TIN

Annual Survey Covering the Year 1972

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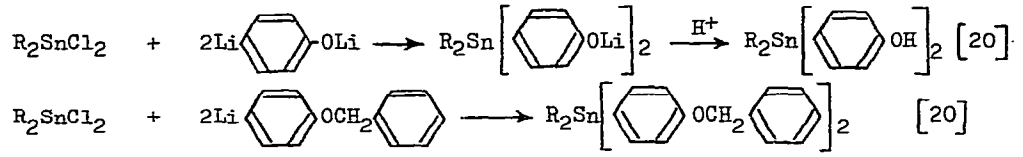
1. Reviews

Articles concerning sulphinato-tin complexes [1], organotin complexes containing intramolecularly coordinated carbonyl groups [2], and the application of topology to the stereochemistry of 4, 5, and 6 coordinate complexes of tin [3] are included in the first issue of a new review journal dealing solely with the chemistry of the Group IV metals. Other subjects which have received attention are: organotin halides and pseudohalides [4], aspects of five-coordination in organotin chemistry [4a], the preparation, structure, and reactions of organotin compounds [5], the formation and cleavage of the tin-carbon bond [6], the use of organotin compounds in organic synthesis [7,8,9], tin-transition metal bonded compounds [10], O- and C-isomerism in keto-enol tin systems [10a], stannyl Grignard reagents [11], organotin peroxides [12], commercial aspects of organotin compounds [13], tin-119m Mössbauer spectra [14], and radical reactions [15]. Bibliographies of organotin structures determined by X-ray diffraction, comprehensive upto 1971, [16] and toxicities of organotin compounds [17] have been compiled.

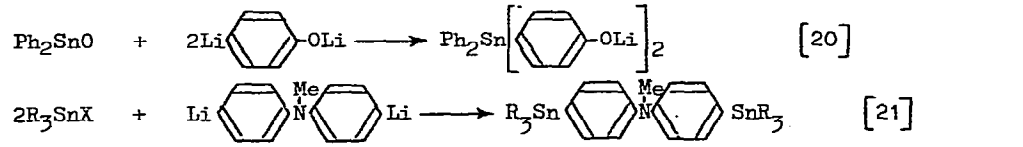
2. Compounds with Four Tin-Carbon Bonds

Two patents have described the synthesis of tetraalkylstannanes. Stannane adds to α-olefins at low temperatures using tert-butyl peroxide and cobalt naphthenate as catalysts [18]. A more efficient process employs the reaction between trialkylalanes and tin(IV) chloride [19].

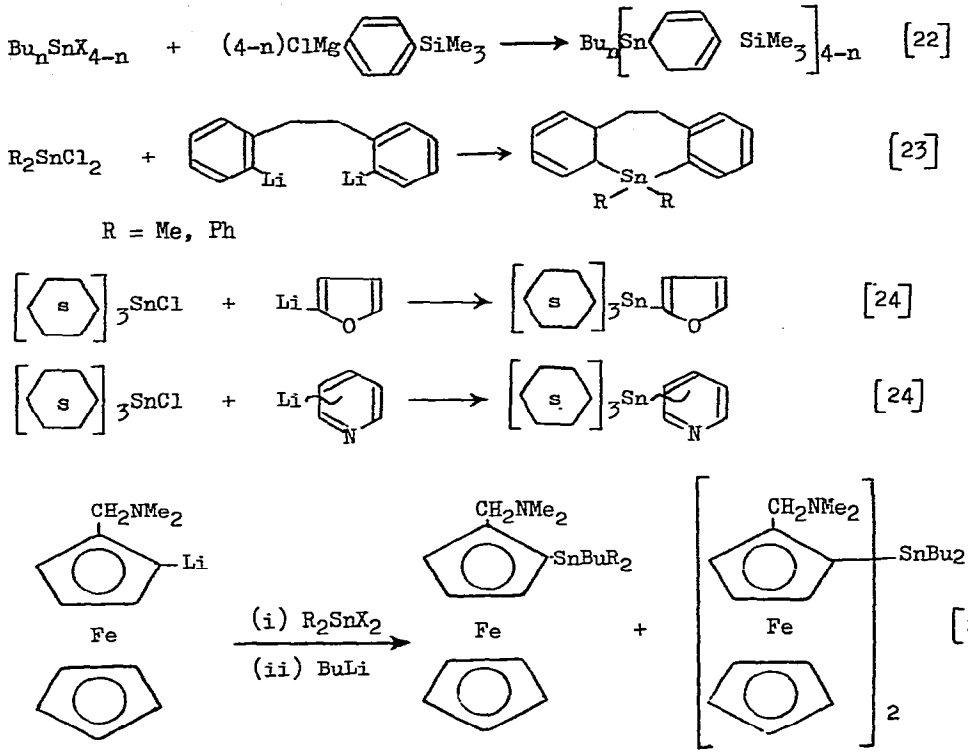
Grignard and organolithium reagents have been used extensively in the formation of functionally substituted arylstannanes and similar compounds, viz.:



R = Me, Ph



R = Me, Ph; X = Cl, Br



Sterically hindered triorganotin halides yield either the tetraorganostannane or the coupled product depending on the degree of crowding. Thus with tert-BuMgX or tert-BuLi, tert-BuR_2SnX (R = Ph, $PhCH_2$, ^nBu) affords $(tert\text{-}Bu)_2R_2Sn$, whilst $(tert\text{-}Bu)_2RSnX$ gives $[(tert\text{-}Bu)_2RSn]_2$. These latter products arise by initial halogen-lithium exchange producing $(tert\text{-}Bu)_2RSnLi$, which can then react further, viz.:

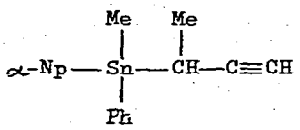
$$^tBu_2PhSnCl + {}^tBuLi \longrightarrow {}^tBu_2PhSnLi + {}^tBuCl$$

$$^tBu_2PhSnLi + {}^tBu_2PhSnCl \longrightarrow {}^tBu_2PhSn\text{-}SnPh{}^tBu_2 + LiCl$$

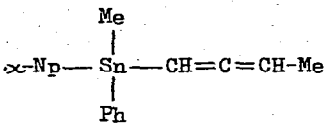
Reaction of tert-amyl Grignard reagents with Ph_2RSnI results in the formation of the coupled product when R = tert-Bu or neophyl, but forms the normal substitution product when R = $PhCH_2$. Normal substitution products are also obtained from the reactions between tri-iso-butyl-, trineophyl-, or tri-tert-butyltin chloride and phenyllithium [27,28]. The potassium reduction

of 1,1-diphenyl-dibenzostannol in DME produces a red solution, but no radical anion can be detected. Oxidation with benzoyl peroxide is chemiluminescent [28a].

Both the propargyl (I) and allenyl (II) isomers are obtained



(I)



(II)

when α-NpPhMeSnI is treated with HC≡C.CHMe.MgBr. The relative proportions of each isomer produced depends on the reaction conditions, although I is readily converted into II by warm methanol. Both exhibit erythro-threo isomerism [29]. The reaction of the allylic Grignard reagent $MeCH{=}CH.CH_2.MgBr$ with R_3SnX (R = Me, Ph; X = Cl, Br) preferentially gives the branched product, $R_3SnCHMe.CH{=}CH_2$, whilst R_3SnLi and $MeCH{=}CH.CH_2X$ preferentially yield the linear isomer, $R_3SnCH_2CH{=}CHMe$. R_3SnLi also reacts with $CH_2{=}CH.CD_2O_3SMe$ to give 70-85% $R_3SnCD_2CH{=}CH_2$ and 30-15% $R_3SnCH_2CH{=}CD_2$ [30]. Unsaturated compounds of the type $Me_3SnQSnMe_3$ ($Q = (CR^1R^2CR^3{=}CR^4CR^5R^6)_n$, R^1 - R^6 = H, Me, aryl; n = 2 - 8) are obtained by treating Mg with a diolefin in THF in the presence of ethyl bromide or 1,2-dibromoethane, and treating the resulting Grignard reagent with Me_3SnCl [31]. A number of triethylstannyl derivatives of dialkynes have been synthesised using liquid ammonia as solvent:

$$Et_3SnNa + BrC{\equiv}C.C{\equiv}CR \longrightarrow Et_3Sn.C{\equiv}C.C{\equiv}CR$$

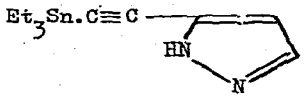
$$Et_3SnBr + HC{\equiv}C.C{\equiv}CH \xrightarrow{Na} Et_3Sn.C{\equiv}C.C{\equiv}CR$$

$$Et_3Sn.C{\equiv}C.C{\equiv}CH + NaNH_2 + Et_3SnCl \longrightarrow Et_3Sn.C{\equiv}C.C{\equiv}C.SnEt_3$$

$$Et_3.C{\equiv}C.C{\equiv}CH + NaNH_2 + EtBr \longrightarrow Et_3Sn.C{\equiv}C.C{\equiv}C.SnEt_3 + Et_3Sn.C{\equiv}C.C{\equiv}CEt$$

$$Et_3SnNa + Et_3Sn.C{\equiv}C.C{\equiv}CH + MeI \longrightarrow Et_3Sn.C{\equiv}C.C{\equiv}C.SnEt_3 + Et_3Sn.SnEt_3$$

1,3-Dipolar addition of diazomethane takes place with the terminal alkyne group of $Et_3Sn.C{\equiv}C.C{\equiv}CH$ producing the ethynylpyrazole derivative III. The same product is also obtained by treating the intermediate formed



III

from $(C{\equiv}CH)_2$ and diazomethane with bis(triethyltin)oxide [32].

Functionally substituted methyltin derivatives continue to arouse interest. α-Sulphonylmethyl- and α-thiolatomethylstannanes are readily obtained using the respective lithium reagents:

$$Bu_3SnCl + RSO_2CH_2Li \longrightarrow Bu_3SnCH_2SO_2R \quad [33]$$

$$Bu_nSnCl_{4-n} + PhSCH_2Li.TMED \longrightarrow Bu_2Sn[CH_2SPh]_{4-n} \quad [34]$$

$$Bu_3SnCl + MeSCH_2Li.TMED \longrightarrow Bu_3SnSCH_2Me \quad [35a]$$

$$Bu_3SnCl + RSCH_2Li \longrightarrow Bu_3SnCH_2SR \quad [35b]$$

$R = Me, Ph, p\text{-}MeOC_6H_4$

α-Thiolatomethyltin compounds may also be synthesised by the substitution of the corresponding bromomethyltin derivatives using the sodium thiolate [34]:

$$(BrCH_2)_4Sn + 4RSNa \longrightarrow (RSCH_2)_4Sn$$

$R = Bu, Ph$

$$(BrCH_2)_2SnBr_2 + 4RSNa \longrightarrow (RSCH_2)_2Sn(SR)_2$$

Organozinc compounds are the preferred reagents for the synthesis of halomethyltin derivatives [36]. Iodomethylzinc iodide produced by the reaction of ethylzinc iodide and diiodomethane is to be preferred to the previous diiodomethane-zinc/copper couple method, enabling Me_3SnCH_2I and $Me_2Sn(CH_2I)_2$

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to be prepared in >70% yield. The reaction of ethylzinc iodide with Me_3SnCHI_2 in THF gives good yields of $Me_3SnCHIZnI$, which reacts further with Me_3SnCl to give $(Me_3Sn)_2CHI$ in high yield:

$$Me_3SnCHI_2 \xrightarrow{EtZnI} Me_3SnCHIZnI \xrightarrow{Me_3SnCl} (Me_3Sn)_2CHI \quad (83\%)$$

$Me_3SiCHISnMe_3$ and $Me_3SnCHIMe$ are prepared similarly:

$$CH_2I_2 \xrightarrow{EtZnI} MeCHIZnI \xrightarrow{Me_3SnCl} MeCHISnMe_3 \quad (75\%)$$

$$Me_3SiCHI_2 \xrightarrow{EtZnI} Me_3SiCHIZnI \xrightarrow{Me_3SnCl} Me_3SiCHISnMe_3 \quad (91\%)$$

Trimethyltindihalomethyllithium reagents have been obtained in moderate yields by the reaction of BuLi with bis(trimethyltin)dihalomethanes in THF at low temperatures:

$$(Me_3Sn)_2CXY + BuLi \longrightarrow Me_3SnCXYLi + BuSnMe_3$$

X, Y = Cl_2, ClBr, Br_2

Me_3SnCBr_2Li is also produced by bromine-lithium exchange between Me_3SnCBr_3 and BuLi. The lithium derivatives are stable only in THF-rich media at temperatures of -95° or below. Their reactions with quenching agents such as trimethylchlorosilane and methyl iodide are very complicated, since the products of such reactions (eg. $Me_3SiCX_2SnMe_3$) are of comparable reactivity towards the lithium reagents [37]. Arenethiols add to allyltrialkylstannanes under free-radical conditions to form 3-(trialkylstannyl)-propyl aryl sulphides:

$$R_3Sn.CH_2CH{=}CH_2 + HSAr \xrightarrow{UV} R_3Sn.CH_2.CH_2.CH_2SAr$$

R = Me, Et, Bu; Ar = Ph, p-tolyl

Prefential cleavage of the allyl group occurred when R = R' = Bu or Ph:

$$R_3Sn.CH_2CH{=}CH_2 + R'SH \longrightarrow R_3SnSR' + CH_3CH{=}CH_2$$

Whilst diallyltin dibromide and benzenethiol yielded stannous bromide [38]. Treatment of the β- and γ-hydroxystannanes $PhR_2Sn(CH_2)_nCR'_2OH$ (R = Me, Ph; R' = H, Me; n = 1, 2) with CX_4 (X = Cl, Br) and triphenylphosphine results in the formation of moderate yields of $PhR_2Sn(CH_2)_nCR'_2X$ [39]. Similar halogenated products are obtained from the insertion of dichlorocarbene (derived from phenyl-bromodichloromethylmercury) into the β-C-H bonds of $Me_3SnCHMeCH_2CH_3$ and $Me_3SnCDMeCH_2CH_3$:

$$Me_3SnCXMeCH_2CH_3 \xrightarrow{[:CCl_2]} Me_3SnCXMe.\underset{CCl_2H}{CH}.CH_3$$

X = H, D

Nmr data (^{13}C and ^{1}H) suggests no deuterium rearrangement to the β-position takes place, and hence a process which involves stabilisation of the transition state by metal-carbon bond hyperconjugation, rather than a stannacyclopropenium ion intermediate, is preferred [40]. In contrast, ethoxycarbonylnitrene, generated under a variety of conditions, is inert to insertion into the α-C-H bonds of Me_4Sn and the β-C-H bonds of trimethylisobutyltin [41]. Perfluoroalkynyltin derivatives react with trimethyltrifluoromethyltin at 150° to give perfluorocyclopropyltin derivatives:

$$Me_nSn(C{\equiv}C.R_f)_{4-n} + (4-n)Me_3SnCF_3 \longrightarrow Me_nSn\left[C{=}\underset{F_2}{C}{-}C.R_f\right]_{4-n}$$

$R_f = CF_3, CF_2CF_3, CF(CF_3)_2$

presumably by the addition of difluorocarbene to the triple bond. Thermolysis of Me_3SnCF_3 produces difluorocarbene probably in its singlet state, since it adds stereospecifically to the double bonds of both cis- and trans-butene. Addition of difluorocarbene also takes place to the double bond of trimethylvinyltin, but not to cyclopropenylstannanes [42].

Trialkylstannylacetic esters of alkynyl alcohols are formed when ketene is passed into the trialkyltin alkoxides at 10-15° [43]:

$$Et_3SnO(CR_2)_n.C{\equiv}C.R' + CH_2{=}C{=}O \longrightarrow Et_3SnCH_2.CO_2(CR_2)_n.C{\equiv}C.R'$$

R = H, Me; n = 1, 2; R = H, $SnEt_3$

The reactions of similar trialkylstannylacetic esters with halosilanes has been investigated in some detail [44]. Initially the O-silylation

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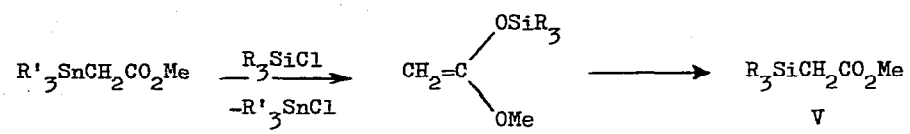
product IV is formed, which subsequently rearranges to the isomeric silylated acetic ester V:



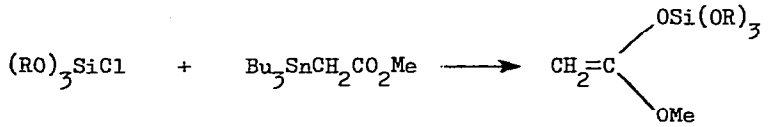
IV

When R = Cl_3Si, Cl_2MeSi, or $ClMe_2Si$, the O-isomers may be isolated by performing the reactions under mild conditions. The inclusion of a hydrogen bonded to silicon ($HSiCl_3$, $MeSiHCl_2$, Me_2SiHCl) precludes the isolation of O-isomeric products, the intermediate nature of which may only be detected by infra-red spectroscopy. The use of excess tin compounds facilitates the replacement of all chlorine atoms bound to silicon:

$$MeSiHCl_2 + 2Bu_2SnCH_2CO_2Me \longrightarrow MeSiH(CH_2CO_2Me)_2 + 2Bu_3SnCl$$

$$HSiCl_3 + 3Et_3SnCH_2CO_2Me \longrightarrow HSi(CH_2CO_2Me)_3 + 3Et_3SnCl$$

The less reactive trimethylchlorosilane reacts only under more severe conditions giving the C- isomer $Me_3SiCH_2CO_2Me$, although the O-isomer may be obtained using the more reactive trialkyliodosilane. Trialkoxychlorosilanes afford stable O-isomeric products which could be isolated in 60-80% yields.



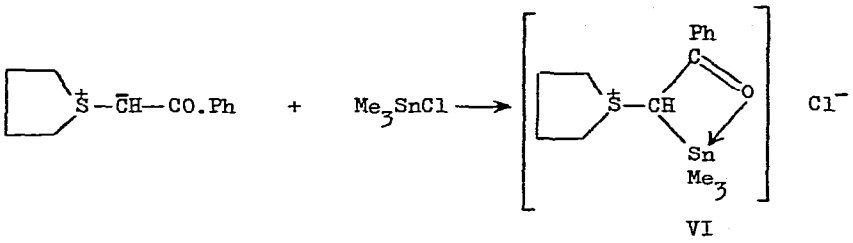
R = Me, Et

Alkynylstannylacetal derivatives have been prepared by treating trialkyltin alkoxides or oxides with an acetylene [80]:

$$R_3SnOR' + HC{\equiv}CX.OCHR''OR \longrightarrow R_3SnC{\equiv}CX.OCHR''OR + HOR'$$

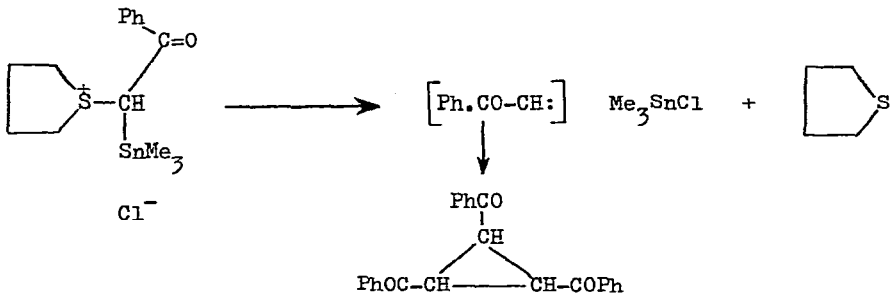
X = CH_2, CH_2CH_2, CHMe, CMe_2

Treatment of trimethyltin chloride with tetramethylenesulphonium phenacylide gives the sulphonium salt VI. The low value of the infra-red carbonyl stretching frequency (1524, 1487 cm^{-1}) suggests strong intramolecular coordination.

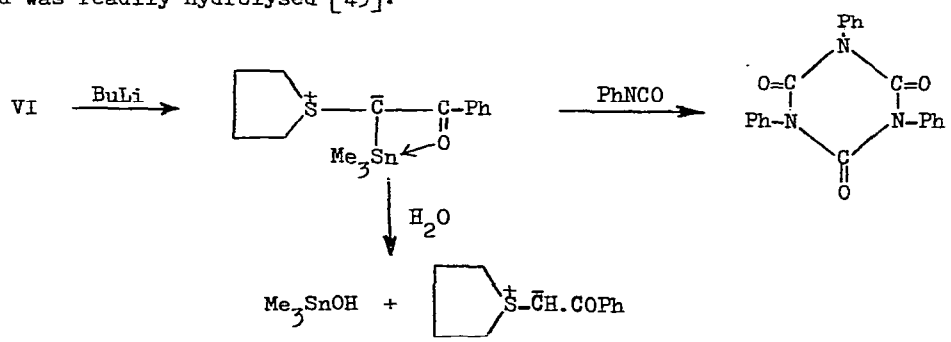


VI

Thermolysis at 150° or irradiation of VI affords tribenzoylcyclopropane, trimethyltin chloride, and tetramethylene sulphide, via nucleophilic attack of the chloride anion at tin:



Butane was liberated upon treatment of VI with BuLi gave the stannyl ylide VII, which converted phenyl isocyanate to the corresponding isocyanurate and was readily hydrolysed [45].



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The pyrolysis of tetramethyltin has been studied in a toluene carrier flow system from 803-941°K using total pressures of 10.6 to 52.4 mm. Methane, ethane, ethylene, and ethylbenzene were formed consistent with the release of four methyl groups for each molecule of tetramethyltin reacting [46]. Thermal decompositions of tetraorganostannanes has been studied at 400° in the presence of amines and alcohols. Metallic tin and radical products are again produced. Similar pyrolysis of dibutyltin diacetate gives stannous oxide [47]. Tributyl-, -octyl-, and -phenyltin compounds are stepwisely degraded by ultra-violet irradiation via di- and mono-derivatives to metallic tin. Dialkyltin derivatives appear to be the most sensitive to UV decomposition [48]. Price has demonstrated that triphenyltin compounds are degradated to inorganic tin compounds [49].

The tin-carbon bond is cleaved under a variety of conditions. Studies of cleavage by electrophilic reagents have been extended. The iodination of propargyl- and allenyltriphenylstannanes produces, respectively, iodoallenes and propargyl iodide [50].

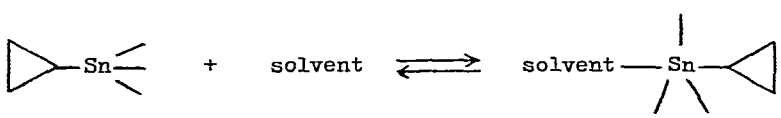
$$Ph_3Sn-\underset{\underset{R}{|}}{CH}-C\equiv CH \xrightarrow{I_2} Ph_3SnI + ICH=C=CH-R$$

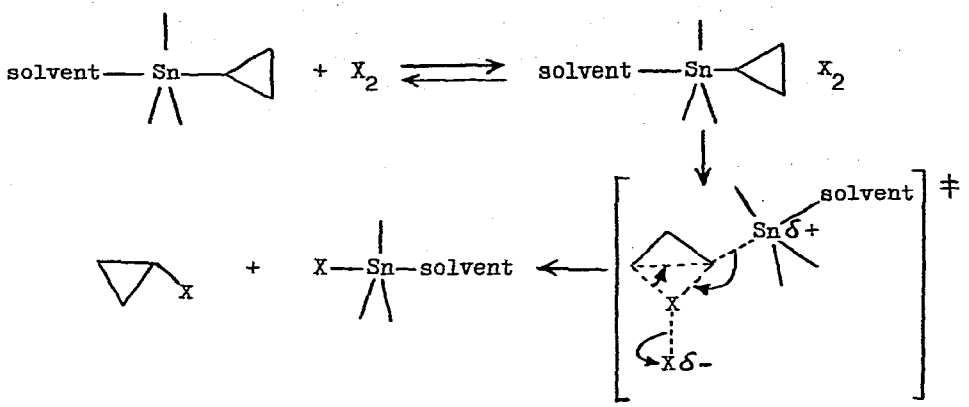
$$Ph_3Sn-CH=C=CH-R \xrightarrow{I_2} Ph_3SnI + \underset{\underset{R}{|}}{IC}-C\equiv CH$$

R = H, Me

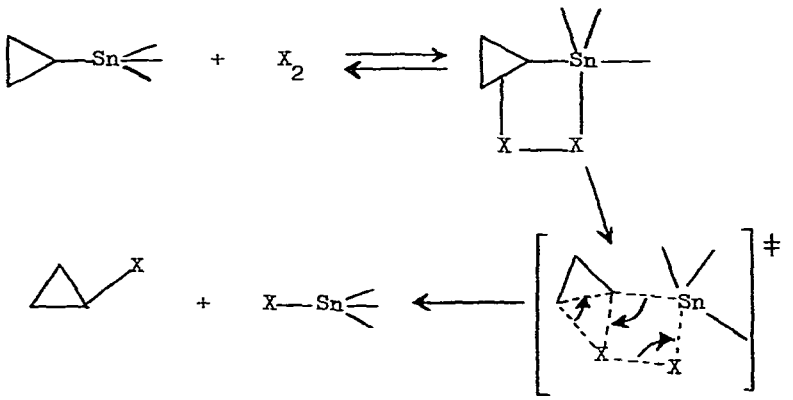
The bimolecular halodemetallation of substituted cyclopropyltrialkylstannanes is stereospecific, and proceeds with retention of configuration at carbon in methanol, acetic acid and chlorobenzene [50]. Two possible mechanisms, both involving the participation of ring orbitals, are postulated depending on the polarity of the solvent.

Polar solvents:





Less polar solvents:



Phenyltrimethylstannane reacts with cyanogen chloride in the presence of aluminium trichloride to give benzonitrile. Similarly tolyltrimethylstannanes afford toluonitriles, but cyanogen bromide affords aryl bromides [51]. Unsaturated groups such as cis- or trans-2-butenyl, 2-propynyl, or allenyl are cleaved from tin by thiocyanogen. Rearrangement accompanies fission and α-methallyl, allenyl, and 2-propynyl thiocyanates, respectively, are produced.

$$R_3Sn\text{-}CH_2\text{-}CH{=}CH\text{-}Me + (SCN)_2 \longrightarrow R_3SnNCS + CH_2{=}CH\text{-}\underset{SCN}{CH}\text{-}Me$$

$$R_3Sn\text{-}CH_2\text{-}C{\equiv}CH + (SCN)_2 \longrightarrow R_3SnNCS + CH_2{=}C{=}CH\text{-}SCN$$

$$R_3Sn\text{-}CH{=}C{=}CH_2 + (SCN)_2 \longrightarrow R_3SnNCS + HC{\equiv}C\text{-}CH_2\text{-}SCN$$

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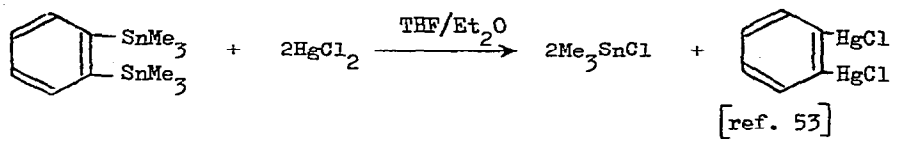
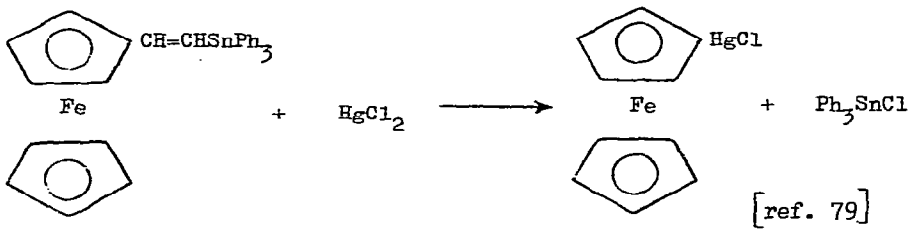
With Me_4Sn and Me_3SnCH_2Ph, no cleavage and polymerisation of thiocyanogen took place. cis- and trans-Styryltrimethylstannanes are cleaved with retention of configuration at the vinylic carbon [52]. Mercuric chloride and acetate cleave aryl-tin bonds to afford useful syntheses of mercuriated derivatives:



[ref. 53]



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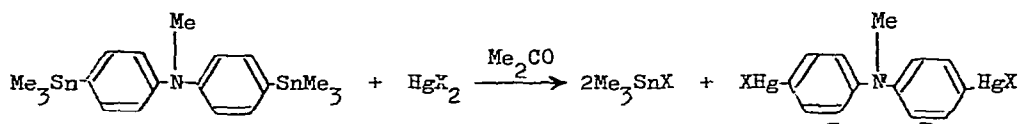
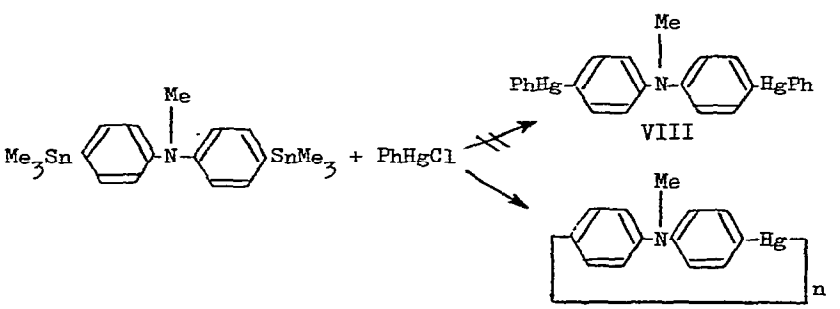


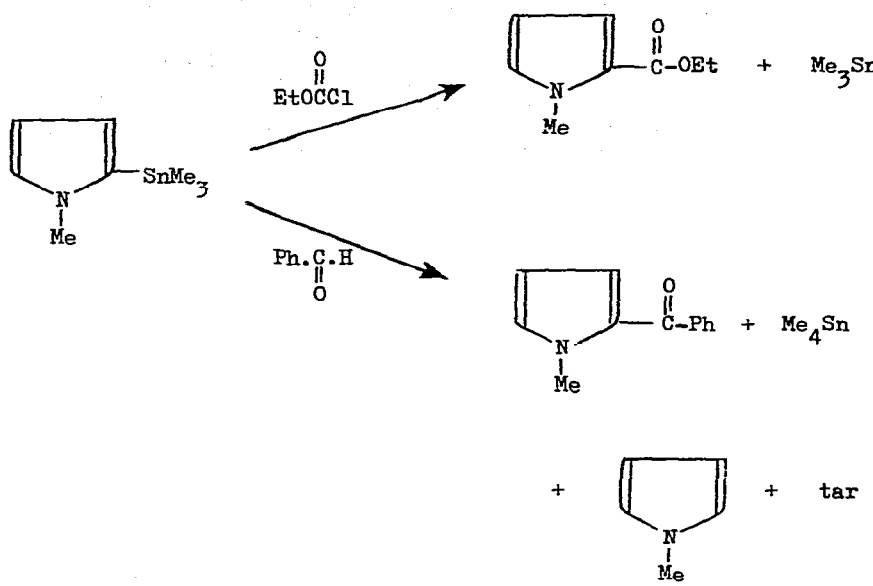
X = Cl, OAc

[ref. 21]

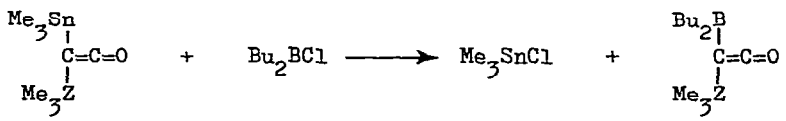
With phenyl mercuric chloride, para-bis(trimethylstannyl)methylamine does not yield the expected product VIII, but a colourless, high-melting solid, insoluble in all common solvents save pyridine and DMF, and for which structure IX is proposed 21 .



