Homolytic Organometallic Reactions. Part 13.[1,2] The Homolytic Reactivity of Stannacycloalkanes

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t-Butoxyl, trimethylsiloxyl, benzoyloxyl, and phenylthiyl radicals, X·, were generated by photolysis of the appropriate precursor, X_2, and caused to react with the acyclic butyltin compounds Bu_nSnCl_{4-n} (n = 1—4) and the cyclic 1,1-dialkylstannacycloalkanes $R_2\overline{Sn[CH_2]}_n$ (R = Me, Et, Bu^n, or Bu^t, n = 4, 5, or 6). The resulting radicals were observed by e.s.r. spectroscopy.

t-Butoxyl and, particularly, trimethylsiloxyl radicals react with tetra-n-butyltin at hydrogen in the α-methylene group to give the radical $Bu_3Sn\dot{C}HPr$. The stannacycloalkanes, on the other hand, react also at the tin centre to yield the ring-opened radicals $XSnR_2[CH_2]_{n-1}CH_2\cdot$, and this tendency increases as the size of the ring is reduced. The stannacyclopentanes $R_2\overline{Sn[CH_2]}_4$ react with the radicals $Me_3CO\cdot$, $PhCO_2\cdot$, and PhS· exclusively by ring opening, and the rate constants of the reaction of t-butoxyl radicals with 1,1-dimethyl- and 1,1-dibutyl-stannacyclopentane have been measured to be 1.0×10^6 and 5.5×10^5 l mol^{-1} s^{-1}, respectively, at 213 K. This reactivity is ascribed mainly to the relief of angle strain in the formation of a five-co-ordinate transition state or intermediate.

Abstraction of hydrogen from an α-methylene group in organotin compounds is accompanied by abstraction from the β-methylene group to give the radical $R_3SnCH_2\dot{C}HR'$, but this radical apparently rapidly undergoes fragmentation to give the trialkylstannyl radical $R_3Sn\cdot$ and the alkene $CH_2{=}CHR'$.

We have shown previously that if t-butoxyl radicals (or ketone triplets) are generated in the presence of tetra-alkyltin compounds, hydrogen is abstracted from the α- or β-positions of the alkyl groups [equation (i)], but under the same conditions, alkyltin halides or alkyltin carboxylates may undergo attack at the tin centre with displacement of an alkyl radical [equation (ii; n = 1—3)].[3]

$$Me_3CO\cdot + R_3SnCH_2CH_2R' \longrightarrow Me_3COH + R_3Sn\dot{C}HCH_2R' \text{ or } R_3SnCH_2\dot{C}HR' \qquad \text{(i)}$$

$$Me_3CO\cdot + R_nSnX_{4-n} \longrightarrow Me_3COSnR_{n-1}X_{4-n} + R\cdot \qquad \text{(ii)}$$

On the other hand, bromine radicals[4] and succinimidyl radicals[5] react with tetra-alkyltins at the tin centre rather than at hydrogen, and do not react with the derivatives R_3SnX. The various factors which control this selectivity are not completely understood, but those which have been considered include the availability of tin 5*d* orbitals for establishing a five-co-ordinate transition state or intermediate, the mutual accommodation of the electronegativity characteristics of reagent and substrate, the conjugative, hyperconjugative, or homoconjugative stabilisation of the side-chain radicals, and the relative steric demands of the various possible processes.[6]

A further factor that might be expected to influence the balance between these alternatives of attack at tin *versus* attack at hydrogen in an alkyl ligand is that of ring strain in the stannacycloalkanes. It is well known that the stannacyclopentanes and, to a lesser extent, the stannacyclohexanes, exhibit an enhanced reactivity under a variety of conditions;[7-9] most of the reactions involved are clearly heterolytic, but the unusual sensitivity to air might reflect a high reactivity towards alkoxyl or alkylperoxyl radicals.

We report here a study, largely by e.s.r., of the interaction of certain free radicals with stannacycloalkanes; some results with acylic compounds have also been included for comparison.

