KINETICS AND MECHANISMS OF CLEAVAGE OF ALLYLIC DERIVATIVES OF GROUP IVA ELEMENTS BY MERCURIC SALTS
III. ALLYLIC AND HOMOALLYLIC TIN COMPOUNDS

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SUMMARY

The cleavage of allylic derivatives of trialkyl- and triphenyltin compounds by mercuric salts in solvent ethanol has been examined using spectrophotometric and chromatographic techniques.

The overall process at low temperatures (25–40°) and low concentrations (10^{-4} M) can be represented by the following equations:

$$R_3SnCH_2CH=CHR' + HgX_2 \xrightarrow{\text{slow}} R_3SnX + XHgCH_2CH=CHR' \qquad (1)$$

$$HgX_2 + R_3SnX \underset{\text{rapid}}{\rightleftharpoons} R_3SnX \cdot HgX_2 \qquad (2)$$

where $R = $ Et, n-Bu, Ph; $R' = $ H, Me, Ph; $X = $ Cl, Br, I.

At higher temperatures and concentrations, a subsequent slow reaction occurs between the reaction products in the triphenyl series to liberate phenylmercuric halide, possibly by electrophilic aromatic substitution

$$Ph_3SnX + R'CH=CHCH_2HgX \rightarrow PhHgX + Ph_2(R'CH=CHCH_2)SnX \qquad (3)$$

For reaction (1) the sequence $HgCl_2 > HgBr_2 > HgI_2$ was established and for $R' = $ H, CH_3, the ratio $k_2(H)/k_2(Me)$ had a value of 200. Previous work has already established a value of 0.24 for the cleavage of the corresponding germanes. The difference is thought to arise from competition between the electrophile and the heteroatom (Si, Ge, Sn) for the olefinic π-electrons. In the case of the silanes and germanes, the reaction proceeds via π-complex formation with the mercuric salt, resulting in $S_E'2$ cleavage, whereas for the tin analogues, donor acceptor interactions between the π-electrons and the central tin atom channel the reaction via an assisted S_E2 pathway.

Further evidence for such interaction was obtained from the corresponding cleavage of other derivatives containing π-donor systems *viz.*:

$$R_3Sn(CH_2)_2CH=CHPh + HgX_2 \rightarrow R_2[PhCH=CH(CH_2)_2]SnX + RHgX \quad (4)$$

$$R_3Sn(CH_2)_4Ph \qquad + HgX_2 \rightarrow R_2[Ph(CH_2)_4]SnX + RHgX \qquad (5)$$

where $R = $ Et, Ph; $X = $ Cl, Br, I.

The following order of decreasing ease of cleavage was found: $Et_3Sn(CH_2)_4Ph$ > $Et_3Sn(CH_2)_2CH=CHPh$ ≫ Et_4Sn; $Ph_3Sn(CH_2)_4Ph$ ∼ $Ph_3Sn(CH_2)_2CH=CHPh$ > $Ph_3Sn-n-Bu$.

INTRODUCTION

A previous investigation of the cleavage of trialkylallylsilicon and -germanium compounds by mercuric salts in various solvents revealed mechanistic differences which were dependent both on solvent and the central Group IV atom[1]. These studies have now been extended to the organotin analogues, and incorporate details of the reactivity of some homoallylic derivatives of trialkyl- and triaryltin compounds.

The reactivity sequence for S_E2 cleavage of organometal systems has been clearly established as $R_3Sn- > R_3Ge- > R_3Si-$ in keeping with the electron releasing properties of the groups[2-4]. In particular, this order has been demonstrated for the cleavage of allylic groups by mercuric salts in solvent acetonitrile[1]. Triethylallyl-germane reacted rapidly but measurably [$k_2(25°) = 39$ l·mole^{-1}·sec^{-1}], whereas the reaction of triethylallyltin proved too fast to be followed by conventional methods. S_E2 reactions are highly solvent dependent, being faster in more polar media. Accordingly, to achieve a measurable rate of cleavage, solvent ethanol was used. The corresponding cleavage of triethylallylgermane revealed a complicating side reaction, namely acidolysis of the product mercurial by acid liberated in the solvolysis of the triethyl-halogermane formed in the initial cleavage. However, owing to the high reactivity of the tin analogues, and the correspondingly low concentration of reagents employed (*ca.* 10^{-5} M), acidolysis[5] is likely to be slow compared with Sn−C bond fission. Such a complication does not arise in the case of the triphenyltin analogues because the corresponding triphenyltin halides are stable in ethanolic solution, presumably due to inhibition of nucleophilic attack at the central tin atom caused by electron donation from the aromatic rings to the tin via $p_π-d_π$ overlaps.

RESULTS AND DISCUSSION

Cleavage of trialkyl- and triarylallyltin derivatives by mercuric salts in ethanol

The reactions were followed using four independent analytical methods: (*i*) direct spectrophotometric measurement, (*ii*) quenching in aqueous KI/CHCl$_3$ and estimating [HgX_2] from the absorbance of [HgI_4]$^{2-}$ at 323 mμ, (*iii*) gas–liquid chromatography (GLC), (*iv*) TLC; the latter two were not used as kinetic tools, but to analyse completed reaction mixtures.