1-Methyl-2-(trimethylstannyl)pyrrole reacts with ethyl chloroformate to give 1-methylpyrrole-2-carboxylate, but with benzaldehyde phenyl-1-methyl-2-pyrrolyl-ketone is unexpectedly produced, presumably via the

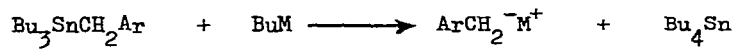


oxidation of the stannyl ether intermediate under the reaction conditions used. 2-Trimethylstannylthiophene is similarly cleaved by benzoyl chloride to yield Me_3SnCl and phenyl 2-thienylketone. Phenyl chloroformate gives Me_3SnCl and diphenylcarbonate [54]. The reaction of the stannylketene derivatives X (Z = Si, Ge) and dibutylchloroborane results in tin carbon-bond fission [55]:



Trityl perchlorate reacts with Me_4Sn to give a low yield of Ph_3CMe, but with Pr_4Sn and Bu_4Sn proton abstraction takes place, and triphenylmethane, trialkyltin perchlorate, and the appropriate olefin are formed [56].

Transmetallation occurs with alkali metal alkyls. 1- and 2-Naphthylmethyllithium, -sodium, and -potassium may be obtained by the reaction [57]:



M = Li, Na, K; Ar = 1- or 2-naphthyl

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p-Silylstannylbenzenes [22] and perhalomethyltin compounds [37] react similarly with lithium reagents:

$$Bu_nSn\left[C_6H_4SiMe_3\right]_{4-n} + (4-n)BuLi \longrightarrow Bu_4Sn + (4-n)Me_3SiPh \quad [22]$$

$n = 0, 2, 3$

$$Me_3SnCCl_2H + BuLi \longrightarrow \underset{47\%}{BuSnMe_3} + LiCCl_2H \xrightarrow{Me_3SiCl} \underset{42\%}{Me_3SiCCl_2H} \quad [37]$$

$$Me_3SnCBr_2H + LiCCl_2H \longrightarrow \underset{76\%}{Me_3SnCCl_2H} + LiCBr_2H \xrightarrow{Me_3SiCl} Me_3SiCBr_2H \quad [37]$$

The rates of cleavage of cinnamyl- and benzyltin derivatives have been measured in strongly aqueous or alcoholic DMSO media. Kinetic isotope effects support the mechanism

$$RO^- + R_4Sn \longrightarrow \left[RO^{\delta-}\cdots Sn(R)(R)\cdots R^{\delta-}\right]^{\ddagger} \longrightarrow ROSnR_3 + R^-$$

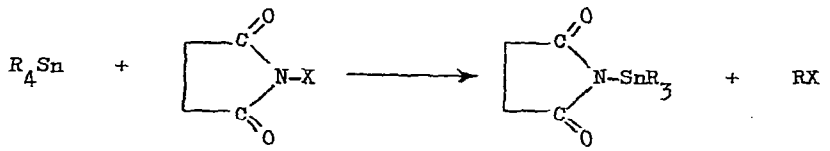
Analogous cinnamyl-silicon and germanium derivatives undergo cleavage much more slowly. Relative rates in 68.3 mole% aqueous DMSO at 40° are Et_3Si, 50; Et_3Ge, 1.0; Et_3Sn, 2.8 10^5 [58]. In contrast, phenyltrimethylsilane is ca. 9 times as reactive as its tin analogue under similar conditions (0.05M KOH in DMSO containing 3% water). Such an unusual order of reactivity has been attributed to the smaller degree of proton transfer to the separating carbon atom in a medium of low hydroxylic content [59].

An estimation of the effective steric bulk of the Me_3Sn group has been obtained from the exo/endo ratio of products of epoxidation and hydroboration reactions of syn-7-substituted norbornenes. The data indicate an effective steric order tert-Bu > Me > Br > $SnMe_3$ > Cl > H [60].

Tetraorganotins have been used as alkylating agents towards transition metal derivatives. Thus $\left[(\pi\text{-}C_6H_6)RuCl_2\right]_2$, triphenylphosphine, and Me_4Sn or Me_3SnCl yields $(\pi\text{-}C_6H_6)RuMeCl(PPh_3)$, and tetraallyltin and

$[(\pi\text{-}C_6H_6)RuCl_2]_2$ afforded $(\pi\text{-}C_6H_6)RuCl(\pi\text{-}C_3H_5)$. No reaction could be observed with tetramethallyltin [61]. When a mixture of aluminium trichloride and $ClCCo_3(CO)_9$ is treated with Me_4Sn, $MeCOCCo_3(CO)_9$ rather than $MeCCo_3(CO)_9$ is produced [62]. Heating mixtures of $[CH_2{=}CHCH_2PdCl]_2$ and $(Me_2CHCH_2CH_2)_4Sn$ or Ph_4Sn result in the formation of the triorganotin chloride and unstable palladium compounds which decompose at the temperatures used to Pd metal [63].

N-Halogenosuccinimides react with tetraalkyltins to give the corresponding alkyl halide and N-trialkylstannylsuccinimides:



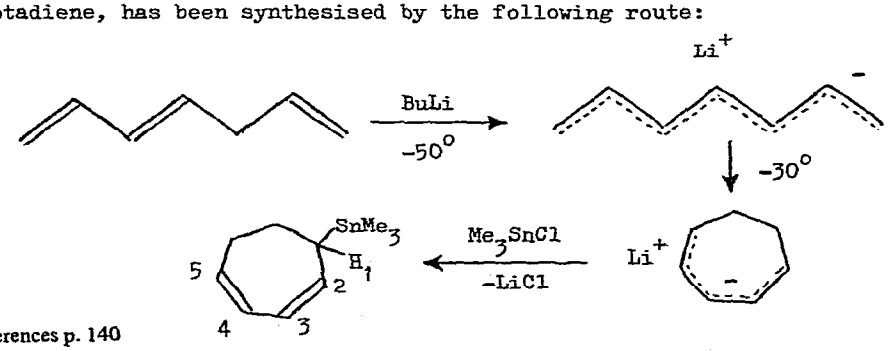
The displacements are inhibited by galvinoxyl and accelerated by di-t-butyl hyponitrite and phenylazotriphenylmethane, and proceed by a radical chain process in which the chain is propagated by the steps

$$(CH_2CO)_2N\cdot + SnR_4 \longrightarrow (CH_2CO)_2NSnR_3 + R\cdot$$

$$R\cdot + (CH_2CO)_2NX \longrightarrow RX + (CH_2CO)_2N\cdot$$

The rates of homolytic attack of the succinimidyl radical at tin decreases in the order $Me > Et > {}^{n}Pr$, ${}^{n}Bu > {}^{s}Bu$ suggesting steric hindrance in the formation of the intermediate five-coordinate species $[(CH_2CO)_2N\dot{S}nR_4]$. Benzyltributyltin reacts essentially only by benzyl-tin bond cleavage at a rate ca. 15 times that of tetrabutyltin, illustrating the effect of the resonance-stabilised incipient benzyl radical [290].

A new fluxional organotin compound, trimethylstannyl-2,4-cycloheptadiene, has been synthesised by the following route:



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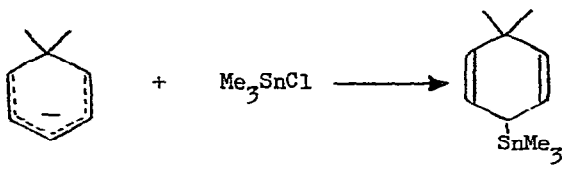
The temperature dependent ^{1}H nmr spectrum is consistent with rapid [1,5] Me_3Sn migration, with an activation energy of 16-19 kcal/mole (cf. 10.1 kcal/mole for the similar [1,5] shift in triphenylstannylcycloheptatriene). The 1,3,5-trimethylcycloheptadienide anion reacted with trimethyltin chloride or bromide to give complex mixtures, the major product of which appears to be a mixture of isomeric trimethylcycloheptadienes. Similarly, the 1,1,4-trimethylcyclohexadienide anion and trimethyltin chloride yielded 1,1,4-trimethyl-2,4-cyclohexadiene as the only olefinic product. The 1,1-dimethylcyclohexadienide anion does react with trimethyltin chloride:



XI

As expected, XI does not exhibit fluxional behaviour [64]. The crystal structure of the fluxional compound, triphenyl-7-cyclohepta-1,3,5-trienyltin, shows that the molecule consists of an approximately tetrahedral triphenyltin moiety σ-bonded to the seven-membered ring, which possesses a non-planar boat conformation. Endocyclic bond distances indicate alternate C-C double bonds (Fig. 1) [65].

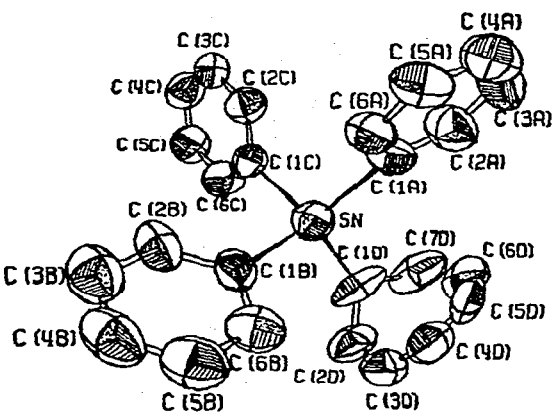


Fig. 1 The structure of triphenyl-7-cyclohepta-1,3,5-trienyltin [65]. (Reproduced by permission of the American Chemical Society).

Tributylcyclopentadienyltin has been obtained from tributyltin chloride and cyclopentadineylthallium(I) [66]. Bistrimethylstannylcyclopentadiene is obtained from cyclopentadiene and excess trimethylstannyldiethylamine [67]. Variable temperature nmr spectra of both this compound and trimethylcyclopentadienyltin show them to be fluxional on the nmr time scale. $Me_3SnC_5H_5$ has been noted previously to display broadening of the ring proton resonance at -70°. At lower temperatures the broadening increases, and at -150° an AA'BB'X spectrum is obtained (Fig. 2). Although a complete analysis of the spectrum was not possible, an analysis of the germanium analogue, $Me_3GeC_5H_5$, showed that the Me_3Ge group migrates via a 1,2 shift. The methyne proton exhibits $^{117,119}Sn$ satellites $J(^{117,119}Sn$

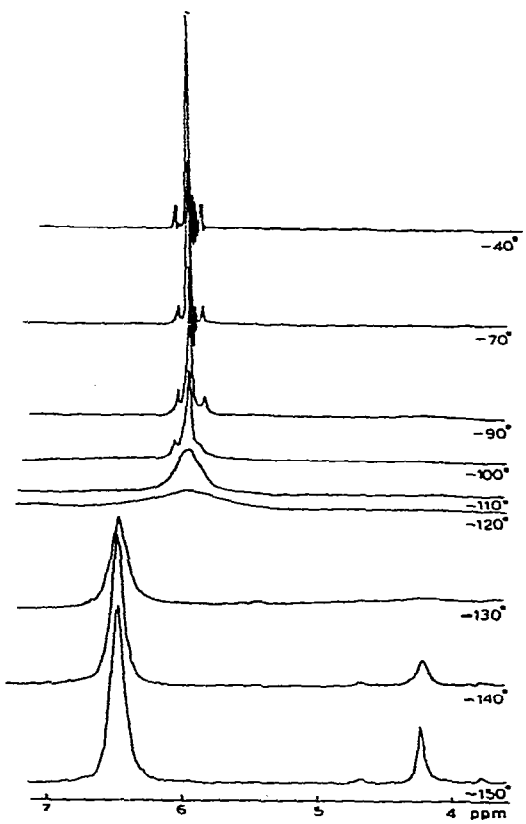
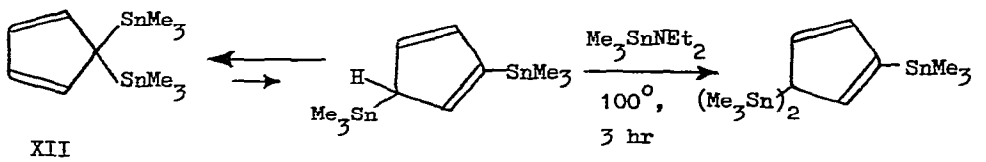


Fig. 2 PMR spectra of cyclopentadienyl protons in $Me_3Sn(C_5H_5)$ at various temperatures [68].

$-^1H_5$) = 91 Hz) [68]. The spectrum of $(Me_3Sn)_2C_5H_4$ consists of an AA'BB' multiplet at lower field to the methyltin singlet, corresponding to structure XII. Complete analysis of the spectrum was possible in this case, and δ(AA') = 6.57, δ(BB') = 6.30 ppm; J(AA') = J(BB') = 2.7 Hz; J(AB) = J(A'B') = 4.4 Hz; J(AB') = J(A'B) = 1.2 Hz. Tin satellites are apparent for both pairs of olefinic protons: $J(^{117,119}Sn-^1H_A)$ = 8.4 Hz; $J(^{117,119}Sn-^1H_B)$ = 6.4 Hz.



XII XIII XIV

The 5,5 isomer XII is in equilibrium with the 2,5 isomer XIII, although the latter is present in such small quantities that it cannot be detected by nmr. Its presence, however, can be verified by the formation of the tris(trimethylstannyl)cyclopentadiene XIV on treatment of the tautomeric mixture with Me_3SnNEt_2. Similar evidence for a 1,5 isomer could not be detected. No conclusive evidence is available to support either a [1,3] shift or two successive [1,2] shifts for the rearrangement XII $\rightleftarrows$ XIII [67]. Sequential [1,2] shifts are, however, favoured for the metallotropic Me_3Sn migration in trimethylstannylindene on the basis of semi-quantitative PMO theory [69] and in addition the measured activation energy, 13.8 kcal/mole, deduced from the temperature-dependent ^{13}C nmr spectrum (cf. 7.1 kcal/mole for the corresponding cyclopentadienyl compound). The ^{13}C-H satellite magnetic resonance spectrum of trimethylcyclopentadienyltin has been obtained and analysed. The evaluation of the coupling constants J^1 and J^2 in this and other model σ- and π-cyclopentadienylmetal compounds yield criteria for the distinction of the two types [71].

Diastereotopic non-equivalence has been demonstrated for molecules of the type $RMe_2SnCHYMe$ (Y = Et, Ph; R = alkyl, aryl), meso-$R'_2Sn(CHYMe)_2$ (R = Me, CH_2Ph), and for diastereoisomers such as $Me_{4-n}Sn(CHZMe)_n$ (Z =

Et, Pr; n = 2, 3) and Me-iso-Pr-cyclo-HexylSnCHMePh [72]. These compounds were obtained by the general routes:

$$AlkSnMe_3 \xrightarrow[MeOH]{Br_2} AlkSnMe_2Br \xrightarrow{PhYCHMeMgCl} AlkMe_2SnCHPhYMe$$

$$EtMeHCSnMe_3 \xrightarrow[MeOH]{Br_2} EtMeHCSnMe_2Br \xrightarrow{AlkMgBr} AlkMe_2SnCHEtMe$$

$$Ar_2SnMe_2 \xrightarrow[MeOH]{Br_2} ArSnMe_2Br \xrightarrow{MeYCHMgCl} ArSnMe_2CHYMe$$

$$PhMe_2SnCHYMe \xrightarrow{Cr_2(CO)_9} (OC)_3Cr\ PhMe_2SnCHYMe$$

Tetramethyl- and -ethylstannanes react with lead tetraacetate under mild conditions to form the trialkyltin acetate, lead(II) acetate, and alkyl acetate, via the unstable alkyllead triacetate [73].

$$R_4Sn + Pb(OAc)_4 \xrightarrow[benzene]{20^\circ} \left[RPb(OAc)_3\right] + R_3SnOAc$$

$$\left[RPb(OAc)_3\right] \rightarrow AcOR + Pb(OAc)$$

Pereyre has studied the stereochemistry of the addition of cis/trans mixtures of tributylcrotyltin to aldehydes.

$$Bu_3SnCH_2.CH{=}CHMe + RCH{=}O \longrightarrow RCH(OSnBu_3).CH(Me).CH{=}CH_2 \xrightarrow{CH_2(COOH)_2} RCH(OH).CH(Me).CH{=}CH_2$$

The addition is stereospecific, the trans isomer giving rise to the threo alcohol and the cis isomer to the erythro alcohol [74].

Several stannylcarboranes have been synthesised. The lithium derivatives of 1-phenyl-1,6- or 1,10-dicarbaclovodecaboranes react with

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dimethyltin dichloride forming $Me_2Sn(CB_8H_8CPh)_2$ [235]. Mironov has synthesised stannyl-substituted carboranes by the protolysis of stannylamines by o-, m-, and p-carboranes at elevated temperatures [236,237].

$$HCB_{10}H_{10}CH + R_3SnNEt_2 \longrightarrow R_3SnCB_{10}H_{10}CH + R_3SnCB_{10}H_{10}SnR_3 + Et_2NH$$

R = Me, Et, Bu

Temperatures of 90–100° are needed for the formation of the monostannyl derivatives, but more vigorous conditions are required (160–180°) for the introduction of two stannyl groups. Substituted carboranes also react similarly:

$$H_2C{=}CR'CB_{10}H_{10}CH + Et_3SnNEt_2 \longrightarrow Et_3SnCB_{10}H_{10}CR'C{=}CH_2 + Et_2NH$$

1-Vinyl-o-carborane gives a dicarboranyl-tin derivative with $Et_2Sn(NEt_2)_2$, but o- and m-carboranes yield low molecular weight polymers [237]:

$$Et_2Sn(NEt_2)_2 + HCB_{10}H_{10}CCH{=}CH_2 \longrightarrow Et_2Sn(CB_{10}H_{10}CCH{=}CH_2)_2$$

$$Et_2Sn(NEt_2)_2 + HCB_{10}H_{10}CH \longrightarrow \left[CB_{10}H_{10}CSnEt_2\right]_n \quad n \leqslant 7$$

3. Hydrides

Lead tetraacetate acylates di- and trialkyltin hydrides in benzene [73]:

$$Et_3SnH + Pb(OAc)_4 \xrightarrow{20^\circ} Et_3SnOAc + HOAc + Pb(OAc)_2$$
91% 97%

$$2Et_3SnH + Pb(OAc)_4 \xrightarrow{50^\circ} 2Et_3SnOAc + H_2 + Pb(OAc)_2$$
99% 98% 98%

$$Et_2SnH_2 + Pb(OAc)_4 \xrightarrow{25^\circ} Et_2Sn(OAc)_2 + H_2 + Pb(OAc)_2$$
86% 94% 95%

$$2Ph_2SnH_2 + Pb(OAc)_4 \xrightarrow{25^\circ} Ph_2(AcO)Sn\text{-}Sn(OAc)Ph_2 + 2H_2 + Pb(OAc)_2$$

40% 85% 92%

Tributyltin hydride adds to arenesulphonylisocyanates at room temperature to give the arenesulphonamide derivatives XV. At ca. 60° these adducts are in equilibrium with the isomeric species XVI [75]:

$$Bu_3SnH + ArSO_2NCO \longrightarrow Bu_3SnO.CH{:}N.SO_2Ar \underset{}{\overset{60^\circ}{\rightleftharpoons}} ArSO_2N(SnBu_3)CHO$$

XV XVI

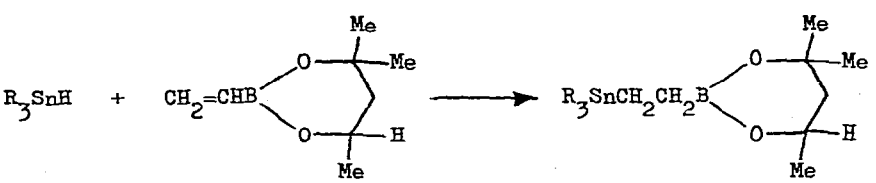
Ar = Ph, p-MeC_6H_4, p-$MeOC_6H_4$, p-ClC_6H_4

Arene sulphonylazides evolve nitrogen upon treatment with di- and tributyltin hydrides in benzene [76]:

$$Bu_3SnH + ArSO_2N_3 \longrightarrow Bu_3Sn.NH.SO_2Ar + N_2.$$

$$Bu_2SnH_2 + 2p\text{-}MeC_6H_4SO_2N_3 \longrightarrow Bu_2Sn(NHSO_2C_6H_4Me)_2 + 2N_2$$

The hydrostannation of 2-vinyl-4,4,6-trimethyl-1,3,2-dioxaborinane by trialkyltin hydrides gives only β-stannylated products. The rates of addition are accelerated by the addition of ABIBN, retarded by galvinoxyl, and unaffected by changes in solvent polarity, confirming the operation of a free-radical mechanism [77].



R = Me, Et, Pr, Bu, Ph

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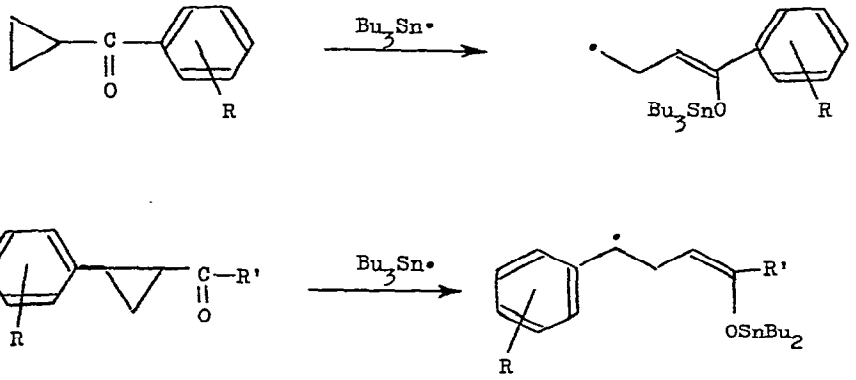
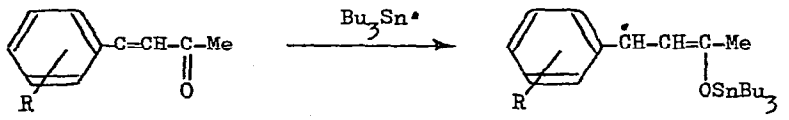
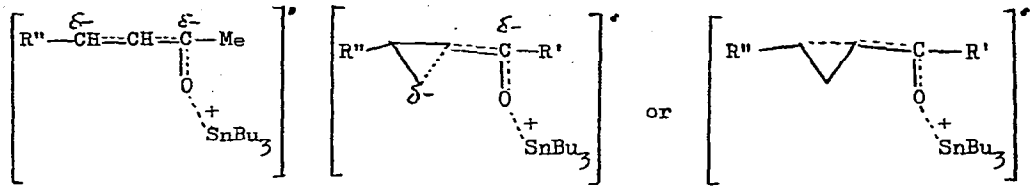
The rate of hydroxtannation of styrene has been studied using infra-red spectroscopy. At 30° the relative rates of reaction followed the order $Ph_2SnH_2 > EtPhSnH_2 > Bu_2SnH_2$ [78]. Tricyclohexyl-2-(2-pyridyl)ethyltin is obtained by the hydrostannation of 2-vinylpyridine [24]. Triphenyltin hydride adds to ferrocenylacetylene (FcC≡CH) to yield $FcCH{=}CHSnPh_3$. $Ph_3SnCFc{=}CH_2$ was obtained by the substitution of $FcCCl{=}CH_2$ by Ph_3SnLi in THF/Et_2O [79]. Organotinacetals, $Et_3SnCH{=}CHXOCHMeOBu$ (X = CH_2, CH_2CH_2, CHMe, CMe_2), have been synthesised by heating triethyltin hydride and the corresponding acetylene [80]. The addition of tributyltin hydride to substituted ben aldehydes, XC_6H_4CHO, may take place by a free-radical or a polar mechanism depending on the conditions used to give the adducts $XC_6H_4CH_2OSnBu$. The relative rates correlate with the Hammett σ and σ^+ constants for X, the polar mechanism being best correlated by σ and the free-radical addition best by σ^+ [81]. The reactivity of tributyltin hydride with two series of aromatic substituted α-cyclopropylketones, 2-phenylacetylcyclopropanes, and benzoylcyclopropanes under radical conditions has been studied [82]. In all cases cyclopropyl-ring opening occurs:



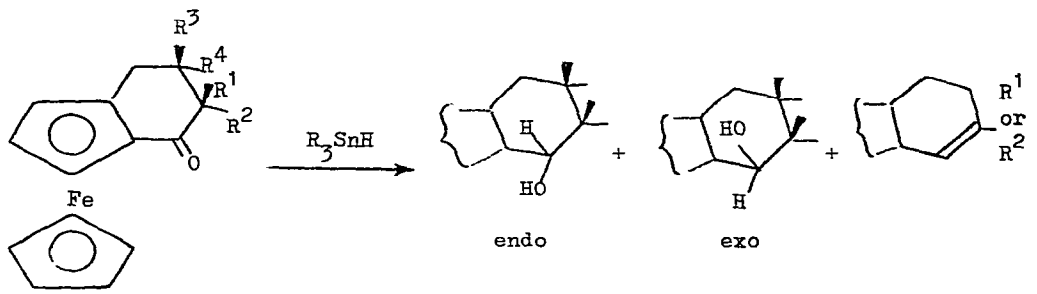
Electron-withdrawing substituents increase the rate of reaction. Similar results are obtained with aromatic-substitued benzalacetones:



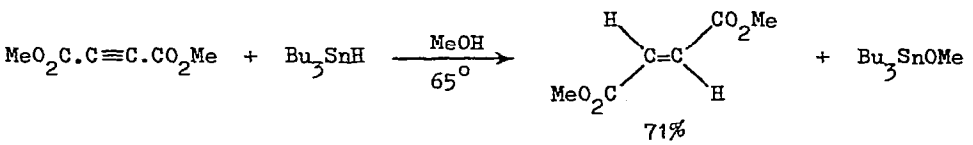
This polar effect on the radical addition may be rationalised by the effective charge delocalisation which is possible in both cases, viz.

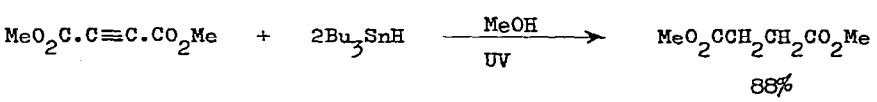


The stereochemistry of the reduction of ferrocenylcyclohexanones by triphenyl- and tributyltin hydride in the absence of solvent has been investigated. The product composition depends on the nature and position of the substituents R^1-R^4 and the presence or otherwise of free-radical initiators.