EXPERIMENTAL

Starting Materials.—1,1-Dimethyl-, 1,1-diethyl-, and 1,1-dibutyl-stannacyclopentane, 1,1-dimethyl- and 1,1-dibutyl-stannacyclohexane, and 1,1-dimethylstannacycloheptane were prepared by methods in the literature.[10] We are grateful to Dr. W. McFarlane (Sir John Cass College) for a sample of 1,1-di-t-butylstannacyclopentane.

Bistrimethylsilyl peroxide was prepared from chlorotrimethylsilane and the diazabicyclo-octane–hydrogen peroxide complex.[11]

E.s.r. Spectroscopy.—E.s.r. spectra were recorded using a Varian E4 spectrometer fitted with a Philips SP 500 W a.c. high pressure mercury capillary lamp focused on the cavity through a system of quartz lenses. The technique for determining rate constants has been described previously.[12] The rate constant for the t-butoxydealkylation of tri-isobutylborane was taken to be 5.0×10^5 l mol^{-1} s^{-1} at 213 K.

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[1] Part 12, A. G. Davies, B. Muggleton, B. P. Roberts, M.-W. Tse, and J. N. Winter, *J. Organometallic Chem.*, 1976, **118**, 289.

[2] Preliminary note, A. G. Davies, G. R. Parry, B. P. Roberts, and M.-W. Tse, *J. Organometallic Chem.*, 1976, **110**, C33.

[3] A. G. Davies and J. C. Scaiano, *J.C.S. Perkin II*, 1973, 1777.

[4] S. Boué, M. Gielen, and J. Nasielski, *J. Organometallic Chem.*, 1967, **9**, 461, 491.

[5] A. G. Davies, B. P. Roberts, and J. M. Smith, *J.C.S. Perkin II*, 1972, 2221.

[6] A. G. Davies, 'Organotin Compounds: New Chemistry and Applications,' ed. J. J. Zuckerman, A.C.S. Advances in Chemistry Series no. 157, 1976, p. 26.

[7] B. C. Pant, *J. Organometallic Chem.*, 1974, **66**, 321.

[8] E. J. Bulten and H. A. Budding, Abstracts of Papers, 7th International Conference on Organometallic Chemistry, Venice, 1975.

[9] D. Hänssgen and E. Odenhausen, *J. Organometallic Chem.*, 1977, **124**, 143.

[10] H. Zimmer, C. W. Blewett, and A. Brakas, *Tetrahedron Letters*, 1968, **13**, 1615.

[11] P. G. Cookson, A. G. Davies, and N. Fazal, *J. Organometallic Chem.*, 1975, **99**, C31.

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

Reaction of Thiols with Dibutylstannacyclopentane.—(*a*) Two solutions in n.m.r. tubes were prepared containing dibutylstannacyclopentane (100 μl), butane-1-thiol (40 μl), and benzene (400 μl). Azobisisobutyronitrile (*ca.* 5 mg) was added to one of the solutions, and the n.m.r. spectra of both were recorded periodically. No change occurred in either during 0.5 h at 25 °C but in 1 h at 60 °C the solution containing the initiator showed a shift of the triplet at τ 7.80 (CH_2SH) downfield to τ 7.41 (CH_2SSn).

Next day, the solvent was removed, and the residual oil was identified as butylthiotributyltin by comparison (i.r. and n.m.r. spectra) with an authentic sample (b.p. 100 °C at 0.05 mmHg) prepared by azeotropic dehydration of a mixture of bistributyltin oxide and butane-1-thiol in toluene.

The reaction between the stannacyclopentane and butanethiol was similarly initiated by di-t-butyl hyponitrite at 35 °C.

(*b*) Two solutions were prepared containing dibutylstannacyclopentane (100 μl), benzenethiol (33 μl), and benzene (400 μl), and to one was added di-t-butyl hyponitrite (5 mg). The solution containing the initiator reacted rapidly at 35 °C as shown by the loss of the SH resonance at τ 6.73.

The solvent was removed leaving phenylthiotributyltin, which was identified by comparison (i.r. and n.m.r. spectra) with an authentic sample (b.p. 141—142 °C at 0.3 mmHg) prepared by Abel and Brady's method; [13] we are grateful to Dr. B. Muggleton for preparing this compound.

