TIN

ANNUAL SURVEY COVERING THE YEAR 1971

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Books, reviews

In 1971 the first two volumes appeared of a new monograph entitled "Organotin Compounds", edited by A. K. Sawyer [1, 2]. Authors of a variety of well-known organotin research centers have contributed to this up-to-date monograph which covers the entire field of organotin chemistry. Volume I deals with the organotin hydrides, halides and oxygen derivatives (oxides, alkoxides). Volume II contains chapters on organotin oxygen (carboxylates, salts, complexes), sulfur, selenium, tellurium, nitrogen, phosphorous, arsenic, antimony and bismuth compounds. Much attention is given to reaction mechanisms and physical methods like IR and NMR spectroscopy. Tables of physical constants of compounds have been added to many chapters Complexes of organotin halides with amines have not been included. Volume III, containing among others a chapter on applications and biological effects of organotins will appear within short.

Sharp et al. composed a review with 458 references on inorganic, organic and organometallic compounds containing elements of Group I-VIII [3].

Less specific review articles on organometallic chemistry, organotin chemistry included, have been prepared by Stone [4, 5] and Rochow [6]. Heterocyclic compounds of the Group IV elements have been surveyed by Yoder and Zuckerman on the basis of 390 references [7].

Review papers on specific classes of organotin compounds are being mentioned below under the relevant headings.

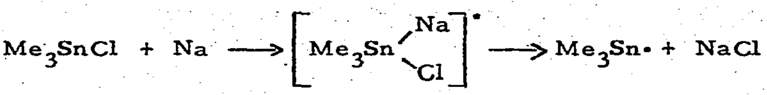
Direct syntheses. Matsuda prepared a review in Japanese on the methods of preparation of organotin compounds such as R_2SnX_2, $R_2R'SnX$, R_3SnH, R_4Sn and $(R_2Sn)_n$, together with reactions of tin-carbon bonds [8].

Organoantimony compounds have been found to be very effective catalysts in the direct synthesis of dialkyltin dibromides and dichlorides (cf. AS 69; 486) [9]. Reaction of tin powder with octyl chloride, initiated by octyl iodide and catalyzed by PCl_3 gives a mixture of Oct_2SnCl_2 (about 58%) and $OctSnCl_3$ (about 15%), whereas no Oct_3SnCl is formed [10]. Rather complex catalyst systems for the reaction of tin with alkyl halides have been described in a German patent application [11]. For example, reaction of tin (15 parts) with octyl chloride (56 parts) for 4 h at 155° in the presence of H_3BO_4 (0.6 parts), $OctNH_2$ (10 parts), red P (0.5 parts), I_2 (1.5 parts) and 1-octanol (1.7 parts), gave 94% conversion of tin to give 34% of $OctSnCl_3$, 47% of Oct_2SnCl_2 and 12% of Oct_3SnCl.

Reaction of tin with alkyl iodides to give alkyltin iodides may be catalyzed by amines (cf. AS 69; 486 and AS 70; 249) [12], by organic acids and alcohols (cf. AS 69; 486) [13] and by zinc together with alcohols [14, 15]. Another direct synthesis process involves reaction of tin/zinc or tin/magnesium mixtures with alkyl halides in the presence of a catalyst mixture comprising a quarternary ammonium salt and an ether, thioether or amine [16].

As regards the direct synthesis of dialkyltin dibromides under the influence of γ-irradiation (cf. AS 70; 249), Popova et al. determined the optimum ratio r of diameter to height for ^{60}Co γ-radiation chemical reactors [17].

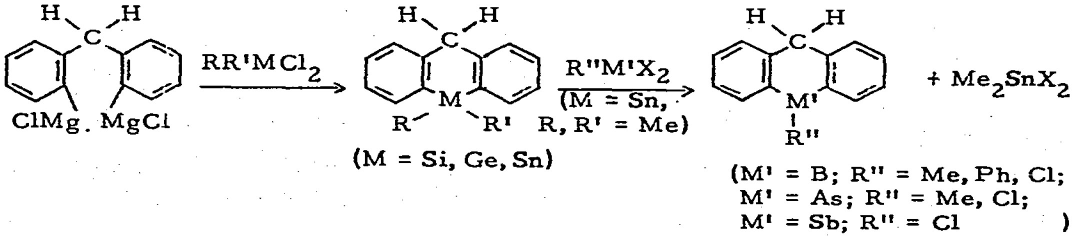
Alkylation and arylation. Rate studies of the gas-phase reaction of trimethyltin chloride with sodium were interpreted on the basis of attack of the sodium on tin instead of on chlorine, viz. [18]:



$$Me_3SnCl + Na \longrightarrow \left[Me_3Sn\begin{matrix}Na\\Cl\end{matrix}\right]^{\bullet} \longrightarrow Me_3Sn\bullet + NaCl$$

Russian authors reported a slightly modified Barbier synthesis of tetrabutyltin by reacting simultaneously magnesium, butyl bromide and tin tetrachloride in hydrocarbon solvent containing ten percent of dibutylether [19]. By means of Grignard procedures a series of alkoxyphenyltin derivatives, $(o\text{-}RO\text{-}C_6H_4)_4Sn$, have been synthesized [20].

According to Gotze [21] reaction of neopentylmagnesium bromide with tin tetrachloride gives 82% of tetraneopentyltin together with only a trace of hexaneopentylditin. In contrast, reaction of neopentylmagnesium chloride with tin tetrachloride has previously been reported to give trineopentyltin chloride (62%), hexaneopentylditin (32%) and only a trace of tetraneopentyltin [G. Zimmer. et al. J. Org. Chem., 29 (1964) 2632]. Grignard techniques were also applied by Jutzi in the synthesis of 9-sila, -germa and -stanna-dihydroanthracenes [22].



Tin-hydrogen compounds. Seyferth composed a review of reactions of Group IV hydrides and halides with diazoalkanes, carbenes, halomethylzinc compounds and sodio-trichloroacetate and the formation of carbenes from mercurials [23]. In reactions of organosilicon and organotin hydrides with zinc carbenoids generated from diethylzinc and geminal diazoalkanes it was observed that with Et_3SnH reduction of the organic iodide predominates over methylene insertion into the Sn-H bond [24]:

$$\begin{tikzcd} & \mathrm{Et_3SnMe}\ (21\%) & \\ \mathrm{Et_3SnH + CH_2I_2 + Et_2Zn} \arrow[ur] \arrow[dr] & & \\ & [\mathrm{Et_3SnI}] \arrow[r, "\mathrm{EtZnX}"] & \mathrm{Et_4Sn}\ (53\%) \end{tikzcd}$$

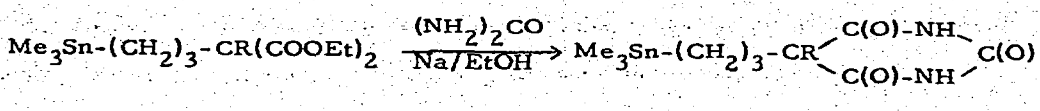
By conventional techniques some mixed alkyl and alkylaryltin dihydrides, $RR'SnH_2$ (R = Et, R' = Bu, Ph; R = Bu, R' = Ph) have been synthesized [25, 26]. A patent application has been filed on the preparation of cyclohexyltin trichloride (4% yield) and iso-propyltin trichloride (8% yield) by reaction of tin foil with hydrochloric acid and cyclohexene or propene, respectively, in diethyl ether. The reaction is suggested to proceed by addition of intermediately formed $HSnCl_3$ following Markovnikov's rule [27]. According to the same team addition of SnH_4 to olefins such as 1-butene, is effectively catalyzed by a mixture of $t\text{-}Bu_2O_2$ and cobalt-naphthenate to give unlikely high yields of the corresponding tetraalkyltin compounds, e.g. 73% of Bu_4Sn [28].

In an attempt to synthesize organotin barbiturates Maire et al. performed the hydrostannation reaction [29]:

$$\mathrm{R_3SnH} \;+\; \mathrm{CH_2{=}CH\text{-}CH_2\text{-}CR'(COOet)_2} \xrightarrow{\mathrm{AIBN}} \mathrm{R_3Sn(CH_2)_3CR'(COOEt)_2}$$

$$(\mathrm{R = Me,\ Bu,\ Ph;}\ \ \mathrm{R' = H,\ Me,\ Et})$$

Cyclization of these adducts with ureum failed with the butyl and phenyl derivatives, but succeeded with the methyl compound [30].



$$Me_3Sn\text{-}(CH_2)_3\text{-}CR(COOEt)_2 \xrightarrow[Na/EtOH]{(NH_2)_2CO} Me_3Sn\text{-}(CH_2)_3\text{-}CR\begin{matrix}C(O)\text{-}NH \\ C(O)\text{-}NH\end{matrix}C(O)$$

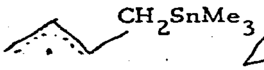
(R = H, Me)

Japanese workers reported on γ-induced addition of R_3SnH (R = Et, Bu) to carbon-carbon double bond systems, e.g. [31]:

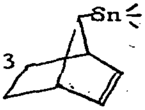
$$Bu_3SnH + CH_2{=}CHR \xrightarrow{\gamma} Bu_3SnCH_2CH_2R \ (R = COOEt,\ CH_2OOCCH_3)$$

Investigations into the relative reactivity of alkenylsilanes towards Group IV hydrides such as Et_3SnH, showed the order of reactivity of the unsaturated substituents to be ethynyl > vinyl > allyl > methallyl [32].

By ESR spectrometry Kawamura et al. determined that the principal adduct formed in the addition of Me_3SnH to 1, 3-butadiene is the trans-α-substituted allylic radical (I) rather than the cis-isomer, as reported previously by Kuivila et al. (cf. AS 67; 361). Presumably in the latter studies isomerization had occurred [33]. UV catalyzed addition of Me_2XSnH (X = me, Cl, Br, I) and of $MeCl_2SnH$ to norbornadiene afforded in each case four isomers (II-V). Mechanism and structure are discussed in detail [34]. Russian groups studied the hydrostannation of some acetylenic [35] and vinylacetylenic alcohols [36] as well as of enyne hydrocarbons containing Group IV substituents (C, Si, Sn) at the triple bond [37], viz. $RC{\equiv}C\text{-}CH{=}CH_2$ (R = alkyl, $R_2'R''Si$, R_3Sn). With the tin derivatives relatively



(I)



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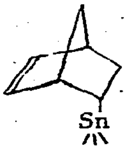

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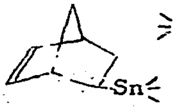

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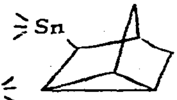
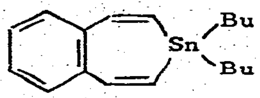


(V)

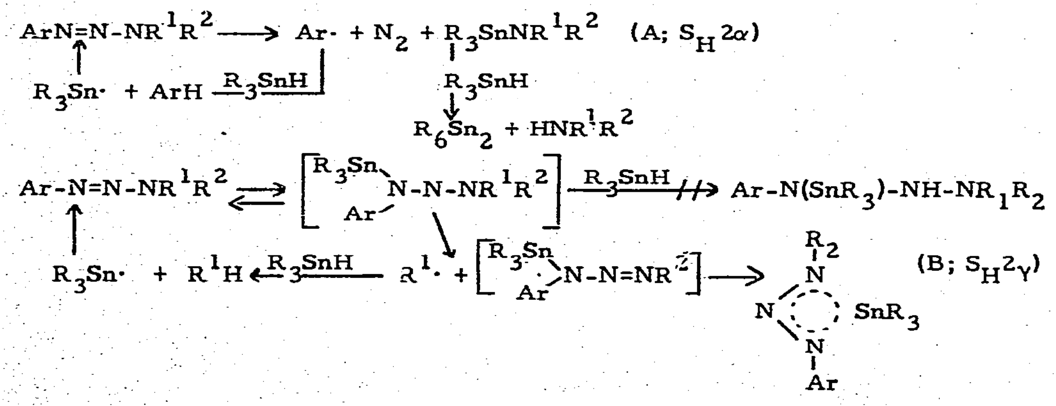
large proportions of allylic products are formed. Next to inductive effects steric effects were concluded to be of great importance as regards the product distribution obtained.

Axelrad et al. [38] used the adduct obtained on addition of Bu_2SnH_2 to o-diethynylbenzene, VI, as an intermediate for the preparation of 3-H-3-benzoborepin-3-ol. Insufficient credit was given to Leusink et al. who made detailed studies of this particular tin-hydride addition reaction (cf. AS 70; 254) and who prepared the very first example of an aromatic benzoborepin (cf. AS 67; 292).



(VI)

As reported by Neumann et al. [39] free radical displacement reactions of triorganotin radicals with triazene systems can proceed in two different ways:



With R^1, R^2 = alkyl reaction proceeds exclusively according to (A), whereas reaction (B) becomes preponderant when at least one of the groups

R^1 or R^2 is stabilized in its radical form, e. g. $PhCH_2$, Ph_3C or Me_3Sn.

Like in 1970, numerous papers dealing with the application of organotin hydrides in organic chemistry appeared in 1971, viz. the reduction of 7, 7-dibromo-2, 2-dimethyl-2-silanorcarane with Bu_3SnH [40], the reduction of specific types of organomercurials with R_3SnH and R_3SnD [41], the photoreduction of α,β-oxido-steroid-ketones with Bu_3SnH to give the corresponding β-hydroxysteroid-ketones [42], the reduction of steroid vicinal halohydrins with Bu_3SnH [43], organotin hydride reduction of geminal dihalides [44] (cf. AS 70; 256), the Bu_3SnH reduction of some heterocyclic carboxylic acid chlorides to give the corresponding aldehydes [45] and the photoreduction of benzophenone [46] and of acenaphthene, benzanthracene and phenanthrene with Bu_3SnH [47]. Reaction of the two isomers of 7-bromo-7-chloronorcarane with Ph_3SnH gave selective reduction of the bromine atom [48]. Triethyltin hydride was reported to be much more reactive than tripentyltin hydride in the reduction of dialkylchlorophosphites [49, 50]:

$$(RO)_2PCl + R_3SnH \xrightarrow[< 30^\circ]{Et_2O} (RO)_2PH + R_3SnCl$$

At Bordeaux Pereyre and coworkers studied the use of Bu_3SnD for the selective deuterium labelling of α,β-unsaturated ketones, esters and nitriles and the reduction of α-cyclopropyl ketones to α or γ-deuterated ring-opened ketones and labelled cyclopropyl alcohols [51].

Tin-metal compounds. Davis and Gray prepared a review on alkali-metal and magnesium derivatives of organosilicon, -germanium, -tin, -lead, -phosphorous, -arsenic, -antimony and -bismuth compounds [52]. According to Zavgorodnii et al. reaction of triethyltin sodium with enynes proceeds mainly by terminal addition to the carbon-carbon triple bond:

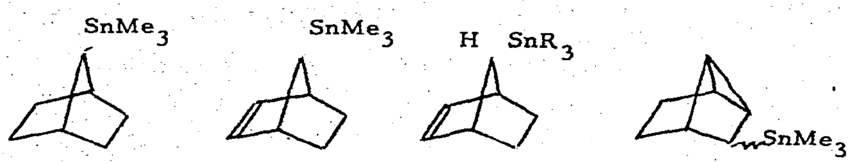
$$Et_3SnNa + MeC{\equiv}C\text{-}CH{=}CH_2 \xrightarrow[(H_2O)]{\text{liq. }NH_3} Et_3SnCMe{=}CH\text{-}CH{=}CH_2$$

With triethyltin lithium the reaction is less selective, *viz.* [53, 54]:

$$Et_3SnLi + MeC{\equiv}C\text{-}CH{=}CH_2 \xrightarrow[(H_2O)]{\text{liq. }NH_3} \underset{(3)}{Et_3SnCMe{=}CH\text{-}CH{=}CH_2} + \underset{(1)}{MeCH{=}C(SnEt_3)\text{-}CH{=}CH_2}$$

Triorganotin alkali metal compounds have been used in the synthesis of the novel bicyclic organotin compounds VII-X [55] (*cf.* ref. 34).