With a radical initiator, the product mixture usually consists of 70% endo and 30% exo ferrocenyl alcohols. Ionic reduction produces only small amounts of the endo alcohol (10-40%) and the olefin product (<10%), and no exo isomer [83]. Pereyre has studied the tributyltin hydride reduction of α-acetylenic esters and nitriles in methanol in detail [84]. The reactions may be summarised as follows:





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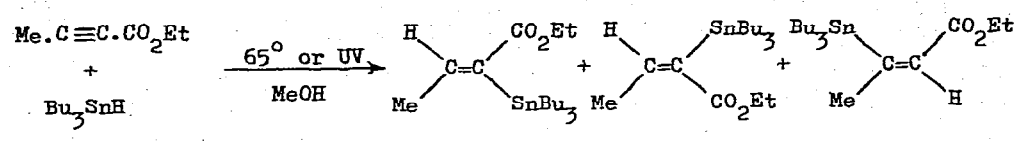
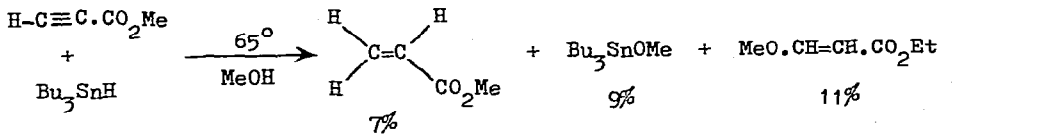
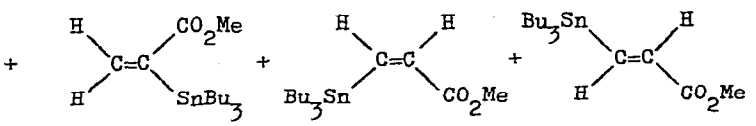
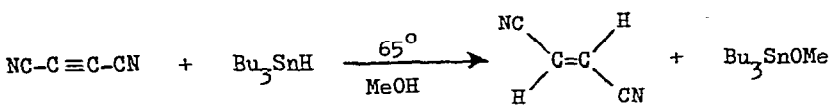


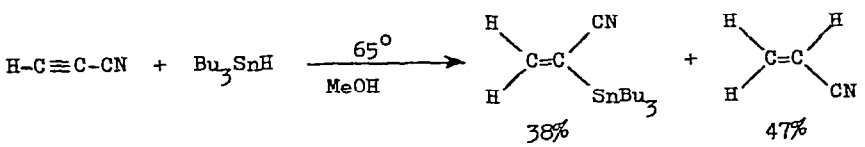




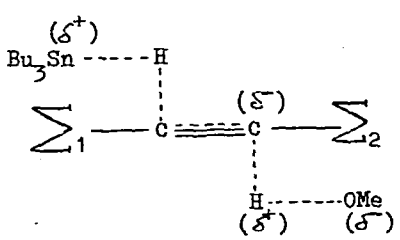
+ $Bu_3SnCH_2CH_2CO_2Me$

6%





The ester products cannot be interpreted on the basis of an intermediate hydrostannation adduct or reduction by nascent hydrogen. Instead, the transition state

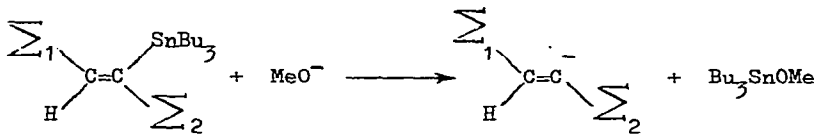


involving solvent participation is preferred, which also rationalises the formation of trans isomers. Ethyl tetrolate gives only hydrostannation products, which did not decompose even after prolonged reflux in ethanol. The reaction with methyl propiolate affords small quantities of $MeO.CH{=}CHCO_2Et$, $Bu_3Sn.C{\equiv}C.CO_2Me$, and $Bu_3SnCH_2CH_2CO_2Me$. The former arises from tributyltin methoxide-catalysed addition of methanol to methyl propiolate, whilst the formation of the two latter products arise from the reactions

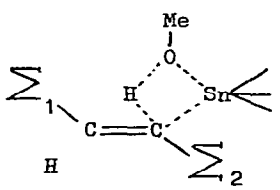
$$Bu_3SnOMe + H.C{\equiv}C.CO_2Me \longrightarrow Bu_3Sn.C{\equiv}C.CO_2Me$$

$$Bu_3SnCH{=}CH.CO_2Me \xrightarrow{Bu_3SnH} [Bu_3Sn.CH_2.CH(SnBu_3).CO_2Me] \xrightarrow{MeOH} Bu_3SnCH_2CH_2CO_2Me$$

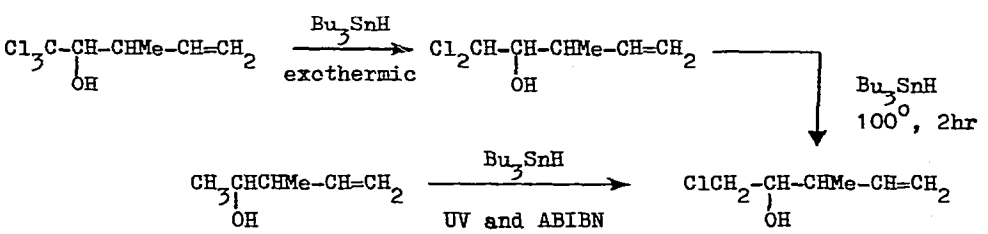
The nitrile reductions proceed via initial hydrostannation of the C≡C triple bond, followed by Sn-C bond cleavage, either by nucleophilic attack of MeO^- (or MeOH) on tin:



or by a concerted mechanism involving a four-centre transition state with solvent participation:



Tributyltin hydride selectively reduces the chlorine function of unsaturated chlorinated alcohols [74]:



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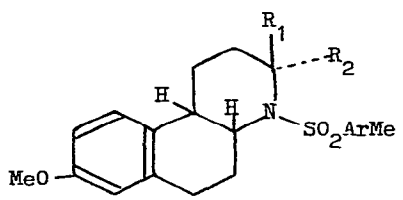
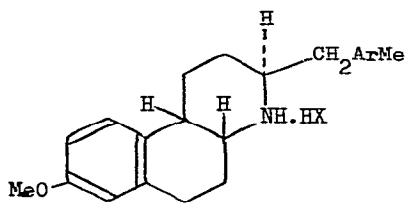
The reduction of 7-halonorcaranes by tributyltin hydride under free-radical conditions gives predominantly the endo-substituted isomer (> 90%), due presumably to the greater steric repulsion in the hydrogen transfer from the tin hydride to the endo side of the radical than to the exo side [86]. Chlorodeoxysugars may be reduced to deoxy sugars under similar conditions [87]. Cyclisation accompanies the radical reduction of $CH_2=CH(CH_2)_3COCl$ producing cyclohexanone (36%). Similarly $Me_2C=CH(CH_2)_2CHMeCH_2COCl$ gives menthone (43%), and $Me_2CH(CH_2)_2CH=Me_2$ (27%) via the decarbonylation of the intermediate acyl radical [87]. The reduction of the dichloromethyl derivative XVII (R_1 = H; R_2 = $CHCl_2$) by Bu_3SnH yields the monochloroderivative XVII (R_1 = H; R_2= CH_2Cl), which could be reduced further in refluxing anisole to XVII (R_1 = H; R_2 = Me). However, the chloromethyl derivative

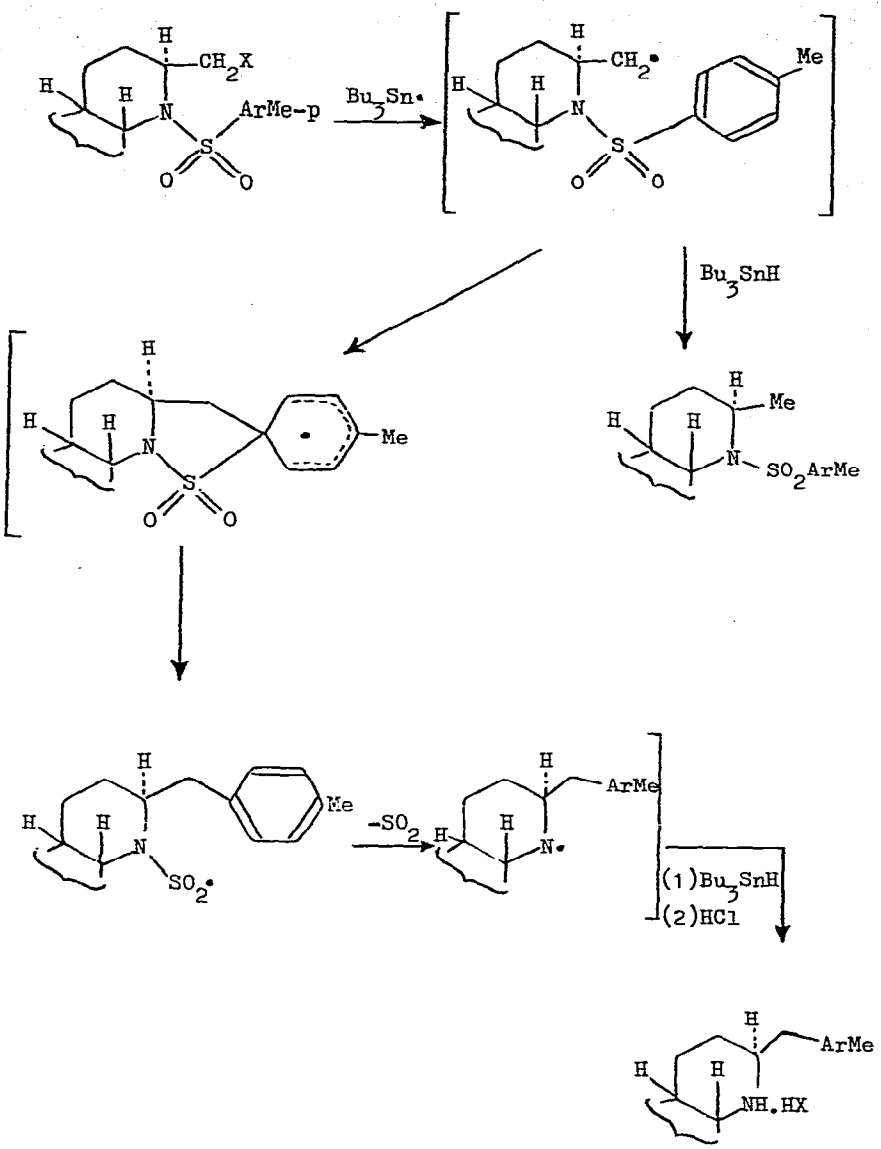


XVII

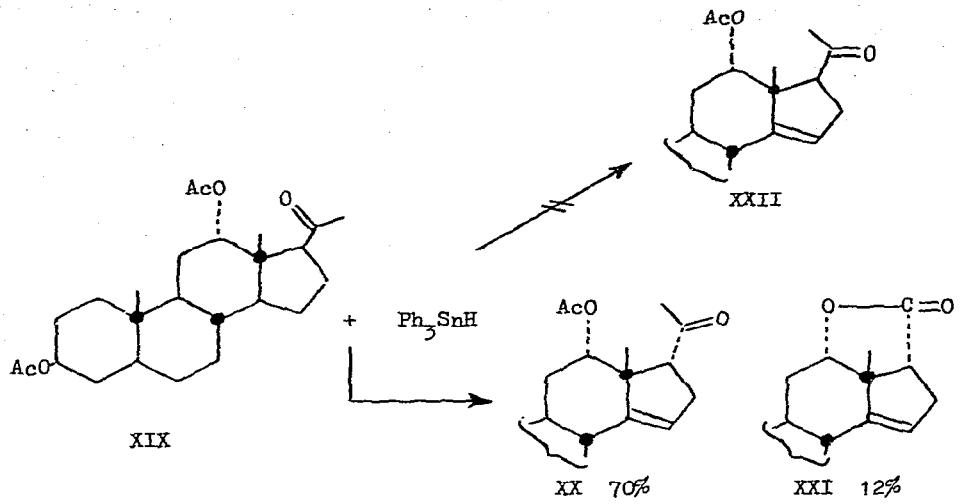


XVIII

XVII (R_1 = CH_2Cl; R_2 = H), under identical conditions, afforded a 50% yield of XVIII (X = Cl) instead of the expected product XVII (R_1 = Me; R_2 = H). A nearly quantitative yield of XVIII (X = Br) was similarly obtained from XVII (R_1 = CH_2Br; R_2 = H). When the reactions were carried out with pure Bu_3SnH, 30% yields of the rearranged products were obtained. These results can be rationalised in terms of the scheme [88]:



Triphenyltin hydride reduction of XIX similarly produced the unexpected products XX and XXI rather than XXII [89]:



4. Halides

Several patents refer to the direct synthesis of alkyltin halides. Thus, tin metal and butyl chloride heated for 14hr at 180° in the presence of hexamethylphosphoramide and iodine resulted in 93% tin conversion to Bu_2SnCl_2 (20%), Bu_3SnCl (21.5%), and a hexamethylphosphoramide complex of Bu_2SnCl_2 (48%) [89]. Powdered tin and octyl chloride with a catalyst formed in situ from octylamine, octanol, boric acid, iodine and red phosphorus heated for 4hr at 155° gave 94% tin conversion to $OctylSnCl_3$ (34%), $Octyl_2SnCl_2$ (47%), and $Octyl_3SnCl$ (12%) [90]. A 99% tin conversion was obtained using compounds possessing an oxirane ring as catalyst. Heating tin and butyl iodide with glycidyl acrylate at 160° for 3hr gave 87% of Bu_2SnI_2 [91]. Mono- and dibutyl- and -octyltin chlorides and bromides are obtained by heating tin, alkyl halide, alkyl iodide, and tributyl antimony under pressure [92]. The use of antimonites or arsenites with iodine gave 14-46% yields of $Octyl_2SnBr_2$ [93]. Similar yields (15-57%) of dibutyl- and -octyltin dichlorides and dibromides are obtained using titanium tetraalkoxides and iodine [94]. Chloromethylsilanes react with metallic tin at temperatures of 150-200° with tin(IV) iodide and triethylamine or piperidine as catalysts to give 50-70% yields of bis(silylmethyl)tin dichlorides, together with small (~5%) yields of mono- and trialkyltin products [95].

$$Cl_nMe_{3-n}SiCH_2Cl + Sn \longrightarrow (Cl_nMe_{3-n}SiCH_2)_2SnCl_2 +$$
$$(Cl_nMe_{3-n}SiCH_2)_3SnCl + Cl_nMe_{3-n}SiCH_2SnCl_3$$

Methyltin trihalides may be obtained in ca, 90% by the exchange reaction [96]:

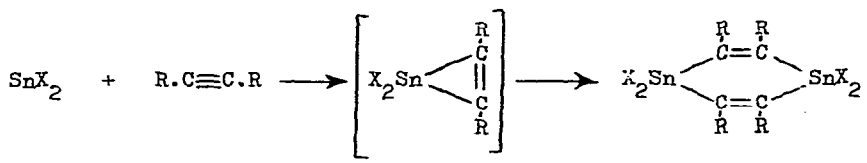
$$Me_2SnBu_2 + 2SnX_4 \longrightarrow 2MeSnX_3 + Bu_2SnCl_2$$
X = Cl, Br

High yields of the unsymmetrical dialkyltin dichlorides $BuRSnCl_2$ are produced by the analogous reaction:

$$BuSnR_3 + 3BuSnCl_3 \xrightarrow{20\text{-}140^\circ} BuRSnCl_2$$
89-95%

R = Et, allyl, Ph, ∝-thienyl

Under the same conditions $RSnCl_3$ and $RSnBu_3$ gave complex mixtures containing R_2SnCl_2, Bu_2SnRCl, and Bu_2SnCl_2 [97]. Stannous halides react with dimethylacetylene dicarboxylate in refluxing THF to give 1:1 adducts formulated as the 1,1,4,4-tetrahalodistannacyclohexadienyl derivatives XXIII.



R = CO_2Me; X = Cl, Br, I — XXIII

XXIII are thought to be polymeric via intermolecular carbonyl→tin coordination. Consistent with this the derivatives are insoluble in all but the most strongly coordinating solvents such as DMSO and DMF which can break down the coordination [98].

Tetramethyltin is solvolysed in anhydrous HF at 25° producing trimethyltin fluoride. When the reaction is carried out at 130°, substantial amounts of the difluoride are formed.

$$Me_4Sn + HF \xrightarrow{25^\circ} Me_3SnF + CH_4$$
$$\xrightarrow{130^\circ} Me_2SnF_2 + 2CH_4$$

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The solvolysis of methyltin chlorides at 25° results in the cleavage of one Sn-Cl bond Me_3SnF and the novel mixed chlorofluorides Me_2SnFCl and $MeSnFCl_2$.

$$Me_nSnCl_{4-n} \xrightarrow[25^\circ]{HF} Me_nSnFCl_{3-n} + HCl \qquad n = 1 - 3$$

Higher temperatures cause further Sn-Cl or Sn-C bond fission:

$$Me_3SnCl \xrightarrow{HF;\ 130^\circ} Me_2SnF_2 + HCl + CH_4$$

$$Me_2SnCl_2 \xrightarrow{HF;\ 130^\circ} Me_2SnF_2 + HCl$$

$$MeSnCl_3 \xrightarrow{HF;\ 130^\circ} MeSnF_3 + HCl$$

The conversion of $MeSnCl_3$ to the fluoride in this way is synthetically useful, however the conversion of di- and trialkyltin chlorides to the corresponding fluorides is more conveniently accomplished using aqueous rather than anhydrous HF [98a].

The structure of chloromethyltin trichloride, determined by electron diffraction in the gas phase, consists of a distorted tetrahedral arrangement of groups about tin ($\angle ClSnCl = 105^\circ$; $\angle CSnCl = 113^\circ$) (Fig. 3). The bond distances are of normal length (Sn-C = 2.23Å; Sn-Cl = 2.34Å), but there appears to be restricted rotation about the Sn-C bond [99].

Trimethyltin and triethyltin chloride solvent interactions have been studied through $^1H - \{^{119}Sn\}$ heteronuclear double resonance. The solvents studied fall into three categories: (i) 'neutral' solvents such as carbon tetrachloride and methylene chloride, which do not significantly

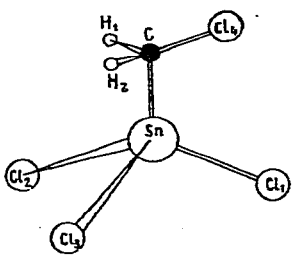

Fig. 3 The structure of chloromethyltin trichloride [99]. (Reproduced by permission of the Consultants Bureau, New York).

affect the ^{119}Sn chemical shifts; (ii) polar solvents, such as acetone, acetonitrile, dioxane, which form complexes; and (ii) alcohols (methanol, ethanol) which probably cause ionisation of the solute. Molar enthalpies of complex formation were estimated to be 4 - 5 kcal/mole for the trimethyltin chloride complexes and 3 kcal/mole for the triethyltin chloride complexes [100].

The crystal structure of the trimethyltin chloride complex of the phosphorus ylide triphenylphosphine-acetylmethylene shows that the ylide residue is bonded to tin via the carbonyl oxygen atom rather than the ylidic carbon atom (Fig. 4). Coordination about tin is almost perfectly

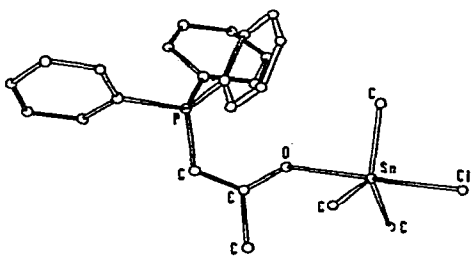

Fig. 4 The structure of $Ph_3PCH.CO.Me\text{-}Me_3SnCl$ [101]. (Reproduced by permission of the Chemical Society).

trigonal bipyramidal with a planar trimethyltin moiety. The Sn-Cl bond distance is longer (2.57Å) than that of the analogous pyridine complex (2.42Å), and the bond distances of the ylide skeleton indicate concentration of electron density away from the phosphorus atom [101]. 4-Picoline forms a similar 1:1 complex with trimethyltin chloride, but 4-aminopyridine forms a 1:2 adduct for which the ionic structure $[Me_3Sn.2(4\text{-aminopyridine})]^+Cl^-$ is proposed. Trimethyltin nitrate forms an analogous complex. Dimethyltin dichloride forms 1:2 adducts with a wide variety of picolines, aminopyridines, and 2-, 3-, and 4-substituted pyridine-N-oxides [102]. Both 1:1 and 1:2 adducts of dimethyltin and diphenyltin dichloride are formed with oxygen donor molecules of the general type R_nEO (E = C, N, P, S). The 1:2 adducts have octahedrally-coordinated tin atoms with trans-methyl or phenyl groups, and cis chlorines and cis donor molecules, except for the pyridine-N-oxide complex. The 1:1 complexes have trigonal bipyramidal structures in which the two organic groups and a chlorine atoms occupy

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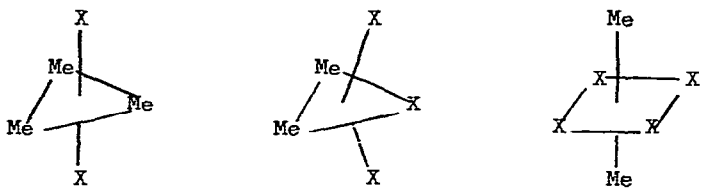
equatorial positions. The pyridine-N-oxide complex is again exceptional with both chlorine atoms occupying the apical positions [103, 103a]. Dipole moments and Molar Kerr constants show that six-coordinate dimethyltin tropolonate exists exclusively as the cis isomer [109a]. Methyltin chlorides, Me_nSnCl_{4-n} (n = 0, 1, 2, 3), form 1:1 complexes with S,S-dimethyldiimide, $Me_2S(NH)_2$ [104]. Infra-red tin-ligand stretching vibrations have been used to assign the geometries of complex organotin anions derived from $R_4N^+Cl^-$ and organotin halides. The $Me_3SnX_2^-$ (X = Cl, Br, I), $Me_2SnX_3^-$ (X = Cl, Br) and $Ph_2SnCl_3^-$, and $Me_2SnX_4^{2-}$ (X = Cl, Br, I) anions were deduced to have structures XXIV (D_{3h}), XXV (C_{2v}), and XXVI (D_{4h}), respectively. The $^2J(Sn^{117,119}-C-^1H)$ coupling constant for methyltin



XXIV XXV XXVI

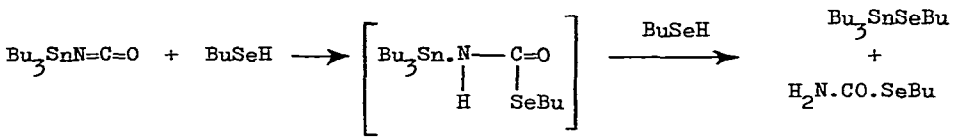
compounds increases as the coordination number at tin increases, consistent with a dominant Fermi contact mechanism. The effect is paralleled by a decrease in the tin-carbon bond distance and an increase in the tin-chlorine bond distance which is expected on the basis of isovalent hybridisation [105]. 2,2,6,6-Tetramethylpiperidine-1-oxo-ammonium chloride $[TMPNO]^+Cl^-$ reacts with dimethyltin dichloride and phenyltin trichloride to give the complexes $[TMPN^+{=}O][Me_2SnCl_3]^-$ and $2[TMPNO^+{=}O][PhSnCl_5]^{2-}$ respectively [106]. Thermogravimetric analysis has been used to study the mode of decomposition of the adducts $R_2SnCl_2.4L$ and $RSnCl_3.4L$ (R = Pr, Ph; L = γ-picoline, morpholine). The picoline adducts pyrolyse to give 1:2 adducts, but the morpholine adduct decomposition is complex [107].

Complex cations are present when ethyltin chloride is dissolved in basic aqueous ethanol. The polycation $[(EtSn)_{10}(OH)_{28}]^+$, present in neutral media, slowly depolymerises on increase of pH. With potentiometry, the cation $[(EtSn)_8(OH)_{23}]^+$, the acid $[(EtSn)_m(OH)_{3m}]$, and the anion $[(EtSn)_3(OH)_{10}]^-$ have been found. The value of m depends on concentration and pH, and in dilute solutions m = 1 and 8. The anion $[EtSn(OH)_4]^-$ is the only species present in 1N NaOH [108]. Dimethyltin dichloride has been studied polarographically in aqueous solution, giving rise to an anodic wave due to chloride anions, and three or four cathodic waves [109].

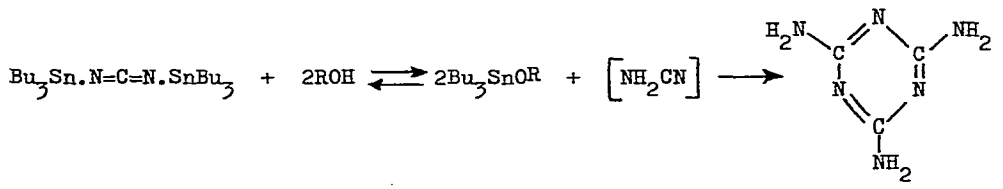
5. Pseudohalides

The structures of some trimethyltin pseudohalides has been the subject of a thesis [110]. In dimethyltin dicyanide, strong N----Sn intermolecular interactions occur giving rise to nearly octahedrally coordinated tin and planar $[Sn(CN)_2]_n$ sheets [111].

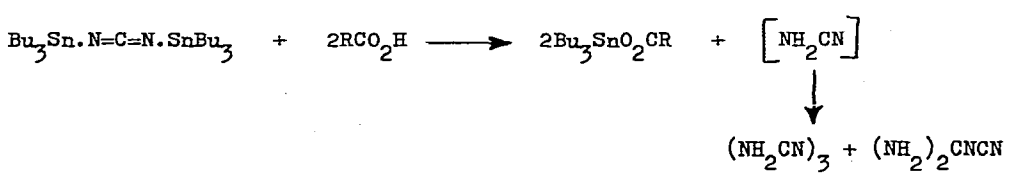
Butaneselenol reacts with tributyltin isocyanate to form tributyltin butylselenide and Se-butyl selenocarbamate. The most probable course of the reaction involves initial addition of the selenol to the isocyanate to form the stannylselenocarbamate, which is then rapidly cleaved by further selenol [112]:



Analogous unstable stannylurea and -carbamate intermediates have been detected by infra-red spectroscopy in the reactions of tributyltin isocyanate with primary or secondary amines and alcohols respectively [113]. The tin-nitrogen bonds of bis(tributylstannyl)carbodiimide are cleaved by a number of reagents. Butyl and methyl alcohols form the corresponding tributyltin alkoxide and cyanamide, which is converted into melamine und the reaction conditions (125-130° for 12hr):



The reaction is reversible, and the carbodiimide is reformed in high yield when the tin alkoxide and cyanamide are mixed at room temperature. Carboxylic acids react under milder conditions (benzoic acid, 80-85° 5hr; acetic acid, room temperature) forming the tributyltin carboxylate, melamine and cyanodiamide [114]:



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Hydrogen chloride at room temperature gives tributyltin chloride and cyanamide dihydrochloride [115]:

$$Bu_3Sn.N{=}C{=}N.SnBu_3 + 4HCl \longrightarrow 2Bu_3SnCl + NH_2CN.2HCl$$

Ethyl and pentyl bromides react with bis(tributyltin)carbodiimide when heated in a sealed ampoule to form the corresponding dialkylcyanamide in ca. 70% yield, rather than the dialkylcarbodiimide. It was postulated that the unsymmetrically substituted intermediate undergoes a carbodiimide → dicyanamide rearrangement [115]:

$$Bu_3Sn.N{=}C{=}N.SnBu_3 + 2RBr \xrightarrow[8hr]{110\text{-}120^{\circ}} \left[Bu_3Sn.N{=}C{=}N.R\right]$$

$$\left[\begin{array}{l} Bu_3Sn \\ \quad\diagdown \\ \quad\quad N{-}C{\equiv}N \\ \quad\diagup \\ \quad R \end{array}\right] \xrightarrow{RBr} 2Bu_3SnBr + R_2N.CN$$

Trityl chloride, however, reacts smoothly in ether at room temperature with bis(triphenylstannyl)carbodiimide to give bistritylcarbodiimide:

$$Ph_3Sn.N{=}C{=}N.SnPh_3 + 2Ph_3CCl \longrightarrow \underset{78\%}{Ph_3SnCl} + \underset{74\%}{Ph_3C.N{=}C{=}N.CPh_3}$$

When the reaction is carried out in a 1:1 molar ratio, the unsymmetrical carbodiimide XXVII is obtained:

$$Ph_3Sn.N{=}C{=}N.SnPh_3 + Ph_3CCl \longrightarrow \underset{\substack{63\% \\ \text{XXVII}}}{Ph_3C.N{=}C{=}N.SnPh_3} + \underset{59\%}{Ph_3SnCl} + \underset{11\%}{Ph_3C.N{=}C{=}N.CPh_3}$$

XXVII reacts further with trityl chloride to afford bistritylcarbodiimide in high yield:

$$Ph_3Sn.N{=}C{=}N.CP_3 + Ph_3CCl \longrightarrow \underset{61\%}{Ph_3SnCl} + \underset{85\%}{Ph_3C.N{=}C{=}N.CPh_3}$$

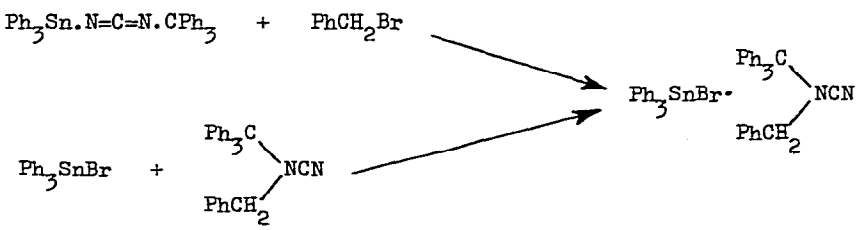
No reaction occurs between bis(triphenylstannyl)carbodiimide and benzyl bromide in ether at room temperature. When the reaction is carried out in refluxing acetonitrile, triphenyltin bromide and its complex with dibenzylcyanamide XXVIII are isolated:

$$Ph_3Sn.N{=}C{=}N.SnPh_3 + PhCH_2Br \longrightarrow \underset{98\%}{Ph_3SnBr} + \underset{\underset{XXVIII}{57\%}}{Ph_3SnBr.(PhCH_2)_2NCN}$$

XXVIII is stable in air and may be recrystallised unchanged from pentane, but recrystallisation from isopropanol results in decomposition to its components, from which it may be synthesised in boiling acetonitrile.

$$Ph_3SnBr + (PhCH_2)_2NCN \underset{\text{refluxing acetonitrile}}{\overset{\text{isopropanol}}{\rightleftharpoons}} XXVIII$$

A similar complex is obtained in low yield ($\sim$ 25%) from (triphenylstannyl)-tritylcarbodiimide and benzyl bromide or triphenyltin bromide and benzyl-tritylcyanamide:



Bis(triphenylstannyl)carbodiimide and ethyl iodide in refluxing acetonitrile gave a 77% yield of triphenyltin iodide, but no complex. No reaction whatsoever occurred with ethyl bromide under the same conditions. The varying modes of reaction are probably due to the differences in steric bulk of the trityl group which prevents two trityl groups occupying the same nitrogen atom. Consistent with this hypothesis, triphenylstannylcyanamide and trityl chloride give rise to carbodiimide products:

$$Ph_3Sn.NH.CN + Ph_3CCl + 2NEt_3 \xrightarrow[\text{benzene}]{26^\circ} \underset{56\%}{NEt_3H^+Cl^-} + \underset{5\%}{Ph_3SnNCNCPh_3} + \underset{38\%}{Ph_3CNCNCPh_3}$$

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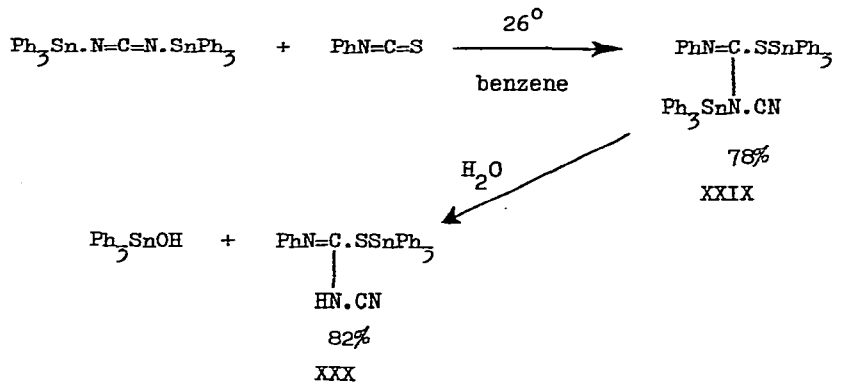
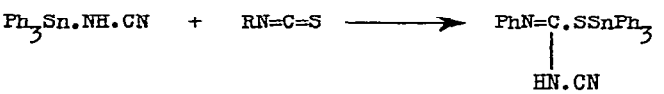
Nmr and infra-red studies indicate that the nitrile nitrogen rather than the amino nitrogen atom is coordinated to the tin in the cyanamide complexes.