RESULTS AND DISCUSSION

Homolytic Reactions of Acylic Butyltin Compounds.—Our previous studies on acyclic organotin compounds [3] were limited to their reactions with t-butoxyl radicals (and ketone triplets). For subsequent comparison with the stannacycloalkanes, this study has now been extended. t-Butoxyl, trimethylsiloxyl, benzoyloxyl, and phenylthiyl radicals (X•) were generated photolytically from the appropriate precursors (X_2) in the presence of the butyltin compounds Bu_nSnCl_{4-n} (n = 1—4) between 0 and −120 °C, and the radicals formed were observed by e.s.r. spectroscopy. The results are summarised in Table 1.

TABLE 1

Radicals observed from the interaction of oxygen- and sulphur-centred radicals with the compounds Bu_nSnCl_{4-n} [a]

	$Me_3CO\cdot$ [b]	$Me_3SiO\cdot$ [b]	$PhCO_2\cdot$ [c]	$PhS\cdot$ [c]
Bu_4Sn	$Bu_3Sn\dot{C}HCH_2Et$ [d,e] (*W*)	$Bu_3Sn\dot{C}HCH_2Et$ [d] (*S*)	*f*	(0)
Bu_3SnCl	Bu• (*S*)	Bu• (*M*)	Bu• (*W*)	(0)
Bu_2SnCl_2	Bu• (*M*)	Bu• (*M*)	(0)	
$BuSnCl_3$	Bu• (*W*)	Me• (*M*)	(0)	

[a] Intensities of the spectra are denoted by *S* (strong), *M* (medium), *W* (weak), 0 (no spectrum). [b] In cyclopropane. [c] In toluene. [d] a (H_α) 20.0 G, a ($2H_\beta$) 25.8 G at −70 °C, g *ca.* 2.000 5. [e] A strong broad singlet slowly develops at g *ca.* 1.99. [f] Very weak spectrum which might be ascribed to Bu•, but little stronger than that from a blank reaction in the absence of the peroxide.

Benzoyloxyl and phenylthiyl radicals showed no significant reaction with any of the butyltin compounds, but the low solubility of benzoyl peroxide and diphenyl disulphide at low temperature even in toluene is a restricting factor. Trimethylsiloxyl radicals, like t-butoxyl radicals, react by an S_H2 process at the tin centre in tributyltin chloride and dibutyltin dichloride to displace a butyl radical, but the siloxyl radicals reacted with butyltin trichloride to afford methyl radicals; tin tetrachloride in fact is even more effective in inducing the formation of the methyl radical.

Trimethylsiloxyl radicals abstracted hydrogen from the α-methylene group of tetrabutyltin to give the 1-tributylstannylbutyl radical (1), with a characteristically low *g*-factor of *ca.* 2.000 5 (*cf.* $Me_3SnCH_2\cdot$, g 2.000 8 [14]). A

$$Me_3SiO\cdot + Bu_4Sn \longrightarrow Me_3SiOH + \underset{(1)}{Bu_3Sn\dot{C}HCH_2CH_2CH_3} \quad \text{(iii)}$$

weak spectrum of the radical (1) could then be identified from the interaction of t-butoxyl radicals with tetrabutyltin; apparently trimethylsiloxyl radicals are more effective than t-butoxyl radicals in abstracting hydrogen from the α-position of the alkyl group in tetra-alkyltins.

Homolytic Ring Opening of Stannacycloalkanes.—The results of interaction of t-butoxyl, trimethylsiloxyl, benzoyloxyl, and phenylthiyl radicals with a variety of 1,1-dialkylstannacycloalkanes, studied by the same method, are given in Table 2. Many of the systems showed a spectrum consisting of a triplet of triplets with a pronounced alternating line-width effect at low temperatures, and which we ascribe to the radicals (2) resulting

$$X\cdot + R_2\overline{Sn[CH_2}]_n \longrightarrow XR_2Sn[CH_2]_{n-1}CH_2\cdot \ (2) \quad \text{(iv)}$$

from ring opening by the S_H2 reaction of the radicals X• at the tin centre. The intensities of the spectra are indicated in Table 2 by *S*(strong), *M*(medium), *W*(weak), and 0(no spectrum). A typical strong spectrum (for $Me_3COSnBu_2CH_2CH_2CH_2CH_2\cdot$) is illustrated in our preliminary note.[2] For a weak spectrum the weakest lines might be lost in the instrumental noise.

