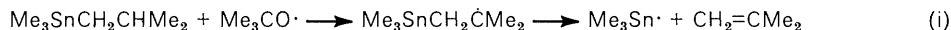


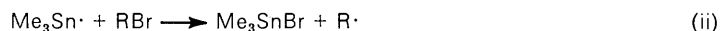
Homolytic Organometallic Reactions. Part 14.¹ Homolytic Reactivity of β -C-H Groups in Organotin Compounds. An Alternative Source of Trialkyltin Radicals

By Alwyn G. Davies,* Brian P. Roberts, and Man-Wing Tse, Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ

Rate constants (at -84°) for the reaction of t-butoxyl radicals with tetraethyltin at the α -methylene group to give the radical $\text{Et}_3\text{Sn}\dot{\text{C}}\text{HCH}_3$, and at the β -methyl group to give the radical $\text{Et}_3\text{SnCH}_2\dot{\text{C}}\text{H}_2$, are 1.2×10^4 and 4.8×10^3 $\text{l mol}^{-1} \text{s}^{-1}$, respectively *ca.* 10^3 and 5×10^2 times greater (per hydrogen atom) than the reaction of t-butoxyl radicals with ethane. The abstraction of hydrogen from the β -position in alkyltin compounds is followed by reversible elimination to give an alkene and a trialkyltin radical, and, if di-t-butyl peroxide is photolysed in the presence of trimethylisobutyltin, the e.s.r. spectrum of the trimethyltin radical can be observed [reaction (i)]. This reaction



provides a useful alternative source of trialkyltin radicals for e.s.r. studies, particularly for the generation of alkyl radicals by the reaction with alkyl bromides [reaction (ii)]. This formation of a β -trialkylstannylalkyl radical and



thence of a trialkyltin radical and alkene can constitute two of the three steps of a radical chain reaction with the overall equation $\text{Me}_3\text{SnCH}_2\text{CHMe}_2 + \text{X-Y} \longrightarrow \text{Me}_3\text{SnY} + \text{CH}_2=\text{CMe}_2 + \text{HX}$, and examples of these reactions have been established where $\text{X-Y} = \text{Cl-CCl}_3$, Br-CCl_3 , and Cl-OCMe_3 .

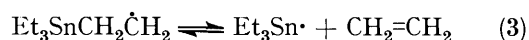
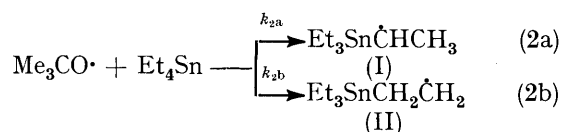
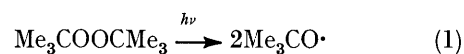
THERE has been a lot of interest recently in the formation, structure, and thermodynamic and kinetic stability of the α - and β -stannylalkyl radicals, $\text{R}_3\text{Sn}\dot{\text{C}}\text{HCH}_2\text{R}^2$ and $\text{R}_3\text{SnCH}_2\dot{\text{C}}\text{HR}^2$.² The former are the principal species which are observed by e.s.r. spectroscopy when free radicals such as $\text{Me}_3\text{CO}\cdot$ react with tetra-alkyltin compounds,³⁻⁵ and the latter are most commonly encountered as products of the addition of trialkylstannyl radicals to alkenes.²⁻¹⁴ Both have been reported to be formed in the γ -irradiation of organotin compounds.^{10,12}

In a recent study of the homolytic reactions of the stannacycloalkanes,¹ we were led to postulate that if attack of alkoxy radicals at the tin, or at the hydrogens of the α -methylene groups, was sterically hindered, reaction occurred principally at the hydrogen of the β -methylene groups.

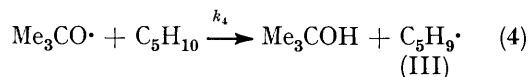
We report here a study of the reactivity of the β -CH group in acyclic organotin compounds towards free radicals, and of the subsequent reactions which may take place.

E.s.r. Studies on Tetra-alkyltins.—Photolysis of di-t-butyl peroxide in the presence of tetraethyltin in cyclopropane at -84° shows the e.s.r. spectrum of the α -stannylethyl radical (I), together with a relatively

small concentration of the β -stannylethyl radical (II); details of the spectra are collected in the Table.



