducts of trimethyltin alkylideneamines with PhNCO, $CH_2{=}CHCN$; $(Ph_3P)_2Pt(SnMe_3)[N{=}C(CF_3)_2]$;[240] $(Me_3Sn)_3P{:}M(CO)_5$ (M = Cr, Mo);[249] mixed germyl stannylarsines;[252] products of the addition of Et_3SnNa with alkyl alkynyl sulphides[253] and ethers;[255] $(^{t}Bu_3Sn)_2Hg$;[257] μ-$Me_3SnC_2B_4H_7$;[260] $(Me_3Sn)_3Sb$, $(Me_3Sn)_3Sb{:}M(CO)_5$ (M = Cr, Mo, W) (IR and R);[275] $Me_2ClSnMn(CO)_5$ (R);[280] $Me_5C_5M(CO)_3SnPh_3$ (M = Cr, Mo);[282] $cpW(CO)_2(phosphine)SnMe_3$;[284] $Os(CO)_4(SnPh_3)_2$;[3 $cp(RCl_2Sn)(Ph_3P)Ni$ (R = Et, Bu);[299] $[R_2SnFe(CO)_4]_2$ and $py.R_2SnFe(CO)_4$ (R = Me, ^{t}Bu, Ph);[323] cp_2Sn, $(MeC_5H_4)_2Sn$ (IR and R);[408] $(MeC_5H_4)_2Sn;AlCl_3$;[325] tin halide complexes of phosphorus(V) thio and dithio esters;[331] $Me_2Sn(C_6H_4)_2X$ (X = O, S, SO_2), $Me_2Sn(C_6H_4O_{\frac{1}{2}})_2$;[332] $^{n}PrSnCl_3$ (IR and R; normal coordinate analysis);[355] $Me_3SnCl_2^{-}$, $Me_2SnCl_3^{-}$, $MeSnCl_4^{-}$, $MeSnCl_5{}^{-}$, $Me_2SnCl_4{}^{2-}$ (IR and R);[359] organotin sulphides (IR and R);[361] $R_2Sn(SCH_2)_2$ (R = Me, Et) (IR and R);[362] $Me_3SnB[NMeCH_2]_2$;[364] $Me_3SnMn(CO)_5$ (IR and R);[365] $IrCl(H)(SnR_3)(CO)(PPh_3)_2$ (R = Me Et);[367] tetraallyltin (IR and R);[371] organotin ketones;[375] $R_3Sn.C{\equiv}CH$ (R = Me, Ph);[376] $Ph_3SnMn(CO)_5$, $Ph_3SnMn(CO)_4PPh_3$, $Ph_3SnFe(CO)_2cp$ (IR and R);[392] $Ph_3SnRe(CO)_5$ (R);[397] methylvinyltin compounds (IR and R).[400]

(iii) Nmr Data.