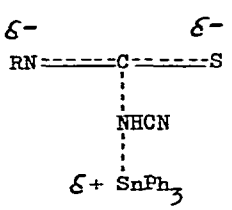
Bis(triphenylstannyl)carbodiimide readily reacts with phenyl isothiocyanate to form the 1:1 addition product XXIX, which may be hydrolysed to give the derivative XXX:



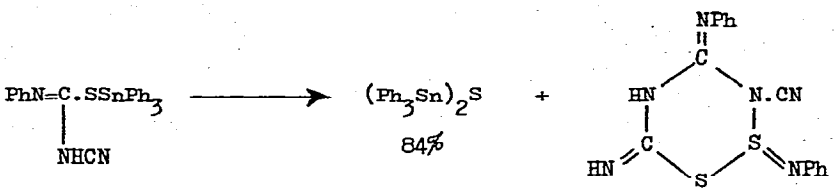
XXX and analogous N-substituted N'-cyano-S-(triphenylstannyl)thioureas can also be prepared from triphenylstannylcyanocyanamide and organic isothiocyanates:



The rates of these reactions vary with the nature of R in the order $p\text{-}O_2NC_6H_4NCS > PhNCS > PhCH_2NCS \sim p\text{-}EtOC_6H_4NCS > EtNCS$, consistent with a mechanism which involves the slow formation of the polar transition state

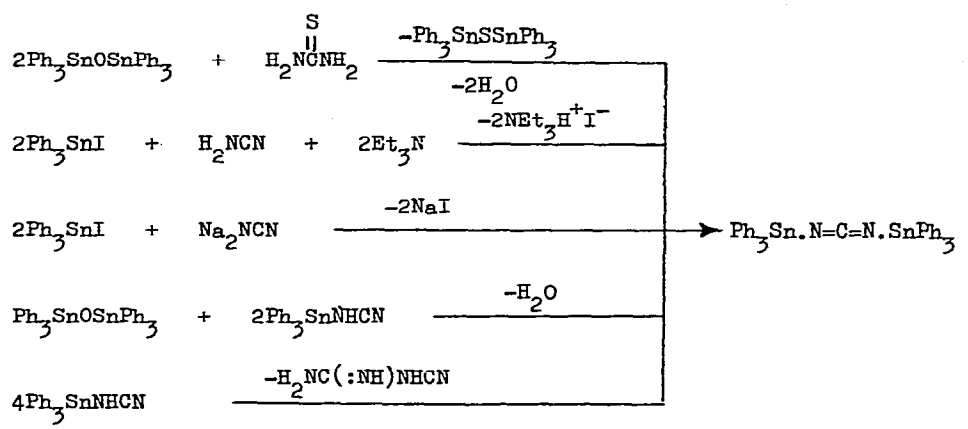


The adduct XXX decomposed in refluxing benzene to give bis(triphenyltin) sulphide and the heterocycle XXXI, which may also be obtained in 24% yield from bis(triphenylstannyl)carbodiimide, cyanamide, and two moles of phenyl isothiocyanate. Similar decomposition of XXIX gives bis(triphenyltin) sulphide (63%) and an unidentified yellow solid [116].

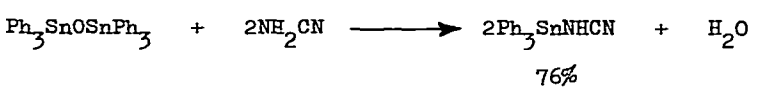


XXXI

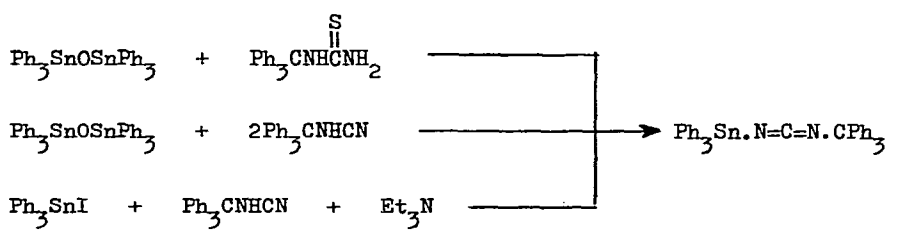
Bis(triphenylstannyl)carbodiimide has been synthesised by several methods:



Triphenylstannylcyanamide is obtained by allowing bis(triphenyl)tin oxide to react with excess cyanamide in refluxing ether:



Trityl(triphenylstannyl)carbodiimide may be obtained by a similar series of reactions:



The reaction of 1,3-disubstituted thioureas with bis(triphenylstannyl)-carbodiimide gives the corresponding N,N'-disubstituted-N"-cyanoguanidine:

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$$Ph_3Sn.N{=}C{=}N.SnPh_3 + RNHC(=S)NHR \longrightarrow Ph_3SnSSnPh_3 + RNHC(=NCN)NHR$$

Thiourea itself gives bis(triphenyltin) sulphide and triphenylstannylcyanamide [117]. Tetrameric dibutyltin carbodiimide may be obtained using the silver salt [118]:

$$Bu_2SnCl_2 + Ag_2NCN \longrightarrow \tfrac{1}{4}[Bu_2SnNCN]_4 + AgCl$$

Novel sulphinylaminotin derivatives have been synthesised by exchange between tin alkoxides and the corresponding sulphinylaminosilanes. The compounds are pale yellow liquids which react with chlorosilanes to regenerate the sulphinylaminosilanes [119];

$$Bu_3SnOMe + Me_3SiNSO \longrightarrow Bu_3SnNSO + Me_3SiOMe$$

$$Me_3SnOEt + Me_3SiNSO \longrightarrow Me_3SnNSO + Me_3SiOEt$$

$$Bu_3SnNSO \xrightarrow{Me_3SiCl} Me_3SiNSO + Bu_2SnCl$$

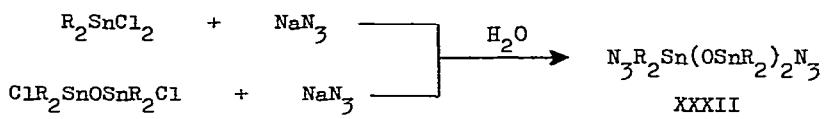
$$Bu_3SnNSO \xrightarrow{Me_2SiCl_2} Me_2Si(NSO)_2 + 2Bu_3SnCl$$

The terdentate ligands, terpyridyl and 8-(2-pyridylmethyleneamino)quinoline (PMAQ), form neutral seven-coordinate complexes with dibutyl- and diphenyltin diisothiocyanates. Infra-red and Mössbauer data indicate a pentagonal bipyramidal arrangement with trans axial C-Sn-C bonds. This has been confirmed by an X-ray diffraction study of $Me_2Sn(NCS)_2$.terpyridyl, for which the C-Sn-C bond angle is 173.7°. The five nitrogen atoms occupy equatorial sites at distances of less than 2.6Å. Appreciable ionisation of the complexes occurs in DMF solution. The use of excess sodium tetraphenylborate in the synthesis of the terpyridyl complexes yields the ionic species $[R_2Sn(NCS).terpyridyl]^+[BPh_4]^-$. The first reported complex of dibutyltin difluoride, with phenanthroline, is precipitated when concentrated DMSO solutions of the reagents are mixed. The infra-red spectrum suggests seven-coordination with fluorine bridging is present in this complex also [120].

6. Oxides, Hydroxides, Peroxides, and Alkoxides

Davies et al. have investigated the trialkyltin hydroxide - bis(trialkyltin)oxide equilibrium by infra-red and Mössbauer spectroscopies. Bis(trialkyltin)oxides react with water at 0-5° to give the corresponding trialkyltin hydroxides. The oxides show a characteristic strong band in the infra-red in the region 740-770 cm^{-1} $\left[\nu_{as}(SnOSn)\right]$, whereas the hydroxides exhibit bands at 3610-3630 cm^{-1} $\left[\nu(OH)\right]$ and 880-920 cm^{-1} $\left[\delta(OH)\right]$. Trimethyl- and triphenyltin hydroxides are stable at room temperature, but triethyl-, tripropyl-, and tributyltin hydroxides are low-melting solids, which are in equilibrium with the corresponding oxides. The Mössbauer spectra of the bis(trialkyltinoxides, which contain four-coordinate tin, have quadrupole splittings of 1.18-1.63 mm/s. In contrast, the hydroxides probably contain chains of oxygen bridged trialkyltin groups with five-coordinate tin. Consistent with this formulation, they exhibit quadrupole splittings 2.78-2.99 mm/s [121]. This type of chain structure is present in the mixed compound $Me_3SnNCO.Me_3SnOH$, in which trimethyltin groups are bridged alternately by nitrogen atoms (from NCO) and oxygen atoms (from OH). The tin-oxygen bond distances are more or less equal (2.14, 2.15Å), but the tin-nitrogen bonds are inequivalent (2.43, 2.75Å). Adjacent chains are interconnected by NCO···HO hydrogen bonding to form a layered structure [122]. Triphenyl- and tri-p-tolyltin hydroxides have been prepared from the organotin bromides and sodium hydroxide in aqueous solution [123]. The addition of 0.2-2% of alkyl acetates effectively stabilises bis(trialkyltin)oxides with respect to precipitate formation on long storage [124].

Dialkyltin dichlorides or tetra-1,3-dichlorodistannoxanes react with sodium azide in the presence of water to give haxealkyl-1,5-diazidotristannoxanes XXXII [125]:



$R_2SnCl_2 + NaN_3$

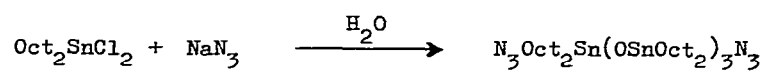
$ClR_2SnOSnR_2Cl + NaN_3$

$\xrightarrow{H_2O}$ $N_3R_2Sn(OSnR_2)_2N_3$

XXXII

R = Me, Et, Pr, Bu

Dioctyltin dichloride yields the octaoctyl-1,7-diazidotetrastannoxane XXXIII:

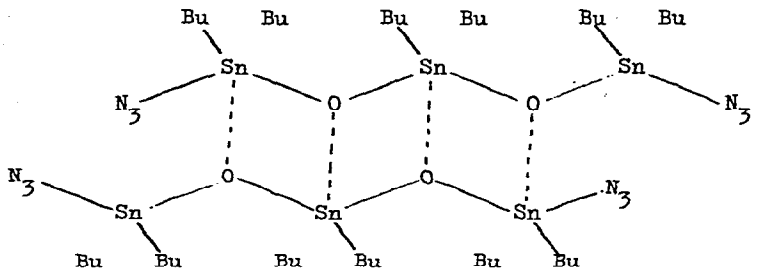


$Oct_2SnCl_2 + NaN_3 \xrightarrow{H_2O} N_3Oct_2Sn(OSnOct_2)_3N_3$

XXXIII

References p. 140

Preliminary X-ray data for the butyl derivative indicate a centrosymmetric dimeric tristannoxane structure XXXIV, similar to those already characterised for the 1,3-disubstituted distannoxanes.



XXXIV

When treated with refluxing methanol XXXII (R = Me) gives the azide methoxide XXXV:

$$N_3Me_2Sn(OSnMe_2)_2N_3 \xrightarrow[\text{methanol}]{\text{refluxing}} N_3Me_2Sn(OSnMe_2)_2OMe$$

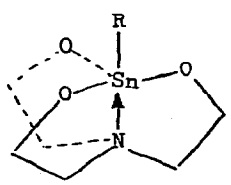
XXXV

Mössbauer data for the organostannonic acids $RSn(O)OH_n$ (R = Me, Et, Bu, C_8H_{17}, Ph) indicate the presence of four coordinate tin in these compounds, but five coordination cannot be excluded. Alkyltin trichlorides react with the sodium derivative of triethanolamine to give organostannatranes XXXVI, which may also be obtained by the azeotropic dehydration of the organostannonic acid and triethanolamine in boiling toluene.

$$RSnCl_3 + (NaOCH_2CH_2)_3N \longrightarrow RSn(OCH_2CH_2)_3N \longleftarrow RSn(O)OH + (HOCH_2CH_2)_3N$$

XXXVI

Mössbauer data suggest that phenylstannatrane is probably tetrahedral, but significant intramolecular N→Sn interaction occurs in the alkylstannatranes as in XXXVII [126].



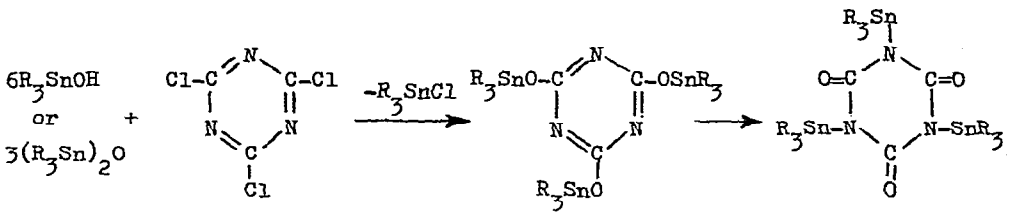
XXXVII

Bis(trialkyltin)oxides and dialkyltin oxides are readily converted into the corresponding chlorides in quantitative yield by thionyl chloride [127]:

$$R_3SnOSnR_3 + SOCl_2 \longrightarrow 2R_3SnCl + SO_2$$

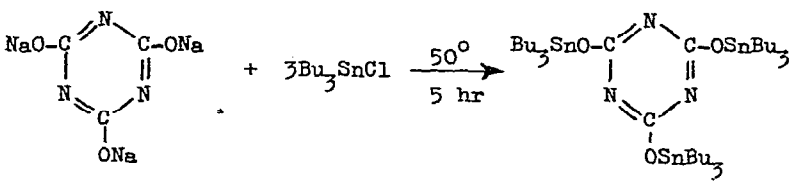
$$R_2SnO + SOCl_2 \longrightarrow 2R_2SnCl_2 + SO_2$$

Heating methyl tripropylstannylacetate with bis(triethyltin)oxides at 115° affords triethyltin tripropylstannylacetate [43]. Triethyltin hydroxide, tribenzyltin hydroxide, and bis(tributyltin)oxide react with cyanuric choride in boiling toluene to give the tris(trialkylstannyl)isocyanurate XXXVIII, via the thermal isomerisation of the expected tris-stannylcyanurate XXXIX:



XXXIX XXXVIII

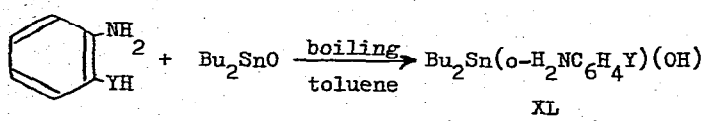
Such a rearrangement has been observed for tris(tributylstannyl)isocyanurate, prepared independetly under mild conditions from sodium cyanurate and tributyltin chloride [128] :

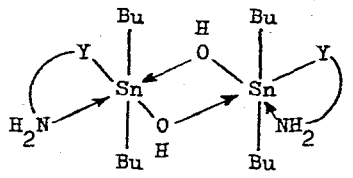


XXXVIII

(R = Bu)

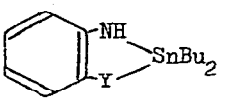
When 1:1 molar ratios of dibutyltin oxide and aminophenol, o-phenylenediamine, or o-aminophenol are heated in boiling toluene, no water is liberated, and the derivatives XL are formed, for which the octahedral binuclear bridged structures XLI are postulated. These compounds may be dehydrated





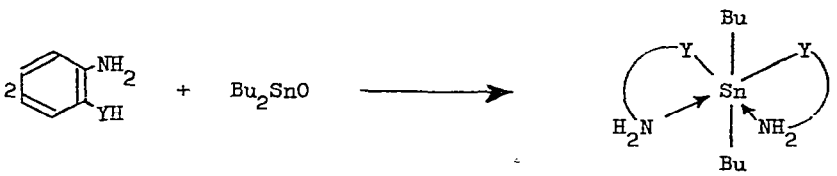
XLI

reduced pressure



XLII

by heating under reduced pressure giving rise to the derivatives XLII. When the reactions are carried out using a 1:2 ration of reactants, water is liberated and the bis substituted compounds XLIII are formed [129].



XLIII

A patent describes the reaction of dialkyltin oxides with zinc chloride and butyl β -mercaptopropionate in the presence of water and sodium bicarbonate to give the compounds $[(BuO_2CCH_2CH_2S)R_2SnO]_2Zn$ [130].

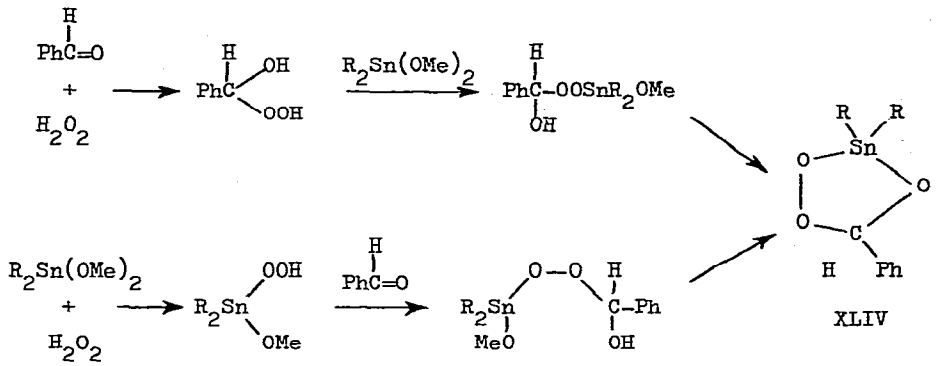
Tert-butylperoxytin derivatives are formed by the protolysis of organotin alkoxides or amines [131a] , eg.

$$Et_3SnNEt_2 + {}^tBuOOH \longrightarrow Et_3SnOO{}^tBu + Et_2NH$$

$$(CH_2{=}CH)Me_2SnOMe + {}^tBuOOH \longrightarrow (CH_2{=}CH)Me_2SnOO{}^tBu + MeOH$$

Triphenyltin hydroperoxide decomposes at 10-40° in benzene, toluene, dioxane and acetonitrile to give diphenyltin oxide, triphenyltin hydroxide, phenol and oxygen [132]. Dialkyltin dimethoxides yields insoluble (probably

polymeric) peroxides when treated with 98% hydrogen peroxide. In the presence of an aldehyde or ketone, peroxides of general formula $\left[-O-CR'R''-O_2-SnR_2-\right]_n$ are obtained. These materials are predominantly simple monomeric heterocycles XLIV, but higher cyclic or linear oligomers may be present. Two possible pathways are envisaged:



Neat dibutyltin benzaldehyde peroxide decomposes thermally in a sealed tube by first-order kinetics:

$$Bu_2SnO_3CHPh \xrightarrow[(2)\ HCl]{(1)\ heat} Bu_2SnCl_2 + O_2 + PhCH{=}O + PhCOOH$$

1.0 0.84 0.31 0.29 0.35

The activation energy for the decomposition is 23 kcal/mole, and 18 kcal/mole for the valeraldehyde analogue [133]. Trimethyltin and aryldimethyltin alkoxides have been synthesised by ligand exchange reactions with tributyltin alkoxides, viz.

$$Me_3SnBr + Bu_3SnOR \longrightarrow Me_3SnOR + Bu_3SnBr$$

R = Me, Et, iso-Pr, tert-Bu

$$p\text{-}RC_6H_4SnMe_2Br + Bu_3SnOMe \longrightarrow p\text{-}RC_6H_4SnMe_2OMe + Bu_3SnBr$$

Polymeric dialkyltin dialkoxides $\left[R_2Sn-OR'-O\right]_n$ are obtained from dialkyltin dichloride and the sodium alkoxide or using interfacial techniques [135,136]. Dialkyltin catecholates and catechol sulphonates are isolated by potentio-

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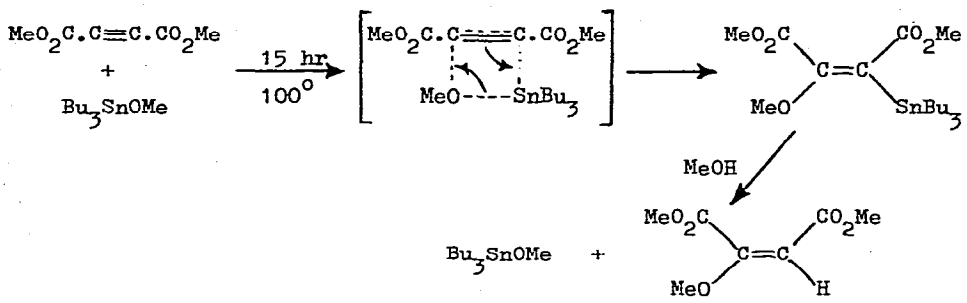
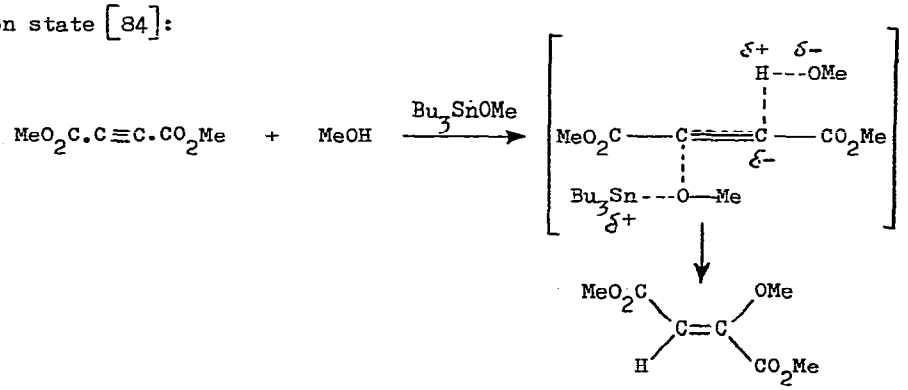
metric titration of mixtures of dialkyltin dichloride and catechol or disodium catechol disulphonate [137,138].

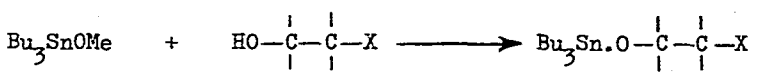
Tributyltin methoxide adds to the triple bond of dimethylacetylene dicarboxylate to give the cis addition product, which may be cleaved



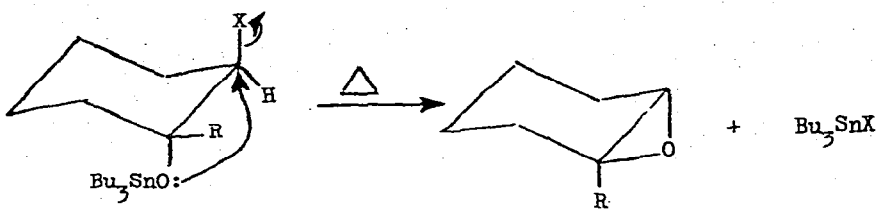
by methanol with retention of configuration. The tributyltin methoxide - catalysed addition of methanol to the acetylene dicarboxylate, however, results in the formation of the trans isomer via a solvent-assisted transition state [84]:



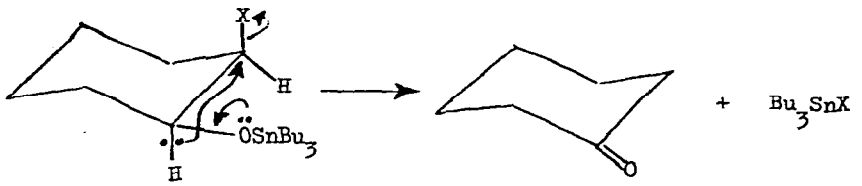
Cyclic and acyclic halohydrins readily displace methanol from tributyltin methoxide to form β-halosubstituted tributyltin alkoxides,



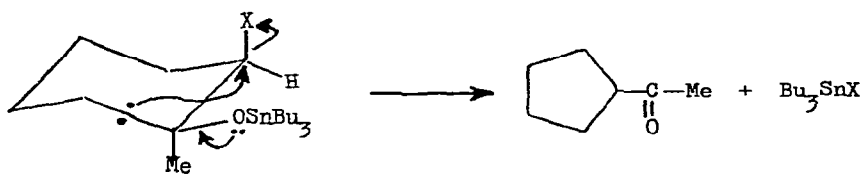
the thermal decomposition of which has been studied in detail [139,140]. Trans cyclohexyl and cyclopentyl derivatives afford excellent yields of the corresponding epoxides, via nucleophilic attack of the oxygen atom at the carbon atom bonded to the halogen, viz.



In contrast, the analogous cis isomers decompose following first-order kinetics affording cyclic ketones. In this case a mechanism involving a 1,2 hydride migration:

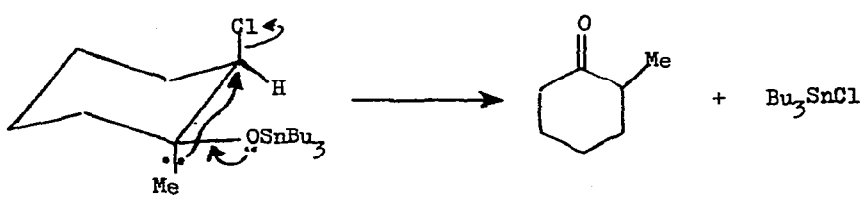


The cis derivatives XLV (X = Cl, Br) undergoes a ring contraction to give cyclopentylmethyl ketone:



XLV

The chlorine derivative also forms methylcyclohexanone by a methyl group migration, presumably due to the higher reaction temperature used.



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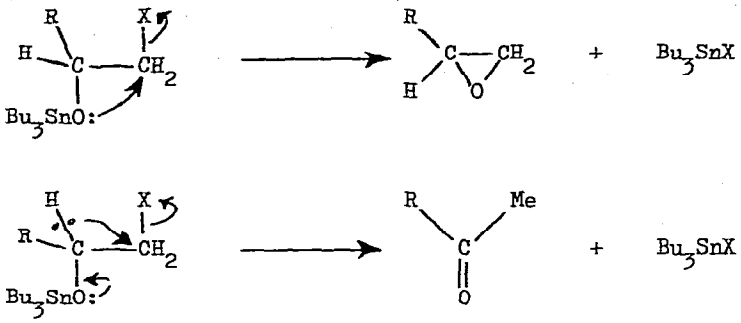
Acyclic 2-haloalkoxytin compounds decompose to give high yields of epoxide, but also appreciable quantities of ketone:



Lithium amides cleave tin-oxygen bonds forming moderate yields of aminostannanes [141]:

$$Bu_3SnOBu + LiNEt_2 \longrightarrow Bu_3SnNEt_2 \quad 38\%$$

$$Bu_3SnOPh + LiNEt_2 \longrightarrow Bu_3SnNEt_2 \quad 78\%$$

$$Bu_2Sn(OPh)_2 + 2LiNEt_2 \longrightarrow Bu_2Sn(NEt_2)_2 \quad 50\%$$

$$Me_3SiOSnBu_3 + LiNEt_2 \longrightarrow Bu_3SnNEt_2 \quad 56\%$$

Triorganotin hydroxylamines are conveniently obtained in high yield by the azeotropic dehydration of the hydroxylamine and the organotin oxide or hydroxide.

$$\begin{matrix} R_3SnOH \\ \text{or} \\ R_3SnOSnPh_3 \end{matrix} + HONR'R'' \longrightarrow R_3SnONR'R'' + H_2O$$

Trimethylstannyl-N,N-diethylhydroxylamine is a monomeric oil which readily reverts to the protic precursors in air. N-Acyl substituted derivatives,

however, very stable in air, and strong intramolecular coordination of the carbonyl oxygen atom to tin is postulated, giving rise to a cis-R_3SnX_2 configuration at tin [142]. An X-ray diffraction has confirmed this type of structure for triphenylstannyl-N-phenyl-N-benzoylhydroxylamine, the first such identified. The structure (Fig. 5) consists of a distorted

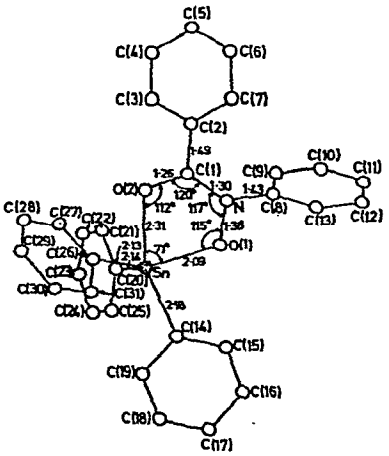
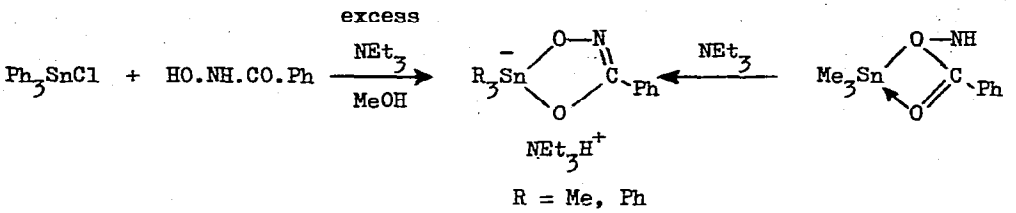


Fig. 5 The structure of $Ph_3Sn.O.NPh.CO.Ph$ [143]. (Reproduced by permission of the Chemical Society).

trigonal bipyramidal arrangement of groups about tin, with two phenyl groups occupying equatorial sites (Sn-C = 2.14, 2.15Å) and the third an axial site at a longer distance (2.18Å). The acylhydroxylamine residue chelates the tin atom via the remaining equatorial site (Sn-O = 2.09Å) and axial (Sn-O = 2.31Å) sites [143]. The tripropyltin analogue slowly disproportionates to give the dipropyltin derivative, whilst attempts to prepare triphenyltin-N-benzoyl- and trimethylstannyl-N-acetyl-hydroxylamine resulted in the formation of tetraorganotin and/or the corresponding di-organotin compound.

$$R_3SnOH + HONR'.CO.R'' \longrightarrow R_3Sn.O.NR'.CO.R'' \longrightarrow R_4Sn + R_2Sn\left[O.NR'.CO.R''\right]_2$$

Anionic species may also be prepared. In this way triphenyltin-N-benzoyl-hydroxylamine may be stabilised [142]:



Organotin nitrosodicyanamide derivatives have been synthesised via the silver salt [144]:

$$R_nSnCl_{4-n} + (4-n)AgNOC(CN)_2 \longrightarrow R_nSn[ONC(CN)_2]_{4-n} + (4-n)AgCl$$

R = Bu, Ph; n = 1, 2

The Schiff base derivative N,N'-ethylenebis(salicylideneiminato) - dimethyltin possesses a distorted octahedral arrangement of groups about tin (Fig. 6). The two methyl groups are mutually trans (Sn-C = 2.07, 2.16Å), and the equatorial coordination atoms are nearly coplanar (Sn-O = 2.19-2.25Å; Sn-N = 2.24-2.27Å) [145].

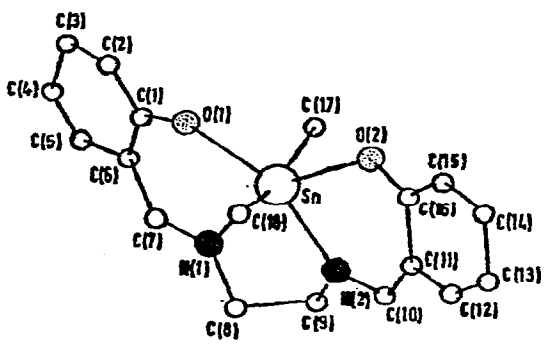
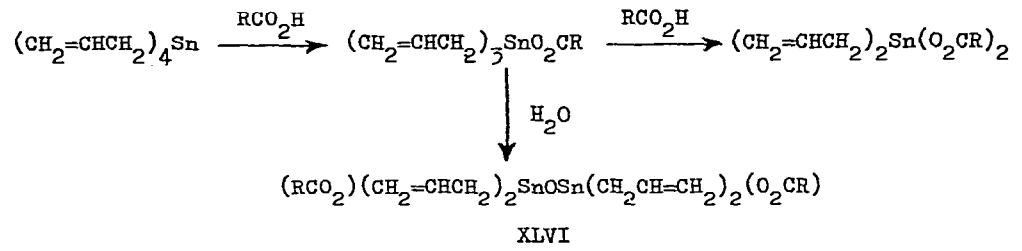


Fig. 6 The structure of N,N'-ethylenebis(salicylideneiminato)dimethyltin [145]. (Reproduced by permission of the Chemical Society).