A correlation between methods (*i*) and (*ii*) is important, since rates of π-complex formation and rates of C−Sn bond fission must be clearly distinguished. Excess KI acts as a sequestering agent for HgI$_2$, trapping out any π-complexed mercury as [HgI_4]$^{2-}$. The observed cleavage rates using methods (*i*) and (*ii*) were in close agreement, and it seems unlikely that a pre-equilibrium involving π-bonded mercury complexes is involved. These results are discussed at length in later sections.

Before describing the cleavage mechanisms in detail, some comment is required on the stoichiometry of the reaction. Analysis of reaction mixtures by methods (*ii*) and (*iii*) show that only one half of each of the reagents was consumed in the initial step. In the cleavage of triphenylallyltin by HgI$_2$, the UV spectrum of the "infinity"

reaction solution was identical with that of a synthetic mixture corresponding to 50% reaction. The addition of an equimolar quantity of Ph_3SnI to the initial reaction mixture reduced the rate of cleavage by a factor of over 100. Moreover, when 10^{-4} M ethanolic solutions of HgI_2 (λ_{max} 267 mμ, ε_{max} 4710) and Ph_3SnI (no λ_{max} above 240 mμ) were mixed, the original HgI_2 peak was replaced by two new maxima at 258 and 305 mμ respectively.

Clearly a complex had been formed, possibly of the type $[Ph_3Sn]^+[HgI_3]^-$. An attempted synthesis of the complex resulted in the isolation of a pink solid (m.p. 107–108°) which was very soluble in ethanol (mercuric iodide itself is only sparingly soluble), and which on treatment with concentrated KI slowly lost its pink colour, liberating Ph_3SnI. In view of these observations, the following reaction sequence is put forward to explain the stoichiometry:

$$R_3SnCH_2CH{=}CH_2 + HgX_2 \xrightarrow{k_2} R_3SnX + CH_2{=}CHCH_2HgX \qquad (1)$$

$$R_3SnX + HgX_2 \underset{rapid}{\overset{K_2}{\rightleftharpoons}} R_3SnX \cdot HgX_2 \qquad (2)$$
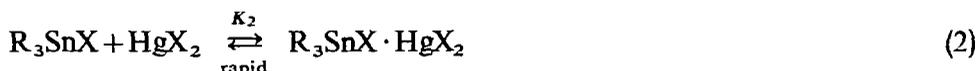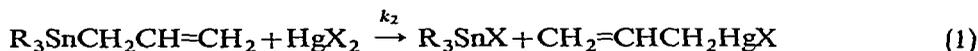
The consequence of this is that for every molecule of substrate consumed, two molecules of electrophile effectively disappear, one due to C–Sn bond fission, and one due to complex formation, assuming K_2 is large. Thus the rate equation used to evaluate the data has the form

$$\frac{2.303}{2a-b} \log \frac{b}{a}\left(\frac{a-x}{b-2x}\right) = k_2 t \qquad (3)$$

a = substrate concentration, b = electrophile concentration

Prolonged reactions at 25° (10^{-4} M solutions) led to 100% product formation via cleavage by either $R_3SnX \cdot HgX_2$ or HgX_2 in the equilibrium concentrations governed by K_2. These observations confirm the conclusions of Abraham et al.[6] on the cleavage of tetraalkyltin compounds by HgI_2 in aq. methanol. The value of K_2 is expected to be much larger in the triphenyl series since the resulting tin cation will be resonance stabilised. At higher temperatures and reagent concentrations, a further reaction occurred between products, in which phenylmercuric iodide was formed. Using

TABLE 1

THIN LAYER CHROMATOGRAPHY OF REACTION MIXTURES OF TRIPHENYLALLYLTIN AND MERCURIC IODIDE AND VARIOUS CALIBRANTS

Spot	R_F	Colour
Compounds		
HgI_2	0.44	Pink
$Ph_3SnCH_2CH{=}CH_2$	0.70	Yellow
PhHgI	0.50	Orange-pink
$CH_2{=}CHCH_2HgI$	0.57	Yellow
Ph_3SnI	0.00	Pink
Reaction mixtures		
5 min at 25°	0.00, 0.57	Pink, yellow
30 min at 78°	0.00, 0.50	Pink, orange-pink

5×10^{-3} M solutions at $40°$, both triphenylallyltin/mercuric iodide mixtures and triphenyltin iodide/allylmercuric iodide mixtures gave phenylmercuric iodide in good yield. Moreover, the UV spectrum of both product solutions was identical, indicating the subsequent reaction to be possibly

$$CH_2=CHCH_2HgI + Ph_3SnI \rightarrow (CH_2=CHCH_2)Ph_2SnI + PhHgI \qquad (4)$$
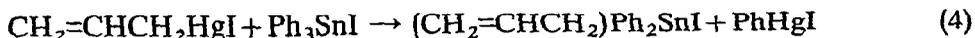
Thus reaction of triphenylallyltin with mercuric iodide $(5 \times 10^{-3} M)$ at room temperature for 5 min yielded allylmercuric iodide (30%), whereas reaction at $40°$ for 24 h yielded phenylmercuric iodide (58%). These product analyses were confirmed by thin layer chromatography (Table 1).