All the radicals, $Me_3CO\cdot$, $Me_3SiO\cdot$, $PhCO_2\cdot$, and PhS• react by the S_H2 mechanism at tin in dimethyl-, diethyl-, and di-n-butyl-stannacyclopentane to give the appropriate ring-opened radical (2). This appears to be the first demonstration that benzoyloxyl or thiyl radicals can displace alkyl radicals from tin. Displacement of an alkyl group R, rather than cleavage of a tin–carbon bond in the ring, appears to be insignificant, although a small proportion of n-butyl radical might be undetected because its hyperfine coupling constants are close to those of the ring-opened radical (2), and the small amount of methyl radical that can be observed in the

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[13] E. W. Abel and D. B. Brady, *J. Chem. Soc.*, 1965, 1192.

[14] T. Kawamura and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 648.

reaction of trimethylsiloxyl radicals with 1,1-dimethylstannacyclopentane could arise from either reagent.

TABLE 2

Radicals $XR_2Sn[CH_2]_{n-1}CH_2\cdot$ (2) and $R_2\overline{Sn[CH_2]_{n-1}C}H\cdot$ (5) resulting from reactions (iv) and (ix) [a]

	$Me_3CO\cdot$ [b] (2) (*S*) [d]	$Me_3SiO\cdot$ [b] (2) (*S*) [d]	$PhCO_2\cdot$ [c] (2) (*M*) [e]	$PhS\cdot$ [c] (2) (*S*)
$Me_2\overline{Sn[C}H_2]_4$		(5) (*M*) [m] Me· (*M*)		
$Et_2\overline{Sn[C}H_2]_4$	(2) (*S*) [d]			
$Bu_2\overline{Sn[C}H_2]_4$	(2) (*S*) [d]	(2) (*S*) [d] (5) (*S*) [m]		(2) (*S*) [f]
$Bu^t{}_2\overline{Sn[C}H_2]_4$	(0)		(0)	
$Me_2\overline{Sn[C}H_2]_5$	(*q*)	(2) (*M*) [g] (5) (*S*) [n] Me· (*W*)	(2) (*M*) [h]	(2) (*M*) [i]
$Bu_2\overline{Sn[C}H_2]_5$	(0)	(2) (*W*) [j] (5) (*M*) [o]	(2) (*W*) [h]	(2) (*M*)
$Me_2\overline{Sn[C}H_2]_6$	(2) (*W*) [k]	(2) (*M*) [l] (5) (*S*) [p,r] Me· (*S*)	(2) (*W*) [g]	(0)

[a] Intensities of the e.s.r. spectra which are observed are denoted by *S* (strong), *M* (medium), *W* (weak), 0 (no spectrum). Hyperfine coupling constants of the radicals (2) *g ca.* 2.002 5 and of the radicals (6) *g ca.* 2.000 5. [b] In cyclopropane. [c] In toluene. [d] a ($2H_\alpha$) 21.9 G, a ($2H_\beta$) 27.8 G, a ($2H_\gamma$) 0.8 G. [e] a ($2H_\alpha$) 21.5 G, a ($2H_\beta$) 27.5 G. [f] a ($2H_\alpha$) 21.6 G, a ($2H_\beta$) 27.5 G, a ($2H_\gamma$) 0.8 G. [g] a ($2H_\alpha$) 22.0 G, a ($2H_\beta$) 28.3 G. [h] a ($2H_\alpha$) 21.9 G, a ($2H_\beta$) 27.9 G, a ($2H_\gamma$) 0.8 G. [i] a ($2H_\alpha$) 21.4 G, a ($2H_\beta$) 27.8 G. [j] a ($2H_\alpha$) 21.8 G, a ($2H_\beta$) 28.2 G. [k] a ($2H_\alpha$) 21.8 G, a ($2H_\beta$) 28.5 G, a ($2H_\gamma$) 0.8 G. [l] a ($2H_\alpha$) 21.9 G, a ($2H_\beta$) 28.9 G. [m] a (H_α) 21.5 G, a ($2H_\beta$) 33.5 G. [n] a (H_α) 20.0 G, av. a ($2H_\beta$) 34.0 G, a (^{117}Sn) 130 G, a (^{119}Sn) 136 G. [o] a (H_α) 20.0 G, a ($2H_\beta$) 34.0 G. [p] a (H_α) 20.2 G, a ($2H_\beta$) 36.0 G. [q] Some strong lines, persisting for 1—2 min after photolysis, were observed at high field, but could not be identified. [r] The spectrum of the radical $Me_3SiOOSiMe_2CH_2\cdot$ could also be observed; a (H_α) 21.4 G (2 H), a (H_γ) 0.7 G (6 H).