7. Carboxylates

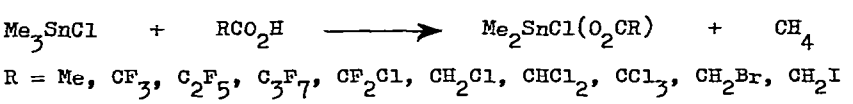
Commercially useful organotin carboxylates have been prepared from the organotin oxide and the carboxylic acid [146] or anhydride [147 148], and from the organotin hydride and the acid [149]. Triallyltin acetate and monochloroacetate may be obtained by the acid cleavage of tetraallyltin in methanol at room temperature. Mono- and dichloroacetic

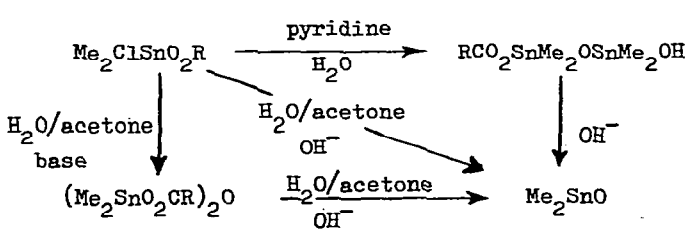
acids cleave two Sn-C bonds when the reaction is carried out using a 2:1 ratio of reactants. In the presence of moisture, 1,3-diacyloxydistannoxanes XLVI are formed. Unusually, the formation of these compounds appears not to involve Sn-O bond cleavage but Sn-allyl cleavage, since the treatment of triallyltin monochloroacetate with moist methanol produces propene and the distannoxane [150].



XLVI

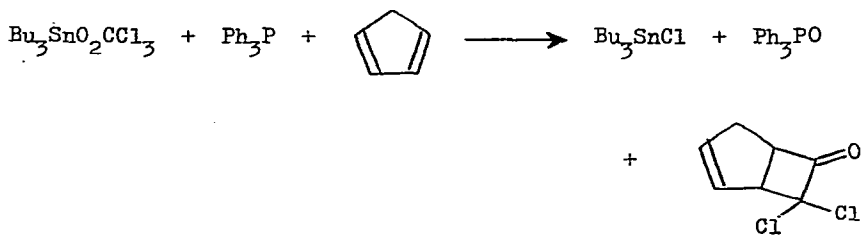
Trimethyltin chloride also undergoes Sn-C bond cleavage by acetic and halogenated carboxylic acids at 100° to afford dimethyltin chloride carboxylates. Spectroscopic data indicate the presence of pentacoordinate tin in both the solid and solution phases. The solids are polymeric with bridging carboxylate groups. In solution, the fluorinated carboxylates are monomeric, while the remainder retain polymeric character [151].





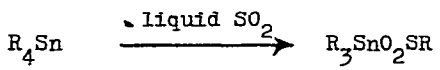
Trimethyltin derivatives of amino acids have been reported by Zuckerman. The O-trimethyltin and tricyclohexyltin derivatives of glycine, DL-α-alanine, DL-α-amino-n-butyric acid, DL-α-valine, DL-α-leucine, L-α-isoleucine, β-alanine, and glycylglycine are obtained by the azeotropic removal of water from the organotin hydroxide and amino acid in

boiling benzene. Bridging by $-NH_2$ rather than $-CO_2$ groups was thought to be present [153]. Triphenyltin acetate is degraded to inorganic tin by irradiation with UV light [154]. The reaction of triphenylphosphine with tributyltin trichloroacetate in the presence of cyclopentadiene produces tributyltin chloride, triphenylphosphine oxide, and the adduct 7,7-dichloro-bicyclo 3,2,0 -hept-2-ene-6one [155].



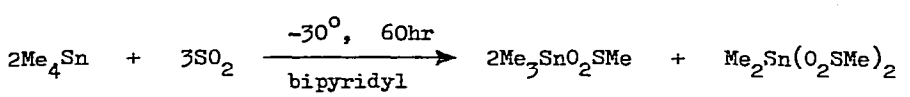
8. Oxyacid Derivatives

Lindner has carried out a detailed investigation of the reaction between liquid sulphur dioxide and tetraorganostannanes. A variety of products are obtained depending on the reaction time and temperature, and the presence or otherwise of water. At low temperatures, SO_2 inserts into one Sn-C bond of tetraalkylstannanes forming trialkyltin alkylsulphinates XLVII. The reactivity of the stannane decreases in the order Et>Me>n-Pr >iso-Pr .



XLVII

As the reaction temperature is raised, bis(trialkyltin)sulphates $(R_3Sn)_2SO_4$ are formed, and at 90° they are the major reactions products. Tetraethyltin is exceptional, giving rise to diethyltin sulphate Et_2SnSO_4 [156]. The addition of bipyridyl suppresses the formation of $(R_3Sn)_2SO_4$. Thus, a 1:1 molar ratio of tetramethyltin and bipyridyl at -30° gives a 2:1 mixture of the mono- and di-insertion products. A decrease in the amount of bipyridyl used results in the formation of $(Me_3Sn)_2SO_4$ [157].



When the reactions are carried out in the presence of water at 60°, the reactions are more complex, and may be summarised as follows:

$$Me_4Sn \xrightarrow{\text{liquid } SO_2/H_2O} (Me_3Sn)_2SO_4 \quad 90\%$$

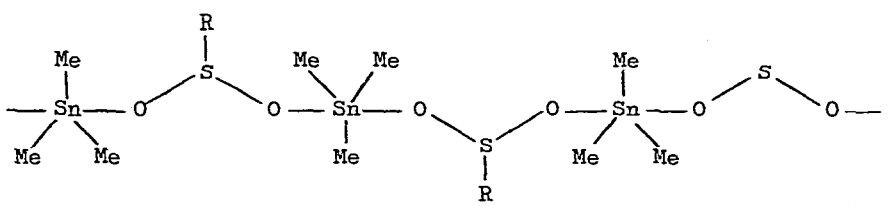
$$Et_4Sn \xrightarrow{\text{liquid } SO_2/H_2O} Et_2SnSO_3\ (50\%) + Et_2Sn(O_2SEt)_2\ (20\%) + Et_2SnSO_4\ (15\%)$$

$$Pr_4Sn \xrightarrow{\text{liquid } SO_2/H_2O} Pr_3SnO_2SPr\ (70\%) + Pr_2Sn(O_2SPr)_2\ (13\%) + Pr_2SnSO_3\ (5\%)$$

$$iso\text{-}Pr_4Sn \xrightarrow{\text{liquid } SO_2/H_2O} {}^{i}Pr_2Sn(O_2S{}^{i}Pr)_2\ (33\%) + ({}^{i}Pr_3Sn)_2SO_4\ (8\%)$$

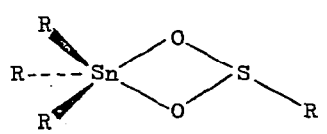
$$Bu_4Sn \xrightarrow{\text{liquid } SO_2/H_2O} Bu_3SnO_2SBu\ (60\text{-}70\%) + Bu_2SnSO_3\ (15\%) + Bu_2Sn(O_2SBu)_2\ (3\%)$$

At 90°, the major products are the dialkyltin sulphates. Trimethyltin methylsulphinate, though tetrameric in benzene solution, is thought to consist of sulphinate-bridged polymeric chains XLVIII in the solid, similar to that deduced crystallographically for trimethyltin propargylsulphinate (R = CH_2-C≡CH) [158]. Higher homologues are monomeric with chelating



XLVIII

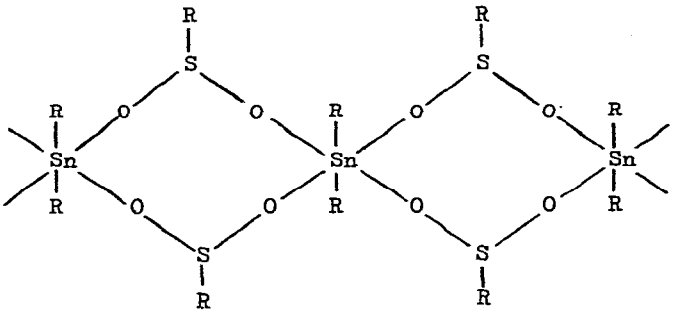
sulphinate groups IL.



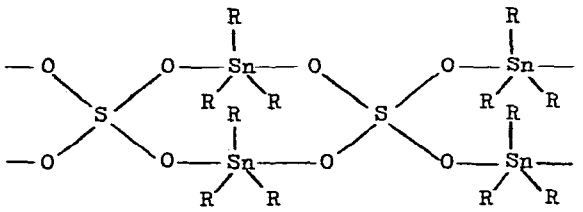
IL

References p. 140

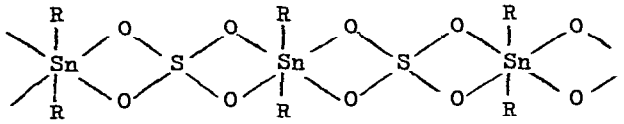
The bis(trialkyltin)sulphates and the dialkyltin sulphates, sulphites, and bis(sulphinates) are usually infusible, and are considered to have the polymeric structures L - LIII involving 5- or 6-coordinate tin [156].



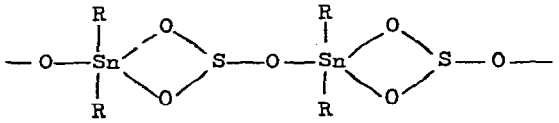
L



LI



LII



LIII

Tetraarylstannanes only give the diaryltin bis(arylsulphinates) when treated with liquid SO_2 at 60°, although at low temperatures ($\leqslant 20°$) tetrabenzyltin affords small quantities of the monosulphinate product. Triaryltin chlorides disproportionate in liquid SO_2 at 20° to yield the disulphinates:

$$Ar_3SnCl + 2SO_2 \xrightarrow[\text{liquid } SO_2]{20°} Ar_2Sn(O_2SAr)_2 + Ar_2SnCl_2$$

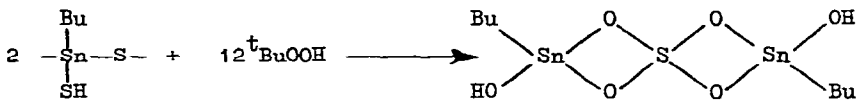
Diaryltin dichlorides are inert, except for di-p-tolyltin dichloride which undergoes di-insertion at 60°:

$$(p\text{-}MeC_6H_4)_2SnCl_2 + 2SO_2 \xrightarrow[\text{liquid } SO_2]{60^\circ} (p\text{-}MeC_6H_4SO_2)_2SnCl_2$$

Mono-, di-, and triaryltin sulphinates are readily obtained by metathesis between the aryltin chloride and sodium sulphinate [159]:

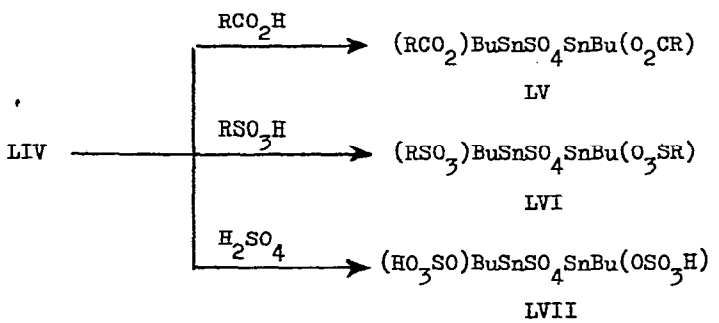
$$Ar_nSnCl_{4-n} + (4-n)NaO_2SAr' \longrightarrow Ar_nSn(O_2SAr')_{4-n} + (4-n)NaCl$$

The oxidation of butyldithiostannonic acid with tert-butylhydroperoxide leads to the formation of bis(butylhydroxytin)orthosulphite LIV



LIV

LIV reacts with carboxylic acids and anhydrides to form the carboxylates LV, and with sulphonic and sulphuric acids to form the sulphonates LVI and sulphate LVII respectively [160];



Dialkyltin salts of strong monobasic sulphonic and phosphoric acids are obtained by the acid solvolysis of tetramethyltin and alkyltin chlorides at 25°, although the monofluorosulphate LVIII may be obtained from Me_4Sn by carrying out the reaction at -80°:

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$$Me_3SnSO_3F \;(LVIII) \xleftarrow[-CH_4]{-80^\circ} Me_4Sn + HSO_3F \xrightarrow[-CH_4]{25^\circ} Me_2Sn(SO_3F)_2 \quad [161]$$

$$Me_3SnCl + 2HSO_3F \longrightarrow Me_2Sn(SO_3F)_2 + HCl + CH_4 \quad [161]$$

$$MeSnCl_3 + 2HSO_3F \longrightarrow MeSnCl(SO_3F)_2 + 2HCl \quad [161]$$

$$R_2SnCl_2 + 2HSO_3F \longrightarrow R_2Sn(SO_3F)_2 + 2HCl \quad [161,162]$$

$$R_2SnCl_2 + 2HSO_3CF_3 \longrightarrow R_2Sn(SO_3CF_3)_2 + 2HCl \quad [162]$$

$$R_2SnCl_2 + HPO_2F_2 \longrightarrow R_2Sn(PO_2F_2)_2 + 2HCl \quad [161]$$

R = Me, Et, Pr, Bu, Octyl

Methyltin fluorosulphates have also been obtained by ligand redistribution, [161], viz.

$$Me_4Sn + Me_2Sn(SO_3F)_2 \longrightarrow Me_3SnSO_3F$$

$$Me_2SnCl_2 + Me_2Sn(SO_3F)_2 \longrightarrow Me_2Sn(Cl)SO_3F$$

$$MeSnCl_3 + Me_2Sn(SO_3F)_2 \longrightarrow MeSn(Cl)_2SO_3F$$

Mössbauer and vibrational spectra indicate polymeric structures with 5- and 6-coordinate tin involving planar Me_3Sn and linear R_2Sn moieties, respectively [161,162].

Trimethyltin nitrate hydrate possesses a trigonal bipyramidal configuration with planar Me_3Sn groups and water molecules and unidentate nitrate groups occupying the apical positions in a disordered manner ($Sn\text{-}O_{water}$ = 2.47Å; $Sn\text{-}O_{nitrate}$ = 2.22Å; Sn-C = 2.11Å). Intermolecular hydrogen bonding (O---O contact = 2.72Å) connects the water of one molecule and the nitrate group of an adjacent molecule [163]. Studies of organotin nitrates have been reported in a thesis [164].

9. Sulphur, Selenium, and Tellurium Derivatives.

Methyldithiostannonic acid is tetrameric and possesses the adamantane structure (Sn-C = 2.136-2.157Å; Sn-S = 2.381-2.395Å) (Fig. 7) [164a].

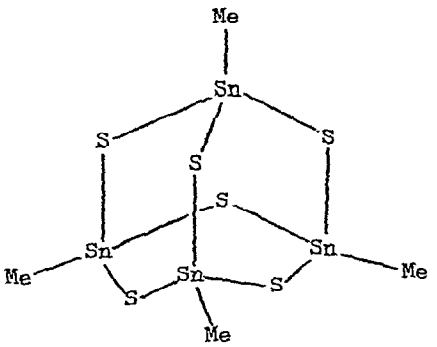


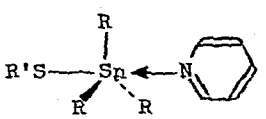
Fig. 7 The structure of $(MeSnS_{1.5})_4$.

Bis(tripentafluorophenyltin)sulphide, -selenide, and -telluride have been synthesised by reacting tripentafluorophenyltin bromide and bistriethylsilyl, -germyl, or -stannyl chalcogenide in toluene at 100° [165].

$$2(C_6F_5)_3SnBr + (Et_3Z)_2Y \longrightarrow (C_6F_5)_3Sn\,Y + 2Et_3ZBr$$

Z = Si, Ge, Sn; Y = S, Se, Te

Several Mössbauer studies of Sn-S bonded compounds have appeared. The similarity of the spectra for the organotin sesquisulphides $(RSnS_{1.5})_4$ (R = Me, Et, Bu, Octyl, Ph) suggest that all are isostructural, having the adamantane structure of the methyl compound [126]. Quadrupole splitting values for the tributyltin and triphenyltin derivatives of benzene thiol, ethane dithiol, and dithioacetic acid are consistent with four coordination at tin. Spectra for pyridine solutions of these compounds exhibit significantly increased splittings due to coordination of solvent producing unstable complexes of the type



The derivatives of 2-mercaptoaniline show similar effects. 2-Triphenylstannylthiolatopyridine appears to be four-coordinate even in pyridine solution presumably due to steric considerations, whereas 4-triphenylstannylthiolatopyridine has five-coordinate tin in the solid [166]. Herber has deduced that carbamates function as weakly bidentate ligands towards tin, forming one strong bond and a second weak interaction [167]. The crystal structure of dimethyltinbis(N,N-dimethyldithiocarbamate) illustrates the anisobidentate nature of the chelation (Fig. 8). The two carbamate groups

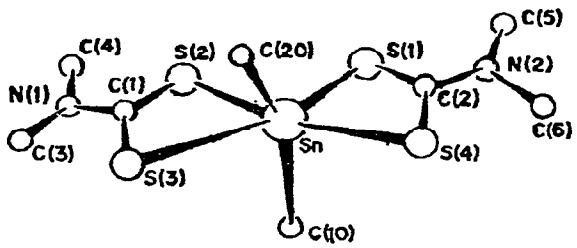
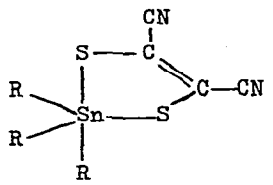


Fig. 8 The structure of dimethyltinbis(N,N-dimethyldithiocarbamate) [168]. (Reproduced by permission of the Chemical Society of Japan).

each form one short bond (2.525, 2.497Å) and one much longer interaction (2.954, 3.061Å) in approximately equatorial sites of pseudo-octahedral coordination. The two methyl groups are trans to each other, but the C-Sn-C bond angle is only 136°. The coordiantion at tin may be considered therefore to be intermediate between tetrahedral and octahedral [168]. For $Ph_2Sn(S_2CNEt_2)_2$, however, the organic groups occupy cis positions in a distorted octahedral configuration with a C-Sn-C bond angle of ca. 101° [169]. Triphenyltin N,N-diethyldithiocarbamate contains a unidentate carbamate [169], which has also been suggested for the diorganotin chloride carbamates $R_2ClSnS_2CNR'_2$ [170].

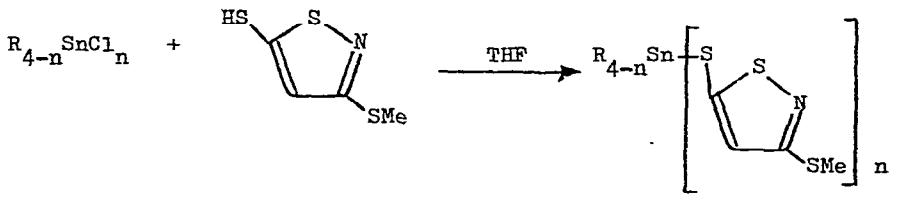
The reaction between disodium dicyanoethylene-1,2-dithiolate (Na_2Mnt) and monoorganotin trichlorides at room temperature results in Sn-C bond cleavage leading to the ionic derivatives $(SnMnt_3)^{2-}$ or $(SnMnt_2Cl_2)^{2-}$ depending on the ratio of reactants used. With triorganotin chlorides, R_3SnMnt^- anions are produced for which the structure LIX is postulated (cf. the structure of $Ph_3Sn.O.NPh.COPh$ - Section 6). Diorganotin dichlorides

afford R_2SnMnt, $R_2SnClMnt^-$, or R_2SnMnt^{2-} depending on the reaction conditions [171,172].



LIX

The preparation of organotin derivatives of 1,2,4-thiadiazoles has been reported in a patent [173]:



Patents also report the synthesis of diorganotin derivatives of mercapto esters from the corresponding oxide [174,175] :

$$R_2SnO + 2HS(CH_2)_nCO_2R' \xrightarrow{Na_2SO_4} R_2Sn[S(CH_2)_nCO_2R']_2 + H_2O$$

R = Bu, Octyl; n = 1, 2; R' = Bu, Octyl, $PhCH_2$

Derivatives of thioglycol, thioglycolic acid and similar compounds have been prepared from the organotin chloride in the presence of triethylamine, eg.

$$R_3SnCl + HSCH_2CH_2OH \xrightarrow{NEt_3} R_3SnSCH_2CH_2OH$$

R = Me, Bu

$$2Me_3SnCl + HS(CH_2)_nCO_2H \xrightarrow{NEt_3} Me_3SnS(CH_2)_nCO_2SnMe_3$$

n = 1, 2

The trimethyltin compounds disproportionate at 110–130° giving tetramethyltin and a dimethyltin derivative [176]:

$$2Me_3SnSCH_2CH_2OH \xrightarrow[10\ hr]{125^\circ} HSCH_2CH_2OH + Me_4Sn + Me_2Sn(SCH_2CH_2O)$$
42% 43%

$$Me_3SnSCH_2CO_2SnMe_3 \xrightarrow[1\ hr]{110^\circ} Me_4Sn + Me_2Sn(SCH_2CO_2)$$
64% 99%

$$Me_3SnSCH_2CH_2CO_2SnMe_3 \xrightarrow[4\ hr]{130^\circ} Me_4Sn + Me_2Sn(SCH_2CH_2CO_2)$$
64% 74%

Phosphorus dithioacids dealkylate tetraethyltin leading to triethyltin dithiophosphorates LX, which are also obtained from triethyltin chloride and ammonium dithiophosphate.

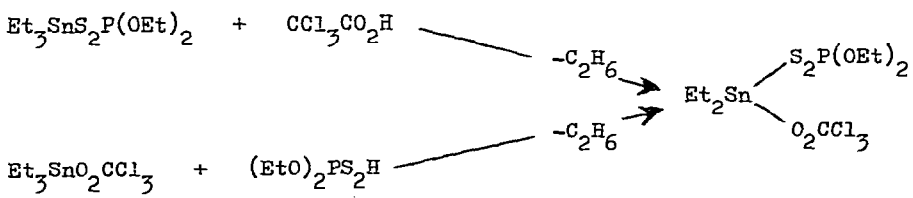
$$Et_4Sn + R'R''P(S)SH \longrightarrow Et_3SnS_2PR'R'' + C_2H_6$$

LX

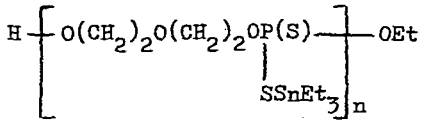
R', R'' = MeO, EtO, PrO, Me

$$Et_3SnCl + NH^+ {}^-S_2PR'R''$$

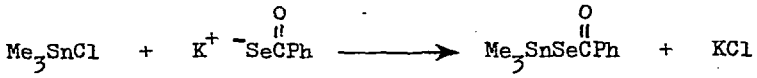
Smaller alkyl groups are cleaved preferentially from tin, thus triethylpropyltin is cleaved to give both ethane and propane in an 8:1 ratio, and butyltripropyltin give propane and butane in a 6:1 ratio. Further Sn-C bond cleavage is effected by trichloroacetic acid yielding LXI, which is also produced from triethyltin trichloroacetate and dithiophosphorus acid [177].



Polymeric triethyltin dithiophosphates such as LXII are similarly prepared [178].

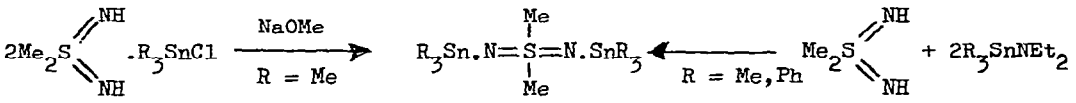


Relatively moisture stable trimethyltin selenobenzoate has been obtained as a pale yellow oil [179]:



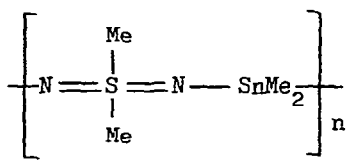
10. Group V Derivatives

Appel has prepared triorganotin dimethylsulphodiimide derivatives LXIII by dehydrohalogenation of the complex LXIV using sodium methoxide, and by transamination of triorganotin amines with S,S-dimethylsulphodiimide, viz.

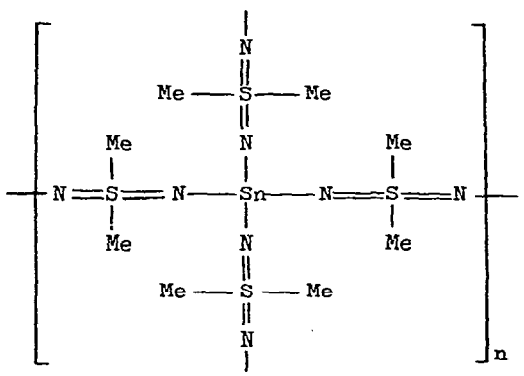


LXIV LXIII

The polymeric materials LXV and LXVI were also obtained using the latter method.

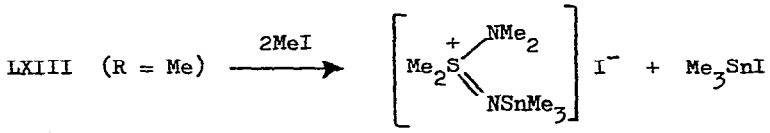


LXV



LXVI

The triphenyltin derivative LXIII (R = Ph) hydrolyses only slowly and gives no reaction with methyl iodide. The trimethyltin analogue, however, hydrolyses rapidly to trimethyltin hydroxide and the parent sulphodiimide, and reacts exothermically with methyl iodide to give trimethyltin iodide and the sulphonium salt LXVII.



LXVII

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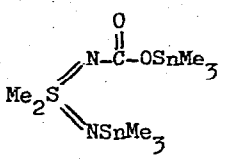
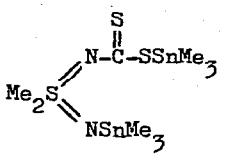
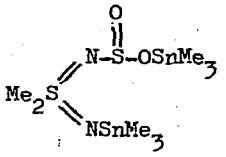
Only one of the Sn-N bonds of LXIII (R = Me) is reactive towards CO_2, CS_2, and SO_2 giving the insertion products LXVIII, LXIX, and LXX, respectively.



LXVIII

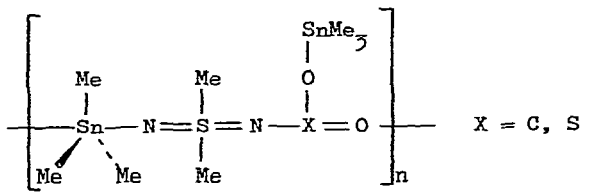


LXIX



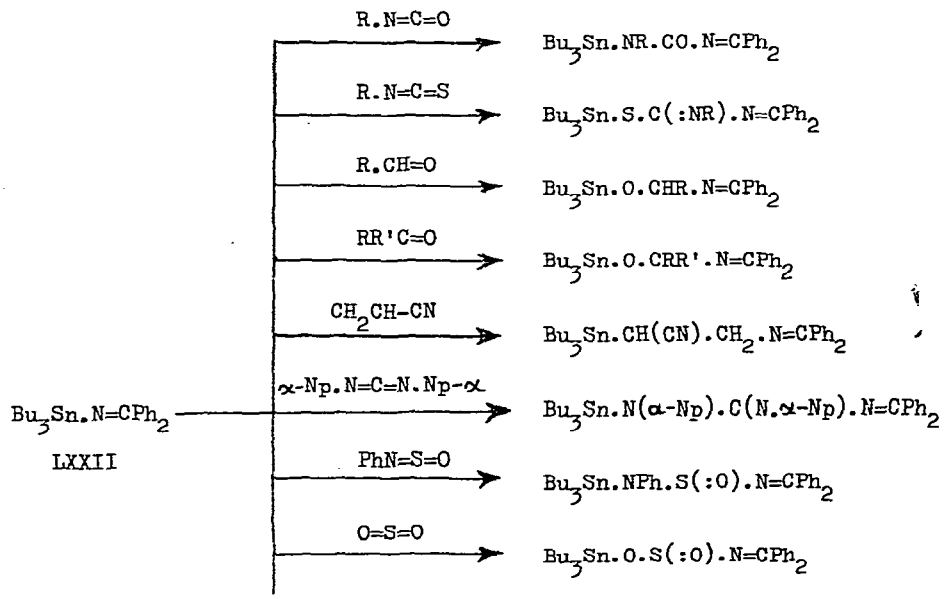
LXX

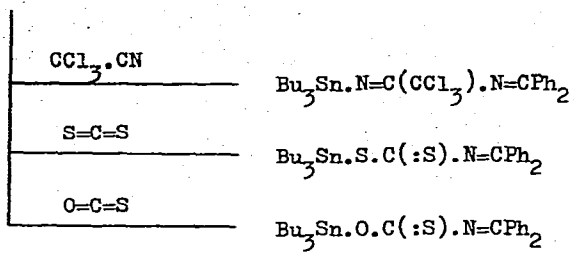
LXIX is monomeric, but LXVIII and LXX are involatile and difficultly soluble, and are postulated to have the intermolecularly coordinated polymeric structure LXXI [104].