Lahournère and Valade continued their investigations on tributyltinmagnesium chloride (*cf.* AS 70; 257, 258). Reaction of this compound



(VII) (VIII) (IX, R = Me, Ph) (X)

with ethylenic ketones proceeds by a 1,2- or a 1,4-addition reaction, depending on the size of the substituents (*cf.* Chart 1) [56]. With epoxides

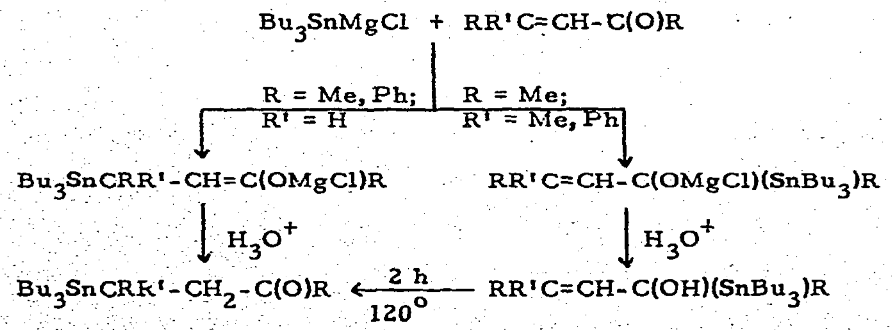
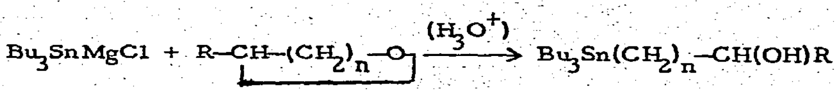


Chart 1. Reactions of $Bu_3SnMgCl$ with ethylenic ketones.

the following reactions take place [57]:



(n = 1, R = H, Me, Et, 55–60%;
n = 2, R = H, Me, 70%)

The preparation and properties of diphenylboryltin compounds by Nöth and coworkers has been discussed previously [58] (cf. AS 69; 493).

$$\mathrm{Me_nSnCl_{4-n}} \xrightarrow{\mathrm{L_2Co(BPh_2)_2}} \mathrm{Me_nSn(BPh_2)_{4-n}}$$

$(X = Ph_2PCH_2CH_2PPh_2,\ n = 0\text{–}3)$

As determined by PMR studies the self-exchange of $(Me_3M)_2Hg$ (M = Si, Ge, Sn) proceeds by a second order process. With the tin compound no quantitative results could be obtained because of its low thermal stability (dec. above −20°). The rate of the group exchange decreases in the order $(Me_3Sn)_2Hg > (Me_3Ge)_2Hg > (Me_3Si)_2Hg > (Me_2ClSi)_2Hg > Me_2Hg$ [59]. Exchange reactions between organotin halides and germyl-mercury compounds have been found to be useful for the preparation of germyl-tin compounds, viz. [60]:

$$\mathrm{(Et_3Ge)_2Hg}\left[\begin{array}{l} \xrightarrow{\mathrm{Me_3SnX}} \mathrm{Et_3GeSnMe_3 + Et_3GeX + Hg} \quad (X = MeO, EtO, Et_2N;\ 60\text{–}90\%) \\ \xrightarrow{\mathrm{Ph_3SnX}} \mathrm{Et_3GeSnPh_3 + Ph_6Sn_2} \quad (X = Cl, NCO;\ 30\text{–}40\%) \\ \xrightarrow{\mathrm{Et_2SnX_2}} \mathrm{(Et_3Ge)_2SnEt_2 + Et_3GeX + Hg} \quad (X = Cl, OMe;\ 54\text{–}66\%) \end{array}\right.$$

The structure of 1,2-diacetoxytetraphenylditin as proposed by Plazzogna et al. (cf. AS 70; 259) was confirmed by X-ray analysis (cf. Fig. 1) [61].

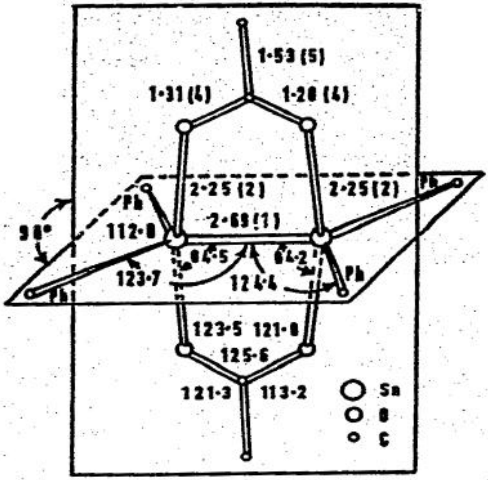
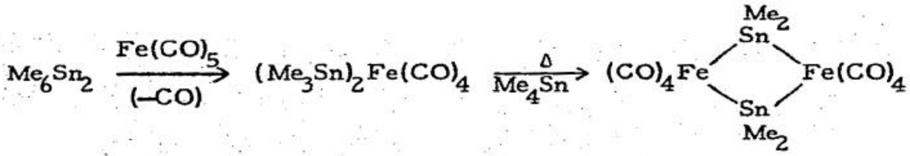
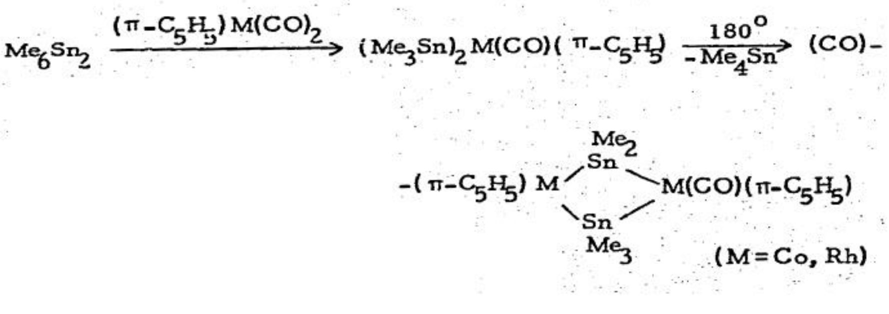


Fig. 1. Crystal structure of 1,2-diacetoxytetraphenylditin from C. Pannattoni, G. Bandoli and D. A. Clemente, J. Chem. Soc. D, (1971) 311.

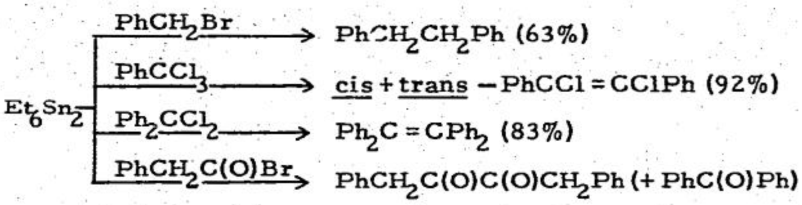
From the results obtained in a gaschromatographic study of compounds of the type $Et_3MM'Et_3$ (M, M' = Si, Ge, Sn) the following electronic polarizability values were derived: Si–Si, 15.4; Si–Ge, 15.8; Ge–Ge, 16.7; Si–Sn, 17.0; Ge–Sn, 19.2; Sn–Sn, 20.6 Å^3 [62].

Abel and Moorhouse reported further studies on reactions of hexamethylditin with transition metal compounds, e.g. [63]:





Dehalogenation of halomethylbenzene derivatives and of acid halides with hexaethylditin gives high yields of the corresponding dimers, for example [64, 65]:



$$\begin{aligned}
&Et_6Sn_2 \xrightarrow{PhCH_2Br} PhCH_2CH_2Ph\ (63\%)\\
&Et_6Sn_2 \xrightarrow{PhCCl_3} \underline{cis} + \underline{trans} - PhCCl{=}CClPh\ (92\%)\\
&Et_6Sn_2 \xrightarrow{Ph_2CCl_2} Ph_2C{=}CPh_2\ (83\%)\\
&Et_6Sn_2 \xrightarrow{PhCH_2C(O)Br} PhCH_2C(O)C(O)CH_2Ph\ (+\ PhC(O)Ph)
\end{aligned}$$

The results obtained in a kinetic study of the iodine cleavage of group IV hexaalkyldimetals, R_3MMR_3 ($M = Si, Ge, Sn$; $R = Me, Et$) have been mentioned previously [66] (cf. AS 70; 259).

Aleksandrov et al. [246] studied the mechanism of ozonolysis of hexaethylditin:

$$Et_6Sn_2 \xrightarrow[-100^\circ]{O_3} (Et_3Sn)_2O + (Et_3SnO)_2 \quad (1/1)$$

Anderson and Drake synthesized some new representatives of compounds containing Sn–As bonds (cf. AS 68; 695), according to [67]:

$$Me_3SnBr + LiAl(AsH_2)_4 \longrightarrow 4\ Me_3SnAsH_2 + LiBr + AlBr_3$$

$$Me_3SnCl + H_3SiAsR_2 \longrightarrow Me_3SnAsR_2 + H_3SiCl$$

$$Me_3SnCl + (H_3Si)_2AsR \longrightarrow (Me_3Sn)_2AsR + H_3SiCl$$

$$\begin{aligned}
&(Me_3Sn)_2AsR + 2K \longrightarrow [Me_3SnAsR]^{\ominus} + Me_3Sn^{\ominus} + 2K^{\oplus}\\
&\qquad\qquad\qquad\qquad\quad\ \ \llcorner \xrightarrow{H_2S} Me_3SnAsHR
\end{aligned}$$

These new trimethylstannyl arsines have a rather low thermal stability.

Schumann et al. [68] studied group IV organometal-stibines as ligands in transition metal carbonyl complexes.

$$(Me_3M)_3Sb + M'(CO)_6 \xrightarrow{UV} (Me_3M)_3SbM'(CO)_5 + CO \quad (M = Ge, Sn;\ M' = Cr, Mo, W)$$

From IR studies (ν_{CO}) it was concluded that substitution of germanium for tin has no appreciable effect on the σ-donor and π-acceptor capacity of the stibine ligand.

Synthesis and spectral characteristics of the following organotin-transition metal compounds have been reported: $Me_nSnPh_{4-n}\cdot mM(CO)_3$ (n = 2,3; m = 1,2; M = Cr, Mo), $(Me_3Sn)_2C_6H_4\cdot Cr(CO)_3$ and $Me_3SnCH_2Ph\cdot Cr(CO)_3$ [69]; $(\pi\text{-}C_5H_5)Fe(CO)(L)SnR_3$ (R = Me, Ph, Cl; L = Ph_3P, Ph_3As, Ph_3Sb) and $(\pi\text{-}C_5H_5)Fe(L)_2SnR_3$ (R = Me, L = Ph_3Sb; R = Ph, L = Ph_2MeP, $PhMe_2P$) [70]; $(\pi\text{-}C_5H_5)Fe(CO)_2SnPh_nCl_{3-n}$ (n = 0-3) [71]; $Ph_3M[Fe(CO)_3NO]_{4-n}$ and $Ph_nSn[Fe(CO)_3NO]_{4-n}$ (M = Ge, Sn, Pb; L = CO, $P(OPh)_3$; n = 0-3) [72]; $(\pi\text{-}C_5H_5)(CO)XRhMX_2R$ (M = Si, Ge, Sn; R, X = Cl; R = Me, X = I) [73]; $[Me_3SnFe(CO)(\pi\text{-}C_5H_5)]_2\cdot L$ and $Ph_3SnFe(\pi\text{-}C_5H_5)L$ (L = butadiene) [74]; $Ph_3SnFe(CO)(\pi\text{-}C_5H_5)L$ (L = Ph_3P, C_2H_4) [75].

Examples of exchange reactions of organotin-transition metal compounds reported by Nesmeyanov et al. [76] are given in Chart 2. Little group exchange takes place between $Ph_3SnRe(CO)_5$ and $NaFe(CO)_2(\pi\text{-}C_5H_5)$.

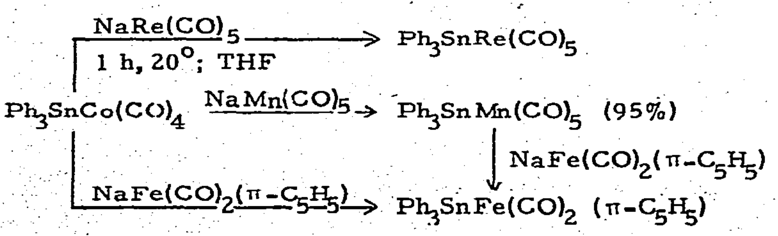


Chart 2. Exchange reactions with organotin-transition metal compounds.

George [77] reported the first example of tin-transition metal compounds exchanging alkyl-metal groups. The mechanism of this reaction was suggested

$$2\,Me_3SnMo(CO)_2(\pi\text{-}C_5H_5)L \xrightarrow{200^\circ} Me_4Sn + Me_2Sn[Mo(CO)_2(\pi\text{-}C_5H_5)L]_2$$
$$(L = Ph_3P)$$

to involve a bimolecular process proceeding through a four-centre activated complex. This type of reaction was also observed by Clark *et al.* [78]:

$$2\,Me_3SnMn(CO)_5 \xrightarrow[130^\circ]{48\,h} (\text{trace})\ Me_4Sn + Me_2Sn[Mn(CO)_5]_2$$

Attempts to insert difluorocarbene into Sn—Mn, Sn—Fe and Sn—W bonds were unsuccessful, but resulted in the discovery of the reactions:

$$Me_3MMn(CO)_5 + Me_3SnCF_3 \longrightarrow Me_2CF_3SnMn(CO)_5 + Me_4M \quad (M = Ge, Sn)$$

$$Me_2CF_3SnMn(CO)_5 + Me_3SnMn(CO)_5 \longrightarrow Me_2Sn[Mn(CO)_5]_2 + Me_3SnCF_3$$

By means of oxidative addition-elimination reactions Lappert *et al.* [79] synthesized some group IV metal cyclopentadienyltricarbonylchromium, -molybdenum and -tungsten derivatives, *e.g.* :

$$Me_3MC_5H_5 + M'(CO)_3(MeCN)_3 \longrightarrow Me_3MM'(CO)_3(\pi\text{-}C_5H_5) + 3\,MeCN$$
$$(M = Ge, Sn;\ M' = Cr, Mo, W)$$

In these reactions the reactivity was found to decrease in the sequence $Cr > Mo \approx W$ and $Sn > Ge \gg Si$ (unreactive). The crystal and molecular structure of di(benzenesulfinato)-μ-(hydroxo-phenylstannio)tetracarbonyl-di-π-cyclopentadienyldiiron have been determined by X-ray analysis [80] (*cf.* Fig. 2).

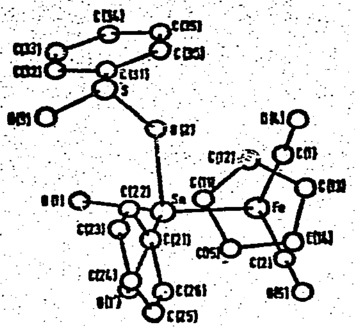


Fig. 2. Crystal structure of di(benzenesulfinato)-μ-(hydroxo-phenyl-stannio)tetracarbonyl-di-π-cyclopentadienyldiiron from R. Restivo and R. F. Bryan, J. Chem. Soc. A, 21 (1971) 3364.

According to Marks [321] reaction of $Na_2Cr_2(CO)_{10}$ with R_2MCl_2 (M= Ge, Sn ; R = Me, t-Bu) yields compounds that were tentatively suggested to

$$R_2MCl_2 + Na_2Cr_2(CO)_{10} \xrightarrow{THF} R_2MCr(CO)_5{\cdot}THF + NaCl + NaCr(CO)_5Cl$$

be pentacarbonylchromium complexes of dialkylgermylenes and -stannylenes. The Mössbauer spectrum of the compounds was stated to be "quite unlike spectra of tin(IV)-transition metal compounds".

From a kinetic study of $Ph_3MMn(CO)_5$ with phosphine ligands no conclusions could be drawn as to a change in bonding properties along the series

$$Ph_3MMn(CO)_5 + L \longrightarrow Ph_3MMn(CO)_4L + CO$$
$$(M = Si, Ge, Sn, Pb;\ L = Ph_3P, Bu_3P)$$

Si, Ge, Sn, Pb [81]. Oxidative addition of hexamethylditin to $Pt(PPh_3)_4$ or $Pt(PPh_3)_2(C_2H_4)$ affords the platinum(II) complex, XI. Hydrogenolysis of XI

$$Me_3SnSnMe_3 + Pt(PPh_3)_4 \longrightarrow \underset{(XI)}{\underline{trans}\text{-}Pt(SnMe_3)_2(PPh_3)_2} + 2\,PPh_3$$

proceeds already smoothly at room temperature according to [82]:

$$(XI) + H_2 \xrightarrow[\text{benzene}]{\text{r.t.}} PtH(SnMe_3)(PPh_3)_2 + Me_3SnH$$

Some of the quite interesting reactions observed by Clemmit and Glockling [83] with trimethylstannylplatinum complexes are compiled in Chart 3 (cf. A 570; 263). Compound XII was found to be stable in air for over 3 months. Attempted recrystallization from benzene resulted in loss of

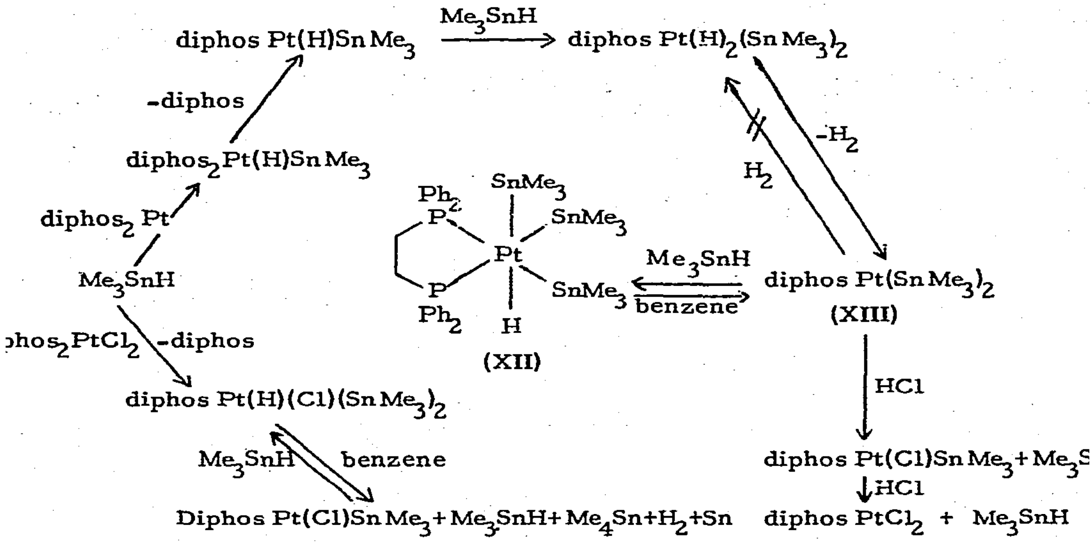
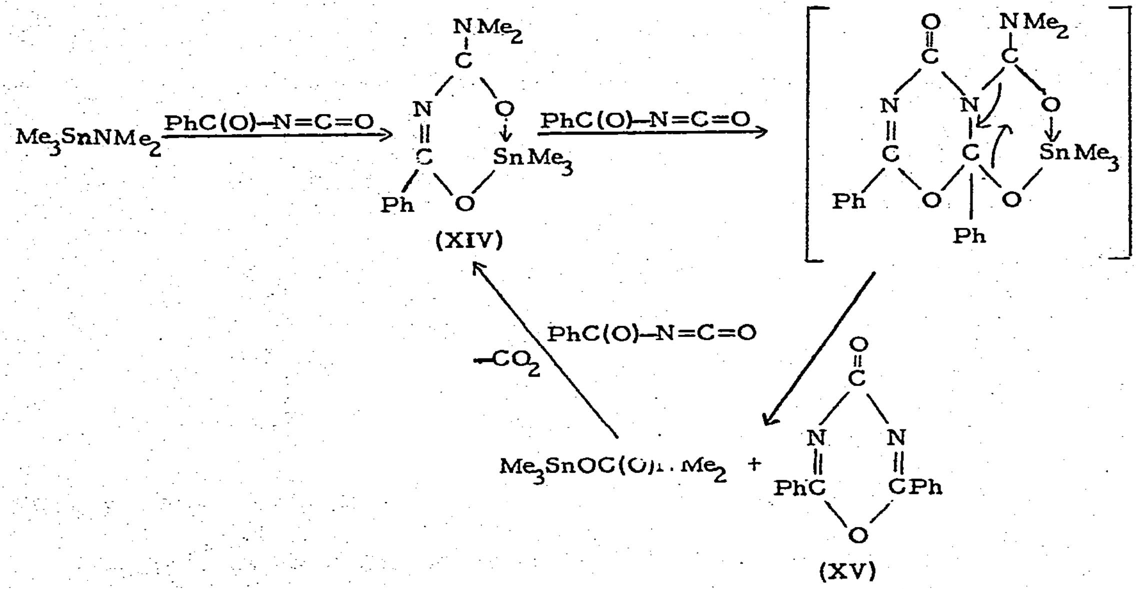


Chart 3. Some reactions with tin-platinum compounds (diphos = $Ph_2PCH_2CH_2PPh_2$).