The rates of the ring-opening reactions between t-butoxyl radicals and 1,1-dimethyl- and 1,1-dibutylstannacyclopentane [equation (iv; $X = Me_3CO\cdot$, $R =$ Me or Bu, $n = 4$)] were determined by causing these reactions to compete with the t-butoxydealkylation of tri-isobutylborane, and determining the relative steady-state concentrations of the radical (2; R = Me or Bu, $n = 4$) and of the isobutyl radical, by e.s.r. spectroscopy. The rate constants for the ring-opening reactions were found to be 1.0×10^6 (R = Me) and 5.5×10^5 l mol^{-1} s^{-1} (R = Bu) at 213 K. For comparison, the rate constant for the abstraction of hydrogen from the α-methylene group of tetrapropyltin is 3.7×10^4 l mol^{-1} s^{-1} at 213 K,[3] and that for the (unobserved) S_H2 reaction at tin cannot be greater than *ca.* 5×10^3 l mol^{-1} s^{-1}: enclosing the tin atom in a five-membered ring has enhanced its S_H2 reactivity at least 100-fold. The effect is paralleled in the stannacyclohexanes, and is weaker, but apparently still present, in the stannacycloheptanes.

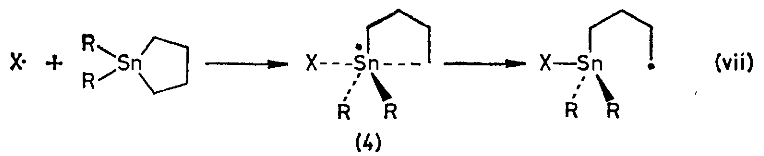
The S_H2 reaction of PhS·, identified in Table 1, implies that thiols should react homolytically with stannacyclopentanes to give acyclic trialkyl(alkylthio)tin compounds. This was confirmed in the reaction between benzene- and butane-thiol and 1,1-dibutylstannacyclopentane. No reaction occurred in the absence of an initiator, but in the presence of t-butyl hyponitrite at 35 °C or of azoisobutyronitrile at 60 °C, a smooth reaction took place to yield the appropriate tributyl alkanethiolate (3) [equations (v) and (vi); R = Bu or Ph].

$$RS\cdot + Bu_2\overline{Sn[C}H_2]_4 \longrightarrow RSSnBu_2CH_2CH_2CH_2CH_2\cdot \quad (v)$$

$$RSSnBu_2CH_2CH_2CH_2CH_2\cdot + RSH \longrightarrow \underset{(3)}{RSSnBu_2CH_2CH_2CH_2CH_3} + RS\cdot \quad (vi)$$

The detailed mechanism of the S_H2 reaction at tin is not known, but evidence appears to be accumulating[6] that it procceds through a five-co-ordinate intermediate with a trigonal bipyramidal structure in which the oxygen or sulphur ligands would occupy an apical site as they do in the analogous phosphoranyl ($X_4P\cdot$) radicals in which the unpaired electron occupies one equatorial site.[15]

The incorporation of tin into a stannacyclopentane ring might enhance the reactivity in two ways. First, molecular models show that the stannacyclopentane ring suffers from angle strain, and this would probably be reduced when the ring bridges apical and equatorial positions in the trigonal bipyramidal intermediate (4), as in the phosphoranyl radicals. Breakdown of (4) would then be expected to occur by preferential cleavage of an apically-directed tin–carbon bond as it does in the radicals $X\dot{P}R'_3$, consistent with our observation that little or no displacement of R· is observed.