If cyclopentane is included in the reaction mixture it competes with the tetraethyltin for reaction with the t-butoxyl radicals, and the superimposed spectra of the α -stannylethyl radical (I) and the cyclopentyl radical (III) are observed.



If the reasonable assumption is made that the rate constants for the removal of the radicals (I) and (III) from solution are similar,¹⁵ the relative concentrations of the radicals are related to the rate constants for their formation by expression (5).¹⁶ By this procedure, the

$$[(\text{I})]/[(\text{III})] = k_{2a}[\text{Et}_4\text{Sn}]/k_4[\text{C}_5\text{H}_{10}] \quad (5)$$

¹ Part 13, A. G. Davies, B. P. Roberts, and M.-W. Tse, *J.C.S. Perkin II*, 1977, 1499.

² Reviewed by A. G. Davies, 'Organotin Compounds: New Chemistry and Applications,' ed. J. J. Zuckerman, *Advances in Chemistry Series 157*, American Chemical Society, Washington, 1976, ch. 2.

³ P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1969, **91**, 6161.

⁴ P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1971, **93**, 846.

⁵ T. Kawamura and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 648.

⁶ W. P. Neumann, H. Nierman, and R. Sommer, *Angew. Chem.*, 1961, **73**, 768.

⁷ A. R. Lyons and M. C. R. Symons, *Chem. Comm.*, 1971, 1068.

⁸ A. R. Lyons and M. C. R. Symons, *J. Amer. Chem. Soc.*, 1971, **93**, 7330.

⁹ M. C. R. Symons, *J. Amer. Chem. Soc.*, 1972, **94**, 8589.

¹⁰ A. R. Lyons and M. C. R. Symons, *J.C.S. Faraday II*, 1972, **622**.

¹¹ M. C. R. Symons, *Chem. Phys. Letters*, 1973, **19**, 61.

¹² S. A. Fieldhouse, A. R. Lyons, H. C. Starkie, and M. C. R. Symons, *J.C.S. Dalton*, 1974, 1966.

¹³ D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, 1973, **95**, 6459.

¹⁴ D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, 1974, **96**, 6715.

¹⁵ K. U. Ingold, 'Free Radicals,' ed. J. K. Kochi, Wiley-Interscience, 1973, vol. 1, ch. 2.

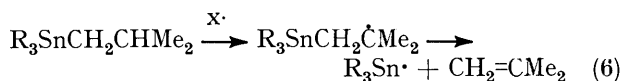
¹⁶ A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc. (B)*, 1971, 1823.

value of k_{2a} was determined to be *ca.* 1.2×10^4 l mol⁻¹ s⁻¹ at -84° .

When the photolysis was carried out in ethylene rather than cyclopropane solvent, the spectrum of the β -stannylethyl radical (II) was relatively intense with $[(I)]/[(II)]$ equal to 2.5. We conclude that $k_{2b} \geq k_{2a}/2.5$, *i.e.* $k_{2b} \geq 4.8 \times 10^3$ l mol⁻¹ s⁻¹; the β -stannylethyl radical however undergoes reversible β -elimination by equation (3) to give ethylene and the triethylstannyl radical,* which is difficult to observe under the usual conditions of the e.s.r. experiment, and, in the present system, is obscured by the spectrum of the radical (I). When ethylene is used as the solvent, the equilibrium (3) is displaced and the relative concentration of (II) increases.

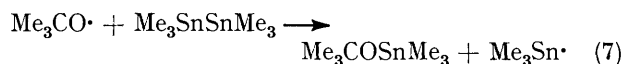
Photolysis of di-*t*-butyl peroxide in the presence of tetra-*n*-butyltin in cyclopropane gave a weak spectrum of the α -tributylstannylbutyl radical, Bu₃Sn \dot{C} HCH₂CH₂CH₃ (see Table), but the spectrum from the equivalent reaction of tetraisobutyltin was too weak to be analysed. Presumably the reactivity of the α -CH groups in these two compounds is reduced by steric hindrance; that of the β -CH groups is enhanced by the presence of the one ethyl or the two methyl substituents in the structures SnCH₂CH₂Et and SnCH₂CHMe₂ respectively, but observation of the β -stannylalkyl radical is precluded by the elimination reaction.

It appeared likely then that isobutyltin compounds might act as useful sources of trialkyltin radicals by the process shown in equation (6).