Interpretation of kinetic data

Using relationships derived from eqn. (3) (see Experimental), values of k_2 were calculated and found to be sensibly constant to variations in substrate and electrophile concentrations (Table 2). A simple bimolecular rate determining cleavage

TABLE 2

VALUES OF SECOND ORDER RATE CONSTANTS k_2 $(l \cdot mole^{-1} \cdot sec^{-1})$ FOR THE CLEAVAGE OF TRIPHENYLALLYLTIN BY MERCURIC IODIDE IN ETHANOL AT $25°$ AT VARIOUS CONCENTRATIONS

$Ph_3SnCH_2CH=CH_2$ $(10^5 M)$	HgI_2 $(10^5 M)$	k_2
2.00	2.00	25.9
3.00	3.00	24.4
3.20	3.20	25.0
4.00	4.00	23.2
4.00	2.00	26.1
6.00	2.00	21.5
20.0	20.0	26.0^a
20.0	20.0	25.0^a
10.0	20.0	27.5^a
4.00	4.00	83^b
20.0	20.0	$0.20^{a,c}$

^{a} Partition method. ^{b} EtOH/H_2O 96/4. ^{c} 2×10^{-4} M Ph_3SnI added $(40°)$.

TABLE 3

EFFECT OF CHANGE OF ELECTROPHILE ON RATES OF CLEAVAGE OF $Ph_3SnCH_2CH=CH_2$ AND $Et_3SnCH_2CH=CHPh$ BY MERCURIC SALTS IN EtOH AT $25°$

$R_3SnCH_2CH=CHR'$	$HgCl_2$	$HgBr_2$	HgI_2
$Ph_3SnCH_2CH=CH_2$	1500	330	25
$Et_3SnCH_2CH=CHPh$	178	13.6	2.8

is indicated. The reaction rate is somewhat sensitive to water content thus necessitating rigorous purification of the solvent prior to use. Change of electrophile produced the expected order of reactivity for an S_E2 process $HgCl_2 > HgBr_2 > HgI_2$ (Table 3).

The trialkyl compounds reacted over one hundred times faster than their

TABLE 4

RATES OF CLEAVAGE OF $R_3SnCH_2CH=CHR'$ COMPOUNDS BY HgI_2 IN ETHANOL

R	R'	Temp. (°C)	k_2 (l·mole^{-1}·sec^{-1})
Et	H	30	2900
Et	CH_3	30	15
Et	Ph	30	3.36
n-Bu	H	30	1020
Ph	H	30	27
Ph	H	25	25
Ph	CH_3	25	0.54
Ph	Ph	25	0.46

triphenyl analogues, reflecting the greater electron releasing property of the trialkyltin group. Table 4 reveals a small steric effect on changing from Et_3Sn- to $n-Bu_3Sn-$. Perhaps more interesting is the variation of rate with substituent on the allylic double bond. For both the triethyl and triphenyl series the order of decreasing reactivity of compound types $R_3SnCH_2CH=CHR'$ is $R'=H > Me \sim Ph$. Indeed, in the triphenyl series the rate of cleavage of the allylic tin–carbon bond drops to such an extent for $R'=Me$, Ph that phenyl tin–carbon bond fission becomes competitive. This throws light on the position of electrophilic attack, since electron releasing substituents (Me) should facilitate S_E2 attack whereas electron attracting substituents (Ph in this case) should inhibit such attack, with the proviso that steric effects may also be important. The ratio k_2 (H)/k_2(Me) of 200 seems too large to be attributed to a steric effect, particularly when one recalls the values of 0.35 and 0.24 obtained for cleavages of the corresponding germanes in acetonitrile and ethanol respectively. One possible rationalisation of these observations is that in the case of the tin compounds in ethanol, the substrates are in a preferred conformation in the transition state due to intramolecular donor–acceptor interactions. This has the effect of reducing the steric effects of the bulky R_3Sn-, $RCH=CH-$ groups on the approach of the electrophile at C_1, since these groups are held back by donor–acceptor interaction. The tin–carbon bond will be labilised both by removal of steric constraints and by electron donation to the tin atom. Any charges developed on the tin atom during bond fission will be partially neutralised by coordination with the olefinic π-electrons. Both silanes and germanes react via π-complex intermediates which produce characteristically
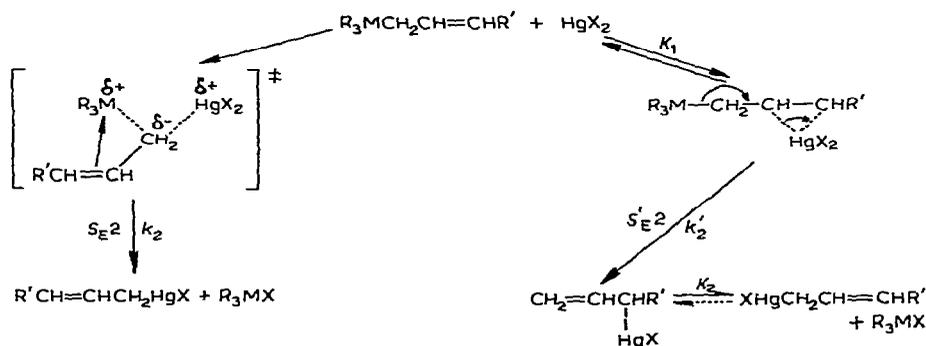
large increases in the absorption spectra of the reaction solutions. No such effects were noted with the tin analogues which undergo rapid S_E2 reactions, probably assisted by the donor properties of the allyl group.