Me_3SnH, this reaction being reversible with Me_3SnH addition (cis-elimination/addition). As regards reaction of compound XIII with hydrochloric acid, it was stated that with a *cis*-chelating phosphine like diphos, the second Pt-Sn bond is cleaved to give the corresponding platinum chloride and tin hydride, whereas with a non-*cis*-chelating phosphine, such as triphenylphosphine, the reaction leads to the platinum hydride and the tin chloride.

Tin-nitrogen compounds. Ishii and coworkers [84] continued their studies of organotin-nitrogen compounds (*cf.* As 70; 264). The applicability of the latter type of compounds in organic synthesis was demonstrated once more by the synthesis of 2,6-diphenyl-1,3,5-oxadiazin-4-one (XV). Addition of



dimethylaminotrimethyltin to benzoylisocyanate gives the pentacoordinate structure (XIV). With an excess of benzoylisocyanate compound (XV) is formed via a cycloaddition across the carbon-nitrogen double bond of (XIV). Reaction of bis(tributylstannyl)phenylamine with chloral proceeds by addition to the carbon-oxygen double bond (Chart 4; *cf.* AS 68; 700, 701) [85]. Hydrostannolysis of Me_3NMe_2 with cyclopentadienylsilanes yields the corresponding silyl-stannyl cyclopentadienyl derivatives. The latter compounds have been used for the preparation of a series of silyl-substituted π-cyclopentadienyl metal carbonyls by methathetical reactions [86].

$$Me_3SnNMe_2 + C_5H_5SiR_3 \longrightarrow Me_3SnC_5H_4SiR_3 + Me_2NH$$

$$Me_3SnC_5H_4SiR_3 + ClM(CO)_3 \longrightarrow \underset{(M = Mn,\ Re)}{(R_3Si\text{-}\pi\text{-}C_5H_4)M(CO)_3} + Me_3SnCl$$

Interesting new information on Group IV substituted hydrazine derivatives was reported by Wiberg and Veith [87, 88]. Reaction of hydrazine with Me_3MCl (M = C, Si, Ge, Sn) or Me_3MNMe_2 (M = Si, Ge, Sn) and reaction of hydrazides of the general formula $(Me_3M)_mN_2H_nLi_p$ (m + n + p = 4) with Me_3MCl yield the thermally stable hydrazines $(Me_3M^1)(Me_3M^2)N\text{–}N(M^3Me_3)(M^4Me_3)$ (M^1 = C, M^2 = Si, M^3 = Ge, M^4 = Sn). The tin derivatives are rather susceptible to solvolysis and oxidation. The synthesis of mixed-group IV

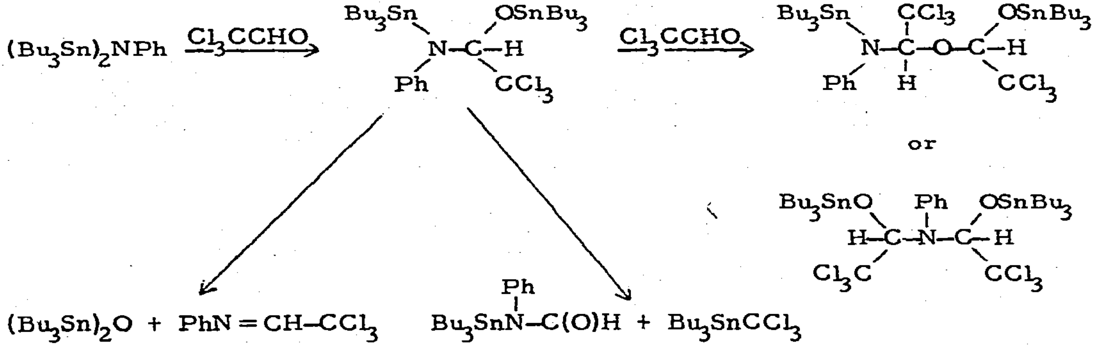


Chart 4. Reaction of bis(tributylstannyl)phenylamine with chloral.

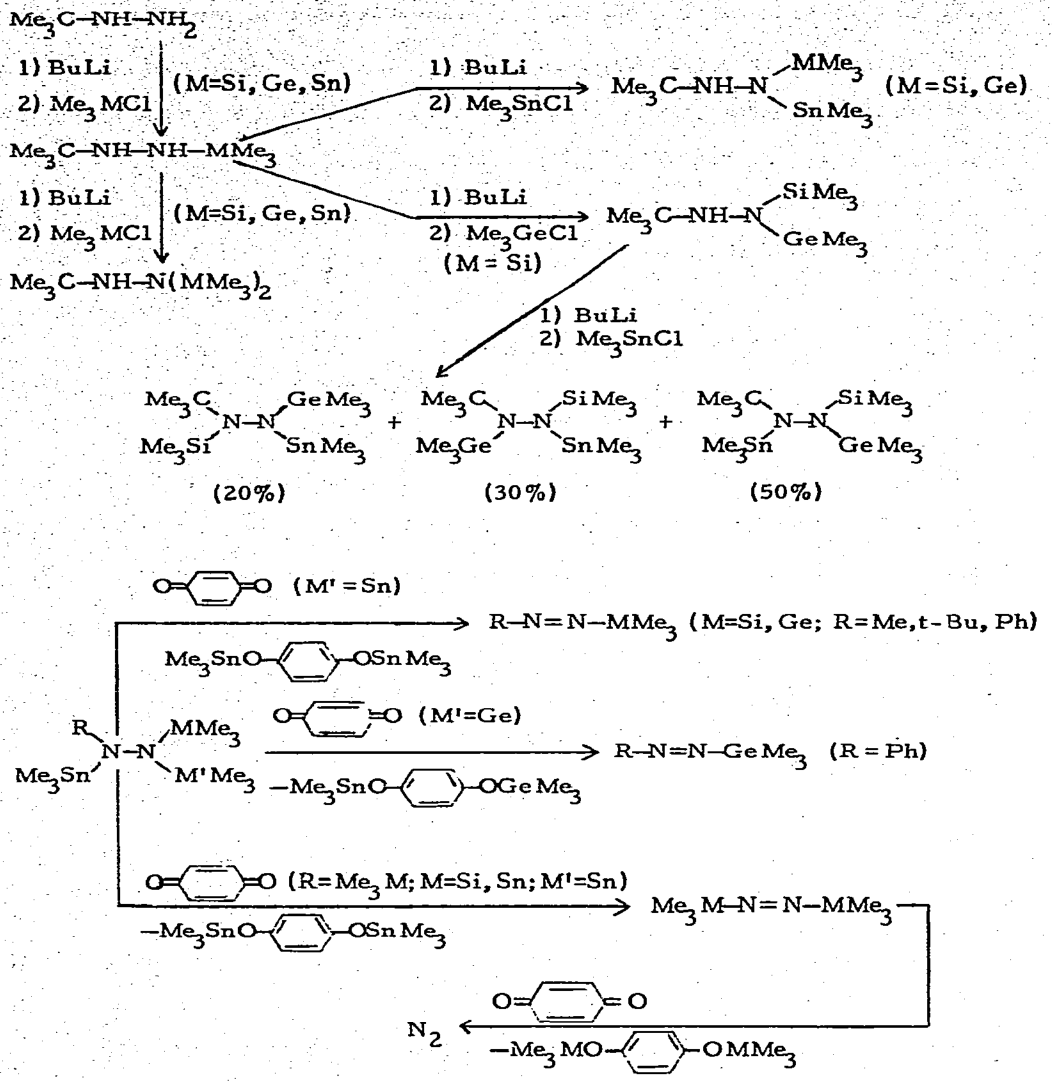


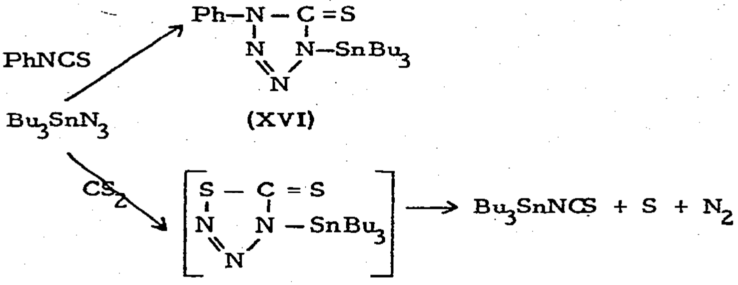
Chart 5. Preparation and reactions of group IV substituted hydrazines.

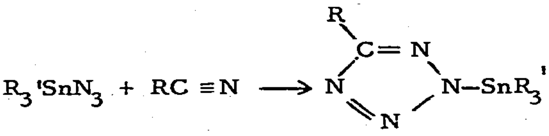
substituted hydrazines and some reactions are given in Chart 5.

The preparation of organometallic polymers of the structure $\left[\mathrm{SnR_2{-}NHR'{-}NH}\right]_n$ by interfacial polycondensation of diamines with R_2SnCl_2

(R = alkyl, aryl) in the presence of organic bases has been studied by Carraher et al. [89, 90] (cf. [103, 104]).

Two research groups reported further studies on the addition of organotin azides to unsaturated systems, as observed initially by Luijten et al. (cf. AS 64; 142). Reaction of Bu_3SnN_3 with phenylisothiocyanate gives the tetrazole (XVI), but from the reaction with carbon disulfide the analogous cyclic adduct could not be isolated as such [91]. Likewise, reaction of tin azides with nitriles affords the corresponding tetrazoles. On the basis of spectral and dipolemoment studies the structure was interpreted to be the 2- rather than the 1-trialkyltin isomer. Like the corresponding imidazole derivatives the tetrazoles have polymeric structures in solution (pentacoordination) [92].


(XVI)



($R' = Me, Bu$; $R = Me, Ph$;
$R' = Bu$, $R = Et, Pr, PhCH_2$,
$CH_2{=}CH$, p-tolyl, p-$NO_2C_6H_4$,
p-$CH_3OC_6H_4$)

The crystal structures of dimethyltin bis(dicyanamide), $Me_2Sn[N(CN)_2]_2$, and of trimethyltin dicyanamide, $Me_3SnN(CN)_2$, have been reported [93]. One of the products formed in the reaction of bis(triethyltin)carbodiimide, $Et_3SnNCNSnEt_3$ (cf. AS 70; 269), with $ZnCl_2$ is $Et_3SnNCNZnCl$ [94, 95]. Reaction of tributyltin isocyanate with amines in the presence of water has been used for the synthesis of some 1,1-disubstituted ureum compounds [96].

$$Bu_3SnNCO \xrightarrow{R_2NH} Bu_3SnNHC(O)NR_2 \xrightarrow[-(Bu_3Sn)_2O]{H_2O} H_2NC(O)NR_2$$

$$(R = Et, t\text{-}Bu, PhCH_2, CH_2{=}CH{-}CH_2)$$

Tin-phosphorous compounds. Scherer *et al.* prepared some group IV substituted phosphazane and phosphazene isomers [97]. Just like trimethyl-

$$t\text{-}Bu_2PNHSiEt_3 \xrightarrow[2)\ Me_3MCl]{1)\ BuLi} t\text{-}Bu_2P(MMe_3){=}N{-}SiEt_3 \quad (M = Si, Ge, Sn)$$

stannylarsine (*cf.* ref. 67), trimethylstannylphosphine has a rather low thermal, oxidative and hydrolytical stability [98]. The inversion energy

$$4\,Me_3SnCl + LiAl(PH_2)_4 \longrightarrow 4\,Me_3SnPH_2 + LiCl + AlCl_3$$

barriers in group IV substituted phosphines of the structure Me_3MPPhR ($M = C, Si, Ge, Sn$; $R = Me, i\text{-}Pr$) have been found to decrease linearly with the Allred electronegativity values of the heteroatoms and with the chemical shift of the Me_3M-protons [99].

Schumann and coworkers continued their studies in the field of organotin-phosphorous chemistry (*cf.* AS 70 ; 268 and AS 69 ; 502). They synthesized some cyclic organotin phosphines according to [100]:

$$R_2SnCl_2 \xrightarrow[Et_3N]{PhPH_2} (R_2SnPPh)_3 \qquad (R = Me, Bu, Ph)$$

Furthermore, new examples were given of the use of organotin-substituted phosphine derivatives as ligands for transition metal carbonyls (*cf.* AS 70; 268 and AS 69; 494), *e. g.* :

$(Me_3M)_3PM'(CO)_5$ ($M = Si, Ge, Sn$; $M' = Cr, Mo, W$) [101], $(Me_3M)_3PCo(NO)(CO)_2$ ($M = C, Si, Ge, Sn$) [102] and $(Me_3M)_3PMn(CO)_2(\pi\text{-}C_5H_5)$ ($M = C, Si, Ge, Sn$) [103].

Tin-oxygen compounds.- Sakai and Ishii prepared a review in Japanese on the application of organotins in chemical synthesis [104].

Bis(triphenyltin)oxide reacts instantaneously with mercuric halides, HgX_2, in diethyl ether to give phenylmercury halide, triphenyltin halide and diphenyltinoxide as the main products. The suggested intermediate, $Ph_3SnOHgX$, could not be isolated or prepared otherwise [105].

$$(Ph_3Sn)_2O + HgX_2 \longrightarrow [Ph_3SnOHgX] \longrightarrow Ph_3SnX + [Ph_2SnO]_n + PhHgX$$

Base-catalyzed hydrolysis of $t\text{-}Bu_2SnCl_2$ gave the first representative of an organotin hydroxide chloride [106]. With an excess of base the corresponding oxide and subsequently the dihydroxide are formed. Russian workers paid considerable attention to experimental details of the base-catalyzed hydrolysis of diorganotin dihalides to give the corresponding oxides [107-112]. Carraher and coworkers extended their studies of the production of organometallic polymers by the interfacial technique (*cf.* refs. 89, 90) to reactions of R_2SnCl_2 with disodio adipate (R = Bu) [113] and with alkylene diols (R = Bu, Ph) [114]. For example, polycondensation of Ph_2SnCl_2 with 1,4-butanediol in the presence of triethyl amine gave a product (XVII) with a softening range > 300°. Matsuda *et al.* prepared a series of alkyl- and arylstannonic acid derivatives, $(RSnOOH)_n$ (R = Me, Bu, Ph, o-, m-, p-tolyl, p-Cl-C_6H_4). The alkyl compounds were reported to be insoluble even in polar solvents like dimethyl sulfoxide. Thermal decomposition occurs at 260-360°, thermolysis

$$t\text{-}Bu_2SnCl_2 \xrightarrow{H_2O/OH^{\ominus}} t\text{-}Bu_2Sn(OH)Cl \xrightarrow{OH^{\ominus}} t\text{-}Bu_2SnO \xrightarrow{OH^{\ominus}} t\text{-}Bu_2Sn(OH)_2$$

$$Ph_2SnCl_2 + HO\text{-}(CH_2)_4\text{-}OH \xrightarrow{Et_3N} \left[O\text{-}SnPh_2\text{-}O\text{-}(CH_2)_4 \right]_n$$

(XVII)

of phenylstannonic acid at 350° yields benzene and water [115].

Davies and Harrison extended their investigations on functionally substituted distannoxanes (cf. AS 70; 270) to sila-, germa- and plumbastannoxanes, for example [116]:

$$Bu_2SnO + R_2MCl_2 \xrightarrow[\text{benzene}]{\text{exothermal}} Bu_2ClSnOMClR_2$$

$$(M = Si, Ge, R = Me;\ M = Pb, R = Bu)$$

In a similar way reaction of dibutyltin oxide with phenylmercuric chloride and with bis(pentafluorophenyl)thallium bromide gave $Bu_2ClSnOHgPh$ and $Bu_2BrSnOTl(C_6F_5)_2$, respectively. No reaction occurred with the less covalent dimethylthallium bromide. Chow [117] determined the crystal and molecular structure of dimeric tetramethyl-1,3-diisothiocyanatodistannoxane (cf. Fig. 3). Mehrotra et al. synthesized some symmetrical distannoxanes by reaction of dibutyltin dichloride with potassium hydrophthalate or with quinaldinic acid [118]. Some oligostannoxanes of the formula $RCH(NHR')-COO(SnBu_2O)_nSnBu_2OOCCH(NHR')R$, wherein the aminoacid moieties are

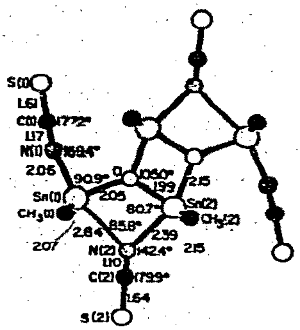


Fig. 3. The molecular structure of $[(Me_2SnNCS)_2O]_2$ [from Y. M. Chow, Inorg. Chem., 10 (1971) 673].

alanine, leucine, phenylalanine, N-benzoylglycine and N-acetylmethionine [119] (cf. AS 69; 507), have also been prepared.