We have confirmed this, particularly for trimethylisobutyltin, and have studied its behaviour in the context of a number of non-chain and chain reactions.

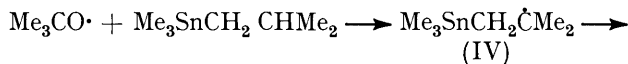
E.s.r. Studies with Trimethylisobutyltin.—Photolysis of di-*t*-butyl peroxide in the presence of trimethylisobutyltin at -120° C in cyclopropane shows the presence at low field of a multiplet of at least eight lines, $a(H)$ 2.75 G, which is characterised by a high g value (2.016 4) and by not being saturated at high microwave power. This spectrum is similar to that which is observed when di-*t*-butyl peroxide is photolysed in the presence of hexamethylditin [equation (7)].^{17,18}



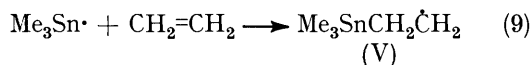
We conclude that this multiplet is associated with the trimethyltin radical formed by fragmentation of the β -stannylalkyl radical (IV) which results from abstraction of hydrogen from the β -position of the trimethylisobutyltin [equation (8)].

* It is interesting that γ -irradiation of tetraethyltin at 77 K has been reported to give a radical identified as Et₃SnCH₂ $\dot{C}H_2$, $a(^{119}Sn)$ *ca.* 409 G, g *ca.* 2.006, and which was long-lived in the solid state. The radicals Bu₃SnCH₂ $\dot{C}HEt$ and Bu₂ClSnCH₂ $\dot{C}HEt$ were similarly identified from the irradiation of Bu₄Sn and Bu₃SnCl respectively.^{10,12}

If the reaction is carried out in ethylene as solvent, one observes instead a strong spectrum of the 2-trimethylstannylethyl radical (V) (see Figure), formed by a combination of reactions (8) and (9). This spectrum



is similar in quality to that which one can obtain by the photolysis of hexamethylditin in the presence of ethylene.⁵

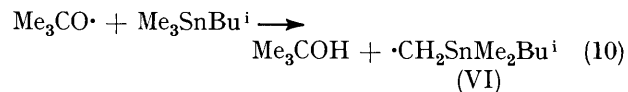


A second radical with Δg -0.001 9, $a(2H)$ 19.2 G, could also be detected in *ca.* 5% relative concentration



E.s.r. spectrum of the radical Me₃SnCH₂ $\dot{C}H_2$ obtained by the photolysis of di-*t*-butyl peroxide in the presence of trimethylisobutyltin in ethylene at -70° C [reactions (8) and (9)]. The arrows indicate two of the three lines of the spectrum of the radical Me₂Bu¹SnCH₂; the third line is obscured by the spectrum of the 2-trimethylstannylethyl radical

(see Figure); this is presumably the dimethylisobutylstannylmethyl radical (VI) resulting from abstraction of hydrogen from a methyl group [*cf.* Me₃SnCH₂ \cdot , $a(2H)$ 20.84 G, g 2.000 8^{5,19}].



(VI)

Under the same conditions, tetraisobutyltin showed the spectrum of the radical Bu₃SnCH₂ $\dot{C}H_2$.

Photolysis of di-*t*-butyl peroxide in the presence of trimethylisobutyltin and 1,1-difluoroethylene gave a weak spectrum of the radical (VII), characterised by a large coupling (101 G) to the α -fluorine atoms, and a

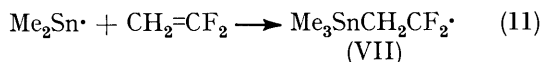
¹⁷ G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, 1972, **94**, 491.

¹⁸ P. M. Blum, unpublished work.

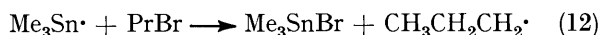
¹⁹ B. Muggleton, Thesis, London, 1975.

very small coupling (5 G) to the β -hydrogen atoms. Kochi has observed couplings of a similar magnitude in other adducts of 1,1-difluoroethylene [*e.g.* $\text{Me}_3\text{SiCH}_2\text{CF}_2\cdot$; $a(2\text{F})$ 98.11, $a(2\text{H})$ 10.85 G; $\text{MeSCH}_2\text{CF}_2\cdot$; $a(2\text{F})$ 88.4, $a(2\text{H})$ 4.3 G], and has attributed the small β -splittings to the fact that the radical centre is pyramidal rather than planar.²⁰