(vii)

Secondly, we have presented evidence previously[5] that the relative reactivity of related organotin compounds may be dominated by repulsion between non-bonded groups in the five-co-ordinate intermediate or transition state, and this repulsion may be reduced if two of the ligands form part of a small ring, as in (4).

Further interpretation of the reactivity of the stannacycloalkanes is difficult because the detailed structure

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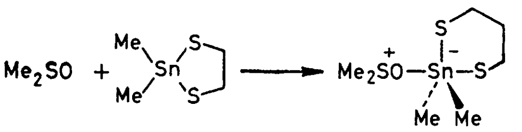
[15] See for example R. W. Dennis and B. P. Roberts, *J.C.S. Perkin II*, 1975, 140; J. W. Cooper and B. P. Roberts, *ibid.*, 1976, 808.

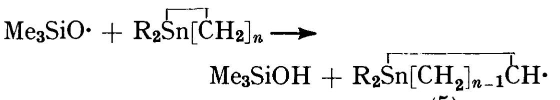
of none has been determined. We are therefore attempting to determine the structure of 1,1-diphenylstannacyclopentane, which is a crystalline solid, by single-crystal *X*-ray diffraction.*

There is an interesting parallel between the tendency of radicals to react at the tin centre in stannacyclopentanes and of ligands to co-ordinate to the tin centre in 1-stanna-2,5-dithiacyclopentanes. The ^{119}Sn n.m.r. signal of the stannadithiacyclopentanes is shifted to high field when the compounds are dissolved in dimethyl sulphoxide, and five-co-ordinate complexes can be isolated. No such interaction occurs with the acyclic analogues, nor with the stannadithiacyclohexanes.[17] It appears that again the transition from pseudo-tetrahedral to pseudo-trigonal bipyramidal geometry at tin is particularly favoured when the tin is located in a five-membered ring [*e.g.* equation (viii)].


(viii)

Abstraction of Hydrogen from the Stannacyclopentane Ring.—The reactions of t-butoxyl radicals with dimethyl-, diethyl-, and dibutyl-stannacyclopentane showed no spectrum which could be ascribed to a stannacyclopentyl radical: apparently the presence of the ring has the effect in these compounds of diverting attack completely from hydrogen on the α-methylene group (though perhaps not the β-group—see below) to the tin centre.

However we obtained evidence above that siloxyl radicals abstracted hydrogen more readily from the α-methylene group of tetrabutyltin, and, consistent with this, we find that siloxyl radicals also abstract hydrogen from the ring of stannacycloalkanes to give the stannacycloalkyl radicals (5), which have characteristically low *g* values [*ca.* 2.000 5; *cf.* $\mathrm{Bu_3Sn\dot{C}HCH_2Et}$ (Table 1)].



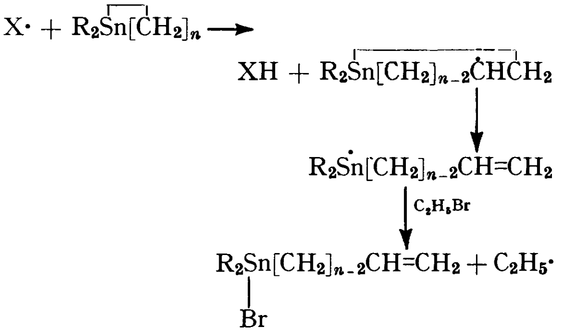
$$\mathrm{Me_3SiO\cdot + R_2\overline{Sn[CH_2]_n} \longrightarrow Me_3SiOH + R_2\overline{Sn[CH_2]_{n-1}\dot{C}H}\cdot} \quad \text{(ix)}$$

(5)

Details of the spectra of the radicals (5) are given as footnotes to Table 2. The values of the hyperfine coupling constants for the stannacyclopentyl radicals [(5; $n = 4$) $a(\mathrm{H}_\alpha)$ *ca.* 21.5 G, a (H_β) *ca.* 33.5 G] are similar to those of the cyclopentyl radical itself (21.5 and 35.2 G, respectively), although the values for the stannacycloheptyl radical [(5; $n = 5$) 20.2 and 36.0 G] are substantially different from those of the cycloheptyl radical (21.8 and 24.7 G).