The reaction of Group IV allylic derivatives with mercuric salts is thus seen as a competition between the electrophile and the hetero atom for the olefinic π-electrons, resulting in the reaction scheme depicted on p. 311.

Donor–acceptor interactions in the cyclic transition state would be rather sensitive to steric factors. Molecular models indicate that even in the less crowded *trans* isomers, steric interaction can occur between R and R', destabilising the transition state. For M = Si, Ge, π-complex formation is dominant and the reaction proceeds via an $S_E'2$ pathway, where $+I$ substituents (R' = Me) would increase K_1, whilst for M = Sn the reaction is channelled via an assisted S_E2 route. Significantly, the cleavage

TABLE 5

RATE CONSTANTS k_2 ($1 \cdot mole^{-1} \cdot sec^{-1}$) AT VARIOUS TEMPERATURES AND ARRHENIUS PARAMETERS FOR THE CLEAVAGE OF SOME ORGANOTIN COMPOUNDS BY HgI_2 IN ETHANOL

Organotin compound	k_2 at (°C)						E_a	$\Delta S^{\neq}$
	25	30	35	40	45	50	($kcal \cdot mole^{-1}$)	(e.u.)
$Ph_3SnCH_2CH=CH_2$	25	27	31	34			4.0	−41
$Et_3SnCH_2CH=CH_2$	2640	3100	3830	4020			5.8	−30
$Et_3SnCH_2CH=CHPh$	2.8	3.3	3.8	5.5	6.0		8.4	−31
$Ph_3Sn(CH_2)_2CH=CHPh^a$		0.137			0.280	0.50 0.69	16.0	−12

^{a} Statistically corrected rate constants.

of the tin compounds is characterised by large negative entropies and small energies of activation which is in keeping with the cyclic nature of the transition state, the removal of steric constraints on the approaching electrophile, and the weakening of the C–Sn bond by donor–acceptor interaction.

Cleavage of homoallylic derivatives of the type $R_3Sn(CH_2)_2CH=CHPh$ *and related compounds*

There is some evidence that the π-electrons in allylic systems promote carbon–metal bond fission by homoallylic interaction[7]. To investigate the effect of this interaction on C–Sn bond fission by mercuric salts, a series of homoallylic compounds of the type $R_3Sn(CH_2)_2CH=CHPh$ was synthesised. If olefinic double bonds could provide such nucleophilic assistance, it was anticipated that aromatic π-donor systems could function in a similar fashion and to investigate this, compounds of the type $R_3Sn(CH_2)_4Ph$ were also prepared. The results of these cleavages appear in Tables 6 and 7. In the case of the triphenyl compounds in solvent ethanol, product analysis showed that the Sn–phenyl bond was cleaved in preference to the Sn–alkyl bond as expected. The ease of cleavage was found to be $Ph_3Sn(CH_2)_4Ph > Ph_3Sn(CH_2)_2CH=$ $CHPh > Ph_3Sn$–n-Bu though the effect was small. The size of the effect was anticipated, since the negative nature of the central tin atom would discourage interaction by π-electron systems. For the triethyl series, tin–carbon bond fission was too slow in ethanol, but in acetone rapid cleavage by $HgCl_2$ occurred to give $EtHgCl$ in 50%

TABLE 6

RATE CONSTANTS (k_2) AND STATISTICALLY CORRECTED RATE CONSTANTS k_2^{stat} (both in $l \cdot mole^{-1} \cdot sec^{-1}$) FOR THE CLEAVAGE OF THE TIN–PHENYL BOND BY HgI_2 IN ETHANOL AT 40° FOR Ph_3SnR' COMPOUNDS
Rate constants derived from the partition method appear in parentheses.

R'	k_2	k_2^{stat}
$-(CH_2)_4Ph$	1.49, (1.62)	0.50, (0.54)
$-(CH_2)_2CH=CHPh$	0.84, (0.82)	0.28, (0.27)
$-(CH_2)_3CH_3$	0.74, (0.74)	0.25, (0.25)
$-Ph$	0.19	0.048

TABLE 7

ANALYSIS OF REACTIONS OF $Et_3Sn(CH_2)_4Ph$, $Et_3Sn(CH_2)_2CH=CHPh$, AND Et_4Sn WITH MERCURIC SALTS (5×10^{-3} M IN BOTH REAGENTS) USING GLC

Compound	HgX₂	% reaction after 5 min	% reaction after 3 h	Solvent
$Et_3Sn(CH_2)_4Ph$	$HgCl_2$	0		Ethanol
$Et_3Sn(CH_2)_4Ph$	$HgCl_2$	49.5	49.5	Acetone
$Et_3Sn(CH_2)_4Ph$	$HgCl_2{}^a$	93.0	100	Acetone
$Et_3Sn(CH_2)_4Ph$	$HgCl_2{}^b$	31	45.5	Acetone
$Et_3Sn(CH_2)_4Ph$	$HgBr_2$	50	51	Acetone
$Et_3Sn(CH_2)_4Ph$	HgI_2	2.0	51	Acetone
$Et_3Sn(CH_2)_2CH=CHPh$	$HgCl_2$	34.0	48.8	Acetone
Et_4Sn	$HgCl_2$	0.0	0.0	Acetone