Trimethylstannyl metaborate, Me_3SnBO_2, was obtained by reaction of trimethyltin bromide with silver metaborate [120].

X-ray analysis confirmed the molecular structure of methyltin trinitrate as proposed earlier on the basis of UV, IR and PMR spectral studies (cf. AS 70; 271). The coordination around tin is approximately pentagonal bipyramidal [121] (cf. Fig. 4).

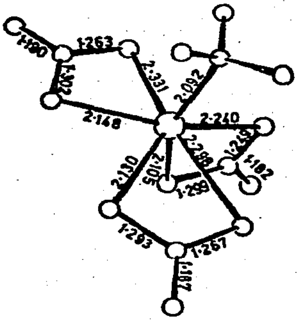


Fig. 4. The structure of methyltin trinitrate [from G.S. Brownlee, A. Walker, S.C. Nyburg and J.T. Szymanski, J. Chem. Soc. D, (1971) 1073].

In a Japanese patent application organotin-sulfamic acid derivatives, $R_nSn(OSO_2NH_2)_{4-n}$ (R = alkyl, Ph; n = 2,3) have been claimed to be useful as fungicides [122]. By conventional methods Lindner et al. [123] prepared some new organotin sulfinates, $PhSn(O_2SR)_3$ (R = Ph, p-tolyl). The same authors reported that the insoluble polymeric triphenyltin-p-tolylsulfinate depolymerizes on heating in benzene solution, whereby the IR spectral characteristics remain unchanged. Under the same conditions triphenyltin-

$$\underset{\text{m.p. } 218\text{-}219^{\circ}}{[Ph_3Sn(p\text{-}O_2S\text{-}C_6H_4\text{-}CH_3)]_n} \underset{-196^{\circ}}{\overset{\text{benzene, } 100^{\circ}}{\rightleftarrows}} \underset{\text{m.p. } 205\text{-}207^{\circ}}{n\,Ph_3Sn(p\text{-}O_2S\text{-}C_6H_4\text{-}CH_3)}$$

phenylsulfinate remains polymeric, but the IR spectrum does change as the result of a phase-transition into a crystal structure of higher symmetry. [124]. Organotin compounds containing fluorine substituents in the anionic group have been prepared by reacting Me_3SnCl, $(Me_3Sn)_2O$ or $(Me_3Sn)_2NMe$ with perfluoro-anhydrides, thiophosphoryl halides and dithiophosphoric acids [125], e.g. :

$$\begin{tikzcd}
(Me_3Sn)_2O \arrow[r, "CF_3SO_2OSO_2CF_3"] \arrow[dr, "SPF_3"'] & 2\,Me_3SnOSO_2CF_3 \\
& Me_3SnOPSF_2 + Me_3SnF
\end{tikzcd}$$

$$Me_3SnCl + HPS_2FX \longrightarrow Me_3SnSPFX + HCl \quad (X = F, Me)$$

An X-ray study showed that dimethyltin bis(fluorosulfate), $Me_2Sn(OSO_2F)_2$, has a structure consisting of polymeric sheets with $FOSO_2$-groups acting as bridging ligands between the linear dimethyltin units [126] (cf. Fig. 5). In accordance with the latter observation, Moessbauer and vibrational spectra of Me_3SnOSO_2X (X = F, Me) were interpreted on the basis of penta-coordinate tin with bridging OSO_2X groups [127].

Garrodd et al. [128] critically discussed the conclusions of Stapfer et al. (cf. AS 70; 271) as to the monomeric structure of bis(tributyltin)sulfate. It was argued that the IR and Moessbauer data do not warrant the conclusion that this compound has a monomeric structure in the solid state. In a reply Herber and Stapfer [129] discussed additional IR, mass- and Moessbauer spectrometric evidence in favour of the monomeric structure.

According to Pommier et al. [130] reaction of (3-haloalkoxy)tributyltin

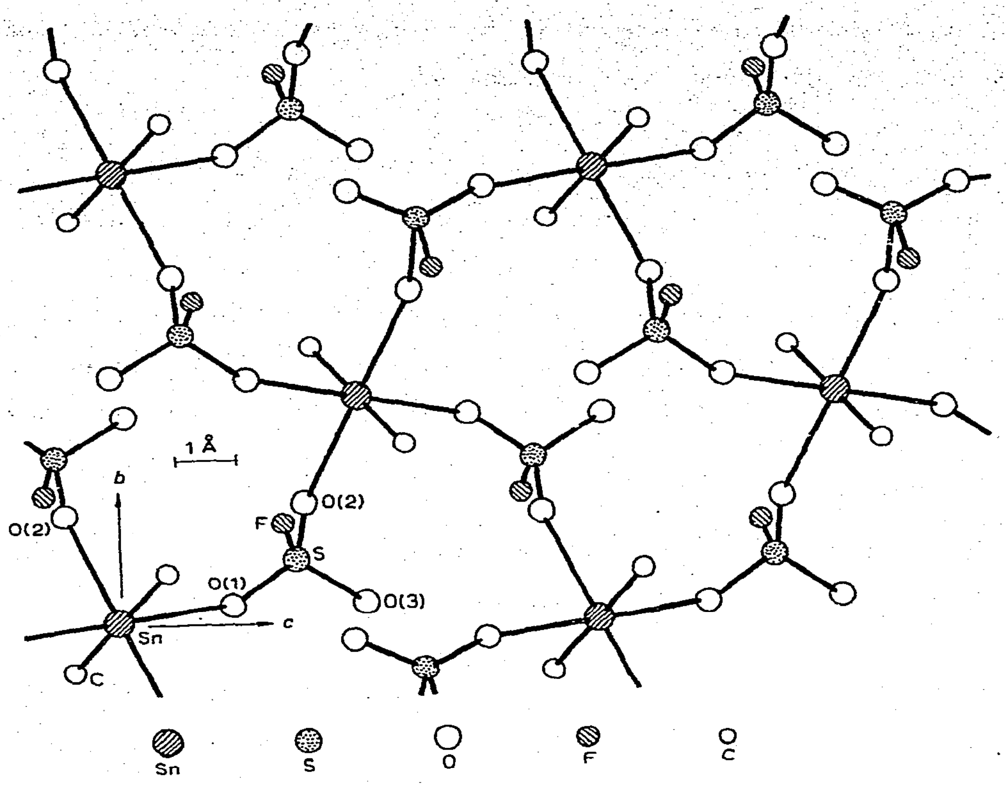


Fig. 5. Crystal structure of $Me_2Sn(OSO_2F)_2$ [from F. H. Allen, J. A. Lerbscher and J. Trotter, J. Chem. Soc. A, (1971) 2507].

compounds with magnesium gives the corresponding (3-trialkylstannyl)propanol derivatives:

$$Bu_3SnO\text{–}CH_2\text{–}CR^1R^2\text{–}CHR^3\text{–}Br \xrightarrow[2)\ H_2O]{1)\ Mg} Bu_3Sn\text{–}CH_2\text{–}CR^1R^2\text{–}CHR^3\text{–}OH$$

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

The synthesis of some oxygen-containing tin-substituted acetylenes was dealt with in a Russian patent application [131].

In a spectrophotometric study of the methanolysis of triphenyltin oxinate the following equilibrium was observed [132]:

$$Ph_3SnOx + MeOH \overset{K_1}{\rightleftharpoons} Ph_3SnOx \cdot MeOH \overset{K_2}{\rightleftharpoons} Ph_3SnOMe + HOx$$

$$(Ox = \text{oxinate};\ K_1 = 5.6 \times 10^{-2};\ K_2 = 4.0 \times 10^{-3})$$

Generally reaction of organotin alkoxides with alkyl halides gives the corresponding organotin halide and the ether. Pommier et al. [133] observed, however, that with polyhalides a free radical oxidation reaction takes place, viz.:

$$Bu_3SnOCH \cdot RR' + CX_4 \xrightarrow[\text{or } \Delta]{h\nu} Bu_3SnX + RR'C{=}O + CHX_3$$

$$(R = H, \text{alkyl, aryl})$$

Ishii and coworkers presented a full account of their interesting new syntheses of spiro-orthocarbonates, by reacting bis(tributyltin)alkylene glycolates having a C_2—C_4 unit with carbon disulfide [134] (cf. AS 70; 273). The same authors concluded from a mechanistic study that reaction of dibutyltin dialkoxides with phenyl isothiocyanate proceeds via the initial

$$Bu_2Sn(OMe)_2 + PhNCS \longrightarrow Bu_2SnS + PhNC(OMe)_2$$

formation of the one/one adduct [135].

Pereyre et al. studied the kinetics and substituent effects of the exchange between trialkyltin alkoxides and optically active silanes, R_3Si^*H, a reaction that proceeds with complete retention of configuration at silicon (cf. AS 70; 275). The results point to a four-centre mechanism with charge distribution in the transition state, the formation of the Si—O bond preceding the formation of the Sn—H bond [136]. Tributyltin methoxide reacts with acylfluorides according to [137]:

$$Bu_3SnOMe + t\text{-}BuC(O)F \longrightarrow Bu_3SnF + t\text{-}BuC(O)OMe$$

In the ethanolysis of tri-isopropyltin halides, $i\text{-}Pr_3SnX$, the reactivity decreases in the order $F > Cl > Br > I$ [138]. Voronkov *et al.* made a comparative rate study of Me_3EOEt ($E = C, Si, Ge, Sn$). With the germanium and tin derivatives, however, hydrolysis in neutral media was too rapid for a kinetic study [139]. Baukov *et al.* [140] used the reactivity of the tin-oxygen bond towards ketenes for the preparation of some new group IV metal-substituted esters, *e.g.*:

$$R_3SnOMe + R_3'MCH{=}O \longrightarrow R_3'MCH(COOMe)SnR_3$$
$$(R = Et\text{-}Bu,\ R' = Me, Et,\ M = Si;\ R' = Et,\ M = Ge)$$

$$(Et_3Sn)_2O + Et_3SiCH{=}C{=}O \longrightarrow Et_3SiCH(COOSnEt_3)SnEt_3$$

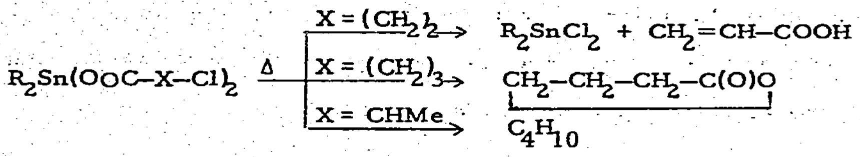
By conventional methods a series of trimesitylalkoxy- and aryloxytin compounds have been synthesized [141].

The structure, thermal stability and fungicidal activity of a series of compounds $R_3SnC(CN){=}CPh_2$ — prepared by thermal decarboxylation of the corresponding esters, $R_3SnOOC(CN){=}CPh_2$ — was studied by Cummins *et al.* [142]. According to Tagliavini and coworkers [143] bis(trialkyltin)oxalates, $(R_3SnOOC)_2$ ($R = Me$—Pr) have a polymeric structure as a result of pentacoordination, the R_3Sn-groups being planar. Alkyltin carboxylates may be used for the preparation of mono- and diketones [144]:

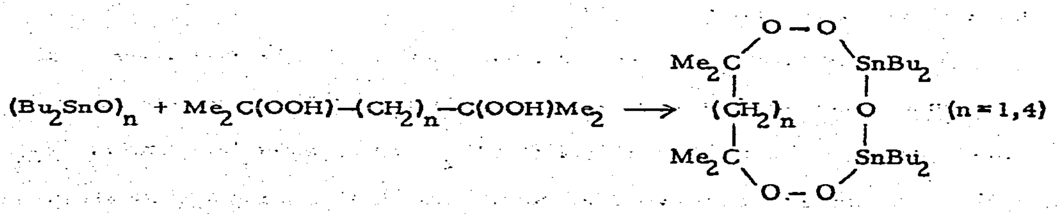
$$Bu_3SnOOC\text{–}(CH_2)_2\text{–}COOSnBu_3 \xrightarrow[2)\ KCl/H_2O]{1)\ BuLi} BuC(O)\text{–}CH_2\text{–}CH_2\text{–}C(O)Bu$$

$$Bu_2Sn(OAc)_2 \xrightarrow[2)\ KCl/H_2O]{1)\ PhLi} PhC(O)Me$$

Thermolysis of alkyltin chlorocarboxylates at 240° results in the elimination of organotin chlorides as the sole chlorine containing products [145]. Free-radical induced copolymerization of trialkyltinmethacrylates with maleic anhydride and with styrene yields ternary copolymers with bactericidal and fungicidal properties [146]. Dannley et al. applied for a patent application on the preparation of (probably cyclic) organotin peroxides from dialkyltin dimethoxides, aldehydes or ketones, and hydrogen peroxide [147] (cf. AS 69; 508). Compound XVIII constitutes another example of a cyclic organotin peroxide [148]. In a kinetic study of the rearrangement of $Ph_3SnOO(O)C\text{–}C_9H_{19}$ into $Ph_2Sn(OPh)OOC\text{–}C_9H_{19}$ among others it was found that the rate of formation [from Ph_3SnOH and $C_9H_{19}C(O)OOH$] is much higher than that of the rearrangement [149].



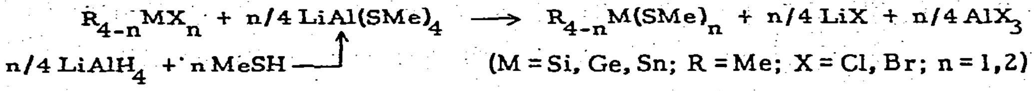
$$R_2Sn(OOC\text{–}X\text{–}Cl)_2 \xrightarrow{\Delta} \begin{cases} X=(CH_2)_2 \rightarrow R_2SnCl_2 + CH_2{=}CH\text{–}COOH \\ X=(CH_2)_3 \rightarrow \underline{CH_2\text{–}CH_2\text{–}CH_2\text{–}C(O)O} \\ X=CHMe \rightarrow C_4H_{10} \end{cases}$$



(XVIII)

Tin-sulfur, -selenium, and -tellurium compounds

As discussed above compounds containing tin-phosphorus and tin-arsenic bonds are readily accessible via the corresponding lithium aluminates [67, 98]. The results of Anderson and Drake show this technique to be generally applicable for establishing tin-heteroelement bonds [150], *viz.*:

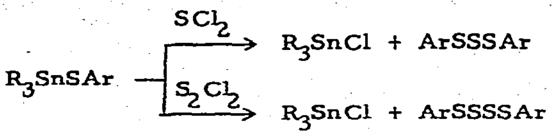


$$\begin{tikzcd} R_{4-n}MX_n + n/4\,LiAl(SMe)_4 \arrow[r] & R_{4-n}M(SMe)_n + n/4\,LiX + n/4\,AlX_3 \\ n/4\,LiAlH_4 + n\,MeSH \arrow[u] & \end{tikzcd}$$

(M = Si, Ge, Sn; R = Me; X = Cl, Br; n = 1,2)

Wardell *et al.* [151] reported further studies into the cleavage of organotin sulfides by aromatic sulfenyl compounds and by divalent sulfur chlorides (*cf.* AS 69; 509). No reaction was observed with sulphenylcyanide, -amide,

$$ArSX + R_3SnSR' \longrightarrow R_3SnX + R'SSAr$$

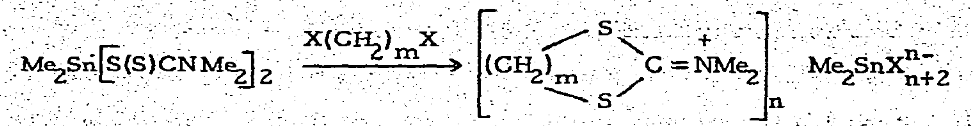


$$R_3SnSAr \begin{cases} \xrightarrow{SCl_2} R_3SnCl + ArSSSAr \\ \xrightarrow{S_2Cl_2} R_3SnCl + ArSSSSAr \end{cases}$$

(Ar = p-tolyl, 2-nitrophenyl, 2,4-dinitrophenyl; R, R' = alkyl, aryl; X = Cl, Br, SCN)

-esters, or -disulfides. Organotins were found to be convenient materials for the synthesis of organic trisulfides and tetrasulfides as well.