$\underline{^{1}H}$: $XMe_2SiCH_2Me_2CH_2Cl$ (X = H, Cl), $Me_3SnCH_2SnMe_3$, $[Me_2SnCH_2]_3$, $(Me_3SnCH_2)_2SnMe_2$;[21] ω-substituted alkyltriorganostannanes;[22] $Ph(PhCH_2)(PhMe_2CCH_2)SnR$ (R = Me, ^{iso}Pr, ^{t}Bu, $MeCH_2CMe_2$), $R(PhMe_2CCH_2)^{t}Bu^{iso}PrSn$ (R = Ph, $PhCH_2$), $Ph(PhCH_2)^{t}Bu(MeCH_2CMe_2)Sn$, $Ph_3(PhMe_2CCH_2)Sn$, $Ph_2(PhCH_2)(MeCH_2CMe_2)Sn$, $Ph_2(PhCH_2)SnR$ (R = ^{t}Bu, $PhMe_2CCH_2$), $[Ph_2(PhMe_2CCH_2)Sn]_2$;[24] adamantyltin compounds;[26] trimethyltin derivatives of the norbornyl skeleton;[28] 9-trimethylstannyl-1,2,3,4-tetrachloro-9,10-dihydro-9,10-etherioanthracene (activation parameters for rotation);[29] Me_3SnCHI_2, $(Me_3Sn)_2CI_2$;[37] 1-trimethylsta ethoxycarbonylcyclopropanes;[38] dialkylcarbamoyltin compounds;[40] di-3-butenyldibutyltin, epoxyalkyltrialkylstannanes, $Bu_3Sn(CH_2)_4OH$;[46] trialkyltin derivatives of pyrazoles and pyrazolenines;[47] propargyl and allenylstannanes;[51] trimethylindenylstannanes (activation energies of fluxional rearrangement);[53] trimethylstannyl - Pt, Rh, Ir acetylides;[58] organotin derivatives of tetrakis(alkoxyboryl)methanes;[59,61] $Me_3Sn{-}\overset{*}{C}HMe{-}CH_2CO_2$-menthyl(−) (in the presence of Eu complexes);[69] the addition products of Et_3SnH with diynes;[73] (α-methoxy- and pyrrolidin-1-ylbenzyl)triorganostannanes;[83] $^tBu(EtO_2C)C{=}C(CO_2Et)SnMe_3$, $\left[(EtO_2C)(Me_3Sn)N\right]_2$;[89] complexes of organotin halides with $Me_2P(X)Y$ ($X = O, S$; $Y = Cl, OMe, SMe$);[120] diastereotopic triorganotin halides and tetraorganostannanes;[121] binary mixtures of trimethyltin halides (activation energies of exchange);[123,124] $Me_n{}^tBu_{3-n}SnBr$ ($n = 1 - 3$);[125] binary mixtures of dimethyltin dihalides (rate constants);[126] Me_2SnCl_2-picolinaldimine adducts;[127] $PhSnX_3$ ($X = Cl, Br, I$) and their adducts with Lewis bases;[128] complexes of R_3SnCl with carbonyl-stabilised phosphorus ylids;[130] $BuCl_2Sn(O_2C_5H_7)$;[131] complexes of tin halides with 1-vinylazoles;[133] $Me_3SnOTeF_5$;[151] organotin trialkoxides and derivatives;[152] organotin alkoxides and phenoxides (exchange);[154] the products of insertion of chloral into oxastannacyclopentanes and -pentenes;[159] organotin stannatranes,[168] (intramolecular motion);[169] dimethyltin derivatives of ONO terdentate Schiff bases;[173] O-trialkyltin hydroxylamines;[178] triorganotin esters of nitronic acids;[179] $Me_3Sn(NO_3)_2$;[193] 1,2-dicyanoethylenedithiolato-diorganotin derivatives;[216] substituted benzoylthiotrimethylstannanes;[217] trimethyltin derivatives of dithioacids;[218] $(Me_3Sn)_2E{:}M(CO)_5$ ($E = S, Se, Te$; $M = Cr, Mo, W$);[220–222] $Me_nSn(SeMe)_{4-n}$ ($n = 0 - 3$);[223] $Me_2Sn(OSeCNR_2)_2$, $Me_3SnOSeCNR_2$, $Me_2ClSnOSeCNR_2$;[225] adducts of CS_2 and PhNCS with oxa-aza- and diazastannacyclopentanes;[230] adducts of Me_3SnX ($X = Me, NMe_2, OMe, SnMe_3$) with sulphodiimides;[231] $Me_3Sn{-}N{=}S{=}N{-}SnMe_3$;[232] $Me_2SnS_2N_2$;[233] $R_3SnCH_2CONMe.COMe$ ($R = Me, Et$);[234] $(Me_3Sn)NMeR$ ($R = P_3N_3F_5, PSCl_2, SO_2C_4F_9$), $(Me_3Sn)_2NR$ ($R = P_3N_3F_5, SO_2C_4F_9, PCl_2{=}NSO_2F$), $Me_3SnPOF_2NP_3N_3F_5$, $Me_3SnN(PCl_2{=}N)_2SO_2$;[235] $Me_3SnBMeBPh_2$, $Me_2ClSnNMeBPh_2$, trimethylstannyltriazaboradecalin;[237] $Me_nSn\left[N{=}C(CF_3)_2\right]_{4-n}$ ($n = 0{-}3$);[239] adducts of trimethyltin alkylideneamines with PhNCO, $CH_2{=}CHCN$, $(Ph_3P)_2Pt(SnMe_3)\left[N{=}C(CF_3)_2\right]$;[240] Me_3SnX ($X = PH_2, P(CF_3)_2$,