A solid, presumably trimethyltin fluoride, was precipitated during the photolysis. Dimethyltin dihydride has been reported to add to difluoroethylene under the influence of u.v. light to give an adduct $\text{Me}_2\text{SnH}(\text{C}_2\text{F}_2\text{H}_3)$ which is unstable and decomposes to give Me_2SnHF and $\text{CH}_2=\text{CHF}$.²¹



Trimethyltin radicals derived from reaction (8) can also be caused to react with alkyl bromides to display the spectrum of the corresponding alkyl radical [*e.g.* equation (12)]. These spectra are substantially better in quality than those which can be obtained with the same apparatus using hexamethylditin as the source of trimethyltin radicals.



t-Butyl chloride showed a rather weak spectrum of the t-butyl radical at -80° , but the spectrum was strong above -60° ; however, n-propyl and isopropyl chlorides did not give satisfactory spectra of the corresponding alkyl radicals at temperatures up to -30° .

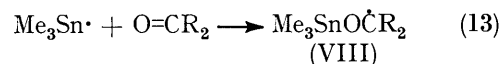
Photolysis of di-t-butyl peroxide in the presence of trimethylisobutyltin and benzophenone gave a strong spectrum of the radical (VIII; $\text{R} = \text{Ph}$).²² We could

Radical ^a	E.s.r. spectra			Notes
	$T/^\circ\text{C}$	$a(\text{H}_\alpha)/\text{G}$	$a(\text{H}_\beta)/\text{G}$	
$\text{Et}_3\text{Sn}\dot{\text{C}}\text{HCH}_3$ (I)	-75	20.5	25.8	c
$\text{Et}_2\text{SnCH}_2\dot{\text{C}}\text{H}_2$ (II)	-75	19.5	16.5	d
$\text{Bu}_3\text{Sn}\dot{\text{C}}\text{HCH}_2\text{Et}$	-75	20.3	25.6	
$\text{Me}_3\text{Sn}\cdot$	-120		2.75	e
$\text{Me}_3\text{SnCH}_2\dot{\text{C}}\text{H}_2$ (V) ^b	-70	19.7	16.9	f
$\text{Me}_2\text{Bu}^i\text{Sn}\dot{\text{C}}\text{H}_2$ (VI)	-70	19.0		
$\text{Bu}_3^i\text{SnCH}_2\dot{\text{C}}\text{H}_2$	-65	19.6	16.0	
$\text{Me}_3\text{SnCH}_2\dot{\text{C}}\text{F}_2$	-70	101 ^g	5	

^a In cyclopropane solvent. ^b In ethylene solvent. ^c $a(^{119}\text{Sn})$ 136 G, g ca. 2.0007. Krusic and Kochi³ report $a(\text{H}_\alpha)$ 20.41, $a(\text{H}_\beta)$ 25.89 G at -104°C . ^d g ca. 2.0020. Krusic and Kochi³ report $a(\text{H}_\alpha)$ 19.77, $a(\text{H}_\beta)$ 16.12 G at -96°C . ^e g 2.0164. Watts and Ingold¹⁷ report $a(\text{H})$ 2.75 G, g 2.017 at -65°C . ^f Kawamura and Kochi⁵ report $a(\text{H}_\alpha)$ 19.69, $a(\text{H}_\beta)$ 15.84 G, g 2.002 05 at -101°C . ^g $a(\alpha\text{-F})$ value.

not obtain a good spectrum by reaction (13) of the adduct (VIII; $\text{R} = \text{Me}$) with acetone, but the spectrum was no better when hexamethylditin, alone or in the

presence of di-t-butyl peroxide, was used as the source of trimethyltin radicals.^{19,23}

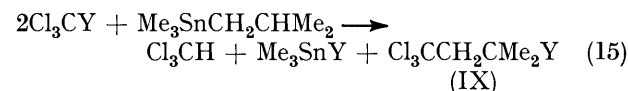


Chain Reactions of Trimethylisobutyltin.—A number of chain reactions can be envisaged in which the formation and β -scission [equation (8)] of the β -stannylalkyl radical are linked by a substitution (or addition) reaction involving the trialkyltin radical [equation (14)].