LXXI

N-Tributylstannyldiphenylmethyleneamine LXXII reacts with a large number of multipy-bonded reagents to form stable adducts [180]:





The bromal adduct reacts with a further molecule of chloral forming the di-adduct LXXIII.

$$Bu_3Sn.O.CHCBr_3.N{=}CPh_2 + CCl_3CH{=}O \longrightarrow \underset{\text{LXXIII}}{Bu_3Sn.O.CHCCl_3.O.CHCBr_3.N{=}CPh_2}$$

With the other aldehyde adducts, however, complete displacement of aldehyde takes place, and the chloral adduct is formed.

$$Bu_3Sn.O.CHR.N{=}CPh_2 + CCl_3CH{=}O \longrightarrow Bu_3Sn.O.CHCCl_3.N{=}CPh_2 + RCH{=}O$$

R = Me, Et, ^{i}Pr, Ph

Only partial displacement of aldehyde usually occurs with perhalogenated ketones, leading to equilibria between the two possible adducts and the two acceptor molecules, eg.

$$Bu_3Sn.O.CHCBr_3 + CCl_2F.CO.CF_2Cl \underset{\text{room temperature}}{\overset{17\text{ hr}}{\rightleftharpoons}} Bu_3Sn.O.C(CCl_2F)(CF_2Cl)-N{=}CPh_2 + \underset{60\%}{CBr_3CH{=}O}$$

Isocyanates and isothiocyanates react in all cases by further addition, eg.

$$Bu_3Sn.OCHMe.N{=}CPh_2 + MeN{=}C{=}O \xrightarrow{\text{exothermic}} Bu_3Sn.NMe.CO.OCHMe.N{=}CPh_2$$

$$Bu_3Sn.OCHCBr_3.N{=}CPh_2 + MeN{=}C{=}O \xrightarrow[33.5^{\circ}]{17\text{ hr}} \underset{75\%}{Bu_3Sn.NMe.CO.OCHCBr_3.N{=}CPh_2}$$

$$Bu_3Sn.OCHMe.N{=}CPh_2 + PhN{=}C{=}S \xrightarrow[\text{room temperature}]{44\text{ hr}} \underset{50\%}{Bu_3Sn.S.N(:CPh).O.CHMe.N{=}CPh_2}$$

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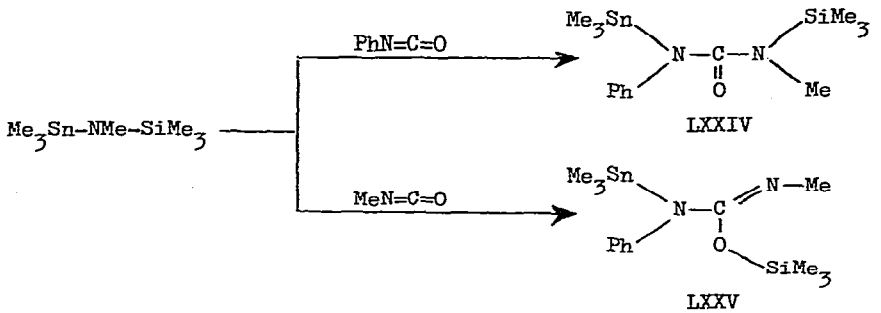
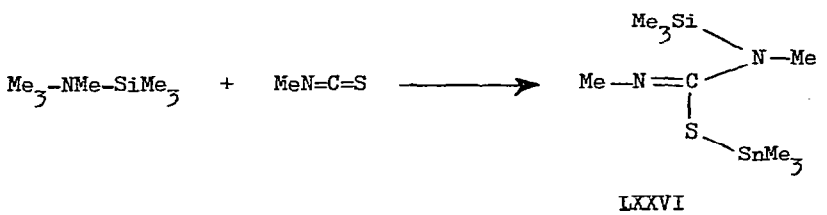
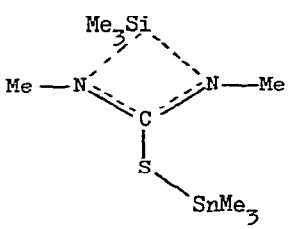
Ishii has investigated the reactions of heptamethylsilastannazane with various heterocumulenes [181]. Initial reaction always takes place at the Sn-N bond, although in several cases, 1,3-migration of the trimethylsilyl group takes place. Thus, whereas phenyl isocyanate gives the adduct LXXIV, methyl isocyanate affords the isomeric product LXXV:



Isothiocyanates not unexpectedly react more slowly. Methyl isothiocyanate gives the stable 1:1 adduct LXXVI, which exhibits only one N-Me resonance in the nmr spectrum, indicating rapid exchange of Me_3Si groups between

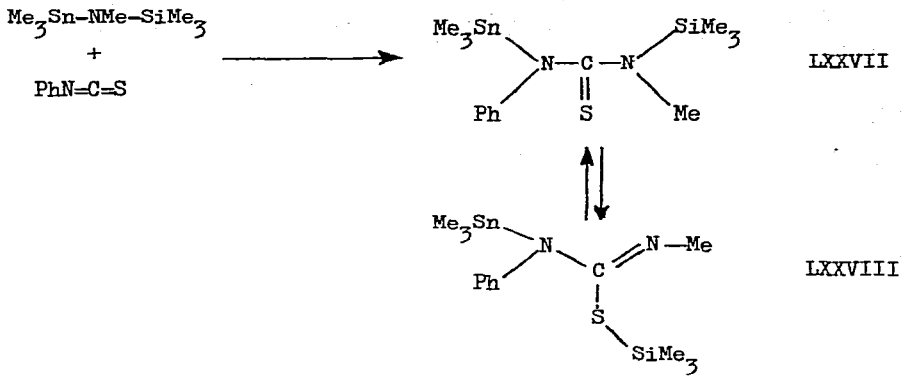


two chemically equivalent nitrogen atoms on the nmr time scale. The structure of LXXVI is therefore best represented as

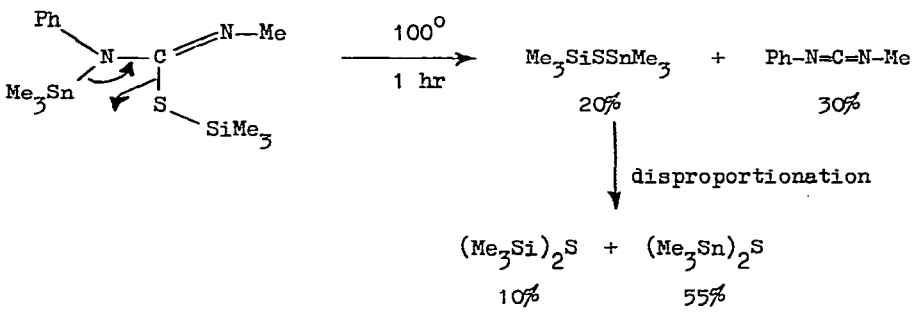


Infra-red and nmr evidence suggests that the similar 1:1 adduct with phenyl

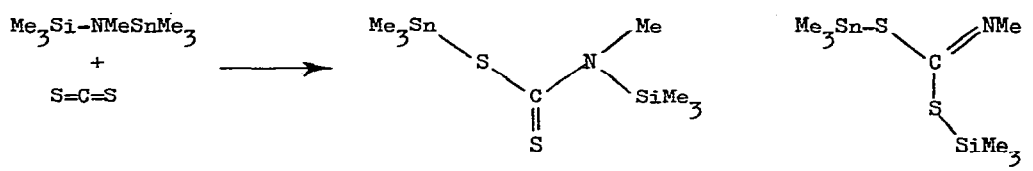
isothiocyanate is composed of a mixture of two interconvertible structures LXXVII and LXXVIII.



The adduct is thermally unstable, and decomposes completely at 100° into phenylmethylcarbodiimide, and a mixture of dimetal-sulphides. This facile decomposition is readily rationalised using the isomer LXXVIII, viz.



The 1:1 adduct with carbon disulphide is similarly considered to be a mixture of both isomers.



Triethylstannyldiethylamine readily reacts with tertbutylhydroperoxide in hexane to form triethylstannyl-tert-butylperoxide.

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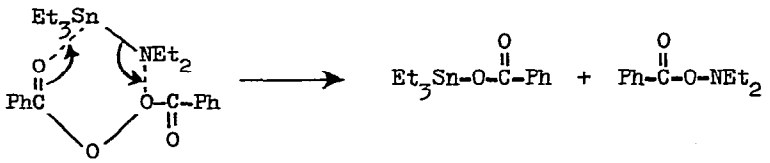
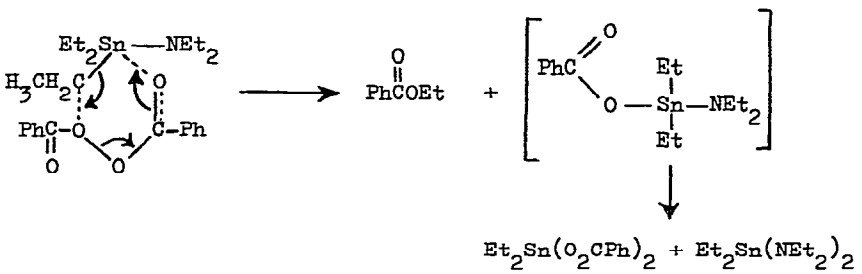
$$Et_3SnNEt_2 + {}^tBuOOH \longrightarrow Et_3SnO{}^tBu + Et_2NH$$

85%

The reaction of the stannylamine with dibenzoyl peroxide was more complex. Using a 1:1 ration of reactants in benzene, triethyltin benzoate (0.72 mole), O-benzoyl-N,N-diethylhydroxylamine (0.75 mcle), N,N-diethylbanzamide (0.05 mole), ethyl benzoate (0.13 mole), and diethyltin products were isolated. The main reaction pathway involves Sn-N bond fission, viz.



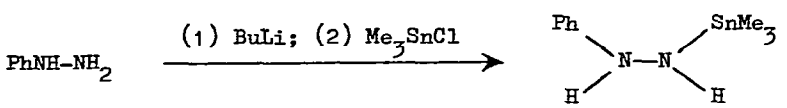
Tin-carbon bond cleavage gives rise to ethyl benzoate and the diethyltin derivatives [131]:

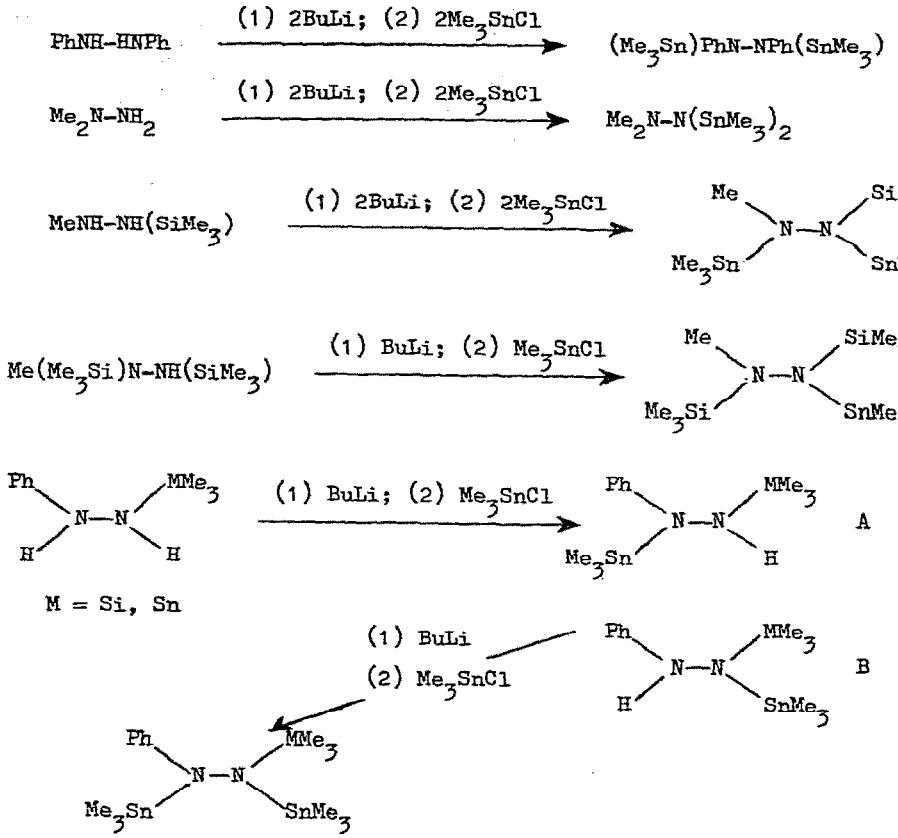


The synthesis and oxidation of organotin hydrazines has received much attention. N-Tributylstannyl-N'-arylhydrazines are conveniently obtained in high yield by the transamination route [182]:

$$Bu_3SnNEt_2 + ArNHNH_2 \longrightarrow Bu_3NHNHAr + Et_2NH$$

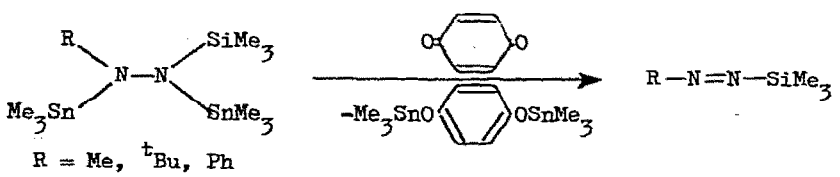
Wiberg has prepared several simple and mixed metallated hydrazines via the lithium salts:



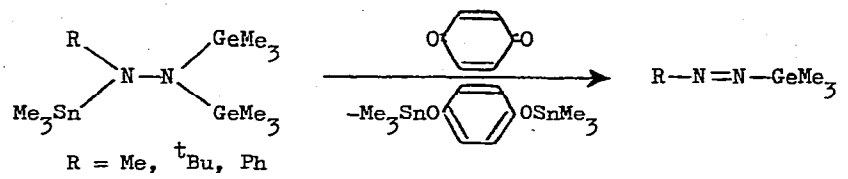


When M = Sn, the isomers A and B are formed in equal proportions, but when M = Si isomer B is favoured (A:B = 40:60). The germylstannylhydrazine $Ph(Me_3Sn)N\text{-}N(GeMe_3)_2$ was synthesised similarly [183].

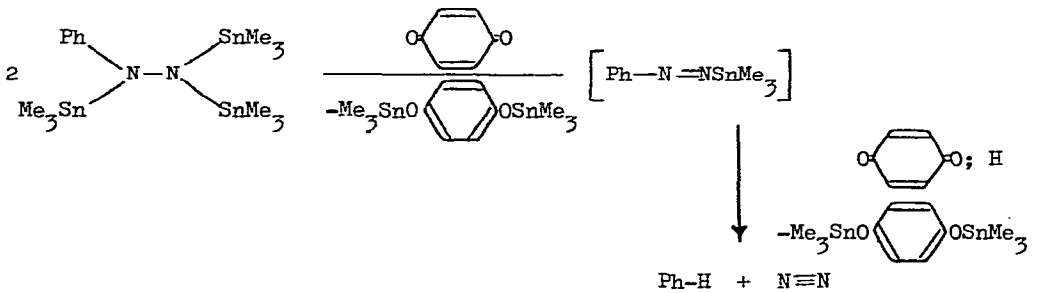
Stannylhydrazines are readily oxidised by a number of reagents. Oxidation by benzoquinone generally leads to substituted diimines via a radical process, viz.



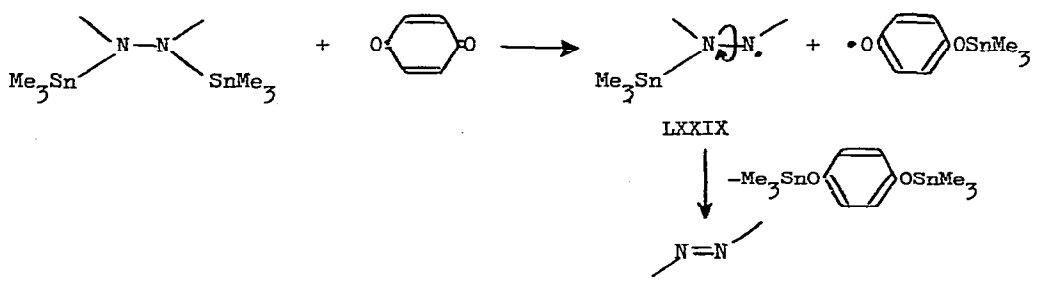
References p. 140



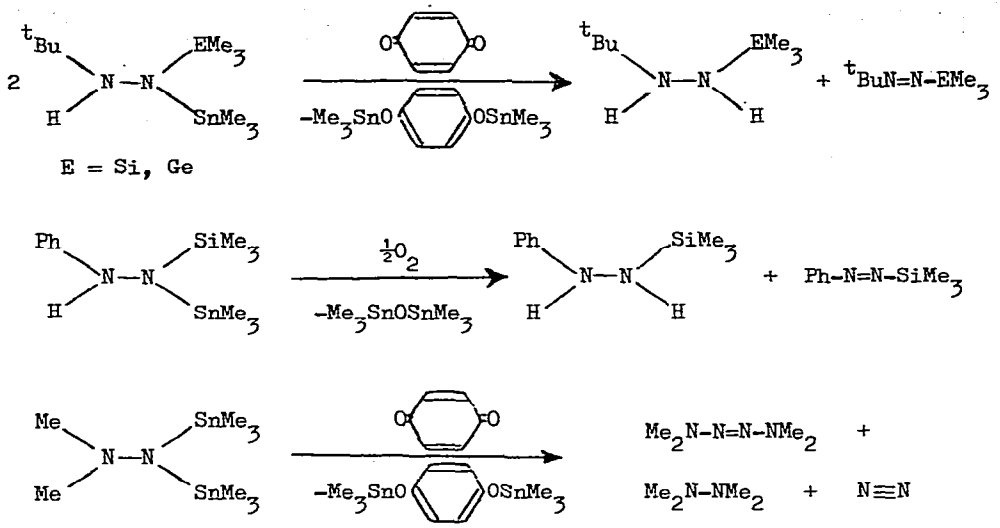
The analogous stannylimine, R-N=N-$SnMe_3$, cannot be obtained by the oxidation of $(Me_3Sn)RN-N(SnMe_3)_2$, and R• radicals and molecular nitrogen are formed by further reaction with benzoquinone.



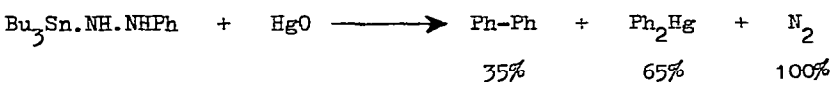
Nitrogen is also produced by the benzoquinone oxidation of tetrasubstituted hydrazines, $(Me_3Sn)(Me_3E)N-N(EMe_3)(SnMe_3)$ (E = Si, Sn), again presumably due to the instability of the incipient diimine. Indeed, the disilyldiimine, $Me_3Si-N=N-SiMe_3$, reacts vigourously even at -70° with benzoquinone to give nitrogen. A concerted mechanism for the oxidation of 1,2-disubstituted hydrazines would lead to cis diimines. However, the oxidation of $Me_3Sn(Ph)N-N(Ph)SnMe_3$ leads only to trans-azobenzene, and the two-stage process



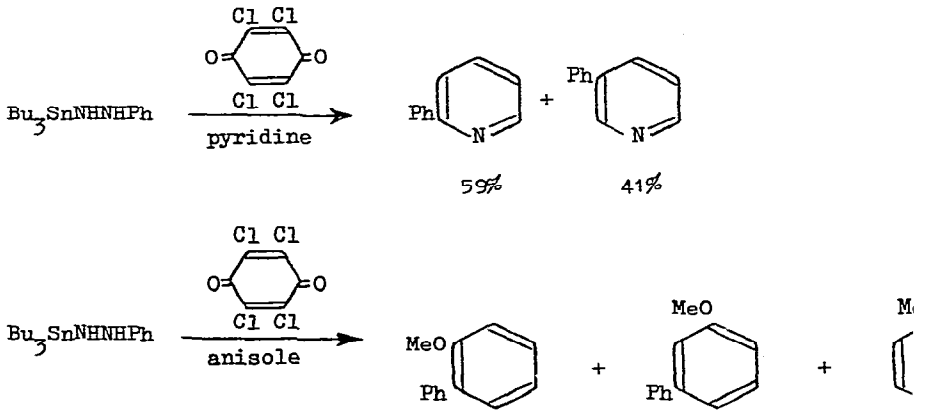
in which free rotation about the N-N bond of the intermediate radical LXXIX can take place, is favoured. 1,1-Disubstituted hydrazines are oxidised by benzoquinone or molecular oxygen to give a mixture of monosubstituted hydrazine and diimine [183]:



The oxidation of N-aryl-N'-tributylstannylhydrazines using a variety of reagents has been used to prepare biphenyl derivatives. With mercuric oxide, $Bu_3SnNH.NHPh$ gives biphenyl, diphenylmercury, and a quantitative yield of nitrogen.



Using chloranil, the yield of biphenyl is increased to 93%. In pyridine or anisole as solvent, a mixture of phenylpyridine and methoxybiphenyls, respectively, are produced.



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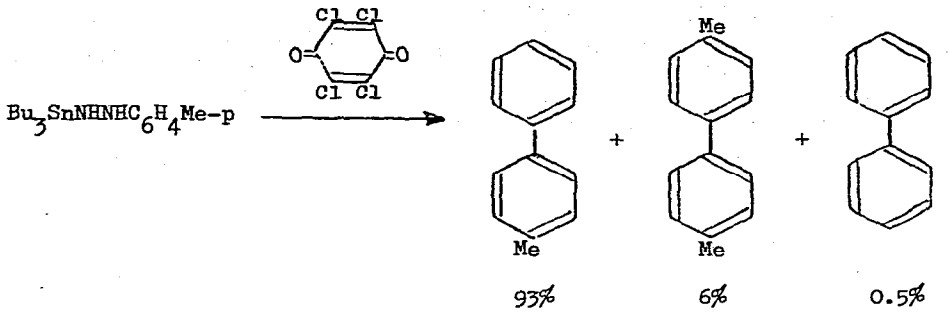
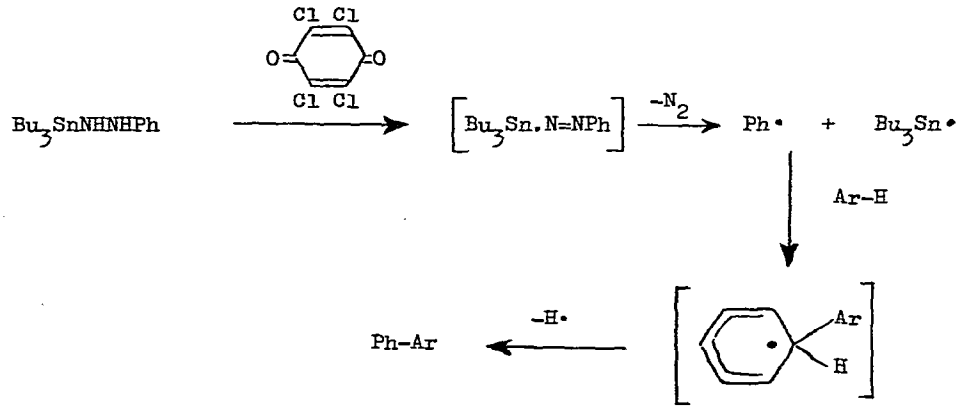


Again, a radical mechanism, with the intermediate formation of the stannyldiimine, $Bu_3Sn.N{=}NPh$, is postulated:



The formation of the polymer $\left[Bu_2Sn{-}NH{-}C_6H_4{-}NH\right]_n$ via the interfacial polycondensation route using a variety of solvent systems has been studied [184].

Several trialkyltin derivatives of azole rings have been synthesised from the sodium salt in liquid ammonia [185]:

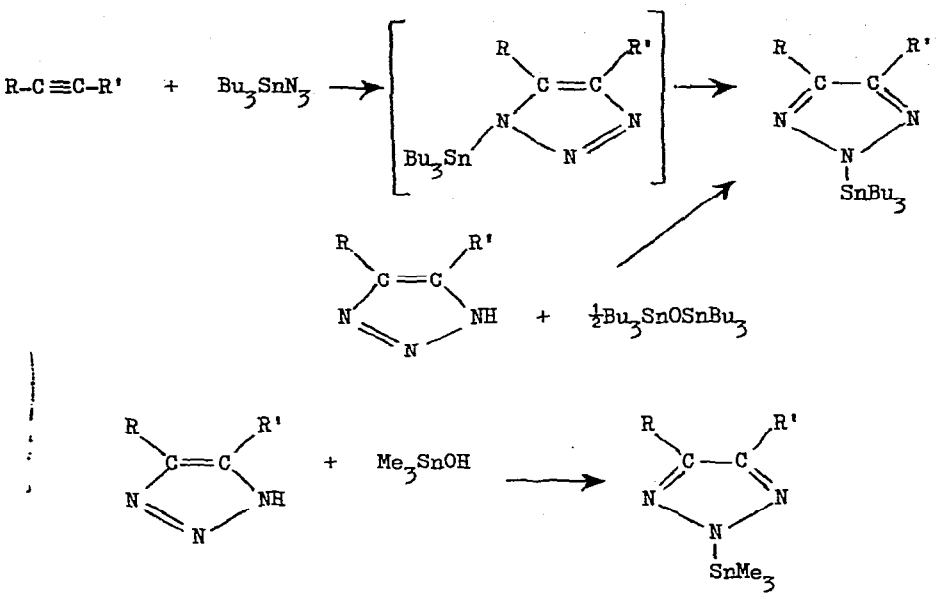
$$R_3SnBr + R'Na \xrightarrow{\text{liquid } NH_3} R_3SnR' + NaBr$$

R = Me, Et, Ph

R' = pyrazole, imidazole, 2-methylimidazole, benzimidazole, benzotriazole

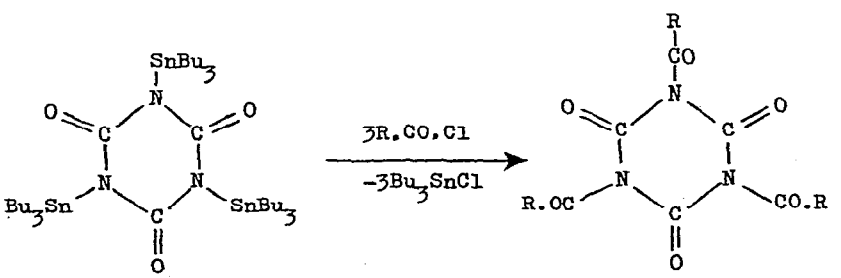
Derivatives of 1,2,3-triazoles are also obtained by the 1,3-cycloaddition of tributyltin azide to alkynes, and also by the condensation of bis(tri-

butyltin)oxide or trimethyltin hydroxide and 1,2,3-triazoles.



Dipole moment, UV, nmr, and viscosity data indicate that the tin atom is attached to the 2-nitrogen atom, hence the cycloaddition must be accompanied by a 1,2-migration of the trialkyltin group [186]. Tributyltin derivatives of 3-phenylpyrazole, 4-phenylimidazole, 3-phenyl-1,2,4-triazole [186], and isatin [187] have also been synthesised by the condensation route using bis(tributyltin)oxide.

The tin-nitrogen bonds of these and similar compounds are easily cleaved by acyl halides in light petroleum or ether to afford high yields of the N-acylated heterocycles, viz.



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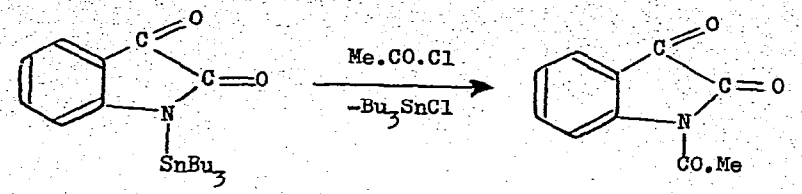
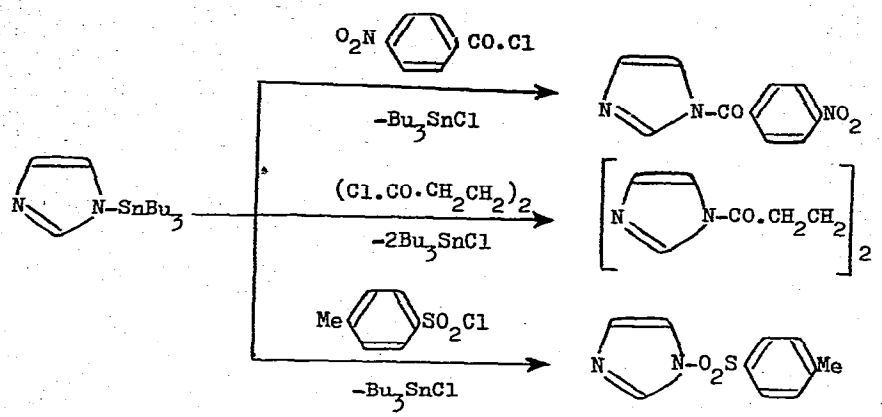
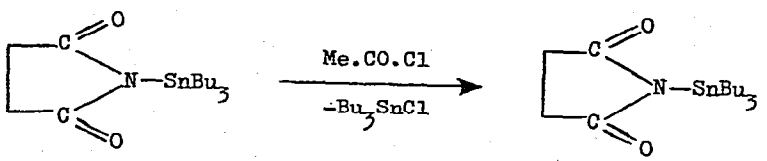
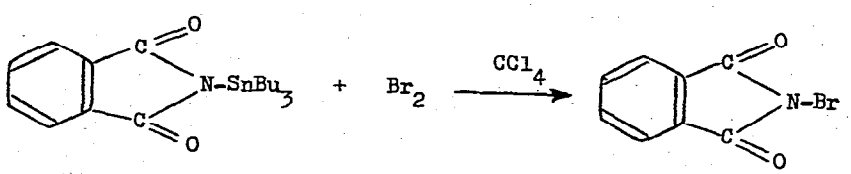
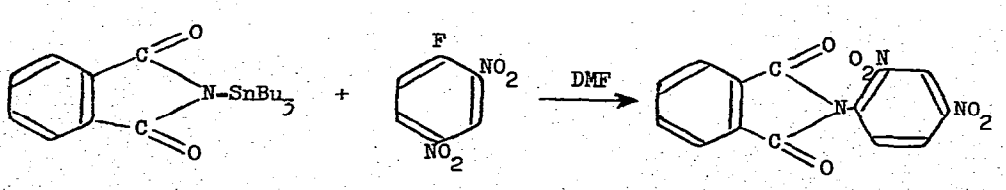

Me.CO.Cl
-Bu3SnCl
SnBu3
CO.Me

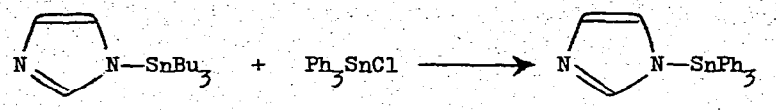

O2N
CO.Cl
-Bu3SnCl
N-SnBu3
(Cl.CO.CH2CH2)2
-2Bu3SnCl
N-CO
NO2
N-CO.CH2CH2
2
Me
SO2Cl
-Bu3SnCl
N-O2S
Me


Me.CO.Cl
-Bu3SnCl
N—SnBu3

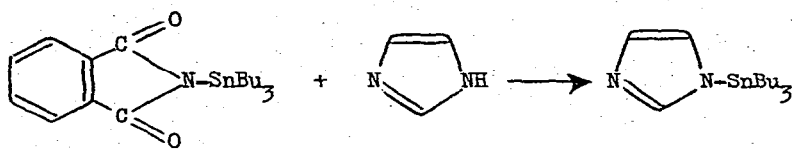

N-SnBu3
+
Br2
CCl4
N-Br


N-SnBu3
+
F
NO2
NO2
DMF
O2N
NO2

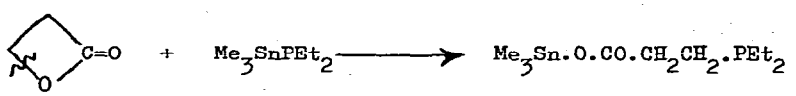
The N-tributylstannyl derivatives undergo metathesis with aryltin chlorides, eg.