[a] 10 fold excess of $HgCl_2$. [b] Solution contains 5×10^{-3} M Et_4Sn.

yield. GLC showed that only 50% of the substrate was consumed, in keeping with the original findings for the allylic series. The data in Table 7 shows the ease of cleavage of the triethyl series to be $Et_3Sn(CH_2)_4Ph > Et_3Sn(CH_2)_2CH=CHPh \gg Et_4Sn$, a sequence which is confirmed by quantitative TLC reported elsewhere. The donor properties of both phenyl and styryl groups clearly assist in C–Sn bond fission. Molecular models of the compounds show that, in the case of the phenylbutenyl derivative, effective overlap of the tin d-orbitals with the ring electrons can only occur for *cis* isomers, and that for the *trans* isomer overlap is restricted to the olefinic π-electrons. These electrons are somewhat delocalised and thus less efficient as a donor system. On the other hand the phenylbutyl compounds can adopt a relatively strain-free conformation with the tin atom almost central over the aromatic ring. In view of this, the above reactivity sequence is not surprising, since the phenylbutenyl compound was shown to be the *trans* isomer from its IR spectrum. The above argument may well explain, in part, the relative inertness of the (*trans*-3-phenylallyl)tin compounds, although a steric effect still seems to be dominant because the *trans*-3-methylallyl derivatives also react much slower.

The recent work of Kieffer *et al.*[8] is particularly relevant in this context. By studying the NMR spectrum of a series of compounds of the type $DCH_2C(Me)(OMe)CH_2A$, where D and A are donor and acceptor atoms respectively, convincing evidence for the following equilibrium was found:

$$\text{CH}_3 \overset{\overset{\displaystyle \text{CH}_2\text{D}}{|}}{\underset{\underset{\displaystyle \text{CH}_2\text{A}}{|}}{\longrightarrow}} \text{OCH}_3 \quad \rightleftharpoons \quad \text{CH}_3 \overset{\text{CH}_2-\text{D}}{\underset{\text{CH}_2-\text{A}}{\diagdown\text{OCH}_3}}$$

(I)   (II)
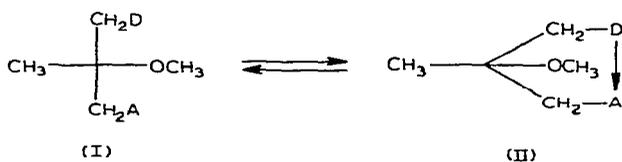
In cases where no donor–acceptor interaction occurs (D = Ph, A = Br), the magnetic non-equivalence of each proton in each flanking methylene group is very small. However, for D = Ph, A = HgCl a very marked change in the spectrum of the methylene groups occurs, two sets of quartets appearing, one of which has associated ^{199}Hg satellites thus enabling the groups to be distinguished. Clearly the magnetic non-equivalence of the protons has greatly increased. Both Br and HgCl have approximately the same steric bulk and the differences between the spectra of the two compounds strongly suggests the presence of a preferred conformation (II) in the case of the mercurial.

A study of the IR[9,10], Raman[11], and UV[12] spectra of a series of compounds of the type $R_3M(CH_2)_nCH=CH_2$, where R = alkyl, halogen; M = C, Si, Ge, Sn; $n = 0,1,2$, revealed trends which suggest that overlap of d-orbitals on the hetero-atom with the olefinic π-electrons is important in the ground state of these molecules, particularly for the allyl series. The IR data in Table 8 show similar trends which could

TABLE 8

OLEFINIC ν(C=C) AND γ(CH) FREQUENCIES OF SOME ALLYL AND HOMOALLYL ORGANOTIN DERIVATIVES (1 % CCl$_4$ SOLUTION)

Compound	ν(C=C) (cm^{-1})	γ(CH) (cm^{-1})
Et$_3$SnCH$_2$CH=CHPh	1634	956
Et$_3$Sn(CH$_2$)$_2$CH=CHPh	1648	960
Ph$_3$SnCH$_2$CH=CHPh	1635	956
Ph$_3$Sn(CH$_2$)$_2$CH=CHPh	1650	972

be open to the same interpretation. However, a more detailed investigation is required, coupled with nuclear magnetic resonance studies. The appearance of strong bands in the 955–975 cm^{-1} region confirms the dominantly *trans* configuration of these molecules.

EXPERIMENTAL

Synthesis of allylic tin compounds $R_3SnCH_2CH=CHR'$

These compounds (R = Et, Ph; R' = H, CH$_3$, Ph) were prepared using standard Grignard methods.