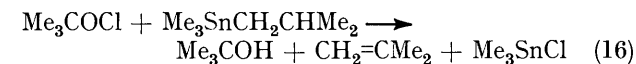
We have established two such types of reaction in which the reagent $\text{X}-\text{Y}$ is a tetrahalogenomethane ($\text{Cl}-\text{CCl}_3$ or $\text{Br}-\text{CCl}_3$), or is t-butyl hypochlorite ($\text{Cl}-\text{OCMe}_3$).

The reaction of an excess of bromotrichloromethane with trimethylisobutyltin [equations (8) and (14; $\text{X} = \text{Cl}_3\text{C}$, $\text{Y} = \text{Br}$)] in the presence of t-butyl hyponitrite as initiator was apparent (n.m.r.) after 1 h at 35°C , and was complete in 48 h. Under the same conditions the reaction involving carbon tetrachloride [equations (8) and (14; $\text{X} = \text{Cl}_3\text{C}$, $\text{Y} = \text{Cl}$)] was ca. 50% complete in 48 h. Both reactions gave quantitatively (n.m.r. integration) chloroform, trimethyltin bromide, or trimethyltin chloride, and the appropriate product (IX) of the homolytic addition of Cl_3CY to isobutene.



Pommier and Chevolleau²⁴ recently reported a similar sequence of reactions between tri-n-butyltin or tri-isobutyltin isopropoxide and polyhalogenomethanes. For example, tri-isobutyltin isopropoxide reacted with bromotrichloromethane in 15 h at 70° under u.v. irradiation to give 39% of (IX; $\text{Y} = \text{Br}$) originating from attack of $\text{Cl}_3\text{C}\cdot$ at the β -position of the isobutyl group [*cf.* equation (15)], together with 27% of acetone *via* attack at CH of the isopropoxy group, and 34% of propan-2-ol possibly arising from an $\text{S}_{\text{H}}2$ reaction at the tin centre. Likewise Vyazankin *et al.* have identified $\text{Cl}_3\text{CCH}_2\text{CH}_2\text{Cl}$ in the products of the reaction of carbon tetrachloride with tetraethyltin.²⁵

The reaction between t-butyl hypochlorite and trimethylisobutyltin took place in the absence of any added initiator. It was complete in 2 days at 35°C and trimethyltin chloride and t-butyl alcohol were the only products (n.m.r.) apart from isobutene which was lost by evaporation.



The only reasonable mechanism for this reaction

²⁰ K. S. Chen, P. J. Krusic, and J. K. Kochi, *J. Phys. Chem.*, 1974, **78**, 2030.

²¹ H. C. Clark, S. G. Furnival, and J. T. Kwon, *Canad. J. Chem.*, 1963, **41**, 2889.

²² H. Hillgärtner, B. Schroeder, and W. P. Neumann, *J. Organometallic Chem.*, 1972, **42**, C83.

²³ J. Cooper, A. Hudson, and R. A. Jackson, *J.C.S. Perkin II*, 1973, 1056.

²⁴ J.-C. Pommier and D. Chevolleau, *J. Organometallic Chem.*, 1974, **74**, 405.

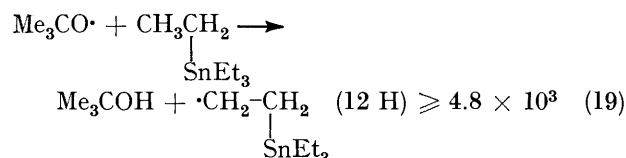
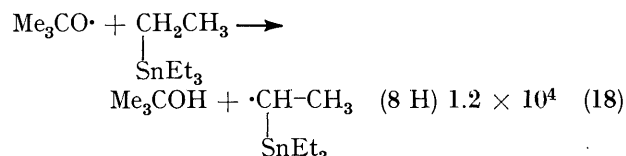
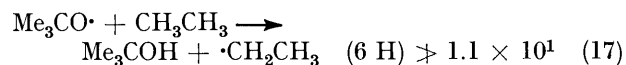
²⁵ N. S. Vyazankin, T. N. Brevnova, and G. A. Razuvaev, *J. Gen. Chem. U.S.S.R.*, 1967, **37**, 187.

appears to be the sequence (8) and (14; $X \cdot = \text{Bu}^t\text{O} \cdot$, $Y = \text{Cl}$). Reactions (8) has been established by e.s.r. spectroscopy (see above), and reaction (14), in which a trimethyltin radical abstracts chlorine from t-butyl hypochlorite, should be exothermic by *ca.* 165 kJ mol⁻¹.