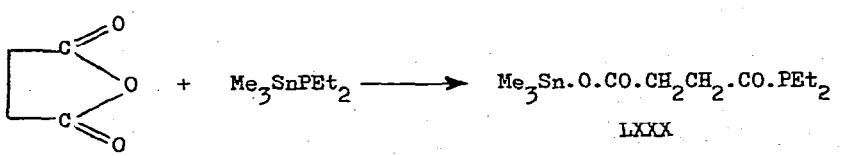
Imidazole displaces phthalimide from its N-tributylstannyl derivatives [187]:



Trimethylstannyldiethylphosphine reacts with β -propiolactone via the cleavage of the alkyl-oxygen bond of the lactone, leading to trimethyltin β -diethylphosphinopropionate [188]:



Acyl-oxygen bond fission is observed for the reaction with succinic anhydride giving the keto-ester LXXX:



The complexes $(Me_3Sn)_3P{:}M(CO)_5$ (M = Cr, Mo, W) undergo tin-phosphorus bond cleavage with diphenylchlorophosphine [189]:

$$(Me_3Sn)_3P{:}M(CO)_5 + 3Ph_2PCl \longrightarrow (Ph_2P)_3P{:}M(CO)_5 + 3Me_3SnCl$$

However, tin-carbon bond fission occurs when the similar stannylphosphine-metal pentacarbonyl complexes LXXXI are treated with boron trihalides. Up to two methyl groups may be removed from tin by BBr_3, although only one is cleaved by BCl_3 [190].

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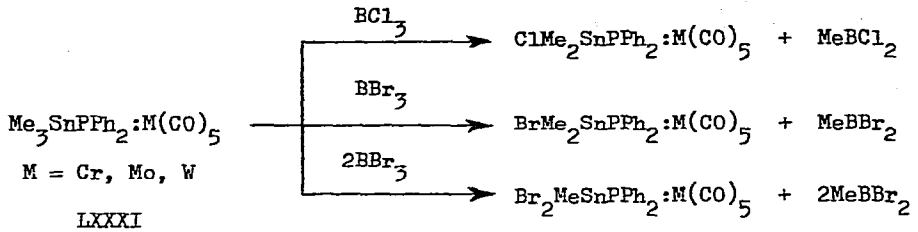
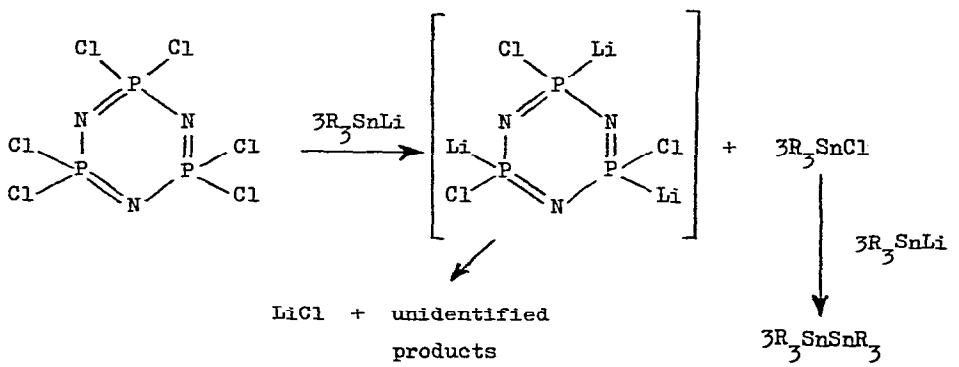


LXXXI

11. Tin-Main Group Metal Bonded Derivatives*

Organostannyllithium and magnesium reagents have been the subject of a thesis [191]. The reaction of triorganostannyllithium reagents with hexachlorotriphosphazenes does not result in the formation of stannyl-substituted phosphazenes. Instead, hexaorganodistannanes are formed in good yield. The most probable mechanism involves initial lithium-chlorine exchange [192]:



Similar exchange reactions have also been postulated by both Traylor [193] and Kuivila [194] to rationalise the stereochemistries of the reactions of trimethyltin alkali metal derivatives with alkyl halides. Carbocyclic bromides react with Me_3SnLi with retention of configuration. However, analogous tosylates react with inversion of configuration (Table 1).

* Including zinc, cadmium, and mercury compounds.

Table 1

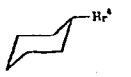
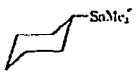
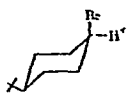
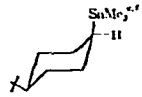
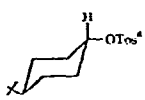
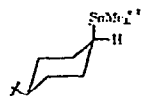
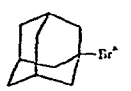
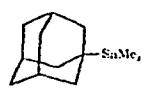
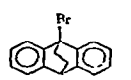
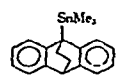
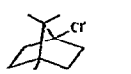
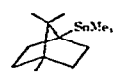
Structure of RX	Reaction time, hr	Yield, %	Product	Stereochemistry
	1–2	51		
	3.5	30		Retention
	12	63		Inversion
	3.5	57		Retention
	2.5	85		Retention
	5	66		Retention

Table 1 Products and stereochemistry of the reaction

$$Me_3SnLi + RX \longrightarrow RSnMe_3 + LiX$$

in THF at 25° [193]. (Reproduced by permission of the American Chemical Society).

Hexamethylditin and olefin are also observed as biproducts [193]. The reaction of syn-7-bromonorbornene with Me_3SnM^I (M^I = Li, Na, K) (from Me_3SnCl and the appropriate alkali metal naphthalene radical anion at -20°) yield mixtures of both syn- and anti-7-norbornenyltrimethyltins, the relative proportions of which depend on the nature of M^I and the cordinating capacity of the solvent. By appropriate choice of gegenion and solvent, the reaction can be made to proceed predominantly by inversion or retention, - sometimes dramatically. Thus, the reaction of trimethyltin sodium in THF proceeds with 90% retention, but addition of 0.053M tetraglyme causes a change to

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91% inversion. Similar experiments with anti-7-bromonorbornene show a great predominance (usually >90%) of retention of configuration, indicating the presence of a severe restraint in the anti bromide against the occurrence of the inversion mechanism. The ease of the retention process is also demonstrated by the high yields of 1- and 2-adamantyltrimethyltins from the corresponding bromoadamantanes [194]. The data indicate the availability of alternative mechanisms for the reaction of the trimethyltin anion with alkyl halides, ie. (1) S_N2 reaction at carbon, giving inversion; and (2) S_N2 reaction at halogen, followed by a rapid coupling reaction, leading to retention of configuration. This scheme also explains the formation of ditin products.

$$RBr + R'_3SnLi \longrightarrow RLi + R'_3SnBr \xrightarrow{R'_3SnLi} R'_3SnSnR'_3$$

$$RLi + R'_3SnBr \xrightarrow{\text{fast}} RSnR'_3 + LiBr$$

Noltes, Van der Kerk and their coworkers have synthesised several tin-zinc and tin-cadmium bonded compounds by hydrostannolysis of the reactive metal-carbon bonds in coordinating solvents [195,196]:

$$Ph_3SnH + R_2M.L \longrightarrow (Ph_3Sn)_2M.L + 2RH$$

R = Et; M = Zn L = THF, DME, TMED, bipyridyl
R = Me; M = Cd

$$Ph_3SnH + EtZnCl.L \longrightarrow Ph_3SnZnCl.L + C_2H_6$$

L = Et_2O, DME, TMED

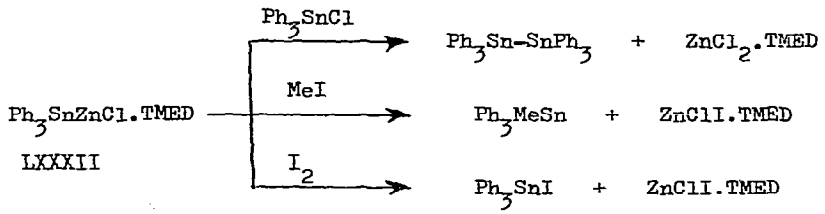
$$2MePh_2SnH + Et_2Zn.TMED \longrightarrow (MePh_2Sn)_2Zn.TMED + C_2H_6$$

$$MePh_2SnH + EtZnCl \xrightarrow{THF} MePh_2SnZnCl + C_2H_6$$

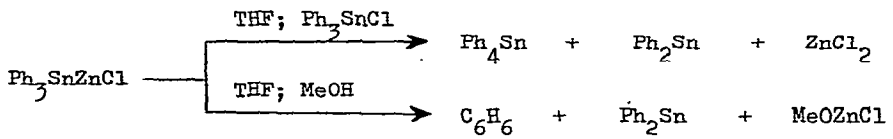
Dimeric, uncomplexed $Ph_3SnZnCl$ may be obtained by removing ether from the corresponding complex in vacuo. Coordination saturation at zinc or cadmium not only promotes reaction (reactions carried out in hydrocarbon solvents result in decomposition to zinc or cadmium metal), but also significantly

enhances the stability of the product. Thus, attempts to remove THF from $(Ph_3Sn)_2Zn.THF$ at $50^\circ/10^{-3}$ mm Hg result in gradual deposition of zinc, whereas the analogous TMED complex melts unchanged at 172.5-174°. Similarly, $Ph_3SnZnCl$ decomposes completely at 102-105°to zinc, but its TMED complex melts at 164-165°, again without decomposition.

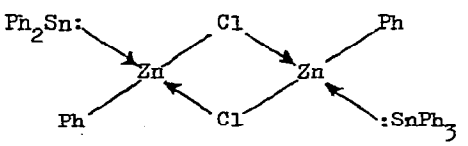
Complexed and uncomplexed triphenyltin-zinc chloride differ considerably in their chemical behaviour. The TMED complex LXXXII behaves as expected for a triphenyltin group attached to a more electropositive metal, eg.



Unsolvated $Ph_3SnZnCl$ in THF, in contrast, displays completely different reactivity:



These reactions indicate a phenyl group migration from tin to zinc, similar to that previously postulated for $Ph_3SnMgBr$, and hence the complex is formulated as the stannylene complex LXXXIII.



LXXXIII

Chemical evidence lends support to this formulation. The products of the reactions with iodine and methyl iodide are readily rationalised on the basis of oxidative-addition of the reagent to a "Ph_2Sn:" species, followed by phenylation of the resultant product by "PhZnCl", viz.:

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$$Ph_2Sn.PhZnCl \xrightarrow[THF]{MeI} ZnClI + Ph_2MeSnI \xrightarrow{[PhZnCl]} Ph_3SnMe$$

36% 52%

$$Ph_2Sn.PhZnCl \xrightarrow[THF]{I_2} ZnClI + Ph_2SnI_2 \xrightarrow{[PhZnCl]} Ph_3SnI + Ph_4Sn$$

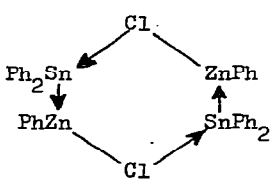
37% 58% 3%

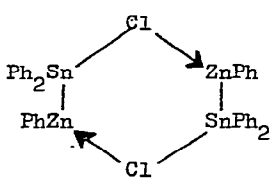
The phenyl migration may be reversed by the addition of strongly coordinating ligands such as TMED. Both methyl and phenyl group migration is observed for $MePh_2SnZnCl$:

$$MePh_2SnH + EtZnCl \xrightarrow{THF} MePh_2SnZnCl \xrightarrow[THF]{2MeOH} CH_4 + C_6H_6$$

12% 88%

Nmr evidence confirms the methyl group migration. Addition of TMED to a THF solution of $MePh_2SnZnCl$ causes a shift of the methyl resonance of δ -0.78 ppm to δ -0.97, the latter position being identical to that in MeZnCl.TMED. Tin-119m Mössbauer evidence, however, does not support formulation as a stannylene complex (formally Sn^{II}), but rather the resonance structures

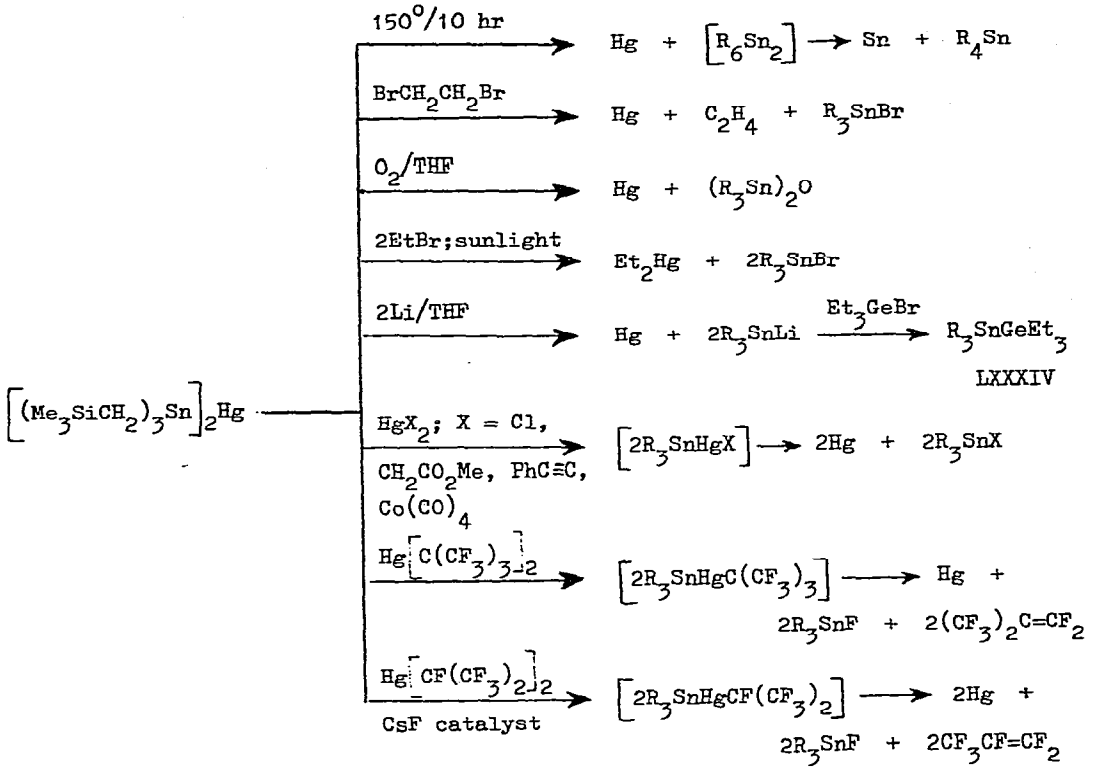




The actual structure most probably possesses phenyl groups bridging both tin and zinc (cf. triphenylaluminium).

The silylmethylstannyl derivatives, $(Me_3SiCH_2)_3Sn_2M$ (M = Cd, Hg), (from hydrostannolysis of Et_2M by $(Me_3SiCH_2)_3SnH$) exhibit markedly enhanced thermal stability over normal alkyl derivatives. Both compounds are stable in polar and non-polar solutions, and melt without decomposition

at ca. 100°. The reactions of the stannyl mercurial have been investigated extensively:



The germylstannane LXXXIV may also be obtained by the reaction [197]:

$$(Et_3Ge)_2Hg + R_3SnCl \longrightarrow Et_3GeCl + [R_3SnHgGeEt_3] \xrightarrow{-Hg} R_3SnGeEt_3$$

The reaction of $(Me_3Ge)_2Hg$ and trialkyltin methoxides yield the mixed mercurials LXXXV, which are in equilibrium with the corresponding symmetrical mercurials:

$$Me_3Ge\text{-}Hg\text{-}GeMe_3 + R_3SnOMe \longrightarrow Me_3Ge\text{-}Hg\text{-}SnMe_3 + Me_3GeOMe$$

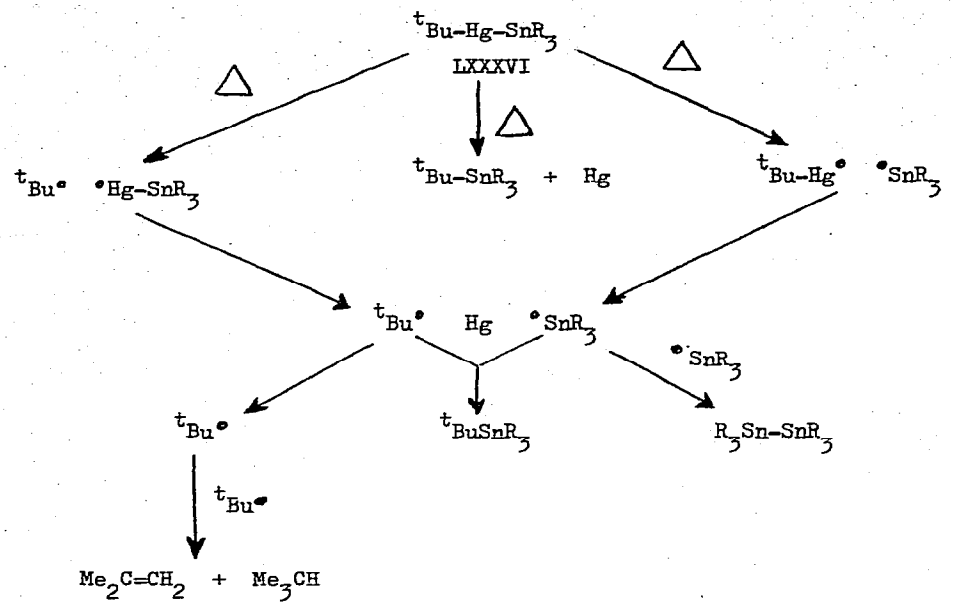
R = Me, Et

$$\tfrac{1}{2}(Me_3Ge)_2Hg + \tfrac{1}{2}(R_3Sn)_2Hg$$

References p. 140

when the reaction mixture was irradiated with a sunlight lamp, mercury, hexamethylditin, $(Me_3Ge)_2Hg$, and $Me_3GeSnMe_3$ are produced [198].

Mitchell [199] has used the phenomenon of CIDNP to demonstrate the free-radical nature of the thermal decomposition of the stannyl-mercurials LXXXVI (R = Me, Et), according to the scheme

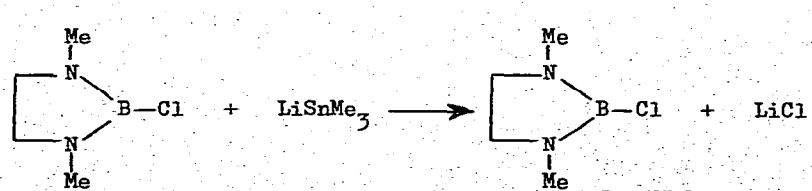


Evidence that the first step involves homolytic Hg-Sn rather than Hg-C bond cleavage comes from the reaction of the stannyl-mercurials with malononitrile derivatives, which afford stannylketeneimines:

$$^tBuHgSnR_3 + XC_6H_4CH{=}C(CN)_2 \longrightarrow XC_6H_4CH^tBu.C(CN){=}C{=}N.SnR_3$$

When the decompositions are carried out with the presence of nitrosobenzene or hexamethylditin, the tert-butylphenylnitroxide radical ^tBuPhNO and $Et_3Sn-SnMe_3$, respectively, are formed.

Treatment of 1,3-dimethyl-2-1,3,2-diazaborolidine with trimethylstannyllithium gives the borylstannane LXXXVII [200].



LXXXVII

Cleavage of the Si-Sn bond of $Me_3SiSnBu_3$ by lithium dibutylamide gives a high yield of the aminosilane [141]:

$$Me_3SiSnBu_3 + Bu_2NLi \longrightarrow Me_3SiNBu_2 \quad (74\%)$$

Lead tetraacetate converts tin-tin bonded compounds to tin acetate derivatives under very mild conditions [73]:

$$Et_3Sn\text{-}SnEt_3 + Pb(OAc)_4 \xrightarrow[\text{benzene}]{20^\circ} 2Et_3SnOAc\ (87\%) + Pb(OAc)_2\ (90\%)$$

$$(Ph_2Sn)_6 + 3Pb(OAc)_4 \xrightarrow[\text{benzene}]{20^\circ;\ \text{exothermic}} Ph_2(AcO)Sn\text{-}Sn(OAc)Ph_2\ (57\%) + 3Pb(OAc)_2\ (77\%)$$

Irradiation of mixtures of hexaalkyldistannanes and diarylketones in benzene at 20-25° affords bis-stannylbenzpinacols LXXXVIII.

$$2Ar\text{-}CO\text{-}Ar + R_3Sn\text{-}SnR_3 \xrightarrow{h\nu} Ar_2C(OSnR_3)\text{-}C(OSnR_3)Ar_2$$

LXXXVIII

The derivatives LXXXVIII are stable in non-polar solvents up to 20°, but on warming the solutions become cherry-red, due to dissociation into the stabilised radicals IXC, which may also be obtained from di-tert-butylperoxide and the organotin alkoxide XC. On heating to 60-70°, the starting ketone and distannane are produced [201]:

$$LXXXVIII \rightleftharpoons 2Ar\dot{C}OSnR_3 \xrightarrow{70^\circ} 2Ar_2CO + [2R_3Sn\cdot] \rightarrow R_3SnSnR_3$$

IXC

$$-2\,{}^tBuOH \uparrow \quad {}^tBuO{}^tBu + 2Ar_2C(OSnR_3)H$$

XC

References p. 140

The reaction of tert-butylperoxy radicals with hexaphenylditin is first order in both radical and distannane concentrations [202]. Ingold has observed a weak esr signal due to $Me_3Sn^{\bullet}$, rather than the expected strong signal due to $Me_3SnSnMe_2\dot{C}H_2$ radicals, when hexamethylditin is photolysed in the presence of di-tert-butylperoxide indicating a S_H2 reaction at the tin centre [203]:

$$^tBuO^{\bullet} + Me_3SnSnMe_3 \longrightarrow Me_3SnO^tBu + Me_3Sn^{\bullet}$$

12. Transition Metal Derivatives

Davison has investigated the stability of seven-coordinate triphenyltin-substituted Group V metal carbonyls. The thermally unstable hexacarbonyl derivatives XCI may be obtained from the corresponding anions, although the presence of water is necessary for the preparation of the vanadium compound.

$$\left[M^I(diglyme)_n\right]\left[M(CO)_6\right] + Ph_3SnCl \xrightarrow{CH_2Cl_2} Ph_3SnM(CO)_6$$

XCI

$M^I = K$, $n = 3$; $M^I = Na$, $n = 2$

$M = V, Nb, Ta$

These compounds undergo facile cleavage of the Sn-M bond in weak donor solvents such as ether and THF. For example, in the latter solvent, $Ph_3SnTa(CO)_6$ is completely dissociated into the $\left[Ta(CO)_6\right]^-$ anion and presumably solvated Ph_3Sn^+ species. This dissociation is reversible, and on removal of the solvent, $Ph_3SnTa(CO)_6$ may be recovered quantitatively. Phosphine substitution at the Group V metal, however, enhanced the stability of the Sn-M bond. Although direct substitution of the Nb and Ta compounds using Ph_3P and $Ph_2PCH_2CH_2PPh_2$ is rapid even at 0^o, substitution of the V derivative is exceedingly slow and is accompanied by much decomposition. Substitution by triphenylphosphite is similar; $Ph_3SnTa(CO)_5\left[P(OPh)_3\right]$ is formed in five hours, but $Ph_3SnV(CO)_6$ is unreactive. The phosphine substituted derivatives are more conveniently synthesised by mixing Ph_3SnCl, the phosphine, and the appropriate hexacarbonyl metallate in methylene chloride. The effect of phosphine substitution on the stability is quite marked. $Ph_3SnV(CO)_5PPh_3$ and $Ph_3SnV(CO)_4(Ph_2CH_2)_2$ are both stable in THF, in which the hexacarbonyl is completely dissociated. $Ph_3SnV(CO)_5PPh_3$ undergoes complete heterolysis in acetone, whereas the diphosphine derivative may be

refluxed in this solvent and acetonitrile without change [204] $Ph_3V(CO)_4$-$(Ph_2PCH_2)_2$ is cleaved by iodine at -60° in methylene chloride to afford $IV(CO)_4(Ph_2PCH_2)_2$ [205].

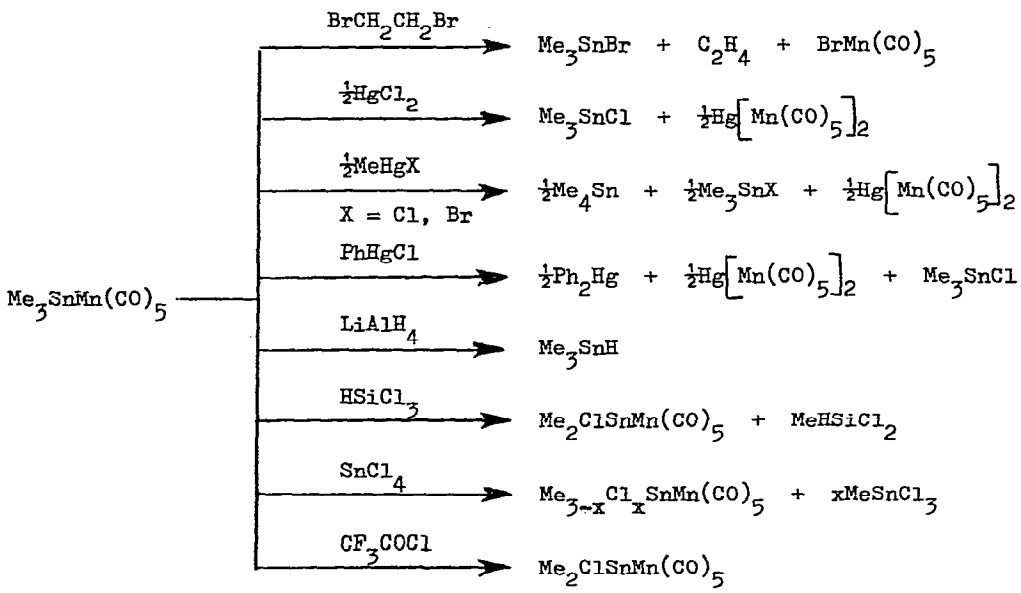
The zirconium and hafnium derivatives XCII are readily obtained by substitution of the metallocene dichlorides with triphenylstannylsodium [206].

$$(C_5H_5)_2MCl_2 + Ph_3SnNa \xrightarrow[THF]{-50^\circ} (C_5H_5)_2M(SnPh_3)Cl + NaCl$$

XCII

M = Zr, Hf

Reaction between trimethyltin hydride and $Mn_2(CO)_{10}$ affords $Me_3SnMn(CO)_5$, but only in poor yields. The compound is unaffected by protic reagents such as water, methanol, and aqueous sodium hydroxide, but undergoes Sn-Mn or Sn-C cleavage with a number of reagents, viz. [207]:



Cleavage of the Mo and W compounds $Me_3SnM(C_5H_5)(CO)_3$ by iodine proceeds with dominant Sn-M bond fission, although some displacement of carbon monoxide occurs in more polar solvents. Mercuric halides react similarly, but

without any CO formation:

$$Me_3SnM(C_5H_5)(CO)_3 + HgX_2 \longrightarrow Me_3SnX + XHgM(C_5H_5)(CO)_3$$

Tin-carbon bond fission occurs with triallyl derivatives:

$$(CH_2{=}CHCH_2)_3SnM(C_5H_5)(CO)_3 + HgX_2 \longrightarrow CH_2{=}CHCH_2HgX + (CH_2{=}CHCH_2)_2Sn(X)M(C_5H_5)(CO)_3$$

Treatment of the trimethyltin derivatives with organomercuric chlorides in acetone rapidly yields the mercurials XCIII, which subsequently undergo slow symmetrisation [208]:

$$Me_3SnM(C_5H_5)(CO)_3 + RHgCl \longrightarrow Me_3SnCl + RHgM(C_5H_5)(CO)_3$$

R = Me, Ph, $CH_2{=}CHCH_2$

$$\downarrow \text{XCIII}$$

$$R_2Hg + Hg[M(C_5H_5)(CO)_3]_2$$

The compounds $(C_5H_5)Mo(CO)_2(L)SnMe_3$ (L = PPh_3, $P(OPh)_3$, $PPhMe_2$, $P(OCH_2)_3CCH_3$, $AsPh_3$, $SbPh_3$) are prepared by the reaction of the anion $[(C_5H_5)Mo(CO)_2L]^-$ with Me_3SnCl. The PPh_3 complex may also be synthesised by the substitution of $(C_5H_5)Mo(CO)_3SnMe_3$ by PPh_3 at 160°. The derivatives disproportionate at 200° giving Me_4Sn and $Me_2Sn[Mo(C_5H_5)(CO)(L)]_2$ [209].

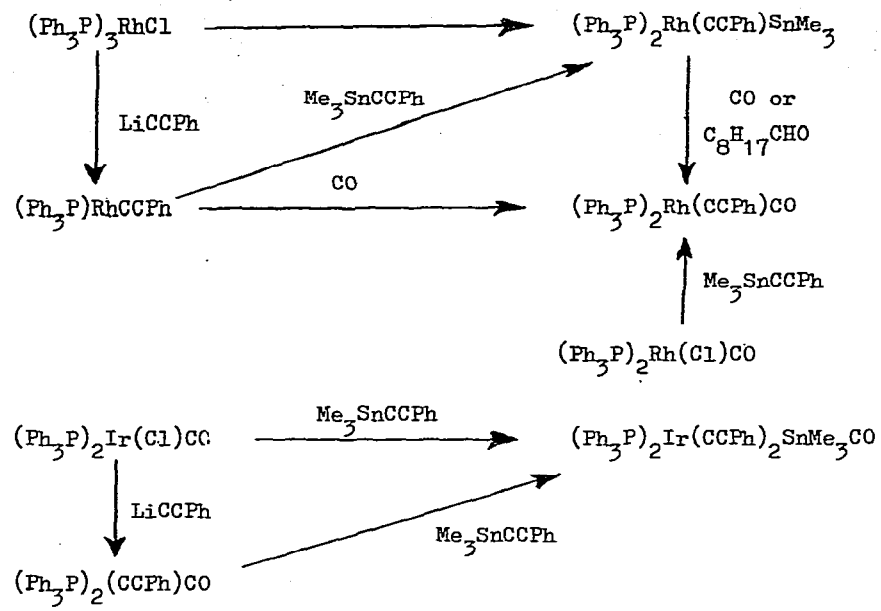
Lappert has synthesised several tin-transition metal derivatives using alkynylstannanes according to the schemes [210]:

$$(C_5H_5)Mo(CO)_3{}_2 + Me_3SnCCPh \xrightarrow[CO;\ 36\ hr]{\text{refluxing diglyme}} (C_5H_5)Mo(CO)_3SnMe_3$$

$$Co_2(CO)_8 + Me_3SnCCPh \xrightarrow{THF;\ 20^\circ;\ \frac{1}{2}\ hr} Me_3SnCo(CO)_4$$

$$(Ph_2RP)_nPt + R'SnCCPh \longrightarrow (Ph_2RP)_2Pt(CCPh)SnR'_3$$

R = Me, Ph; n = 3, 4; R' = Me, Et



The crystal structure of $\left[(Me_2Sn)Fe(CO)_4\right]_2$ has been determined, and is shown in Fig. 9. The four-membered Fe_2Sn_2 ring is planar with a

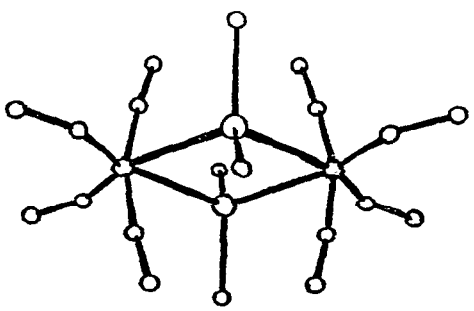


Fig. 9 The structure of $\left[Me_2SnFe(CO)_4\right]_2$ [211]. (Reproduced by permission of the Chemical Society).