The spectra of the stannacyclohexyl radicals are particularly interesting. In the 1,1-di-butyl-1-stannacyclohexan-2-yl radical (5; R = Bu, $n = 5$), all six lines of the spectrum can be identified, but in the 1,1-dimethyl analogue, the lines of the central doublet cannot be seen although the lines of the outer pairs of doublets are strong enough for the ^{117}Sn and ^{119}Sn satellites to be located. It appears that, at low temperature, the two hydrogen atoms ($\mathrm{H}_{\beta1}$ and $\mathrm{H}_{\beta2}$) on the β-carbon atom show different hyperfine coupling constants, but in the range of temperature studied (−60 to −120 °C), configurational inversion at this methylene group occurs to place an out-of-phase modulation on these hyperfine splittings and broaden beyond detection any line associated with non-identical values of $m_\mathrm{I}(\mathrm{H}_{\beta1})$ and $m_\mathrm{I}(\mathrm{H}_{\beta2})$. A similar effect is well recognised in the cyclohexyl radical itself [$a(\mathrm{H}_\alpha) = 21.3$, $a(\mathrm{H}_{\beta1})$ 39.4, $a(\mathrm{H}_{\beta2})$ 5.3 G; average $a(\mathrm{H}_\beta)$ 22.35 G], and the barrier to inversion is 4.9 kcal mol^{-1}.[18] In the dimethylstannacyclohexan-2-yl radical, $a(\mathrm{H}_\alpha) = 20.0$ G, and the average value of $a(\mathrm{H}_\beta)$ is 30.0 G. In the dibutylstannacyclohexyl radical (and in the stannacyclopentyl and dimethylstannacycloheptyl radicals) ring inversion apparently occurs more rapidly, and the two β-protons appear to be equivalent on the e.s.r. time scale, an averaged value of $a(\mathrm{H}_\beta)$ being observed.

No radicals (6) were identified which might be ascribed to the abstraction of hydrogen from a β-methylene group in the ring, although the complicated form which the spectra would take might render detection difficult.



$$\mathrm{X\cdot + R_2\overline{Sn[CH_2]_n} \longrightarrow XH + R_2\overline{Sn[CH_2]_{n-2}\dot{C}HCH_2}} \quad (6)$$

$$\downarrow$$

$$\mathrm{R_2\dot{S}n[CH_2]_{n-2}CH{=}CH_2} \quad (7)$$

$$\Big\downarrow \mathrm{C_2H_5Br}$$

$$\mathrm{R_2Sn(Br)[CH_2]_{n-2}CH{=}CH_2 + C_2H_5\cdot}$$

However, it seemed remarkable that the mixture from photolysis of di-t-butyl peroxide in the presence of 1,1-di-t-butyl-1-stannacyclopentane in cyclopropane did not show the e.s.r. spectrum of any radical, even of the cyclopropyl radical derived from the solvent. This might be explained if the bulky t-butyl groups sterically protected the tin centre and the α-methylene groups, directing attack to the β-methylene group to give the radical (6); this radical then might not be observed if it rapidly underwent β-scission to give the tin-centred radical (7), which would probably not be detectable in solution by e.s.r.

Accordingly, di-t-butyl peroxide was irradiated at

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* We originally reported [2] that 1,1-diphenyl-1-stannacyclopentane did not undergo the $S_\mathrm{H}2$ reaction at the tin centre, but we have since found that the sample we were using was in fact the dimer, 1,1,6,6-tetraphenyl-1,6-distannacyclodecane.[16] The authentic monomer readily undergoes the $S_\mathrm{H}2$ reaction.

[16] A. G. Davies, J. D. Kennedy, M. F. C. Ladd, D. C. Povey, G. S. Pyne, and M.-W. Tse, unpublished work.

[17] J. D. Kennedy, W. McFarlane, and G. S. Pyne, *Bull. Soc. chim. belges*, 1975, **84**, 289.