DISCUSSION

No direct measurement of the rate constant for the abstraction of hydrogen from ethane by the t-butoxyl radical appears to have been reported, but at 40 °C a primary aliphatic CH bond is *ca.* 0.1 times as reactive towards $\text{Bu}^t\text{O} \cdot$ as is a CH bond in toluene,¹⁵ for which $k(40^\circ) = 6.3 \times 10^3$ and $k(-84^\circ) = 1.67 \times 10^1$ l mol⁻¹ s⁻¹ per hydrogen atom. The activation energy for the reaction with ethane would be expected to be greater than that with toluene, and at -84 °C the difference between the rate constants would be more extreme, and $k_{17}(6 \text{ H}) \geq 1.1 \times 10^1$ l mol⁻¹ s⁻¹.

Second-order rate constants (l mol⁻¹ s⁻¹ at -84°) for the abstraction of hydrogen by t-butoxyl radicals from ethane, and from the α - and β -CH groups of tetraethyltin are as in reactions (17)–(19); these figures refine our previous estimates.²



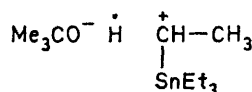
The enhanced reactivity of the CH group α to SnEt_3 may be ascribed to (a) conjugation between the singly occupied p orbital on carbon and $5d$ orbital on the tin, (b) hyperconjugation between the singly occupied $2p$ orbital and the three Sn–Et σ -bonds, and (c) mutual accommodation between the electronic demands of the oxygen and the tin centre, the resonance form (X) being stabilised by inductive electron release by the tin, and making a significant contribution to the structure of the transition state.² The present work contributes little to our understanding of the relative importance of these factors, except to emphasise that a fourth factor, that of steric hindrance, may be important in directing attack away from the α -methylene group if the bulk of the alkyl group is increased.

* It is interesting that dichlorocarbene reacts with tetraalkyltins by insertion into a β -CH bond, and no reaction occurs at the α -CH position. The controlling factor has been suggested to be stabilisation of the structure (XII) by metal–carbon hyperconjugation, and to a lesser extent by inductive electron release by tin.²⁶

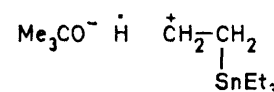
† For the insertion of dichlorocarbene into the β -CH bonds of alkylsilanes, Seyferth found that 1,1-dimethyl-1-silacyclopentane showed low and 1,1-dimethyl-1-silacyclohexane high reactivity.²⁶

The enhanced reactivity of the β -CH groups has tended to be discounted because it is less obvious than is the reactivity of the α -CH groups by the e.s.r. technique on which much of the work in this field has been based. The principal factors which may contribute to this enhanced β -reactivity are (a) homoconjugation between the singly occupied $2p$ orbital on carbon and $5d$ orbital on tin,^{4,5} (b) hyperconjugation between the singly occupied $2p$ orbital and the C_β -Sn σ -bond,^{5,7-12} and (c) mutual accommodation between the electronic demands of the oxygen and the tin centre by both inductive and hyperconjugative release by the unique C–Sn bond in the resonance structure (XI).^{2,*}

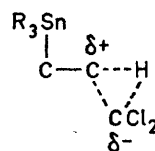
Again it is difficult to assess the relative contributions which these three effects may make, but it is interesting that the high β -reactivity appears to be maintained in the β -methylene groups of the stannacyclopentane ring, which was indeed the system which first drew our attention to this phenomenon.^{1,†} Of the above factors, hyperconjugative release to the carbon radical–carbonium ion centre would appear to be most sterically demanding in that it would need the C–Sn σ -bond to eclipse the p -orbital on the carbon centre; this configuration might be expected to be least accessible in the stannacyclopentanes (XIII), the Sn–C(2) bond lying in the nodal plane of the $2p$ orbital on C(3). This might be regarded as an argument against the importance of the hyperconjugation mechanism, but it should be emphasised that we do not know whether the stannacyclopentyl radical would have a planar ring, whether the radical is a σ - or a π -radical, (XIII), and whether, in these cyclic compounds a further factor, that of angle strain, may not dominate the reactivity.