Synthesis of triphenyl(4-phenyl-3-butenyl)tin[13]

To the Grignard reagent formed from PhCH=CH(CH$_2$)$_2$Br (5 g, 0.0234 mole) and magnesium (0.72 g, 0.030 g-atom) in dry THF (250 ml) was added Ph$_3$SnCl (9 g, 0.0234 mole) in dry THF (100 ml). The mixture was refluxed for 10 h and the THF distilled off and replaced by Et$_2$O. The excess Grignard was destroyed with aqueous NH$_4$Cl and the ether layer separated off. The residue was extracted with

3×50 ml volumes of ether. The aqueous phase was extracted with 2×50 ml chloroform to yield hexaphenyldistannane 3.9 g, m.p. 226–228°. A thin layer chromatogram of the ether layer indicated the presence of three components. The ether extract was passed down a column of alumina followed by elution with chloroform. The chloroform extract contained two components. After pumping off the chloroform and triturating with 30–40° pet. ether, a white crystalline solid was obtained m.p. 75–76°. 1.20 g (10.7%). (Found: C, 69.77; H, 5.36. $C_{28}H_{26}Sn$ calcd.: C, 70.00; H, 5.46%.) The NMR spectrum showed the compound to be pure.

Synthesis of triethyl(4-phenyl-3-butenyl)tin[13]

The compound was prepared from $PhCH=CH(CH_2)_2Br$ (8.9 g, 0.042 mole) and Mg (1.5 g, 0.063 g-atom) in ether (250 ml) followed by addition of Et_3SnBr (10.5 g, 0.037 mole) in ether (100 ml) and refluxing for 10 h. On working up the reaction mixture in the usual way and vacuum distilling the product, a fraction boiling at 137–145° (1 mm) was collected and purified on an Aerograph Autoprep 705, using a column packed with 5% Carbowax on Chromosorb W 100/120 at 200°. Yield 0.23 g (2%). (Found: C, 57.10; H, 7.74. $C_{16}H_{26}Sn$ calcd.: C, 56.95; H 7.54%.)

Preparation of triphenyl(4-phenyl butyl)tin[13]

The compound was prepared using a conventional Grignard method from $Ph(CH_2)_4Br$[15] (5.0 g, 0.024 mole); Mg (0.72 g, 0.030 g-atom) and Ph_3SnCl (9.0 g, 0.023 mole). After passing the final ethereal extract through an alumina column, eluting with chloroform and fractionating, a high boiling fraction [240–245° (1.5 mm)] was obtained. On cooling, a partially crystalline slush was formed. The contaminating solid ($Ph_3SnSnPh_3$) was removed by washing with acetone and filtering the resultant mixture. The filtrate was pumped down on a rotary evaporator to yield a clear colourless liquid. The NMR spectrum showed the compound to be pure, yield 3 g (27%). (Found: C, 69.60; H, 5.85. $C_{28}H_{28}Sn$ calcd.: C, 69.70; H, 5.80%.)

Triethyl(4-phenyl butyl)tin, b.p. 160–166° (2 mm), n_D^{20} 1.5222, was prepared in a 35% yield, using a similar method. (Found: C, 56.81; H, 8.14. $C_{16}H_{26}Sn$ calcd.: C, 56.90; H, 8.29%.)

Attempts to synthesise the corresponding (4-cyclohexylbutyl)tin derivatives using both Grignard and organolithium reagents of 1-bromo-4-cyclohexylbutane[16] have not so far been successful.

Triphenyl-n-butyltin m.p. 62–63° was prepared in 60% yield using a conventional Grignard method. Tetraphenyltin was supplied by Koch–Light Ltd. and crystallised from ethanol prior to use.

Purification of materials

All mercuric salts were crystallised from acetone before use. Solvents methanol and ethanol were purified via their magnesium alkoxides and solvent acetonitrile was purified by refluxing over P_2O_5 and distilling from anhydrous sodium carbonate. Acetone was purified by standard procedures.

Kinetic techniques

(*i*). *Direct spectrophotometric method*. Solutions of reagents were mixed in a

thermostatted cell compartment of an SP 500 spectrophotometer and readings taken at 250 mμ for the triphenylallyltin derivatives, and at 315 mμ for the $R_3Sn(CH_2)_2$-CH=CHPh, $R_3Sn(CH_2)_4Ph$ derivatives. The following equations are postulated to explain the stoichiometry of the reaction[6]:

$$R_3SnCH_2CH=CHR' + HgX_2 \xrightarrow{k_2} R_3SnX + XHgCH_2CH=CHR'$$

$$R_3SnX + HgX_2 \underset{\text{rapid}}{\overset{K_2}{\rightleftharpoons}} R_3SnX \cdot HgX_2$$
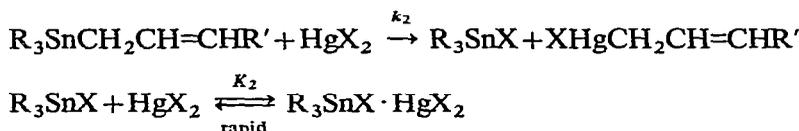
Thus for every molecule of HgX_2 which reacts, a further molecule disappears in the formation of the complex $R_3SnX \cdot HgX_2$. If a and b are the initial concentration in moles/litre of substrate and electrophile respectively, then, assuming K_2 to be large, the concentration of the reactants at time t will be $(a-x)$ and $(b-2x)$ moles/litre. This gives rise to the rate equation:

$$\frac{dx}{dt} = k_2 \cdot (a-x)(b-2x)$$

whose solution is

$$k_2 = \frac{2.303}{(2a-b) \cdot t} \log\left(\frac{b}{b} \cdot \frac{a-x}{b-2x}\right)$$

In terms of absorbance D_t at time t, assuming Beers law to hold for the reaction solution,

$$k_2 = \frac{2.303}{(2a-b) \cdot t} \log\left[\frac{b}{2a} \cdot \frac{(2a/b) \cdot D_\infty - (2a/b-1) \cdot D_0 - D_t}{D_\infty - D_t}\right]$$

Table 9 shows a typical run and values of k_2 computed from the above equation. The constancy of k_2 supports the assumptions made concerning the equilibrium constant K_2.