[18] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147; H. Fischer, 'Free Radicals,' ed. J. K. Kochi, Wiley-Interscience, New York, 1973, vol. II, p. 479.

-60 °C in the presence of di-t-butylstannacyclopentane and ethyl bromide: a strong spectrum of the ethyl radical was observed. No ethyl radical was observed in the absence of the tin compounds, and we believe that the ethyl radical arises from the interaction of the tin-centred radical (6) with ethyl bromide. It appears probable that the abstraction of hydrogen from the β-methylene group of organotin compounds occurs generally more readily than is usually supposed, and that this reaction is obscured by the subsequent rapid reversible β-scission to give an alkene.

Some further miscellaneous radicals were observed in certain of the reaction systems. First, all the reactions involving bistrimethylsilyl peroxide and the 1,1-dimethylstannacycloalkanes showed the presence of the methyl radical. This might in principle originate from either the peroxide or the stannane, but either source is rather surprising. We have never before observed the displacement of methyl from tin even in the methyltin halides; and, although the higher bistrialkylsilicon peroxides do, on irradiation at low temperature, afford alkyl radicals, we have previously detected the formation of methyl radicals from bistrimethylsilyl peroxide only when a Lewis acid such as tin tetrachloride or (Table 1) butyltin trichloride was present.

Secondly, in the reaction of trimethylsiloxyl radicals with dimethylstannacycloheptane, the characteristic spectrum of the radical (8) resulting from abstraction of hydrogen from the parent peroxide was observed; it appears that the hydrogen atoms in the stannacycloheptane ring are less easily abstracted than those in the five- and six-membered rings.

$$\mathrm{Me_3SiO\cdot + Me_3SiOOSiMe_3 \longrightarrow Me_3SiOH + \underset{(8)}{Me_3SiOOSiMe_2CH_2\cdot}} \qquad \text{(xi)}$$

Thirdly, in a number of the reaction systems noted in Tables 1 and 2, as photolysis progressed we observed the development at high field of strong broad singlets or broad low-order multiplets, the presence of which appears to detract from the intensity of signals due to any carbon-centred radical which is also being formed. The spectral data are given in footnotes to Tables 1 and 2. We believe that these spectra may be associated with the $\mathrm{Sn^V}$ radicals $\mathrm{X_5Sn\cdot}$ related to those which we postulate as intermediates when homolytic substitution occurs at a tin centre, but we have not yet been able to observe the satellites due to $^{117/119}\mathrm{Sn}$ coupling, and our identification of these species remains speculative.

Conclusion.—We have demonstrated here that the stannacycloalkanes, particularly the stannacyclopentanes, show an enhanced S_H2 reactivity at the metal centre, which results in ring opening. A similar enhancement of reactivity is apparent in small-ring compounds of other elements.

Within group 4, one of the few examples of S_H2 reaction at a saturated carbon centre is in the cyclopropanes [*e.g.* equation (xii)],[19] and the best evidence for the S_H2 displacement of alkyl from silicon appears to be the fact that the silacyclopropanes react with air to give peroxidic products [equation (xiii)].[20]

$$\mathrm{Br\cdot + \overline{CH_2CH_2CH_2} \longrightarrow BrCH_2CH_2CH_2\cdot} \qquad \text{(xii)}$$

$$\mathrm{X\cdot + \overline{Me_2SiCMe_2CMe_2} \longrightarrow XMe_2SiCMe_2CMe_2\cdot} \qquad \text{(xiii)}$$

In group 6, the thiacyclobutanes (thietans) react with butoxyl and trimethylsiloxyl radicals to undergo ring-opening [equation (xiv)], whereas the thiacyclopentanes (thiolans), thiacyclohexanes (thians), and acyclic dialkyl sulphides undergo hydrogen abstraction.[21] These

$$\mathrm{RO\cdot + \overline{S[CH_2]_3} \longrightarrow ROSCH_2CH_2CH_2\cdot} \qquad \text{(xiv)}$$

ring systems provide an important context within which S_H2 reactions at multivalent centres can be investigated, and their further study should help to elucidate the mechanisms of these processes.

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