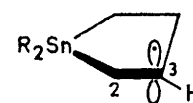
(X)



(XI)



(XII)



(XIII)

Kochi has shown a similar enhancement of the reactivity of the β -CH groups in alkylmercury compounds, reaction (20) occurring 560 times as fast as reaction (21), the value of the rate constants at 95 °C being as shown.^{27,‡}

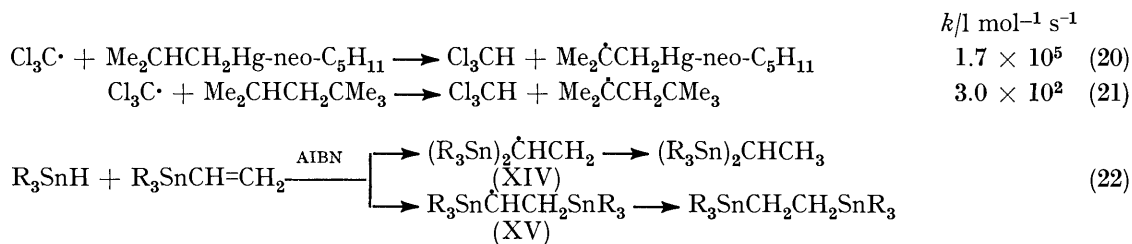
‡ Based on White and Kuntz's determination of $\log(k/\text{l mol}^{-1} \text{s}^{-1}) = 8.8 - (10\,700/\theta)$ (where $\theta = 2.303/RT$ cal mol⁻¹) for the attack of $\cdot\text{Cl}_3$ on cyclohexane.²⁸

²⁶ D. Seyferth, S. S. Washburne, C. J. Attridge, and K. Yamamoto, *J. Amer. Chem. Soc.*, 1970, **92**, 4405.

²⁷ W. A. Nugent and J. K. Kochi, *J. Organometallic Chem.*, 1977, **124**, 327.

²⁸ M. L. White and R. R. Kuntz, *Internat. J. Chem. Kinetics*, 1971, **3**, 127.

There is evidence in the literature that addition reactions, like hydrogen abstraction reactions, can give both α - and β -stannyethyl radicals. Bulten and Budding²⁹ have shown that hydrostannation of trialkylvinyltins [equation (22)] gives the product derived

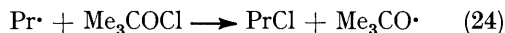


through the radicals (XIV; with two β tin atoms) and (XV; with one α - and one β -tin atom) in the ratio 40 : 60 when R = Me, 22 : 27 when R = Et, and 0 : 100 when R = Ph. The trend in this series probably reflects, at least in part, the steric effect of the R_3Sn group.

The reversibility of the addition of $\text{R}_3\text{Sn}\cdot$ to alkenes was established ten years ago,^{30,31} but attention has focused on the addition rather than the elimination because of the importance of the hydrostannylation synthesis.

This reverse reaction provides a useful alternative to the established ways of generating $\text{R}_3\text{Sn}\cdot$ radicals from hexa-alkylditins or trialkyltin hydrides, particularly for the applications in e.s.r. spectroscopy, because (a) trialkylisobutyltins are easier to make, to store, and to handle, (b) they are more soluble especially in the non-polar solvents which are preferred for e.s.r. spectroscopy, (c) they are less likely to react heterolytically or to enter into homolytic chain reactions with other reagents, and pragmatically, (d) they appear to give rather better e.s.r. spectra from, for example alkyl bromides, than do the alternative reagents.

We have shown previously that tripropyltin chloride reacts exothermically with *t*-butyl hypochlorite to give propyl chloride in at least 70% yield, and we suggested that the most probable mechanism involved an $\text{S}_{\text{H}}2$ reaction by the *t*-butoxyl radical at the tin centre [equation (23)]; this reaction is known from e.s.r. studies to have a rate constant of 1×10^6 at 10 °C.³²



We tried to make use of this type of reaction to determine the relative ease of displacement of different alkyl groups from tin. Various mixed alkyltin chlorides, $\text{R}^1\text{R}^2_2\text{SnCl}$, were caused to react with *t*-butyl hypo-

chlorite, and the alkyl chlorides, R^1Cl and R^2Cl , which of hydrogen from the α - and β -positions of the alkyl groups; this problem would be expected to be particularly severe with branched alkyl groups R^1 and R^2 , which would sterically protect the tin centre, but themselves have a high intrinsic reactivity towards alkoxy radicals.