TABLE 9

SECOND ORDER RATE CONSTANTS k_2 (l·mole^{-1}·sec^{-1}) FOR THE CLEAVAGE OF TRIPHENYLALLYLTIN (4.00 × 10^{-5} M) BY MERCURIC IODIDE (4.00 × 10^{-5} M) IN ETHANOL AT 25.0° (DIRECT METHOD)

Time (sec)	D (250 mμ)	$D_\infty - D_t$	$2D_\infty - D_0 - D_t$	$\log \frac{1}{2}\left\{\frac{2D_\infty - D_0 - D_t}{D_\infty - D_t}\right\}$	k_2
0	0.232	0.299	0.598	0.000	
120	0.291	0.240	0.539	0.050	24.0
240	0.330	0.201	0.500	0.095	22.8
360	0.364	0.167	0.466	0.145	23.2
480	0.388	0.143	0.442	0.188	22.6
600	0.410	0.121	0.420	0.239	23.0
720	0.429	0.102	0.401	0.293	23.5
840	0.442	0.089	0.388	0.339	23.3
960	0.452	0.079	0.378	0.379	22.8
1080	0.462	0.069	0.368	0.426	22.7
1200	0.474	0.057	0.356	0.494	23.8
∞	0.531				av. 23.2

(ii). *Partition method.* Volumes of mercuric salt solution (4.00 ml 10^{-3} M) were added to 10^{-3} M substrate (4.00 ml) and pure ethanol (12.00 ml) at the reaction temperature and timing commenced. Aliquots (1.00 ml) of the reaction mixture were withdrawn at suitable time intervals, and run into a mixture of Analar CCl_4 (5.00 ml) and 0.04 M KI (5.00 ml). The KI solution was made up in boiled-out distilled water. The mixture was shaken and allowed to separate. Any persistent cloudiness was dispersed by warming gently at 40°. The aqueous layer was separated off and the absorption measured at 323 mμ, the λ_{max} of the $[HgI_4]^{2-}$ ion, using 0.04 M KI as the reference. Table 10 shows values of k_2 calculated from the equations derived below.

TABLE 10

SECOND ORDER RATE CONSTANTS k_2 (l·mole^{-1}·sec^{-1}) FOR THE CLEAVAGE OF TRIPHENYLALLYLTIN (2.00 × 10^{-4} M) BY MERCURIC IODIDE (2.00 × 10^{-4} M) IN ETHANOL AT 25° (PARTITION METHOD)

Time (sec)	D (323 mμ)	$D_0 - D_t$	x^a 10^4 M	$\log \dfrac{a-x}{a-2x}$	k_2
0	0.598	0.000	0.000	0.000	
60	0.498	0.100	0.423	0.136	26.1
120	0.456	0.142	0.601	0.244	23.4
180	0.412	0.186	0.787	0.454	29.1
240	0.400	0.198	0.838	0.555	26.6
300	0.392	0.206	0.872	0.644	24.7
360	0.381	0.217	0.919	0.824	26.3
∞	0.367	0.231	0.980		av. 26.0

^{a} Using $x = 4.23 \times 10^{-4} (D_0 - D_t)$ from calibration data.

The readings obtained at 323 mμ are due to the *total* concentration of HgI_2, since the addition of KI disrupts the complex $R_3SnX \cdot HgX_2$. liberating one equivalent of HgI_2. The equations employed for computing k_2 are thus

$$k_2 = \frac{2.303}{(2a-b) \cdot t} \log \left(\frac{b}{a} \cdot \frac{a-x}{b-2x} \right)$$

$$= \frac{2.303}{a \cdot t} \log \left[\frac{1}{2} \frac{D_t - (2D_\infty - D_0)}{D_t - D_\infty} \right] \qquad \text{for } a = b$$

The values of k_2 derived from both of these analytical methods agree to within 10%. Statistical corrections to rate constants have been applied in the cleavage of the phenyl–tin bonds of Ph_3SnR' and Ph_4Sn compounds.

Analytical methods

(i). *Gas–liquid chromatography.* This method was used to investigate the reactions

$$Et_3Sn(CH_2)_2CH=CHPh + HgX_2 \rightarrow EtHgX + Et_2[PhCH=CH(CH_2)_2]SnX$$

$$Et_3Sn(CH_2)_4Ph + HgX_2 \rightarrow EtHgX + Et_2[Ph(CH_2)_4]SnX$$

$$Et_4Sn + HgX_2 \rightarrow EtHgX + Et_3SnX$$
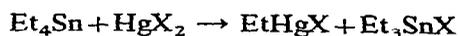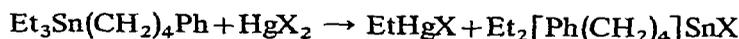
in acetone at 25°.