By conventional techniques a series of trimethyltin derivatives of 4-substituted phenylsulfides, p-$Me_3SnC_6H_4X$ (X = Me, F, Cl, Br, NH_2 NO_2), have been synthesized. On the basis of IR and UV data $p_\pi(S) \rightarrow d_\pi(Sn)$ bonding was suggested to occur [152]. Reaction of dimethyltin dithiocarbamate with dihaloalkanes proceeds according to [153]:

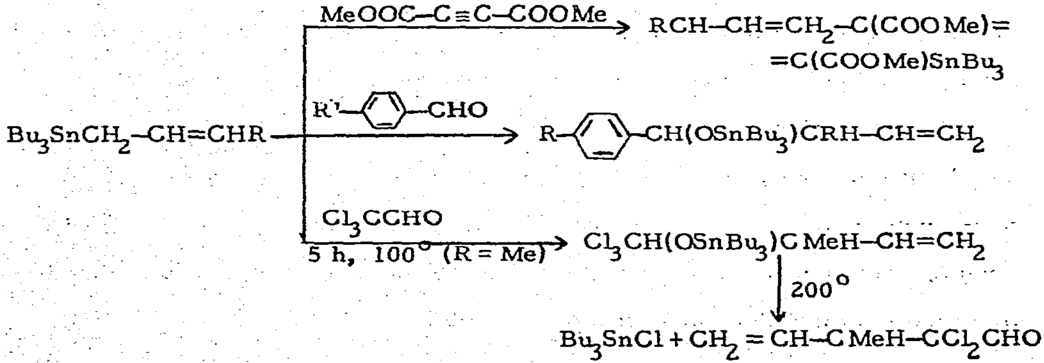


$$Me_2Sn[S(S)CNMePh]_2 \xrightarrow{X(CH_2)_mX} [PhMeNC(S)S(CH_2)_m]_2 + Me_2SnX_2$$

$(X = Cl, Br, I;\ n = 1,2;\ m = 2-4)$

Matsuda et al. [154, 155] investigated the thermal decomposition of several types of dialkyltin mercaptides, $R_2Sn(SR')_2$ (R, R' = alkyl). The thermal stability of these compounds decreases in the order $R_2Sn(SR')_2 > R_2Sn[S(CH_2)_2COOR']_2 > R_2Sn[SCHR''COOR']_2$. Some (trialkyltin)butylselenides, $R_3SnSeBu$, have been prepared by cleavage of Sn—N and Sn—O bonds with γ-butylselenol [156].

Alkenyl- and alkynyl-tin compounds. The Grignard route to tetraallyl group IV metal derivatives has been taken up in Inorganic Synthesis [157]. As found by Pereyre et al. [158] the tin-carbon bond in tributylallyltin compounds is sufficiently reactive to allow addition to the carbon-carbon triple bond of dimethylacetylene dicarboxylate and to the carbon-oxygen double bond of reactive aldehydes. In all cases allylic rearrangement occurs. No



(R = Me, R'=H, Cl; 60-70%)

reaction was observed with methylpropiolate, -maleate, -fumarate and with malonitrile. The reactions were explained on the basis of a reversible addition reaction followed by a direct substitution reaction. For example, with $Cl_3CCOOC_2H_5$ no adduct was observed, only the substitution product:

$$Bu_3SnCH_2{-}CH{=}CHMe + Cl_3CCOOEt \xrightarrow[-Bu_3SnCl]{200^\circ} CH_2{=}CH{-}CHMe{-}CCl_3{-}COOEt$$

According to Abel *et al.* [159] transorganylation reactions between halo--transition metal carbonyls and allyl-, cyclopentadienyl-, indenyl- and fluorenyl-organotin compounds are quite convenient for the preparation of the corresponding transition metal-π-complexes (*cf.* AS 70; 283), *e.g.*:

$$Me_3SnCH_2{-}CH{=}CH_2 + M(CO)_5X \xrightarrow[-Me_3SnX]{-CO} (\pi\text{-}C_3H_5)M(CO)_4 + Me_3SnX$$
$$(M = Mn, Re;\ X = Cl, Br)$$

Likewise, reaction of *trans*-cinnamyltriethyltin with BBr_3 proceeds with the preferential transfer of the *trans*-cinnamyl group from tin to boron [160].

In the ionic polymerization of triethylvinyltin catalyzed by butyl lithium, only low molecular weight poly(triethylvinyltin) is formed. During the process the catalyst lost its reactivity, which was ascribed to complex formation with the triethylvinyltin moieties [161] (*cf.* AS 70; 284). Butyl lithium catalyzed anionic copolymerization of trialkylvinyltin compounds only succeeded with styrene (*cf.* AS 70; 284), not with methyl acrylate or methyl methacrylate [162].

Fitch *et al.* prepared some alkylvinylsilane and -tin complexes of copper(I) chloride, $Me_3SnCH{=}CH \cdot CuCl$ and $R_2Sn(CH{=}CH_2)_2 \cdot 2\,CuCl$ (R = Me, Bu). The divinyl complexes were mentioned to be among the most stable olefin-copper(I) chloride complexes described so far [163].

Mono- and bimetallated germanium and tin-substituted ketenes (*cf.*

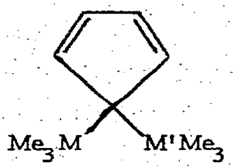
AS 69; 468) have been synthesized by Lutsenko and coworkers [164], according to:

$$\mathrm{BuO{-}C{\equiv}CH} \xrightarrow[\substack{2)\ R_3MX \\ 3)\ 120-130^{\circ}}]{1)\ EtMgBr} \mathrm{(R_3M)_2C{=}C{=}O} \quad (35\%)$$

$(R = Me, Et, Pr;\ M = Si, Ge, Sn)$

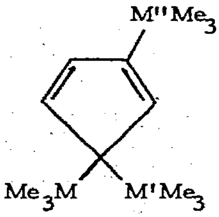
Reaction of styrenyltin trichloride with $PhICl_2$ gave a small amount (5%) of phenyl-ω-styrenyl iodonium iodide, $PhI^{\oplus}CH{=}CHI^{\ominus}Ph$ [165].

The Russian group of Zavgorodnii paid much attention to the preparation [166], polymerization and copolymerization [167,168] of 1- and 2-trialkylstannyl-1,3-butadienes. Another Russian group reported the synthesis of a series of polymetallated cyclopentadienes (XIX, XX) [169].



(XIX)

$(M = Si,\ M' = Si, Ge, Sn;$
$M = Ge,\ M' = Ge, Sn;$
$M, M' = Sn)$



(XX)

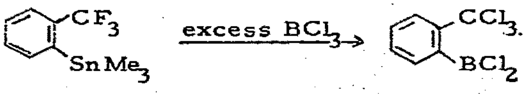
$(M, M', M'' = Sn;\ M, M' = Sn, M'' = Si;$
$M' = Sn, M = Ge, M'' = Si;$
$M, M'' = Si, M' = Sn)$

By conventional methods Zavgorodnii and coworkers prepared some alkynyltin compounds, such as $Et_3SnC{\equiv}CR$ ($R = OMe, SMe, CH_2OMe, CH_2SEt$) [170-172], $Et_3SnC{\equiv}CMR_3$ ($M = Si, Ge$; R = alkyl) [173], $Et_3SnC{\equiv}C{-}R$ ($R = CH_2Cl, CHBrMe$) [174]. According to Cullen et al. the perfluoroalkynyltin compounds, $Me_nSn(C{\equiv}CR)_{4-n}$ ($R = CF_3, CF_2CF_3, CF(CF_3)_2; n = 0-3$) are thermally and hydrolytically unstable, whereas the corresponding silicon and germanium compounds are not so [175] (cf. AS 70; 288).

<u>Carbon-functional tin compounds.</u> The synthesis of the germa- and stanna undecaboranes, $Me_2MB_{10}H_{12}$ (M=Ge, Sn) was reported by Norman *et al.* [176].

Trimethyl(polyfluoroaryl)tin compounds have been used for the preparation of some polyfluorobiaryls (cf. AS 67; 377) [177], *e.g.*:

Furthermore, group IV fluoroorganometallic compounds have been dealt with in a Ph. D. thesis [178]. As reported by Chivers, reaction of *o*-(trifluoromethyl)phenyltrimethyltin with BF_3 gives Me_3SnF and *o*-CF_3-$C_6H_4BF_2$. With BCl_3 the simultaneous occurrence of a halogen-exchange was observed as well [179]:



By reaction of chloro-imines with group IVmetal-lithium derivatives some carbon-substituted imino derivatives of germanium, tin and lead have been prepared [180]. The crystal structure of triethyltin cyanide was determined

$$R_3MLi \xrightarrow{PhCCl=NR'} R_3MC(Ph)=NR'$$

(R = Me, M=Sn; R = Ph, M=Ge, Sn, Pb; R' = Ph, Ch)

by Chow and Britton [181]. By conventional methods Peterson synthesized a series of α-functionally substituted organotins, Bu_3SnCH_2X (X = SCH_3, SO_2R, SO_2NMe_2, SO_2Ph, p-$SO_2C_6H_4Cl$, p-SO_2-C_6H_4OMe, etc.) and studied their reactivity towards solvolysis among others by butanol. The seemingly significant alteration in leaving groups (from CH_2SO_2R to $CH_2SO_2NMe_2$) resulted only in minor changes in the rate of butanolysis [182]. Jutzi et al. developed a direct method for carbamoylation [183], viz.:

$$t\text{-}BuNHLi \xrightarrow{CO} t\text{-}BuNHC(O)Li \xrightarrow{Me_3MCl} Me_3MC(O)NHBu\text{-}t$$

$$(M = Si, Ge, Sn)$$

IR and PMR spectroscopic data of Ph_3MCH_2COOEt (M = C, Si, Ge, Sn; prepared by means of the Reformatski reagent $BrZnCH_2COOEt$) did not provide indications for an intramolecular interaction between the heteroatom and oxygen in these compounds [184]. Such an interaction was not te bo expected in view of the rather unfavourable four-membered ring structure that would have been formed.

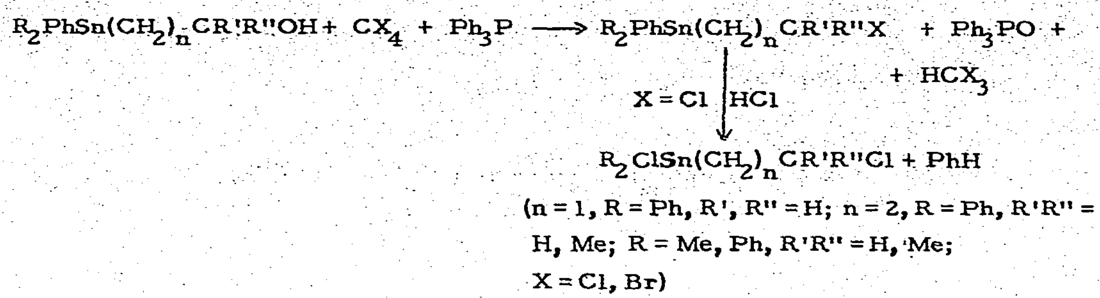
Seyferth et al. [185] successfully applied halomethylzinc halides in the synthesis of monohalomethylgermanium, -tin, -lead and mercury compounds.

$$R_2R'SnX \xrightarrow{ICH_2ZnI} R_2R'SnCH_2I \xrightarrow{AgX} R_2R'SnCH_2X$$

$$(R = Me, R' = Me, Ph; \; R, R' = Ph, Cl) \qquad (R, R' = Me; X = Cl, Br)$$

Good yields were obtained except for the reaction with $SnCl_4$. The mechanism was tentatively proposed to involve a nucleophilic sttack by the organozinc reagent at tin. In the free-radical reaction of benzoyl peroxide with bis-(trimethylstannyl)dichloromethane, $(Me_3Sn)_2CCl_2$, the intermediate formation of the (trimethylstannyl) dichloromethyl radical, $Me_3SnCCl_2\cdot$, was suggested [186].

Gielen and coworkers reported a convenient method for the synthesis of haloalkyltin compounds [187]:



$$\begin{array}{l} R_2PhSn(CH_2)_nCR'R''OH + CX_4 + Ph_3P \longrightarrow R_2PhSn(CH_2)_nCR'R''X + Ph_3PO + HCX_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad X = Cl \Big\downarrow HCl \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad R_2ClSn(CH_2)_nCR'R''Cl + PhH \end{array}$$

(n = 1, R = Ph, R', R'' = H; n = 2, R = Ph, R'R'' = H, Me; R = Me, Ph, R'R'' = H, Me; X = Cl, Br)

The PMR spectrum of $Me_2PhSnCH_2CH_2CHMeOH$ shows two diastereotopic methylgroups at tin with $\Delta\delta = 0.3$ Hz. $Me_2BrSnCH_2CH_2CHMeOH$ showed no detectable non-equivalence, not even in the presence of tris(dipivalomethanato)-europium(III). The latter tin compound was concluded to have largely a five-membered ring structure [188].

Redistribution and cleavage reactions. Moedritzer published another review article (with no less than 495 references) on redistribution equilibria of organometallic compounds [189] (cf. AS 68; 718).

In a patent application a variety of inorganic metal salts (Lewis acids) and complexes, such as $AlCl_3$, $GaCl_3$, $TaCl_5$, BF_3, $BF_3 \cdot Bu_2O$, $NaAlCl_4$, were claimed to be effective redistribution catalysts, for example:

$$3\,Ph_4Sn + SnCl_4 \xrightarrow[\substack{2)\ 1\%\ GaCl_3\ \text{at}\ 150^\circ \\ 3)\ 15'\ \text{at}\ 110^\circ}]{1)\ 0.5\ \text{h at}\ 200^\circ} Ph_3SnCl\ (96\%)$$

Without a catalyst the yield in the latter reaction was only some 10% lower [190]. Aluminium trichloride can also be used for the preparation of mixed alkyl-phenyl substituted compounds, such as $Ph_2BuSnCl$ [191]. According to Mel'nichenko et al. (cf. AS 70; 290) this type of compounds can be prepared

$$2\,Ph_3SnCl + Bu_3SnCl \xrightarrow{AlCl_3} 3Ph_2BuSnCl$$

as well without a catalyst, but a rather specific alternating heating process seems to be required [192].

$$2\,Ph_3SnEt + EtSnCl_3 \xrightarrow[\substack{\text{2) 4 h at } 210^{o} \\ \text{3) 3 h at } 150^{o}}]{\text{1) 0.5 h at } 120^{o}} 3\,Ph_2EtSnCl\ (77\%)$$

$$Me_2Bu_2Sn + Bu_2SnCl_2 \xrightarrow[\substack{\text{2) 3 h at } 140^{o} \\ \text{3) } 200^{o}}]{\text{1) 3 h at } 80^{o}} 2\,Bu_2MeSnCl\ (87\%)$$

The same authors studied some redistribution reactions of tetraalkyltins with tin acylates [193]:

$$Et_4Sn + Cl_2Sn(OAc)_2 \xrightarrow[175^{o}]{2h} 2\,Et_2Sn(OAc)Cl\ (86\%)$$

$$Et_4Sn + Sn(OAc)_4 \xrightarrow[210^{o}]{10\text{ h}} 2\,Et_2Sn(OAc)_2\ (71\%)$$

Abraham and coworkers have continued (cf. AS 70; 294 and AS 69; 519) their mechanistic studies on bimolecular electrophilic substitution reactions of tetraalkyltins by inorganic and organic mercuric compounds, HgX_2, in different polar solvent systems [194-197]

$$R_4Sn + HgX_2 \longrightarrow R_3SnX + RHgX$$

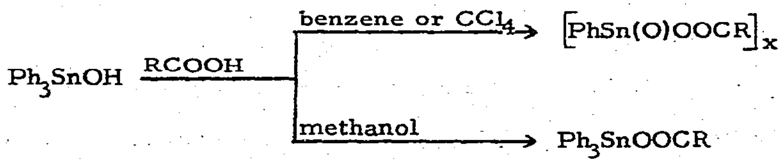
$$(R = Me, Et, Pr, i\text{-}Pr, Bu, i\text{-}Bu;\ X = Cl, I, OAc)$$

In the solvent systems: methanol, aqueous methanol, tert-butanol, methanol/ /tert-butanol and acetonitrile the reactions with $HgCl_2$ and with HgI_2 proceed by the S_E2 (open) mechanism of electrophilic substitution at carbon, through a transition state in which there is considerable charge separation. In the reaction with $Hg(OAc)_2$ in tert-butanol solution a cyclic S_E2 mechanism may be involved. The relative rate coefficients for these reactions in acetonitrile were determined to be 4.5 (X = OAc), 1.0 (X = Cl) and 1.8 (X = I), whereas in methanol they are 250 (X = OAc), 1.0 (X = Cl) and 0.8 (X = I) [197].

A kinetic study has been reported of mercury- and iododestannylation reactions of Me_3SnR (R = Me, Bu, Pent, $(CH_2)_4Ph$, $(CH_2)_2CH{=}CH_2$, $(CH_2)_3CH{=}CH_2$, $(CH_2)_2COOMe$, norbornenyl and norbornadienyl derivatives) [198]. As was to be expected on the basis of previous studies of Abraham *et al.* (*cf.* AS 70; 294) and Gielen and Nasielski *et al.*, it was found that with exception of the latter two derivatives, almost exclusively demethylation occurs. The stereochemistry and mechanism of bromodestannylation has been studied with different tetraalkyltins [199]. Russian authors prepared a review (in Russian) with 250 references on reactions of organometallic group I-IV derivatives with polyhalomethanes [200].

The rather unexpected solvent effects observed with cleavage reactions of aryltrimethyltin compounds, $Me_3SnC_6H_4X$ (X = H, p-F, m-Cl, m-Br, p-Me, p-SMe), with aqueous ethanolic perchloric acid were discussed on the basis of counteracting effects of water on the acid proton and on the transition state involved [201]. The base-catalyzed hydrolytic cleavage of these aryltrimethyltin derivatives in aqueous dimethylsulfoxide has been studied by the same group [202].

On heating triphenyltin hydroxide with strong carboxylic acids in non-coordinating solvents like benzene or carbon tetrachloride tin-carbon bond cleavage occurs, whereas in methanol or ethanol at room temperature the corresponding triphenyltin carboxylates are formed [203].