The type of homolytic chain reactions which we have identified may well be significant in the environmental autoxidative and biological^{34,35} degradation of organotin compounds to inorganic tin, alongside the alternatives of unimolecular photolysis of R-Sn bonds, and of $\text{S}_{\text{H}}2$ dealkylations at the tin centre.

EXPERIMENTAL

Preparation of Starting Materials.—Tetraisobutyltin, b.p. 70 °C at 0.1 mmHg, was prepared from the reaction of tin tetrachloride with isobutylmagnesium bromide in tetrahydrofuran (Found: C, 56.1; H, 10.5. Calc. for $\text{C}_{16}\text{H}_{36}\text{Sn}$: C, 55.4; H, 10.4%); ¹³C n.m.r. (C_6H_6) δ 23.2 (CH_2), 27.2 (CH), and 2.65 (Me_2), ¹J(Sn-C) 310 and ²J(Sn-C) 36 Hz.

Trimethylisobutyltin, b.p. 38 °C at 9 mmHg, was prepared from the reaction between trimethyltin chloride and isobutylmagnesium bromide in ether (Found: C, 37.5; H, 8.2. Calc. for $\text{C}_7\text{H}_{18}\text{Sn}$: C, 38.0; H, 8.2%); ¹³C n.m.r. (C_6H_6) δ -9.54 (Me_3), 23.17 (CH_2), 27.35 (CH), and 26.59 (Me_2). Mitchell reports δ -9.6, 23.2, 27.2, and 26.5 respectively.³⁶

E.s.r. Spectroscopy.—Spectra were recorded with a Varian E4 spectrometer fitted with a Philips SP 500 W a.c. high pressure mercury capillary lamp for photolysis within the cavity. The technique for determining rate constants has been described previously.¹⁶

Reaction of Trimethylisobutyltin with Carbon Tetrahalides.—Trimethylisobutyltin [τ 9.95 (Me_3) and 7.85–9.85 (Bu^1), ²J(¹¹⁹Sn-Me) 52.8 Hz] and 5 mole % of di-*t*-butyl hyponitrite were dissolved in an excess of bromotrichloromethane at 35 °C and the reaction which ensued was monitored by

³² A. G. Davies and J. C. Scaiano, *J.C.S. Perkin II*, 1973, 1777.

³³ T. Maki, Thesis, London, 1973.

³⁴ R. H. Fish, E. C. Kimmel, and J. E. Casida, *J. Organometallic Chem.*, 1976, **118**, 41.

³⁵ R. H. Fish, E. C. Kimmel, and J. E. Casida, ref. 2, ch. 14.

³⁶ T. N. Mitchell and G. Walter, *J. Organometallic Chem.*, 1976, **121**, 177.

²⁹ E. J. Bulten and H. A. Budding, *J. Organometallic Chem.*, 1976, **111**, C33.

³⁰ H. G. Kuivila and R. Sommer, *J. Amer. Chem. Soc.*, 1967, **89**, 5616.

³¹ W. P. Neumann, H. J. Albert, and W. Kaiser, *Tetrahedron Letters*, 1967, 2041.

^1H n.m.r. spectroscopy. Reaction was apparent after 1 h and was complete after 48 h yielding trimethyltin bromide, τ 9.26 (Me_3), $^2J(^{119}\text{Sn}-\text{Me})$ 57.6 Hz, 1,1,1-trichloro-3-bromo-3-methylbutane [τ 6.43 (CH_2) and 7.81 (Me_2)], and chloroform (τ 2.68).

Under similar conditions, the reaction with carbon tetrachloride was 50% complete in 48 h, yielding trimethyltin chloride [τ 9.35 (Me_3), $^2J(^{119}\text{Sn}-\text{Me})$ 58.2 Hz], 1,1,1,3-tetrachloro-3-methylbutane [τ 6.59 (CH_2) and 8.11 (Me_2)], and chloroform (τ 2.68).

Reaction of Trimethylisobutyltin with t-Butyl Hypochlorite.—A solution of equimolar amounts of trimethyliso-

butyltin and t-butyl hypochlorite (τ 8.83) in benzene was kept at 35° and monitored by ^1H n.m.r. spectroscopy. In 2 days, reaction was complete yielding t-butyl alcohol [τ 8.81 (Me_3) and 6.64 (OH)] and trimethyltin chloride (τ 9.50). The identity of the products was confirmed by adding samples of the authentic materials.

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