Fe-Sn-Fe bond of 103°. The Fe-Sn bond distance corresponds closely to the sum of the covalent radii of Fe^{II} and Sn^{IV} [211]. Marks has reported that compounds of this class undergo rapid homolytic cleavage of the metal-metal bond in solution in the presence of Lewis bases (L) to give 'stannylene' complexes:

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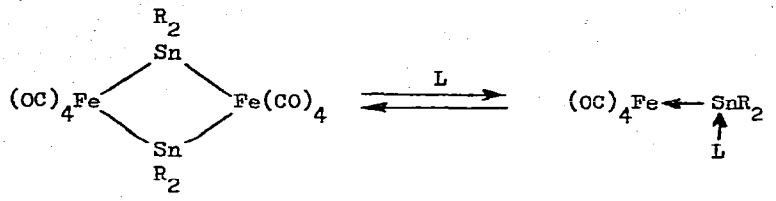
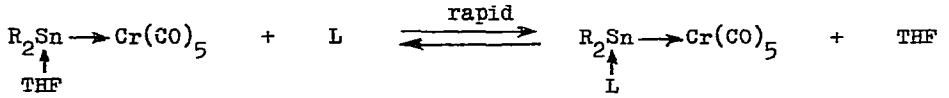
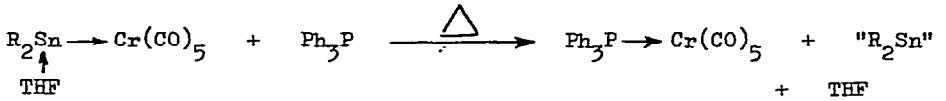


Similar equilibria may also be detected for stannylene-chromium carbonyl complexes:

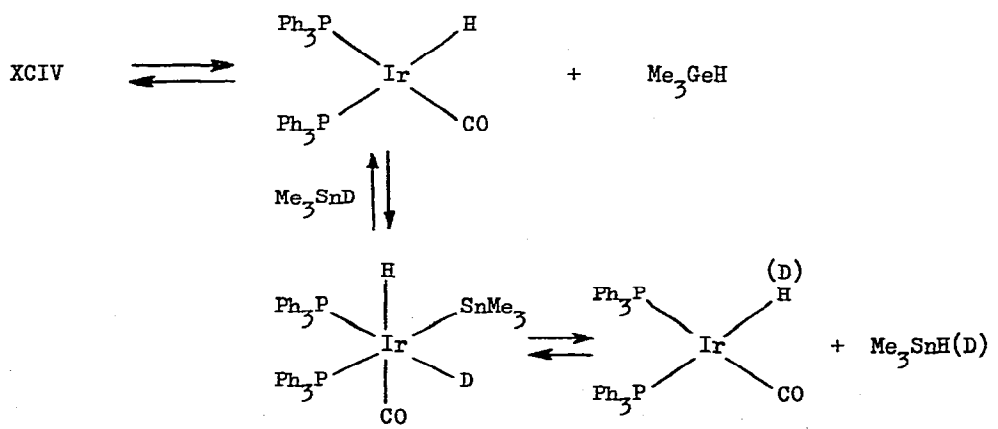


Triphenylphosphine, however, causes displacement of the stannylene [212]:



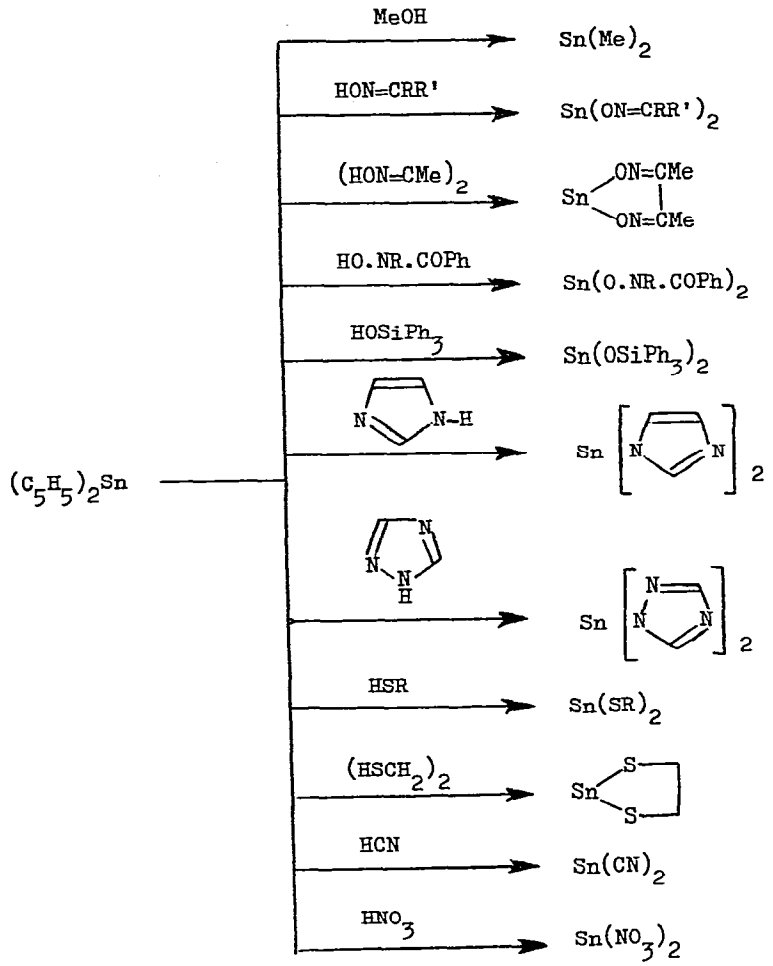
Tris(triphenylphosphine)nickel undergoes double oxidative-addition of R_3SnCl (R = Me, Ph) to give the stable complexes $Ni(PPh_3)_2(SnR_3)_2Cl_2$. Preliminary X-ray analysis of the trimethyltin derivative indicates a trans,trans,trans octahedral configuration about nickel [213].

The reaction of trialkylstannanes to trans-$(Ph_3P)_2(CO)ClIr$ are complex. However, with the dihydroiridium complex $(Ph_3P)(Me_3Ge)(CO)(H)_2Ir$ XCIV, displacement of trimethylgermane occurs and the analogous trialkylstannyl complex is formed. Using Me_3SnD, both Me_3GeH and Me_3GeD are formed and both iridium protons are equally deuterated, suggesting a mechanism involving reversible dissociation and reversible oxidative-addition steps [214]:



13. Divalent Derivatives

The cyclopentadienyl rings of dicyclopentadienyltin are easily removed by protic reagents leading to a wide range of previously inaccessible inorganic tin(II) derivatives [215,216].



Halide-ring exchange takes place with stannous halides in THF producing mono-organotin(II) halides as white crystalline solids:

$$(C_5H_5)_2Sn + SnX_2 \longrightarrow C_5H_5SnX$$

X = Cl, Br

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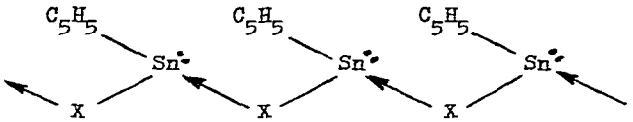
Mono-organotin derivatives may also be prepared by protolysis:

$$C_5H_5SnOPh \xleftarrow{PhOH} (C_5H_5)_2Sn \xrightarrow{HCl} C_5H_5SnCl$$

Although monomeric in solution, the solid state structure of the mono-organotin halides is thought to involve halide bridges [217]:



Amma has synthesised and determined the structures of two more arene-tin(II) derivatives. The complexes $[Ar.SnCl(AlCl_4)]_2$ (Ar = Ph, p-MeC_6H_4Me) (from $SnCl_2$ and a deficiency of $AlCl_3$ in the aromatic solvent) exhibit distorted octahedral coordination at tin. In both complexes the C_6 ring is axially symmetric (viz. Fig. 10) [218].

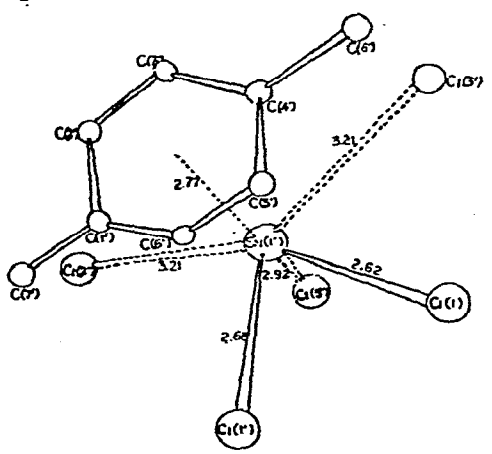


Fig. 10 The structure of $[p\text{-}MeC_6H_4Me.SnCl(AlCl_4)]_2$ [218]. (Reproduced by permission of the American Chemical Society).

14. Applications

A tunsten hexachloride - tetramethyltin mixture is a catalyst for the metathesis of methyl esters of unsaturated fatty acids. Thus, the methyl esters of cis and trans-octadec-9-enoic acid are converted into octadec-9-ene and the dimethyl ester of octadec-9-ene-dioic acid [219].

Several patents report application as pesticides [35b, 220-226], fungicides [24, 33, 35, 227-229], lubricant antioxidants [230], stabilizers for halogen-containing resins [130], epoxide polymerisation catalysts [231,232], catalysts for polyurethane foam production [233]. A report documents attempts to prepare organotin compounds possessing antimalarial activity [234].

15. Physical Measurements

(i) Bond Energies

Pedley has evaluated the thermochemical bond energy terms E(Sn-X) for a number of compounds: Me_3SnOH, E(Sn-O) = 77 kcal/mole; Me_3SnOEt, E(Sn-O) = 66 kcal/mole; Me_3SnCl, E(Sn-Cl) = 75 kcal/mole; Me_3SnBr, E(Sn-Br) = 61 kcal/mole; Me_3SnI, E(Sn-I) = 45 kcal/mole; Me_3SnSBu^n, E(Sn-S) = 52 kcal/mole; Me_3SnNMe_2, E(Sn-N) = 41 kcal/mole; $(Me_3Sn)_2NMe$, E(Sn-N) = 48 kcal/mole; $(Me_3Sn)_3N$, E(Sn-N) = 42 kcal/mole [238]. Sisler has estimated the bond dissociation energy of the Sn-P bond to be 44 kcal/mole [192]. $D(Me_3Sn-Me)$ has been estimated to be 64.5 kcal/mole [46].

(ii) Infra-red and Raman Spectra

The following compounds have been the subject of study in varying degrees of detail: Ph_3RSn (R = ^tBu, ^iBu, Neophyl)(IR) [28]; stannylcarboranes (IR) [237]; organotin ferrocenes (IR) [25]; $Et_3SnCH_2CO_2Me$ (IR) [239]; benzyltin (IR, R) [240] and para-substituted benzyltin (IR, R) compounds [241]; Me_nSnF_{4-n} (n = 3,2,1), Me_2SnClF, $MeSnCl_2F$ (IR, R) [98a]; Me_2SnF_2, $Me_2Sn(C_5H_7O_2)_2$ and $Me_2SnCl_2.2DMSO$ (single crystal R) [242,243]; adducts of stannous halides with dimethylacetylene dicarboxylate (IR, R) [98]; $R_2SnCl_2.mR_nEO$ (R = Me, Ph; m = 1, 2; E = C, N, P, S) (IR) [103,103a]; organotin complex anions and cations (IR) [105,106]; substituted cyanamide-Ph_3SnBr complexes and N'-cyano-S-(triphenylstannyl)-isothioureas (IR) [116]; diorganotin diisothiocyanate complexes of terpyridyl and 8-(2-pyridylmethyleneamino)quinoline (IR) [120]; $(Bu_3Sn)_2NEt$, Bu_3SnNRR' and $Bu_2Sn(NR_2)_2$ (IR, R) [244]; $Me_3SnPHPh$ (IR) [245]; Bu_3SnNSO (IR) [119]; trialkyltin pyrazoles, imidazoles, and triazoles (IR) [185,186]; adducts of $Bu_3SnN{=}CPh_2$ (IR) [180] and $Me_3SnNMeSiMe_3$ (IR) [181] with various unsaturated acceptor molecules; $Me_3SnO_2CCH_2CH_2PEt_2$ and $Me_3SnO_2CCH_2CH_2COPEt_2$ (IR) [188]; triorganotin oxides and hydroxides (IR) [121]; $Bu_2Sn(o\text{-}XC_6H_4NH_2)(OH)$ (X = O, NH), $Bu_2Sn(o\text{-}C_6H_4NH)$, $Bu_2Sn(o\text{-}YC_6H_4NH_2)$ (Y = O, S) (IR) [129]; trialkyltin derivatives of thioglycol, glycollic acid and thioglycollic acid (IR) [176]; $Me_3SnONEt_2$,

$R_3SnONR'.COPh$ (R = Me, Pr, Ph; R' = H, Ph), NEt_3H^+ $Ph_3\overline{SnONCO}Ph^-$ (IR) [142]; $R_nSn[ONC(CN)_2]_{4-n}$ (R = Bu, Ph; n = 2, 3) (IR) [144]; $Me_2Snsalen$ (IR) [246]; dimethyltin phthalate, molybdate, and oxalate hydrate, o-phenylenedioxy- and 2,2'-biphenylenedioxydimethyltin (IR) [247]; dimethyltin chlorocarboxylates (IR) [151]; 1,3-bis(dicarboxylato)tetramethyldistannoxanes (IR) [152]; allyltin carboxylates (IR) [150]; R_3SnO_2SR, $R_2Sn(O_2SR)_2$ (R = Me, Et, ^nPr, ^iPr, Bu), $(R_3Sn)_2SO_4$ (R = Me, Et, ^nPr, ^iPr) (IR) 156,157 ; $Ar_nSn(O_2SAr)_{4-n}$ (n = 2, 3; Ar = Ph, $PhCH_2$, o-, m-, p-Tolyl) (IR) [159]; methyltin chlorosulphonato compounds (IR, R) [161]; dialkyltin bisfluorosulphates, bistrifluoromethanesulphonates, and bisdifluorophosphates (IR, R) [162]; organotin dithiocarbamates (IR) [167]; Et_4N^+ $R_3Sn(S_2C_2(CN)_2)^-$ (IR) [172]; $Me_3SnSeCOPh$ (IR) [179]; $(Ph_3Sn)_2M.L$ (M = Zn, Cd; L = TMED, bipyridyl) (IR) [196]; $(CO)_5M.PPh_2SnMe_nX_{3-n}$ (M = Cr, Mo, W; n = 3, 2, 1; X = Cl, Br) (IR) [190]; $Ph_3SnM(CO)_6$, $Ph_3SnM(CO)_5PPh_3$, $Ph_3SnV(CO)_5PBu_3$, $Ph_3SnTa(CO)_5P(OPh)_3$, $Ph_3SnM(CO)_4(Ph_2PCH_2)_2$ (m = V, Nb, Ta) (IR) [204]; $(C_5H_5)Mo(CO)_2(L)SnMe_3$ (L = PPh_3, $PPhMe_2$, $P(OCH_2)_3CCH_3$, $P(OPh)_3$, $AsPh_3$, $SbPh_3$), and $Me_2Sn[(C_5H_5)Mo(CO)_2L]_2$ (L = PPh_3, $P(OCH_2)_3CCH_3$) (IR) [209]; $allyl_3SnW(C_5H_5)(CO)_3$ (IR) [208]; $(PPh_3)_2Pt(CCPh)(SnR'_3)$, $(PPh_3)Rh(CCPh)_2SnMe_3$, $(PPh_3)Ir(CCPh)_2SnMe_3CO$ (IR) [210]; $(PPh_3)_2(Me_3Sn)(CO)(H)_2Ir$ (IR) [214]; $Me_2ClSnMn(CO)_5$ (R) [207]; $Ph_3SnMn(CO)_5$, $Ph_3SnMn(CO)_4(PPh_3)$, and $Ph_3SnFe(CO)_2(C_5H_5)$ (IR, R) [248]. The basicities of alkenylstannanes [249], tributyltin aryloxides and dimethylaryltin methoxides [250] have been determined. As expected, for the two series of organotin alkoxides, the elctron releasing substituents on the aryl groups increase the availability of the oxygen lone pairs [250].

(iii) Nmr Spectra

Much chemical shift and coupling constant data has been accumulated during 1972, and is listed here according to the nucleus under examination.

^1H:

Tetracyclopropyltin [251]; $Me_3SnC_5H_5$, $Sn(C_5H_5)_2$, and $(C_5H_5)_2Sn$-$Fe(CO)_2C_5H_5$ 2 [68,71]; $C_5H_4(SnMe_3)_2$ [67]; trimethylstannyl-2,4-cycloheptadiene, 1,1-dimethyl-4-trimethylstannyl-2,5-cyclohexadiene [64]; R_3PhSn (R = ^tBu, ^iBu, Neophyl) [28]; α-NpMePhSnR (R = CH_2=C=CHMe, CHMeC≡CH) [29]; $R'Me_2SnCHYMe$ (Y = Et, Ph; various R'), meso-$R''_2Sn(CHYMe)_2$ (R" = Me, CH_2Ph), $Me_{4-n}Sn(CHZMe)_n$ (Z = Et, Pr,; n = 2, 3), and $Me^iPr^{cyc}HexSnCHMePh$ [72]; dimethyltin derivatives of substituted ferrocenes [26]; 2-vinyl-4,4,6-trimethyl-1,3,2-dioxaborinane - triorganotin hydride adducts [77]; sec-butyl- and α-deuterio-sec-butyltrimethyltin [40]; $R_3Sn(CH_2)_nCH=CHR'$ (R = Me, Et;

R' = H, Ph; n = 1, 2) [256]; cis- and trans-4-tert-butyl-cyclo-hexyltrimethyltin [193]; $MeSnR_3$ (R = Me, $CH{=}CH_2$, Ph, 2-thienyl, 3-thienyl, 2-furyl, 3-furyl), $Sn(C_6H_4X\text{-}p)_4$ (X = OMe, Me, D, Cl) [257]; $(YC_6H_4CH_2)_nSnCl_{4-n}$ (Y = H, F, Cl; n = 2, 3, 4) [258]; tert-butylphenylneophyltin iodide [259]; Me_4Sn, Me_nSnX_{4-n} (X = Ph, Cl, Br, I), Et_4Sn, $EtSnMe_3$, Et_3SnMe, Et_3SnX (X = Cl, Br, I), Et_2SnCl_2 [260]; Bu_3SnCH_2Ph and tributyltin succinimide [290]; mixed tetraorganotins [252]; Me_3SnR (R = Me, $PhC{\equiv}C$, PhS, PhO, Cl, Br, I) [253]; Ph_4Sn, $Ph_3SnCH{=}CH_2$, Ph_3SnN_3, Ph_2SnCl_2 [254]; Me_3SnNSO [119]; $Me_nSnCl_{4-n}.(NH)_2SMe_2$ (n = 1,2,3) [104]; N-trialkyltin derivatives of imidazoles, pyrazoles, and triazoles [186]; addition compounds of $Bu_3SnN{=}CPh_2$ [180] and $Me_3SnNMeSnMe_3$ [181] with various unsaturated acceptor molecules; $Me_3SnPHPh$ and $Me_3SnOPHPh$ [245]; Me_3SnPPh_2, $(CO)_5M.PPh_2SnMe_nX_{3-n}$ (M = Cr, Mo, W; X = Me, Cl, Br; n = 3, 2, 1) [190]; $Me_3SnO_2CCH_2CH_2PEt_2$ and $Me_3SnO_2CCH_2CH_2COPEt_2$ [188]; $(R_3SnOCAr_2)_2$ [202]; bis(acetylacetonato)organotin compounds [255]; organotin carbamates [167]; $Me_3SnSeCOPh$ [179]; Et_4N^+ $Me_3SnS_2C_2(CN)_2^-$ [172]; trialkyltin derivatives of thioglycol, glycolic acid, and thioglycolic acid [176]; $Me_3SnONEt_2$, $Me_3SnONR.CO.Ph$ (R = H, Ph) [142]; dimethylchlorotin carboxylates [151]; $Me_3SnS.CO.NMe_2$, $Me_3SnE_2CNMe_2$ (E = O, S) [261]; o-, m-, and p-tolyltin chlorides and arylsulphinates [159]; Et_3SnOH [121]; $(TMPN{=}O)^+(Me_2SnCl_3)^-$ [106]; $Me_3SnM(CO)_3C_5H_5$ (M = Mo, W) [208]; $(C_5H_5)Mo(CO)_2(L)SnMe_3$ (L = PPh_3, $P(OCH_2)_3CCH_3$, $P(OPh)_3$, $PPhMe_2$, $AsPh_3$, $SbPh_3$), $(C_5H_5)Mo(CO)_2(L)\ SnMe_2$ (L = PPh_3, $P(OCH_2)_3CCH_3$) [209]; $(Ph_3P)_2(Me_3Sn)(CO)(H)_2Ir$ [214]; $Ph_3SnM(C_5H_5)_2Cl$ (M = Zr, Hf), $Me_3SnZr(C_5H_5)_2Cl$ [205]; $Ni(PPh_3)_2(SnMe_3)_2Cl_2$ [213]; $^tBuHgSnR_3$ [199]; $Me_3GeHgSnMe_3$ [198]; $MePh_2SnZnCl$ [195]; C_5H_5SnX (X = Cl, Br) [217].

^{13}C:

$Me_3CXMe.CHMe.CCl_2H$, $Me_3SnCXMeCH_2Me$ (X = H, D) [40]; trimethylstannylindene [70]; Me_3SnSPh [295].

^{14}N:

Ph_3SnN_3 [254].

^{19}F:

Ph_3SnSAr (Ar = C_6H_4F-4, $C_6H_2Me_2$-2,6-F-4, $C_6H_2Br_2$-2,6-F-4) [262]; trimethylstannyl [263] and triphenylstannylmethyl [264] fluoronaphthalenes, fluorobenzenes, and fluorobiphenyls; $Me_3SnCF_2CF_2Mn(CO)_5$, $Me_3SnC(CF_3)C(CF_3){=}C(CF_3)C(CF_3)Mn(CO)_5$ [265].

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^{31}P:

$(R_3Sn)_nPX_{3-n}$ (R = H, Me, Bu, Ph; X = H, Me, Ph; n = 3, 2, 1) [266]; Me_2SnPPh_2, $(CO)_5M.PPh_2SnMe_nX_{3-n}$ (M = Cr, Mo, W; X = Me, Cl, Br; n = 1, 2, 3) [190].

^{55}Mn:

$Ph_3SnMn(CO)_5$ [267].

^{119}Sn:

Me_3SnCl/solvent interactions [101]; ethyl- [268] and benzyl- [258] tin compounds; di- and trialkyltin alkoxides [269]; organotin carboxylates [270]; $Me_3Sn(CH_2)_nCH=CH_2$ (n = 1, 2, 3) [256]; $RSnCl_3$ (R = Me, Et, Bu, octyl, Ph) [126].

Ulrich and Dunnell have studied molecular motions of trimethyltin fluoride by continuous wave and pulsed nmr methods. Their results show that the trimethyltin group rotates about its chain axis at high temperatures, with relatively free methyl group rotation even at 77°K [271].

(iv) Tin-119m Mössbauer Spectra

Tin-119m Mössbauer studies of organotins have been the subject of a thesis [272]. Bancroft has deduced the quadrupole moment of ^{119}Sn to be $-0.062\pm0.02\times10^{-28}$ m^2 [273]. Clark et al have used a simple molecular orbital model for the correlation of Mössbauer quadrupole splitting with stereochemistry in organotin(IV) compounds [274].

Data is available for the following compounds: $R_3Sn(CH_2)_3SR'$ (R = Me, Et, Bu; R' = Ph, p-tolyl), Bu_3SnSR' [38]; $(RSCH_2)_4Sn$ (R = Bu, Ph), Bu_2SnCH_2SPh, $[PhSCH_2Sn(O)O_2CMe]_x$, $(PhSCH_2)_2SnO$ [34]; $(C_5H_5)Fe\ C_5H_3(CH_2NMe_2)SnBu_3$ (^{57}Fe and ^{119}Sn) [25]; organotin derivatives of o-, m-, and p-carboranes [275]; triphenyltin compounds [276]; triorganotin derivatives of imidazoles, pyrazoles, and triazoles [185]; $R_2Sn(NCS)_2.L$ (R = Me, Bu, Ph; L = bipyridyl, terpyridyl, 8-(2-pyridylmethyleneamino)quinoline), $[R_2Sn(NCS)terpyr]^+[BPh_4]^-$, Bu_2SnF_2.o-phenanthroline [120]; R_3SnOH, $R_3SnOSnR_3$ (R = Me, Et, Pr, Bu, octyl, Ph) [121]; di- and trialkyltin alkoxides [269]; $Me_3SnONEt_2$, $R_3SnONR'.COPh$ (R = Me, Pr, Ph; R' = H, Ph), $NEt_3H^+\ Ph_3SnONCOPh^-$ [142]; dimethylchlorotin carboxylates [151]; monoalkyltin orthosulphites [160]; dialkyltin bisfluorosulphates, bistrifluoromethane sulphonates, and bisdifluorophosphates [162]; $Me_nSnCl_m(SO_3X)_{4-(n+m)}$ (n,m = 0, 1, 2; X = F, CF_3) [161]; dimethyltin oxalate monohydrate, phthalate, molybdate, tungstate, and carbonate, o-phenylenedioxydimethyltin [247]; $Me_2Snsalen$ [246]; organostannonic acids, organo-

stannatranes, and organotin sesquisulphides, $BuSn(OMe)_3$ [126]; R_3SnR' (R = Bu, Ph; R' = Ac, $CH_2CH_2SSnBu_3$, Ph, C_6H_4-NH_2-2, $Ph_3SnSC_5H_4N$-2, $Ph_3SnSC_5H_4N$-4 [166]; organotin dithiocarbamates [167]; diorganochlorotin dithiocarbamates [170]; Et_nSnX_{4-n} (n = 4, 3, 2; X = Cl, Br, I) [277]; Me_3SnF, $MeSnF_3$, $MeSnCl_2F$, Me_2SnClF, R_2SnF_2 (R = Me, Et, Pr, Bu, octyl) [98a]; stannous halide adducts of dimethylacetylene dicarboxylate [98]; $R_2SnCl_2.nR'_mEO$ (n = 1, 2; E = C, N, P, S) 103,103a ; tin-manganese [278-282] and tin-iron [281,282] bonded compounds; C_5H_5SnX (X = Cl, Br) [217].

(v) Mass Spectra

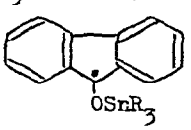
PhR_3Sn (R = ^tBu, ^iBu, Neophyl) [28]; trimethylstannyl-2,4-cycloheptadiene and 1,1-dimethyl-4-trimethylstannyl-2,5-cyclohexadiene [64]; 5,10-dihydrophenazastannanes [283]; 10,11-dihydro-5H-dibenzo[b,f]stannepins [283]; mixed tetraalkyltins and trimethyltin halides [284]; $Ph_2SnCl(S_2CNEt_2)$ [170]; 2-(tributylstannyl)-4,5-diethyl-1,2,3-triazole [186].

(vi) Ultra-violet Spectra

PhR_3Sn (R = ^tBu, ^iBu, Neophyl) [28]; trialkyltin triazoles [186]; $(Ph_3Sn)_2M.L$ (M = Zn, Cd; L = bipyridyl, TMED) [196]; $(PPh_3)_2Ni(Cl)_2(SnR_3)_2$ [213]; $(C_5H_5)Mo(CO)_2(L)SnMe_3$ (L = PPh_3, $P(OPh)_3$, $PPhMe_2$, $P(OCH_2)_3CCH_3$, $AsPh_3$ $SbPh_3$) [209].

(vii) Electron Spin Resonance

Spectra due to the following organotin radicals have been observed: $Et_3\dot{S}nCHCH_3$, $Bu_3SnO\dot{C}HCH_2CH_3$ [285]; $Bu_3SnCH_2\dot{C}H{=}CH\dot{C}H_2$ [286]; $Me_3SnCH_2\dot{C}H_2$ [287]; $Me_3Sn\dot{C}H_2$ [288]; $Bu_3SnCH_2\dot{C}HEt$, $Et_3SnCH_2\dot{C}H_2$ [289]; $Me_3Sn\bullet$ [203]; $R_3SnO\dot{C}Ar_2$ (R = Me, Et, Ph; Ar = Ph, p-tolyl, p-$Me_3SnC_6H_4$),



(R = Me, Et) [202]

(viii) Kinetic Data

Rate constants have been determined for the following reactions: Homolytic substitution of tetraalkyltins by N-halogenosuucimides [290]; reaction of tert-peroxy radicals with $^nPr_3SnCl$ [285] and hexaphenylditin [202]; hydrostannation of 2-vinyl-4,4,6-trimethyl-1,3,2-dioxaborinane with R_3SnH (R = Me, Et, Pr, Bu, Ph) [77]; ozonolysis of hexaethylditin [291]; self-reactions of $Me_3Sn\bullet$ and $Me_3S\dot{n}CH_2$ radicals [203]; the pyrolysis of tetramethyltin [46]; the cleavage of cinnamyl- and benzyltin derivatives

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in strongly basic aqueous or alcoholic DMSO [58]; the cleavage of $PhMe_3Sn$ by KOH in aqueous DMSO [59].

(ix) Miscellaneous

Dipole moments have been evaluated for the following compounds: Me_nSnCl_{4-n} (n = 1-3) [255]; $Bu_3SnN_3C_2RR$ (R = Et, Ph), $Bu_3SnN_3C_2HPh$ [186]; iron-, molybdenum-, and tungsten-tin bonded compounds [292].

Molar conductances have been measured for $R_2Sn(NCS)_2.L$ (R = Me, Bu, Ph; L = terpyridyl, 8-(2-pyridylmethyleneamino)quinoline) [120]; $NEt_4^+ R_3SnS_2C_2(CN)_2^-$ (R = Me, Ph) [172].

Polarography has been applied to Me_2SnCl_2 [109] and $EtSnCl_3$ [108] in aqueous solution.

The ^{35}Cl nuclear quadrupole resonance frequency of $p\text{-}Me_3SnC_6H_4Cl$ has been measured [293].

The helium-(I) photoelectron spectrum of tetramethyltin has been reported and assigned using a simple molecular orbital model [294]. The $S_{2p_{\frac{3}{2}}}$ ESCA ionisation energy of Me_3SnSPh has been determined [295].

Crystal data for Ph_4Sn have been compared with other Group IV tetraphenyls [296]. X-ray powder data are available for $Et_4N^+ R_3SnS_2C_2(CN)_2^-$ (R = Me, Ph) [172].

Optical, electro-optical, and electrical properties of single crystal of Ph_4Sn have been investigated [297].

The Del Re method has been used to predict bond orders [298], nmr spectra [299], and chemical reactivity [300] of organotin compounds.

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