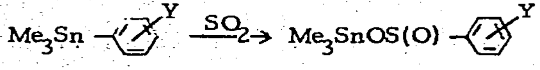


(R = Me, CH_2I, CH_2Br, CH_2Cl, $CHCl_2$, CF_3)

Lindner et al. made further studies on the behaviour of tetraorganotins towards sulfur dioxide (cf. AS 70; 295) [204]. Fong and Kitching investigated

$$R_4Sn \xrightarrow[60^\circ]{\text{lig. }SO_2,\ H_2O} R_2SnSO_3 \quad (R = Et, 50\%;\ Bu, 15\%)$$

the kinetics and mechanism of the insertion of sulfur dioxide into the carbon-tin bond of a variety of aryltrimethyltin compounds.



$(Y = m\text{-}Me, \text{-}OMe, \text{-}Cl, \text{-}CF_3, p\text{-}Me, \text{-}OMe, \text{-}Cl, \text{-}CF_3)$

The results obtained were interpreted on the basis of an electrophilic substitution at carbon (S_Ei), involving some charge-separation in the transition state [205]. Similar conclusions were reached with respect to sulfur dioxide insertion reactions into the phenyl-tin bond in some iron-tin derivatives [206].

$$(\pi\text{-}C_5H_5)(CO)_2FeSnPh_3 \xrightarrow{SO_2} (\pi\text{-}C_5H_5)(CO)_2FeSn(SO_2Ph)Ph \xrightarrow{SO_2}$$

$$(\pi\text{-}C_5H_5)(CO)_2FeSn(SO_2Ph)_2$$

Aleksandrov prepared a review article on the oxidation of organometallic group IV derivatives by ozone [207]. The same author reported that the ozonolysis of $Et_{4-n}SnCl_n$ ($n = 0\text{-}2$) proceeds as a bimolecular reaction, the reactivity of the tin compounds towards ozone decreasing with increasing number of chlorine atoms [208, 209].

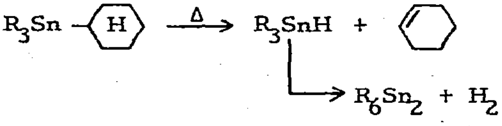
Peterson reported details on the preparation of N,N-disubstituted aminomethyllithium compounds by cleavage of the corresponding tin compounds,

Bu_3SnCH_2NRR', with butyllithium (cf. AS 70; 296) [210].

$$Bu_3SnCH_2NRR' + BuLi \longrightarrow Bu_4Sn + LiCH_2NRR'$$
$$(R, R' = Me, Ph, (CH_2)_5, CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2)$$

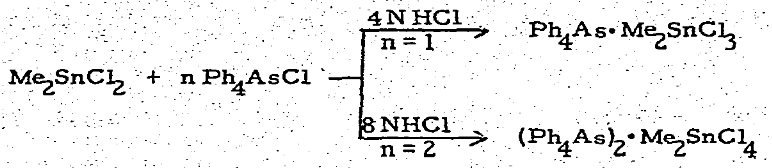
Seyferth gave a summary of his research on divalent carbon intermediates formed by α-elimination from organometallics [211].

As observed by Kochetikhina [212], in addition to homolytic fission group IV organometallics (M=Ge,Sn) also undergo decomposition by metal-hydride elimination, viz.:



Complexes and coordination. Zahrobsky discussed the application of a stereochemical model to several mono-nuclear complexes of tin that had been studied by X-ray diffraction. For the octahedral complexes the calculated bond angles are generally within the experimental error with those observed by X-ray [213].

Several groups reported investigations into the complex formation of diorganotin diisothiocyanates with nitrogen or oxygen containing ligands [214-216] (cf. AS 69; 521). Comparison of the stability constants of 2,2'-bipyridyl adducts of diorganotin diisothiocyanates and dichlorides in benzene and toluene solutions showed that the diisothiocyanates are much better acceptors (by factors of about 500) than the dichlorides. Reaction of dimethyltin dichloride with tetraphenylarsonium chloride gives rise to the formation of the corresponding penta- or hexacoordinated complexes, depending on the reaction conditions employed [217].



$$Me_2SnCl_2 + n\,Ph_4AsCl \xrightarrow[n=1]{4\,N\,HCl} Ph_4As \cdot Me_2SnCl_3$$

$$Me_2SnCl_2 + n\,Ph_4AsCl \xrightarrow[n=2]{8\,N\,HCl} (Ph_4As)_2 \cdot Me_2SnCl_4$$

Barbieri and coworkers made further spectroscopic studies into both the solid state configuration (cf. Fig. 6) [218], and the structure in methanolic solution [219] of a series of one to one adducts of R_2SnCl_2 (R = Me, Et, Bu, Ph)

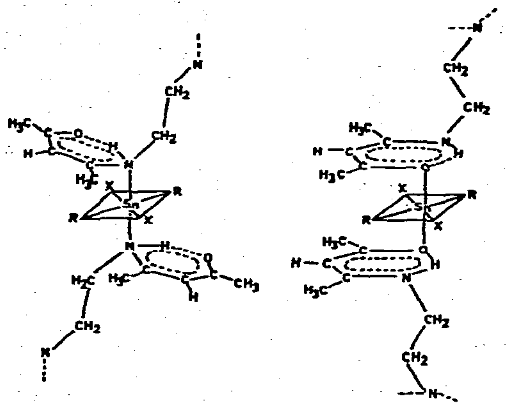


Fig. 6. Suggested solid-state configurations of R_2SnCl_2-bis(acetylacetone)ethylenediimine adducts [from R. Barbieri, R. Cefalu, S. C. Chandra and R. H. Herber, J. Organometal. Chem., 32(1971)97]

with bis(acetylacetone)ethylenediimine (cf. AS 69; 521). In methanol complete dissociation into the free ligand and the solvated organotin halide moieties was inferred. From PMR spectral data of the very same compounds Smith et al. [220] concluded also that these adducts are largely dissociated even in non--coordinating solvents. However, conductivity studies in nitrobenzene solution indicated that the species in solution are non-ionic. The complex formation of dimethyltin derivatives has been the subject of two doctoral dissertations [221, 222].

Other papers dealing with molar conductance and/or spectroscopic studies of complexes of organotin halides with donor ligands include: a cryoscopic study of the complex formation of $Bu_{4-n}SnCl_n$ (n = 1-3), Bu_3SnBr, $Bu_2Sn(OAc)_2$, Et_3SnCl and Et_2SnCl_2 with a wide range of oxygen and nitrogen containing ligands [223], complexes of the types $R_2SnX_2 \cdot 2\,DMF$ [224], $R_2SnX_2 \cdot 2,2'$-bipyridine [225] and $R_2SnX_2 \cdot 1,10$-phenanthroline [226] (R = Ph, $PhCH_2$, o-, m-, p-tolyl; X = Cl, Br, I), one to one adducts of $PhPrSnCl_2$ with α- and β-picolines and one to two adducts of $PhRSnCl_2$ (R = Et-Bu, $PhCH_2$) with pyridine, quinoline, isoquinoline, morpholine, piperidine or aniline [227, 228] (cf. AS 70; 297), complex formation of Me_2SnCl_2 with N,N-dimethylpicolinamide, -isonicotinamide and N-methyl-N-benzyl derivatives in benzene/methylene chloride solution (rapid equilibrium) [229] as well as with some peculiar Schiff bases [230]. On the basis of IR, conductivity and molecular weight data for diaryltin bis(acetylacetonates), $R_2Sn(acac)_2$ (R = Ph, o-, m-, p-tolyl) a hexacoordinated octahedral structure was concluded [231].

Physico-chemical investigations. By conformational analyses and lattice energy calculations the crystal and molecular structure of tetraphenylcarbon, -silicon, -tin and -lead have been determined [232]. The calculated structure of tetraphenyltin was in good agreement with that determined experimentally by X-ray analysis [233] (cf. AS 70; 301). Other compounds of which the crystal and molecular structures have been determined are tetrabenzyltin [234], triphenyltin chloride [235] and a series of (4-halo-1,2,3,4-tetraphenyl-cis,cis-1,3-butadienyl)dimethylphenyltins [236] (cf. Fig. 7 and AS 70; 284, 285). As determined by an electron diffraction study of the structure of gaseous trimethylcyclopentadienyltin the cyclopentadienyl moiety

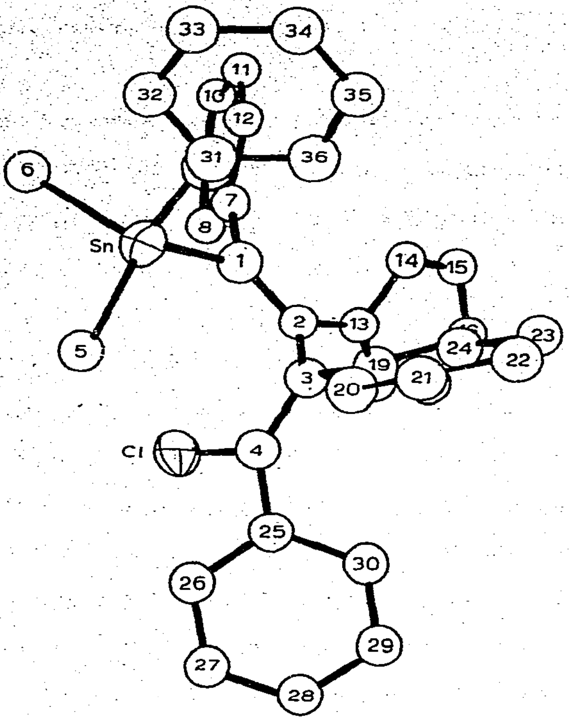


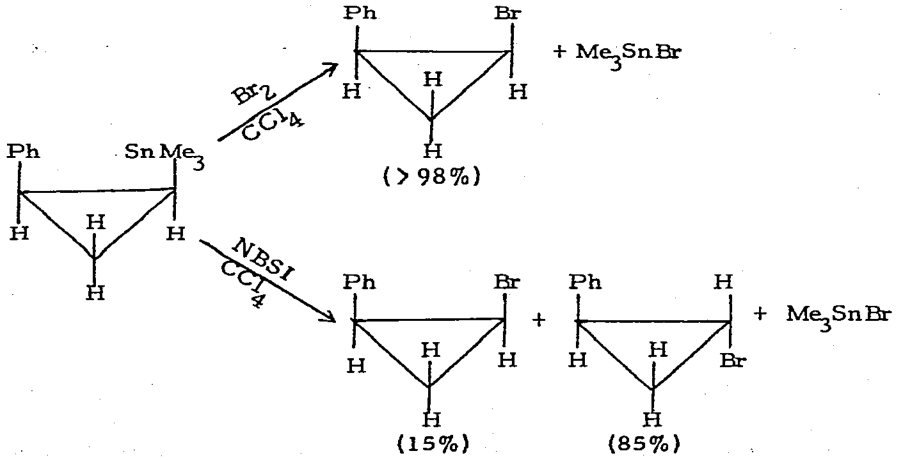
Fig. 7. The structure of $Me_2PhSnC(Ph){=}C(Ph){-}C(Ph){=}C(Ph)Cl$ [from F. P. Boer, F. P. Van-Remoortere, P. P. North and G. N. Reeke, Inorg. Chem., 10 (1971) 529].

is not planar [237]. A gas-electron diffraction study of dimethyltin dichloride confirmed the occurrence of a regular bond contraction in going from Me_3SnCl to $SnCl_4$, as pointed out previously by Skinner and Sutton in 1944 [238].

Perkins and Wall presented an analysis of the charge distributions in $Me_{4-n}SnH_n$ (n = 0-4) and $Me_{4-n}SnX_n$ (n = 0-4, X = halogen). Replacement of halogen atoms by methyl groups reduces the polarity of the tin-halogen bond, because methyl groups act in this context as sources of electrons, largely via the π-type orbitals. The involvement of 5 d orbitals is small in $Me_{4-n}SnH_n$ (n = 0-4), larger in the tetrahalides SnX_4 and largest in the hexahalide anions SnX$_6^{2-}$ [239]. Quite remarkably, the opposite was concluded by Gupta et al. [240]. On the basis of electric dipole moment calculations these authors concluded that the bond polarity of the tin-chlorine bond decreases in the order R$_3$SnCl > R$_2$SnCl$_2$ > RSnCl$_3$ > SnCl$_4$.

A Russian group studied the polarografic behaviour of R$_3$SnCl (R = Bu, Ph) and R$_2$SnCl$_2$ (R = Et, Bu) [241-243].

In a review article Aylett discussed the stereochemistry of the main group IV elements on the basis of 310 references [244]. Likewise, Nasielski dealt with the structure, mechanism and stereochemistry of organotins [245]. Sisido and coworkers [247] reported that bromine cleavage of cis- and trans--(2-phenylcyclopropyl)trimethyltin in the dark proceeds with >98% retention of configuration (cf. AS 70; 300). This result is in agreement with previous



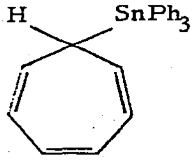
observations of Baekelmans et al. (cf. AS 67; 380), viz. halogen cleavage of (cyclopropyl)trimethyltin derivatives proceeds by an ionic mechanism provided that the maximum precautions are taken to avoid free radical reactions. Under free radical conditions (NBSI) a racemic mixture is formed. Valade and Calas et al. studied the asymmetric hydrostannation of (—)-menthyl-

-trans-crotonate with tributyltin hydride; on subsequent reduction with $LiAlH_4$(–)(R)-2-tributylstannylbutane was obtained [248]. Optically active compounds have also been prepared by coupling reactions of triphenyl-group IV metal alkali metal compounds [249], viz:

$$Ph_3M^{\ominus} + (S)\text{-}(+)\text{-}sec\text{-}BuBr \longrightarrow (R)\text{-}(-)\text{-}sec\text{-}BuMPh_3 + Br^{\ominus}$$
$$(M = Si, Ge, Sn, Pb)$$

Allred et al. [250] discussed the factors influencing the magnitude of diastereotopic non-equivalence in the PMR spectra of asymmetric tin compounds. From a comparison of a variety of such compounds it was among others concluded that the large anisotropy of the phenyl-ring is important in establishing a sufficient difference in shielding for diastereotopic non-equivalence to be observed (cf. AS 70; 300).

A fluxional sigmatropic rearrangement has been observed with triphenyl-7-cyclohepta-1,3,5-trienyltin (XXI) [251].



(XXI)

The experimental evidence on the ability of group IV metals to use their empty d-orbitals to form (p →d)π bonds with ethylenic systems has been discussed in a review [252]. On the basis of an IR spectral study of mixtures of $CDCl_3$ with different organosilicon, -germanium and -tin compounds, it was concluded that (p→d)π conjugation does occur, this interaction being greater with silicon than with germanium or tin [253]. Using the shift in the visible absorption maximum of hexanitrodiphenyl amine the order of base strengths for Me_3MX was concluded to be $Me_3SiSMe < Me_3CSMe < Me_3SnSMe \approx Me_3SiNMe_2$ [254].

Gupta *et al.* developed a method for calculating the heats of atomization of organotin compounds [255].

Miscellaneous physico-chemical studies include the fluorescence quenching of anthracene by Me_2Hg, Me_4Pb and Me_4Sn [256], the mesomorphic behaviour of p-Me_3M- substituted benzaldehydes (M=Si, Ge, Sn) [257] and the solubilities of R_4M (R = Me, Et; M=Si, Ge, Sn) compounds in mixtures of water with methanol, ethanol, dioxane, acetone and acetic acid [258].

Spectral studies. In 1970 W. O. George edited the monograph "Spectroscopic Methods in Organometallic Chemistry" [259]. In 1971 the East German authors K. Licht and P. Reich published the book "Literature Data for IR, Raman and NMR Spectroscopy of Silicon, Germanium, Tin and Lead Organic Compounds" [260]. In the latter book, covering the literature only up to 1966, spectroscopic data of about 5500 compounds have been listed and indexed on the basis of some 2100 references.

IR and Raman studies. A short survey on the application of vibrational spectroscopy to organometallic chemistry has been published by Downs [261]. Furthermore, the vibrational spectra of intra- and intermetal and semi-metal bonds have been reviewed [262]. More specific studies include the following compounds: Me_6M_2 (M=Si, Ge, Sn, Pb) [263]; Ph_6M_2 (M=Sn, Pb) and $(Ph_3Sn)_4Sn$ [264]; $R_3SnMn(CO)_5$ (R = Me, Ph, Cl, Br) [265]; $Me_3MM'(\pi\text{-}C_5H_5)(CO)_3$ (M=Ge, Sn; M' = Cr, Mo, W) [266]; R_3SnF (R = Me—Bu, Ph) [267]; Me_2SnF_2 [268]; Ph_4Sn, Ph_3SnX, Ph_2SnX_2 (X = halogen) [269].

UV studies. In the series Me_3MCH_2Ph (M = C, Si, Ge, Sn) the displacement of the UV spectrum from that of benzene increases when carbon is substituted by Si, Ge or Sn. Replacement of the methyl group by chlorine resulted in a decrease of that displacement. These results were interpreted on the basis of (σ-π) conjugation [270]. The UV spectra observed for a series of 2-substituted pyridines— substituents being CH_3-, $Me_3SiCH_2CH_2$-, Me_3ECH_2- (E = C, Si, Ge), $(Me_3E)_2CH$— (E = Si, Sn) — were likewise interpreted in terms of carbon-metal (σ-π) hyperconjugation [271].