$As(CF_3)_2$, Cl, Br, I);[251] mixed germyl-stannylarsines;[252] products of the additi of Et_3SnNa with alkyl alkynyl sulphides[253] and ethers;[255] $(^tBu_3Sn)_2Hg$;[257] μ-$Me_3SnC_2B_4H_7$;[260] $LiMe_3SnMMe_3$ (Me = Al, Ga, In, Tl);[261] $LiTlMe_4$, Li $(Me_3Sn)_nTlM$ (n = 1, 2);[262] $(Me_3Sn)_3Sb{:}M(CO)_3$ (M = Cr, Mo, W);[275] $Me_3SnM(cp)_2X$ (M = Mo, W; X = halide, H), adducts of $Me_3SnM(cp)_2H$ with $MeO_2C.C{\equiv}C.CO_2Me$;[278] $Me_5C_5M(CO)_3SnPh_3$ (M = Cr, Mo);[282] $cpW(CO)_2$(phosphine)$SnMe_3$;[284] $cpFe\left[P(OPh)_3\right]_2Sn_4Me_9$;[293] $(MeC_5H_4)_2Sn$;[408] cp_nSnX_{4-n} (X = Cl, Br, I; n = 1, 2, 3);[330] tin halide complexes of phosphorus(V) thio and dithio esters;[331] β-phenethyltin compounds;[350] *N*-viny and *N*-ethylimidazole complexes of tri- and diorganotin halides;[351] Me_nSnX_{4-n} (n = 1, 2, 3: X = Cl, Br, I);[352] Ph_3SnX (X = F, Cl, OH) (study of molecular motion),[354] $Me_3SnB(NMeCH_2)_2$;[364] $R_3SnC{\equiv}CH$ (R = Me, Ph);[376] organotin carboranes; organotin selenides;[391] $(Me_3Sn)_2Te$.[396]

^{11}B: $Me_3SnNMeBPh_2$, $Me_2ClSnNMeBPh_2$, trimethylstannyltriazaboradecalin;[237] μ-$Me_3SnC_2B_4H_7$;[260] $Me_3SnB(NMeCH_2)_2$;[364] organotin carboranes.[387]

^{13}C: Adamantyltin compounds;[26] $cpW(CO)_2$(phosphine)$SnMe_3$;[284] $cpFe\left[P(OPh)_3\right]_2\ Sn_4Me_9$;[293] substituted aryltrimethylstannanes;[370,372] (some value in ref. 372 have later been corrected[373]); SnR_4 (R = Me, Et, ^{n}Pr, ^{n}Bu, vinyl, allyl), $Me_3SnC_nH_{2n-1}$ (n = 3, 4, 5, 6)· $Me_3SnCMe{=}C{=}CHMe$, trimethyltin derivatives of the norbornyl skeleton;[374] $R_3SnC{\equiv}CH$ (R = Me, Ph);[376] various organotin derivatives (49 in all);[389] aryl- and benzyltrimethylstannanes;[390] organotin selenide

^{14}N: R_3SnN_3 (R = Me, Et).[360]

^{19}F: $Sn(CF_3)_4$, $Sn(CF_3)_3I$;[18] $(Me_3Sn)NRR'$ (R = Me, $SnMe_3$; R' = $P_3N_3F_5$, $SO_2C_4F_9$);[235] $Me_nSn\ N{=}C(CF_3)_{2\ 4-n}$ (n = 0 – 3);[239] $Me_3SnE(CF_3)_2$ (E = P, As);[251] (4-fluorophenyl)dimethyltin and triaryl(4-fluorophenyl)tin compounds.[380,381]

^{31}P: Complexes of organotin halides with $Me_2P(X)Y$ (X = O, S; Y = Cl, OMe, SMe);[120] $cpW(CO)_2$(phosphine)$SnMe_3$;[284] tin halide complexes of phosphorus(V) thio and dithio esters.[331]

^{55}Mn: $L_3SnMn(CO)_5$ (L_3 = $PhCl_2$, $(C_6F_5)_3$, $Ph(C_6F_5)_2$, Ph_2Cl, $Ph_2(C_6F_5)$, Ph_3).

^{77}Se: Organotin selenides.[391]

^{119}Sn: Butyltin trialkoxides;[153] Me_nSnX_{4-n} (n = 1 – 3; X = Cl, Br, I);[352] organotin carboranes;[387] organotin selenides;[391] $Me_{4-n}Sn(NR_2)_n$ (R = Me, Et; n =

1 - 4);[397,398] $Me_{4-n}SnX_n$ (X = SMe, OMe, OEt; n = 1 - 4).[398]

^{125}Te: $(Me_3Sn)_2Te$.[396]

(iv) Tin-119m Mössbauer Data.