1.00 ml of an acetone solution of mercuric salt (10^{-2} M) was added to 1.00 ml of an acetone solution of Et_3SnR' (10^{-2} M) at 25°. After 5 min $3\mu l$ of the reaction mixture was withdrawn and injected in an F11 GLC, using a 2 m $\times \frac{1}{8}''$ Stainless Steel column containing neopentylglycol adipate and trimer acid on HMDS Chromosorb W 80–100 mesh $3/\frac{3}{4}/96\frac{1}{4}$. The column temperature was maintained at 200° and sensitivity 5×1. (For the cleavage of Et_4Sn a column temperature of 30° was used). The reaction was followed by measuring the peak areas of Et_3SnR', the only volatile species in the reaction mixtures.

The retention times of the substrates used were: $Et_3Sn(CH_2)_2CH=CHPh$ (525 sec at 200°), $Et_3Sn(CH_2)_4Ph$ (340 sec at 200°) Et_4Sn (1320 sec at 30°).

The results listed in Table 7 confirm the stoichiometry described above and also show that the ease of cleavage of the ethyl–tin bond is $Ph(CH_2)_4SnEt_3 >$ $PhCH=CH(CH_2)_2SnEt_3 \gg Et_4Sn$; $HgCl_2 \sim HgBr_2 > HgI_2$.

A slight reduction in rate is observed when equimolar solutions of Et_3Sn-$(CH_2)_4Ph$ and Et_4Sn compete for mercuric chloride, possibly due to intermolecular competition for the ring electrons by the added Et_4Sn.

(*ii*). *Thin layer chromatography.* 0.50 ml of 5×10^{-3} M organotin compound and mercuric salt in ethanol were mixed at the reaction temperature and the reaction mixture spotted on Silica gel "S" (0.25 mm thickness). After drying, the chromatogram was developed in 95/5 cyclohexane/chloroform and after removing the solvent, the plate was sprayed with 0.1% dithizone. Suitable calibrants were spotted on the same plate for identification purposes.

The reaction of triphenylallyltin with mercuric iodide was investigated at 25° (5 min) and at 78° (30 min). The results appearing in Table 1 show that at 25° allylmercuric iodide is formed, whereas at 78° phenylmercuric iodide is formed.

Adopting a similar procedure for the cleavage of $Ph_3Sn(CH_2)_4Ph$, Ph_3Sn-$(CH_2)_2CH=CHPh$, Ph_3Sn–n-Bu, and Ph_4Sn, it could be shown that the first three compounds were cleaved readily in 60 min at 40° to give PhHgI as expected. However, Ph_4Sn was cleaved much less readily (5 days at 40°). The corresponding triethyl series [$Et_3Sn(CH_2)_4Ph$, $Et_3Sn(CH_2)_2CH=CHPh$, Et_4Sn] reacted much more slowly. For the first two substrates, some EtHgI was formed after 24 h at 40° but no reaction was observed for Et_4Sn. After 5 days at 40°, 4.0 μl of each solution was removed, spotted and developed as above. The HgI_2 spots were scraped off the plate and triturated with 3.0 ml ethanol. The absorbance of the resultant filtered solution was measured at 479 mμ (λ_{max} for the dithizone–mercuric iodide complex). By comparison with standard calibrant solutions, the percentage reaction and relative rates of cleavage were found to be $Et_3Sn(CH_2)_4Ph(50\%) > Et_3Sn(CH_2)_2CH=CHPh(35\%) > Et_4Sn$ (12%).

This result confirms the reactivity sequence derived from the GLC data.

Product analyses

Triphenylallyltin (2.00 g, 5.12×10^{-3} mole) and mercuric iodide (2.33 g, 5.12×10^{-3} mole) in pure ethanol (1l) were allowed to react at 0° for 1 h. The reaction mixture was poured into ice water (3 l) giving a yellow-white precipitate which yielded 0.54 g of a yellowish solid m.p. 125°, whose IR spectrum was identical with that of an authentic specimen of allylmercuric iodide. Yield 29%. Further concentration of the mother liquor yielded a pink solid, which on treatment with aqueous KI gave 0.82 g

(33%) Ph_3SnI, m.p. 121°. The filtrate was pumped to dryness to yield 1.4 g of a white solid which contained some unreacted substrate.

Adopting a similar procedure but employing 0.02 M concentrations of reactants at 40° for 24 h, a 65% yield of PhHgI melting at 264° was obtained.

Cleavage of $Ph_3Sn(CH_2)_4Ph$ and $Et_3Sn(CH_2)_4Ph$ by mercuric chloride in acetone at 25° gave 46% and 40% yields of PhHgCl, m.p. 254°, and EtHgCl, m.p. 190°, respectively. $Ph_3Sn(CH_2)_2CH=CHPh$ gave a 53% yield of PhHgCl in ethanol at 40°.

Triphenyltin iodide (2.3 g, $4.8 \cdot 10^{-3}$ mole) and allylmercuric iodide (1.85 g, $4.8 \cdot 10^{-3}$ mole) in pure ethanol (200 ml) were refluxed for 30 min and allowed to cool. White crystals (1.27 g, m.p. 264°) separated out whose IR spectrum was identical with that of PhHgI. PhHgI is thus formed in 65% yield.

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