NMR studies. In the series "Characterization of Organometallic Compounds" (Ed. M. Tsutsui) R. G. Kidd prepared a review on NMR spectroscopy of organometallic compounds [272]. This subject was also reviewed by Mc. Farlane [273]. More specific subjects studied by NMR spectrometry include: the primary isotope effect on the magnetic shielding of ^{117}Sn and ^{119}Sn nuclei [274]; ^{119}Sn chemical shifts in a series of organotin compounds by ^{1}H– ^{119}Sn double resonance experiments [275, 276]; $^{117/119}Sn$ satellite spectra and $^{117/119}Sn$-proton long range coupling constants in tetra(2-furyl)-, tetra(3-furyl)-, tetra(2-thienyl)- and tetra(3-thienyl)tin [277]; $Me_3MM'Me_3$ (M, M' = C, Si, Ge, Sn) [278]; R_6Sn_2 (R = Et, Ph), Ph_3SnMMe_3 (M = Ge, Sn), $Me_3SnGePh_3$ [279]; ^{1}H and ^{55}Mn NMR spectra of $R_{3-n}X_nSnMn(CO)_5$ (R = Me, Ph; X = Cl, Br; n = 0-3) [280]; geminal spin-coupling constants in a series of group IV hydrides by double resonance experiments [281]; halogen-exchange between Me_3SnI and Me_3SnBr [282]; spin-spin coupling constants for $Me_{4-n}SnX_n$ (X = Li, $Re(CO)_5$, $Mn(CO)_5$, $SnMe_3$, SiH_3, $Co(CO)_4$, NMe_2, SMe, OMe, I, Br, Cl; n = 1-3) [283]; ^{1}H, ^{13}C and ^{119}Sn NMR spectra of $Me_nSn(SMe)_{4-n}$ (n = 0-3) [284]; low temperature PMR study of diphenylbis(2,4-pentanedionato)-tin(IV) [285]; ^{119}Sn and ^{31}P spectra of $Me_3SnPHPh$ and Me_3SnPPh_2 [286]; ^{55}Mn spectra of $R_{3-n}X_nSnMn(CO)_5$ (R = Me, Ph; X = Cl, Br; n = 0-3) [287].

Mössbauer studies. Quite a series of Mössbauer studies of organotin compounds have appeared in 1971. Although this technique has been found to be of great help in the elucidation of many structural problems in organotin chemistry, care should be taken in the interpretation of the Mössbauer phenomena observed. For example, on the basis of Mössbauer studies it has been concluded that Ph_2SnCl_2 has a pentacoordinate structure. Recently, however, an X-ray study revealed that there is no molecular association in the Ph_2SnCl_2 crystal. The authors, Greene and Bryan, concluded that anomalous results in Mössbauer spectral measurements of this and similar compounds, having large deviations from regular tetrahedral geometry, are likely to be the rule rather than the exception [288].

Reviews on Mössbauer spectroscopy have been prepared by Herber [289], Gibb [290], Keune and Trautwein [291] and Gol'danskii [292], as well as by Kazimir [293] and Beaumont [294].

In accordance with the results of Greene and Bryan mentioned above, Parish and Platt concluded from a Mössbauer study of different organotin compounds that the stereochemistry plays an important role, viz. the isomer shift of dialkyl- and diaryltin compounds increases with increasing C–Sn–C bond angle. In compounds of the type R_3SnX and, to a lower extent, R_2SnX_2, the isomer shift is insensitive to the nature of the ligand X, owing to changes in electric shielding [295].

The quadrupole splitting data observed for cyclohexyltin derivatives, for $Ph_2XSn(CH_2)_4SnXPh$ (X = I, OH, OAc, Ph), for $Bu_nSn(OAc)_{4-n}$ (n = 2, 3) and for dibutyltin maleate were used empirically to discuss internal association in organotin compounds [296]. Origin and sign of the quadrupole coupling constants in different organotins have been discussed by Parish et al. [297-299], by Greenwood et al. [300, 301] and by Gol'danskii [302].

Malysheva et al. concluded that the temperature dependence of the γ-resonance absorption of organotin compounds cannot be used as a direct method for determining the coordination number of tin(IV) compounds [303, 304].

The isomer shifts observed for the adducts of dicyclopentadienyltin(II) and bis(methylcyclopentadienyl)tin(II) with phenylmagnesium bromide were found to be well below that of β-tin, which points to the structure $(R\text{-}C_5H_4)_2PhSn^{IV}MgBr$ (dimer) rather than $(R\text{-}C_5H_4)_2Sn^{II}\cdot PhMgBr$ (R = H, Me) [305].

Other Mössbauer studies of organotin compounds include: $(RCOO)Ph_2Sn\text{-}SnPh_2(OOCR)$ ($R = Me, CH_2Cl, CCl_3, CF_3, Ph$) [306]; $Me_3SnM(CO)_3(\pi\text{-}C_5H_5)$ (M = Cr, Mo, W), Me_3SnMR_3 (R = Me, Ph; M = C, Si, Ge, Sn), Ph_3SnMPh_3 (M = Si, Ge, Sn), $Ph_3SnIrH(X)(CO)(PPh_3)_2$ (X = Cl, I), $Me_3SnIrX(Cl)(CO)(PPh_3)_2$ (X = H, D), $Ph_3SnIrH(Cl)(CO)(Ph_2RP)_2$ (R = Me, Ph) [307]; compounds of the type $(\pi\text{-}C_5H_5)Fe(CO)_2SnPh_{3-n}Cl_n$ (n = 0-3), $(\pi\text{-}C_5H_5)Fe(CO)_2SnMe_3$, $(CO)_5MnSnX_3$ (X = Me, Ph, Cl) [308]; $R_{3-n}X_nSnMn(CO)_5$ (R = Me, Ph; X = Cl, Br) [280]; complexes of Pr_2SnCl_2, $PrSnCl_3$ and Ph_nSnCl_{4-n} (n = 1-3) with piperidine, morpholine, β-picoline, γ-picoline and isoquinoline [309]; comments on the theory of Williams *et al.* (*cf.* AS 70; 303) on orbital populations derived from the Mössbauer spectra of organotin compounds [310] and a reply to these comments [311]; $Bu_2SnCl_2\cdot 2L$, $Ph_2SnCl_2\cdot L$, $RSnCl_3\cdot 2L$ (R = Bu, Ph; $L = Ph_3PO, Ph_3AsO, Bu_3PO, Ph_3P$) [312]; R_3SnX (R = Me, Ph; X = various anionic substituents) [313]; $Ph_2SnCl_2\cdot R_2SO$, $Ph_2SnCl_2\cdot 2RSO$ (R = Me, Pr, Bu, $(CH_2)_4$ [314]; dialkyltin(IV) complexes with tridentate planar ligands having ONO and SNO donor groups [315]; alkyl- and aryltin cyanates [316]; $(Bu_3Sn)_2SO_4$, Bu_3SnX (X = F, OAc), Bu_2SnX_2 (X = F, OAc) [317]; $R_3SnOOCCH_{3-n}X_n$ (n = 0-3; X = Cl, F; R = alkyl) [318]; $Ph_3SnOOCR$ ($R = Me, CH_2Cl, CH_2Br, CH_2I, CHCl_2, CF_3$) [203]; $(Bu_2XSn)_2O$ (X = halogen) [319].

Aleksandrov *et al.* used γ-resonance spectroscopy in a study of the mechanism of the reaction of a triethyltin derivative of PVC, *viz.* $\left[CH_2-CH(SnEt_3)-CH_2-CHCl\right]_n$, with hydrogen chloride [320] (cf. AS 70; 374).

The vibrational anisotropy and Goldanskii-Karyagin effect in Me_3SnF have been studied by ^{119}Sn Mössbauer spectrometry in the temperature range $7 < T < 296^oK$ [322].

ESR studies. In the series "Characterization of Organometallic Compounds" (Ed. M. Tsutsui) Smentowski published the contribution "Characterization of Organometallic Compounds by ESR" [323]. Jackson prepared a review with 117 references on silicon, germanium, tin and lead radicals [324] (cf. AS 70; 248). The ESR study of the adduct of the trimethyltin radical with butadiene as performed by Kawamura et al. has been dealt with in the section tin-hydrogen compounds [33]. Krusic et al. [325] as well as Lyons et al. [326] studied the ESR spectral phenomena of β-metal substituted alkyl radicals of the structure $R_3M{-}CH_2{-}CH_2\cdot$ (R = alkyl; M = Si, Ge, Sn, P, As, S).

Mass spectral studies. Mass spectra and fragmentation patterns of the following types of compounds have been reported: R_4M (R = Me, M = Sn; R = allyl, M = Si, Ge, Sn) [327]; Me_4M and $Me_3MM'Me_3$ (M, M' = C, Si, Ge, Sn, Pb) [328]; R_6Sn_2 (R = Et, Ph), Ph_3SnMMe_3 (M = Ge, Sn), $Me_3SnGePh_3$ [279]; $Me_3MM'(CO)_3(\pi\text{-}C_5H_5)$ (M = Ge, Sn; M' = Cr, Mo, W) [266]; $(C_6F_5)_{4-n}SnR_n$ (R = Me, Bu, Ph; n = 1-3) and $(Me_3Sn)_2C_6X_4$ (X = F, Cl) [329]; $Bu_2Sn(CH_2{-}CH_2{-}COOCH_3)_2$ [330]; p-trimethyltin-substituted phenyl sulfides [331]; some group IV acetylides [332].

Analytical studies. Luijten composed a bibliography of organotin analysis [550]. Gaschromatographic analysis has been studied with the following organotin compounds: R_3SnMe (R = Et, Pr, i-Pr), Bu_3SnR (R = Me-Pr), R_3SnH (= Et—Bu) and R_6Sn_2 (R = Me—Bu) [333]; $(Et_3M)_2X$ (M = Si, Ge, Sn; X = S, Se, Te) [334]; $Bu_{4-n}SnCl_n$ (n = 0-3) [335]; organotin chalcogenides [336]; $Me_{4-n}SnCl_n$ (n = 0, 4) [337]; $Et_3MM'Et_3$ (M, M' = Si, Ge, Sn) [62].

Thin-layer chromatography has been applied to the separation of eight organotin stabilizers in plastic formulations [338]. Commercial organotin stabilizers have also been identified by chemical break-down and separation of the break-down products [339].

3'-Pyridylfluorone has been found to be useful in the photometric determination of tin in organotin compounds (after destruction) [340].

Booth et al. (cf. AS 70; 304) extended their studies on the application of anodic stripping voltametry to the determination of sub-microgram concentrations of Ph_3SnX (X = OH, OAc) [341]. The latter technique has also been applied to the determination of Bu_3SnCl [342].

Organotin stabilizers can be determined quantitatively by potentiometric titration with sodium methoxide in dimethylformamide, pyridine or THF solution [343].

Polarographic determinations have been studied with the following organotin species: Et_3SnX (X = Cl, OH, $OOC{-}C(Me){=}CH_2$), $(R_3Sn)_2O$ (R = Et, Bu) and Bu_3SnX (X = Cl, $OOC{-}C(Me){=}CH_2$) [344]; organotin stabilizers in PVC [345, 346].

Havranek et al. reported a fast method for X-ray fluorescence analysis of tin in organotin stabilizers as such or in PVC films [347].

A method has been developed for the determination of sulfur in organotin mercaptides by coulometric titration [348].

Applications and biological effects. The rapidly increasing industrial importance of organotin compounds is reflected by the large amount of scientific papers and patent applications dealing with the many different types of applications of organotins as well as with their biological effects.

Several review articles featuring the most important field of application of organotins, viz. the stabilization of PVC have appeared. Yukitomo reviewed both the stabilizing effect of among others organotin compounds [349] and the mechanism of stabilization [350]. Granick and Weisfeld 351 discussed the legal limitations on the use of stabilizers in PVC food packaging, among which the dioctyltin stabilizers. A survey of the recent developments, advantageous and disadvantageous of today's most important types of PVC stabilizers, prepared by Thomas, clearly shows the outstanding properties of the organotin stabilizers. In that paper the most important single development in PVC stabilization of recent years is mentioned to be the acceptance of organotin compounds for food-packaging materials [352]. Furthermore, this type of application of organotins has been treated by Evans in Tin and its Uses [353] as well as in Tin International [354].

According to Rockett and coworkers [355] the reactivity of an organotin mercaptide or carbothiolic acid salt towards hydrochloric acid is a measure of its efficiency as a heat stabilizer for PVC, the stabilizing effect of a given compound increasing with increasing reactivity towards HCl. On the basis of DTA and TGA analysis Zavarova *et al.* concluded that dibutyltin dicaprylate inhibits the HCl cleave either by adding to the double bonds in the polymer, or by forming a complex with the polyene or chlorine atoms [356]. The same research group applied UV and IR spectroscopic methods in studying the mechanism of the stabilization of PVC by organotin compounds. IR spectra showed inhibition of conjugated double bond formation with dibutyltin dioctanoate, maleate and bis(thiododecylate) for one hour at 175°. Under these conditions butylstannonic acid had no effect, whereas bis-(tributyltin) oxide increases the conjugation rate. It was concluded that the stabilizing mechanism involves the formation of stable Cl–Sn–Cl bridges between PVC macromolecules [357]. In a study of the thermal and photo-stabilization of PVC with compounds of the type Bu_2SnX_2 (X = $SC_{12}H_{25}$, $OOCC_{11}H_{23}$, SMe, OAc) the mercaptides were found to be the most effective [358].

Seidler *et al* [359] used ^{14}C labelled dioctyltin stabilizers in studying their migration from hard PVC into edible oil. With similar techniques Figge and coworkers [360, 361] observed that the type of fat in foodstuff has no appreciable effect on the migration, whereas the type of resin is of great importance. The latter group also determined that migration of dioctyltin bis(2-ethylhexylthioglycolate) from PVC bottles in beer after 8 weeks at 20° is far below the limit of 1 mg/l of organotin stabilizer as permitted by the US Food and Drug Administration [362]. Similar migration studies have been performed with different types of liquid foods [363] as well as with various solvents [364]. On the basis of biological inertness and low toxicity the best plastic formulation for use in vascular catheters has been reported to be a dioctyltin distearate containing type of PVC. Polyethylene was stated to be less satisfactory for this medicinal application [365]. In contrast, however, Stetson recommended that no plastic devices that will be in contact with human tissue contain an organotin stabilizer: organotin stabilized PVC devices cause inflammation and necrosis when placed in intimate contact with rabbit muscle [366].

Specific types of organotin compounds claimed to be useful as stabilizers for PVC include: R_3SnNCO (R= Et, Bu, Ph, CH_2Ph) (*cf.* AS 70; 304) [367]; dibutyl- and dioctyltin maleate [368, 369]; dibutyl- and dioctyltin phenolates [370, 371]; metallostannoxanes of the structure $R_2ClMOSnClR_2'$ (R = alkyl, aryl; R' = alkyl), for example $Me_2ClSiOSnClBu_2$, prepared from Me_2SiCl_2 and Bu_2SnO [372]; dimercapto derivatives of distannoxanes or thiodistannoxanes [373] as well as many other types of organotin-sulfur derivatives [374-383]; boron-containing organotins such as $C_{11}H_{23}COOSnBu_2OB(O$-$-SnBu_2SCH_2CH_2OOCCH{=}CHCOOCH_2CH_2SH)_2$ [384] ; fluoroalkyltin compounds of the type $[CF_3CH_2CH_2]_{4-n}SnX_n$ [385]; dialkyltin derivatives containing reactive dienophilic groups, such as, $Bu_2Sn(OOC-CR{=}CR'-COOC_nH_{2n+1})_2$ (R,R' = alkyl; n = 1-5) [386-388]; stabilizer systems consisting of an organotin compound and an acidic phosphoric acid alkyl ester [389]; $R_2Sn(OOCCH_2CH_2OR')$ (R = Me, Bu; R' = Me, Bu, $C_{10}H_{21}$) and $R_2Sn(OOCCH_2CH_2SCH_2CH_2COOR')_2$ (R = Me, Bu; R' = Et, Oct, $C_{12}H_{25}$) [390]. The stabilizing effect of a mixture of dioctyltin oxide/dioctyltin bis(isothioglycolate) = 18/75 has been claimed to be better than that of the latter compound alone [391].

The following monoorganotin dervatives are effective in the thermal stabilization of chlorine containing polymers: $RSnX_2Cl$(R = Bu, Oct; X = octylthio, laurylthio) [392], $[BuSn(S)SCH_2COOR]_x$ (R = different hydrocarbon moieties) [393], $[PhSn(O)OH]_x$ [394].

A synergistic effect has been claimed for mixtures of divalent organic sulfur compounds with conventional dialkyltin stabilizers [395] as well as with butylstannonic acid [396], and for mixtures of dialkyl- and monoalkyltin compounds [397, 398].

Organotin phenolates may be used as UV stabilizers for synthetic polymers like polystyrene [399, 400]. Polyethylene and polypropylene with improved heat and light stability may be obtained by incorporating ditin compounds, R_6Sn_2 (R = Ph, p-Me_2N-C_6H_4, p-Me-C_6H_4, etc.) [401] (cf. AS 70; 305).

The number of papers and patent applications featuring organotin compounds as suitable catalysts or co-catalysts for many different industrially important processes is rapidly increasing.

A mixture of tetraethyltin, aluminium trichloride and dicyclopentadienyltin dichloride has been claimed as a catalyst for the preparation of polyethylene [402]. Complex catalyst systems containing organotin hydrides can be used for the preparation of stereoregular polyethylene (cf. AS 69; 528 and AS 70; 306) [403] and of cis-1, 4-polyisoprene [404], and for the polymerization of cyclopentene [405]. Tetraalkyltin compounds are useful as catalysts or co-catalysts in the telomerization of cyclic olefins with acyclic olefins [406], in the polymerization of butadiene or isoprene [407] and in the polymerization of trioxane [408]. Bu_3SnF is a suitable co-catalysts in the stereospecific (cis) solution polymerization of butadiene [409] (cf. AS 70; 306). Dialkyl- as well as trialkyltin derivatives catalyze the polymerization of formaldehyde [410] (cf. AS 70; 306). Other processes (co-)catalyzed by organotins include: alkylene oxide polymerization ($R_{4-n}SnX_n$, n = 1-3) [411], the polymerization of lactones (R_2SnXY) [412, 413], the polymerization of 2,5-dioxopiperazine ($R_{4-n}SnCl_n$, n = 1-4) [414], the trimerization of isocyanates (Me_3SnSX, X = H, Me_3Sn) [415] and the polymerization of vinylethers [416].