4-Phenoxybutyltrimethyltin;[22] epoxyalkyltriorganostannanes, $Bu_3Sn(CH_2)_4OH$;[46] complexes of organotin halides with $Me_2P(X)Y$ (X = O, S; Y = Cl, OMe, SMe);[120] $R_3SnCl.Ph_3PCHCOMe$, (R = Me, Ph);[129] $BuCl_2Sn(O_2C_5H_7)$;[131] organostannatranes;[168] di- and triorganotin derivatives of Schiff bases;[174] organotin oximates and Schiff base complexes (magnetically perturbed spectra);[175] O-trialkyltin hydroxylamines;[178] triorganotin esters of nitronic acids;[180] organotin mercaptocarboxylates;[190] triorganotin derivatives of amino acids and dipeptides;[191,192] $Me_2Sn(O_2SMe)_2$;[196] $R_3Sn(PO_2H_2)_2$, $R_2Sn(PO_3X)_2$ (X = F, H, OH),$(Me_3Sn)_3(PO_4)_2$;[205] organotin amines, imines, carbamates, and amides;[243] $[^tBu_2SnFe(CO)_4]_2$, $B.^tBu_2SnFe(CO)_4$ (B = DMSO, py); $B.^tBu_2SnCr(CO)_5$ (B = THF, DMSO, py);[324] $(MeC_5H_4)_2Sn$;[408] $[(Me_3Si)_2CH]_2Sn$;[321] tin halide complexes of phosphorus(V) thio and dithio esters;[331] Ph_2SnCl_2 (in depth study as a possible calibrant);[353] $RPhSnCl_2.2B$ (B = py, ½bipy, DMSO);[357] Me_nSnX_{4-n} (X = Cl, Br; n = 1 - 3) in various solvents;[358] organotin sulphides, thiolates and thioacetates;[363] $Me_3SnB(NMeCH_2)_2$;[364] Bu_4Sn, Bu_2SnCl_2, Bu_2SnSO_4;[385] tin-cobalt bonded compounds;[38 organotin carboranes;[387] $R_2SnCl_2(X)salen$ (R = Me, Ph; X = H_2, Ni), $OctSnCl_3H_2salen$, $RSnCl_3Nisalen$ (R = Me,Ph).[403] Bancroft has calculated the quadrupole moment of ^{119}Sn to be $-0.062\pm0.02\times10^{-28}$ m^2,[388] whilst Gupta and Majee have used the Del Re approximation to calculate electron densities at tin nuclei. A value of $+3.2\times10^{-4}$ was calculated for $\Delta R/R$.[404]

(v) Mass Spectra.

$Sn(CF_3)_4$;[18] $XMe_2SiCH_2SnMe_2CH_2Cl$ (X = H, Cl), $Me_3SnCH_2SnMe_3$, $(Me_2SnCH_2)_3$, $(Me_3SnCH_2)_2SnMe_2$;[21] ω-substituted alkyltriorganostannanes;[22] $RSnBu_3$ (R = Me, ^{iso}Pr, $^{cyclo}Hex$), Bu_2SnRR' (R' = Me, Et; R = ^{iso}Pr, $^{cyclo}Hex$, ^{sec}Bu), $EtBu^{iso}Pr^{cyclo}HexSn$, $Et_2Bu^{cyclo}HexSn$, $MeBu^{iso}Pr^{cyclo}HexSn$, $Bu_2{}^{iso}PrSnBr$, $Bu^{iso}Pr^{cyclo}HexSnBr$;[23] trimethylstannylindene and -indane (ionisation potentials);[5 (α-methoxy- and α-pyrrolidin-1-ylbenzyl)triorganostannanes;[83] ^{iso}propyl and ^{tert}butyltin compounds;[125] $Me_3SnS.C(NCN)N(CN)SnMe_3$;[141] O-trialkyltin hydroxylamines;[178] triorganotin esters of nitronic acids;[179] dimethylchlorotin carboxyl and their hydrolysis products;[183] triorganotin derivatives of amino acids and dipeptides, R_3SnOH and $(R_3Sn)_2CO_3$ (R = Me, ^{cyclo}Hexyl);[192] $Me_2Sn(O_2SMe)_2$;[196] 1,2-dicyanoethylenedithiolatodiorganotin derivatives;[216] $Me_3{-}N{=}S{=}N{-}SnMe_3$;[232] $Me_2SnS_2N_2$;[233] $(Me_3Sn)NMeR$ (R = $P_3N_3F_5$, $PSCl_2$, $SO_2C_4F_9$), $(Me_3Sn)_2NR$ (R = $P_3N_3F_5$, $SO_2C_4F_9$, $PCl_2{=}NSO_2F$), $Me_3SnPOF_2NP_3N_3F_5$, $Me_3SnN(PCl_2{=}N)_2SO_2$;[235] $(^tBu_3Sn)_2Hg$;[257] $(R_2Sn)_n$ (R = Et, Bu, ^{iso}Bu, ^{cyclo}Hex, Ph);[271] $Me_2Sn(C_6H_4)_2O$, $\left[Me_2Sn(C_6H_4O_{\frac{1}{2}})\right]_2$;[334] $Me_2Sn(SMe)_2$, $(R_3Sn)_2S$, $(R_2SnS)_3$;[361] $Me_3SnMn(CO)_5$;[365] $R_3SnEC_6F_5$ (R = Me, Ph; E = O, S).[401]

(vi) Ultra-violet Spectra.