In a general survey Evans gave an exposition of the application of dibutyltin dilaurate and tin dioctoate as polyurethane catalysts [417, 418]. Lipatova and coworkers continued their studies of the kinetics of polyurethane formation in the presence of dibutyltin derivatives. The results were interpreted on the basis of the formation of termolecular complexes between the reactants and the catalysts (cf. AS 70; 306) [419, 420]. Similar kinetic studies have been reported by Volodarskaya et al. [421]. The applicability of dialkyltin derivatives as catalysts for the preparation of polyurethanes is claimed in several patent applications [422-425].

The application of dialkyltin compounds as catalysts for the cold-curing of silicones also continues to arouse interest [426]; several patent applications were filed [427-429].

Dialkyl- and monoalkyltin compounds have been found to be highly effective catalysts in the cold-curing of a specific new type of epoxy resins. [430].

Catalysts claimed to be active in transesterification and/or polycondensation reactions to give linear polyesters such as poly(ethylene terephthalate) include $R_3SnOP(O)X_2$ or $(R_3SnO)_{3-n}P(O)X_n$ (R = alkyl, aryl; X = alkoxy, phenoxy; n = 1, 2) [431] (cf. AS 70;307), $R_3Sn(SnR_2)_nSnR_3$(R = alkyl, n = 0, 1) [432], $(R_2XSn)_2O$ (e.g. R = Bu, X = Cl) [433], R_3SnH (R = alkyl, aryl) [434], R_2SnX_2 (R = Bu, Oct; X = Cl, OMe, OBu) [435], compounds of the formula $RO[(R_2SnO)_x(R_2SiO)_y]_nR$ (R = alkyl, aryl) [436]. Ethyleneterephthalate polyesters may be stabilized with R_2SnX_2 (e.g. R = Bu, X = acetate, laurate) [437]. Dibutyltin oxide is useful as a catalyst for the transesterification of methylnicotinate to give benzyl and 2-(diethylamino)ethyl nicotinate, which are useful for pharmaceuticals and cosmetics [438].

Miscellaneous applications of organotins reported include: dibutyltin derivatives as additives for improved workability of crystalline polyolefins [439] and of PVC fibers and filaments [440], tri-isobutyltin carboxylates, sulfonates and phosphates as antistatic finishes for textiles [441], solutions of triorganotin compounds in dimethyl formamide spinning solutions for imparting improved light stability, oxidation resistance and antibacterial properties to polyacrylonitrile fibers [442], incorporation of mono- and dialkyltin compounds in printing ink applied on removable adhesive tapes [443, 444], tri- and tetraorganotin compounds for imparting good storage stability to photopolymerizable mixtures of unsaturated compounds [445], dialkyltin compounds as additives for polysiloxane paper-coatings with improved release properties and abrasion resistance [446], R_3SnX(R = Bu, $PhCH_2$; X = H, OH, OMe) as catalysts for the hydroperoxide oxidation of olefins to epoxides [447, 448], a mixture of Bu_4Sn and $ReCl_5$ for the homogeneously catalyzed disproportionation of 2-pentene into 2-butene and 3-hexene at room temperature [449], trialkyltin oxides as the basic material for the preparation of a catalyst for the conversion of 4,4-dimethyl-1,3-dioxane into isoprene [450] and the use of compounds of the types $R_3SnC_6Cl_5$(R = Pr, Bu) [451] and $R_3SnOOCCH_2SC(S)OR'$ (R, R' = alkyl, aryl) [452] as desiccants.

Sigel prepared a general review of the biological siginificance of organometallic compounds [453], and Thayer discussed the biological aspects of organometallic chemistry [454].

Many papers featuring the biocidal activity of organotin compound have appeared in 1971. Ison et al. studied the fungicidal, insecticidal, acaricidal, molluscicidal and anthelmintic activity of a series of tributyltin sulfur derivatives containing twenty different heterocycles. Within this series little or no effect of the nature of the heterocycle was observed, the pesticidal toxophore being the trialkyltin grouping. These results corroborate the original observations of Luijten and Van der Kerk in the fifties [455]. The same conclusion was reached by Polster et al. in biocidal studies of different tributyl- and triphenyltin compounds towards some 50 types of fungi, yeasts and bacteria [456]. The latter group also made a comparative study of the fungicidal effect of tributyltin compounds and a series of non-metallic fungicides, the tin compounds being the most effective [457]. Compounds of the general formula $R_3SnOMR'_{n-1}$ (R = alkyl; M = Si, B, Ti, Sb, Al, V; R' = alkoxy, vinyl; n = valency of M) are useful for rendering substrates like textile, paper, synthetic resins, cement, paints, adhesives or wood, resistant to fungi and bacteria [458]. Bartl et al. (cf. AS 70; 308) continued their investigations into the use of organotin fungicides in cement, limes and plasters [459-461]. TBTO containing PVC film has been used as a transfer medium for imparting biocidal activity to leather shoes [462]. According to Kochkin et al. [146, 463, 464] copolymers of maleic anhydride (or acid), styrene and triorganotin or -lead acrylates are most effective in antibacterial activity. A specific fungicidal and bactericidal composition based on TBTO has been claimed to be useful for finishing textiles [465]. In laboratory tests effective growth inhibition of slime organisms was observed with Bu_3SnCl (0. 5 ppm), Bu_3SnOAc (4 ppm) and to a lesser extent with TBTO ($>$30 ppm). Triphenyltin hydroxide or acetate were ineffective. None of the compounds, however, were effective (50 ppm) for slime control of the white water in a paper plant. Only as much as 200 ppm of TBTO (1000-2000 ppm for pulp) gives a significant effect [466]. Freyschuss studied the counteraction of fungal attack in groundwood pulp by among others TBTO [467]. Fungal growth in optical and electronic instruments can be prevented by painting with a laquer containing 1-3 wt. % of TBTO [468].

Systemic fungicidal activity has been observed with triphenyltin acetate against cercospora beticola on sugarbeet, but the systemic activity was inferior to that of benomyl [469]. Of twenty-one fungicides tested (among which benomyl) three formulations containing triphenyltin derivatives were found to be the most effective [470]. According to McIntosh the fungicidal activity of tributyltin acetate and of a series of dibutyltin compounds is < 0.1 times the activity of triphenyltin acetate against late blight (potato) [471].

Miscellaneous compounds and formulations for which fungicidal and/or bactericidal activity is claimed are: $R_3SnOOC\text{-}CHR'\text{-}CH_2\text{-}COOSnR_3$ (e.g. R = Bu, R' = octyl, decyl, dodecyl, octadecyl) [472, 473], $R_3SnOOC\text{-}C(CN) = CPh_2$(R = Me-Bu, Ph) [142], diorganotinphthalates (cf. AS 70; 308) [474-476], dibutyltin bis(5-methylthio-4-methylsalicylate) [477], tributyl(2,4-dichloro-6-cyanophenoxy)tin [478], mixtures of Ph_3SnX(X = Cl, OH, OAc) and 1,2-propylenebis(dithiocarbamic acid)--salts of divalent metals (e.g. Zn) [479], partially hydrolyzed triphenyltin chloride [480, 481], $(CF_3CH_2CH_2)_{4-n}SnX_n$(X = H, anionic group; n = 1, 2) [385], $R_nSn(OSO_2NH_2)_{4-n}$ (R = C_{1-4} alkyl or Ph, n = 2, 3) [122].

In a comperative study of marine antifouling systems Sheldon observed excellent activity in excess of two years with TBTO. In particular this compound is very effective in algae control [482]. Very effective ship-bottom paints are prepared by mixing a common vinyl resin varnish with 30% of a trialkyltin compound, such as bis(tripropyltin)succinate [483] and by mixing a polyurethane with a triorganotin fluoride, e.g. Bu_3SnF [484]. Anticorrosive coating compositions obtained by treating an alkyd resin with $(R_3Sn)_2O$(R = Pr, Bu, Oct, Ph) gave eight months of fouling protection on steel sheets and fishing nets [485]. Acrylic plastics pressure treated with TBTO were less effective, viz. after thirty days all panels were covered with marine growth [486].

According to Lorenz optimal results are obtained with antifouling paints containing a mixture of TBTO and triphenyllead acetate [487]. Stronganov c.s. reported a comparative study of the toxicity of $R_{4-n}MX_n$(R = Me-Pr; M = Si, Ge, Sn, Pb; X = Cl, OH, OAc; n = 0-3) against different aquatic organisms such as Scenedesmus quadricauda, Chlorella vulgaris and Daphnia magna [488].

Other compounds claimed to be effective antifouling agents are: triphenyltin derivatives [489], bis(triorganotin)tetrachlorophthalates [490, 491], triorganotin sorbates (synergistic effect) [492], mercury containing stannoxanes of the structure $R_3SnOHgR'$(preferably R = Et, Bu; R' = Et, Bu, Hex, Ph) [493] and combinations of 2-amino-3-chloro-1,4-naphthoquinone, a copper salt like $CuSO_4$ and TBTO [494].

Interest in organotin compounds as wood preservatives, in particular TBTO, is increasing very rapidly. This is partly due to recent governmental regulations in different countries (England, The Netherlands) prescribing the preservation of timber for state-aided buildings. British standard specifications for TBTO have been described [495]. Levi et al. studied the effect of TBTO preservative distribution following different drying techniques, viz. freeze-drying, rapid air-drying and slow air-drying [496]. TBTO based wood-preservatives were also studied by Hof (cf. AS 70; 309) [497] and by Hocking [498]. According to Da Costa et al. [499] tributyltin acetate is slightly more effective as a wood preservative than the corresponding lead compound. Both triphenyltin and -lead compounds are almost completely ineffective. Other organotin containing wood preservatives reported are triorganotin sorbates [492], triorganotin perchlorates [500] and mixtures of compounds like diphenyl(hydroxypropyl)tin bromide and diglycidylether (reduced leaching) [501].

Molluscicidal activity has been claimed for R_3Sn-X-C(X')-NR'R''(X, X' = O, S R = phenyl or substituted phenyl; R, R' = H, alkyl, aralkyl, aryl) (cf. AS 70; 309) [502]. Del Rivero tested the efficacy of 63 different insecticidal formulations against the cabbage worm (Pierris brassicae). All tin containing products were found to be phytotoxic [503].

The recently disclosed Miticidal properties of tricylohexyltin hydroxide (Plictran; cf. AS 69; 725 and AS 70; 310) gave rise to a variety of patent applications on tricyclohexyltin derivatives as pesticides, viz. Ch_3SnX (Ch = cyclohexyl, X = OH) [504], X = OAr (Ar = p-$NO_2C_6H_4$, C_6Cl_5, 2,4,5-$Cl_3C_6H_2$, etc.) [505], X = substituted phenoxy group, such as 4-nitrophenoxy, pentachlorophenoxy [506], X = YR, (Y = O,S; R = organic group) [507], X = CH_2CH_2Y (Y = CN, COOH, COOMe, COOEt, prepared by addition of Ch_3SnH to the corresponding ethylenic compound) [508], X = chlorophenylthio group [509], X = a variety of ester groups, such as ferrocenoate, picolinate, phenoxyacetate, phenylthioacetate, dichlorophenoxyacetate [510], X = heterocyclic group, such as imidazol-1-yl, 4,5-benzotriazol-1-yl, 4,5-benzimidazol-1-yl [511], X = OC(O)R (R = CF_3, C_4F_7, C_6F_5) [512], and compounds of the type $ChSnX_3$ (X = Cl, Br) [513]. According to Trombetti et al. tricyclohexyltin hydroxide causes only a slight delay in the must fermentation of grapevine in laboratory trials, whereas in field tests no such delay was observed [514]. Findlay investigated the toxicity as well as the antifeedant and the reproduction inhibiting effect of Ph_3SnX (X = OH, OAc) on the different stages of the life-cycle of the Egyptian cotton leaf worm, Spodoptera littoralis [515]. As determined in similar studies castor leaf bits dipped in $\leq 0.4\%$ Ph_3SnOAc solutions gave a marked reduction of the leaf area eaten and all larvae exposed to a $> 0.05\%$ solution died in 48 hours without eating at all [516]. Ascher et al. continued their studies of Me_6Sn_2 (Pennsalt TD-5032) (cf. AS 70; 310). This compound was found to be four times as effective as dichlorvos in controlling larvae and eggs of the Egyptian cotton leaf worm [517, 518]. The same group published further data on the effect of fentins on the fertility of the female housefly. In the same paper the influence of fentins on the fertility and fecundity of other insect species was critically reviewed [519].

Other organotin compounds claimed to be useful as insecticides are: R_3SnX and $(R_3Sn)_2Y$ (R = Ph or monosubstituted phenyl; X, Y = mono- and divalent "solubilizing moiety") [520], compounds of the type  for example trineophyltin chloride, $(PhMe_2C-CH_2)_3SnCl$, and $(PhMeCH-CH_2)_3SnCl$ (less phytotoxic than tricyclohexyltin derivatives, more effective than parathion) [521], $R_3SnCH_2SO_2X$ (X = alkyl, aryl, R_2N etc.) [522].

Herbicidal activity has been claimed for compounds of the formula R_3SnX ($X = OH, CN, N_3$) especially Bu_3SnN_3 [523], R_3SnCH_2SR', preferably R = Bu, R' = Me [524] and phenoxytin compounds such as tributyl (2,4-dinitro-6-sec-butylphenoxy)tin [525].

According to Poller et al. [526] Ph_3SnOAc is subject to microbial degradation in soil. By means of ^{13}C labeling it was proved that the carbon dioxide formed stems from the phenyl groups. The rate of degradation slows down after evolution of an amount of carbon dioxide corresponding with one phenyl group.

Cellulose containing material, e.g. sawdust, is an excellent absorbent for organotins and can be used for the purification of solutions and emulsions containing TBTO [527]. Isoamyl gallate has been claimed to be useful for the stabilization of TBTO [528].

On the basis of investigations into the modes of action and the antimicrobial spectra of Pr_3SnOAc and Ph_3PbOAc Kourai et al. concluded that the primary sites of inhibition are the biosynthesis of DNA and RNA (of E. coli K_{12}) [529]. Aldridge gave a review of the inhibitory effects of trialkyltin compounds, their stimulation of ATPase, the chemical binding of $Et_3{}^{113}Sn$ and $Me_3{}^{113}Sn$ and of proteins which combine with Et_3Sn [530]. The latter authors continued their studies on the inhibition of the oxidative phosphorylation by trialkyltin compounds (cf. AS 69; 529) and discussed the relation between the specific binding of Me_3Sn and Et_3Sn to mitochondria and their effects on various mitochondrial functions [531]. Casida and coworkers made a detailed study of the oxidative dealkylation of tetra-, tri- and dialkyitins and tetra- and trialkylleads by liver microsomes. The extent of metabolism was found to decrease with increasing size of the organic substituents, viz. Et_3Sn, Pr_3Sn, $Bu_3Sn > Pent_3Sn > Ch_3Sn > Hex_3Sn \gg Oct_3Sn \gg Ph_3Sn$, the latter species not being metabolized at all. The presence of α-hydrogen atoms is essential for rapid microsomal degradation, for which the following degradation sequence was proposed [532]:

$$(R\text{-}CH_2)_4Sn \longrightarrow (R\text{-}CH_2)_3Sn\text{-}CH(OH)\text{-}R \xrightarrow{-alkene} (R\text{-}CH_2)_3Sn^+ \longrightarrow$$
$$(R\text{-}CH_2)_2Sn^+\text{-}CH(OH)\text{-}R \longrightarrow \text{-------} \longrightarrow R\text{-}CH_2Sn^{3+}$$

As much as twenty papers on toxic effects of organotins have appeared in 1971. Two rather conflicting papers on the toxicity of organotin stabilized PVC to human tissue have been mentioned in the section on organotin stabilizers [365, 366]. A bibliography of organotin toxicity has been composed by Luijten [551].

Different medical research centres reported on studies of the pathobiology of brain eudema in rats as produced experimentally by means of triethyltin compounds [533-541]. According to Zoltan et al. [542] the functional deterioration of the central nervous system induced by triethyltin sulfate poisoning can be decreased (about 40% decrease in mortality) by silylmarin

(Legalon). The protective effect of theophyllin is markedly weaker, whereas manitol is ineffective.

Pelikan et al. studied the effects of low doses of bis(tributyltin)oxide on the skin [543] as well as on the eyes of rats [544]. Horacek et al. reported on the characteristic features of intoxication of some workers handling Brestan, a commercial fungicide based on triphenyltin acetate [545]. The influence of the latter compound on lymphatic tissue and on immune responses in guinea pigs was discussed by Verschuuren and coworkers [546]. The LD_{50} of Bu_3SnX(X = Cl, OAc, OOCPh, oleate, laurate) and of Ph_3SnOAc for mice and rats was determined to be 100-250 mg/kg, whereas for zoo- and phytoplankton and for cold-blooded animals the LC_{50} was found to be 0.002-0.1 ppm [456].

Pelikan et al. studied the toxic effects in white mice of intragastrically administered dioctyltin bis(2-ethylhexylmaleate) (LD_{50} = 2.7 g/kg), dioctyltin bis(butylmaleate) (LD_{50} = 3.75 g/kg) and dioctyltin maleate (LD_{50} = 2.25 g/kg) [547]. The latter authors also reported on analogous studies with some monobutyltin compounds at a 4000 mg/kg dose [548]. Investigations into the effects of peroral administration of dioctyltin bis(isooctylthioglycolate) and of dibenzyltin bis(isooctylthioglycolate) on rats for 3 and 18 months periods learned that the toxicities of these compounds depends on the dose and the period of administration. The benzyl derivative is more toxic than the octyl derivative [549].

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