Dialkylcarbamoyltin compounds;[40] substituted benzoylthiotrimethylstannanes trimethyltin derivatives of dithioacids;[218] $Me_2Sn\left[N{=}C(CF_3)_2\right]_2$;[239] $cp(OC)_2W(phosphine)SnMe_3$.[284]

(vii) Electron Spin Resonance.

$\left[(Me_3Si)_2CH\right]_3Sn^{\bullet}$;[301] $Me_nCl_{3-n}Sn^{\bullet}$ (n = 0 - 3);[302] stannylcyclopentenyl radicals derived from the addition of $Bu_3Sn^{\bullet}$ to C_5H_6 and C_5H_5D;[303] $Et_3Sn\overset{\bullet}{C}HCH_3$, $Pr_3Sn\overset{\bullet}{C}HCH_2CH_3$, $Bu_3SnO\overset{\bullet}{C}HCH_2CH_3$;[309] $Bu_3SnO\overset{\bullet}{C}Me_2$;[310] 2,4,6-$^tBu_3C_6H_2\overset{\bullet}{N}{-}OSnEt_3$;[312] $Me_3SnOO^{\bullet}$;[314] $Me_3SnC_6H_4N^tBuO^{\bullet}$.[349]

(viii) Kinetic Data.

Protolysis of 1-naphthyltrimethyltin;[30] the dealkylation of Et_4Sn by HgX_2 (X = Cl, I, OAc);[34-36] the reaction of propargyl- and allenylstannanes with chloral;[52] alkaline cleavage of o-, m-, and p-carboranyltrimethylstannanes;[63] the reaction between tin hydrides and chromium pentacarbonyl - carbene complexes;[83,84] exchange between alkoxytin compounds and silanes;[156] the inserti of SO_2 into aryl-[200] and benzyl-tin[201] bonds; halogen abstraction from alkyl halides by $Me_3Sn^{\bullet}$ radicals in the gas phase;[307] $^tBuO^{\bullet}$ substitution of R_nSnX_{4-n} (X = halide or carboxylate; n = 1 - 3);[309] reaction of N-chlorosuccinimide and hexalkylditins;[311] decomposition of tert-butyl 3-(trimethylsilyl)peroxypropionat in Et_4Sn and Et_6Sn_2;[317] decomposition of peresters in the presence of Et_3SnH.[318]

(ix) Photoelectron and ESCA Data.

$\left[R_2SnFe(CO)_4\right]_2$ (R = Me, Ph, ^tBu), $B.R_2SnFe(CO)_4$ (B = DMSO, py),

$B.{}^tBuSnCr(CO)_5$ (B = THF, DMSO, py);[324] $[(Me_3Si)_2CH]_2Sn$;[321] Me_4Sn;[332,407] Ph_4Sn, Ph_3SnCl, $(PhCH_2)_3SnCl$, $(PhCH_2)_2SnCl_2$;[383] Bu_3SnR (R = Bu, vinyl, allyl).[384]

(x) Miscellaneous.

The dipole moments of $Me_2Sn(O_2C_5H_7)_2$,[172] $Ph_3SnFe(CO)_2(NO)L$ (L = CO, PPh_3, $AsPh_3$, $P(OPh)_3$),[292] Fe–Sn bonded compounds, $cp(CO)_3MSnPh_3$ (M = Mo, W),[366] and R_nSnX_{4-n} (X = Cl, Br; n = 1 - 3)[394] have been evaluated.

Nqr spectra have been recorded for methyltin chlorides (^{35}Cl) and bromides (^{79}Br and ^{81}Br) Me_nSnX_{4-n} (X = Cl, Br; n = 0 - 3),[356,399] and some of their complexes with DEE, dioxane, acetone, DME, THF, DMF, HMPT, pyridine, DMSO, and TMED.[356]

Crystal dislocations in Ph_4Sn have been studied.[368] The sublimation pressures of solid solutions in the binary Ph_4Si + Ph_4Sn system have been measured.[369]

Gupta and Majee have extended their studies using the Del Re approximation to aryl-,[377] vinyl-,[377] and alkyl-tin[378] bond cleavage. Pitt has discussed the role of hyperconjugation in Group IV chemistry.[379] Force field calculations of the conformational equilibria in organotin hydrides have been carried out.[402]

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