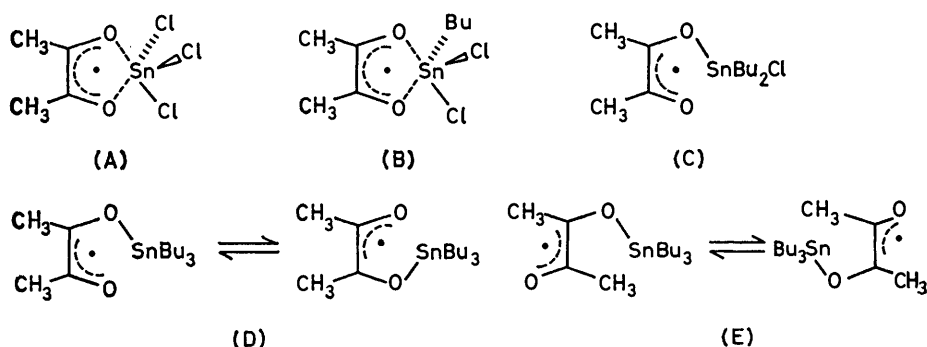


An Electron Spin Resonance Study of the Reactivity of Alkylchlorotin Radicals, $R_nCl_{3-n}Sn^\bullet$ ($n = 0-3$) towards Alkenes, Alkyl Bromides, and Biacetyl. The Spectra and Structures of the Alkylchlorotin Derivatives of Butane-2,3-semidione, $R_nCl_{3-n}SnOCMeCMeO^\bullet$

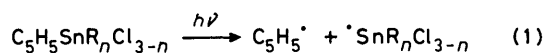
By Philip J. Barker, Alwyn G. Davies,* Jalal A.-A. Hawari, and M.-W. Tse, Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ

The radicals $Bu_nCl_{3-n}Sn^\bullet$ were generated by photolysis of the appropriate [cyclopentadienyltin compounds, $Bu_n(C_5H_5)SnCl_{3-n}$], and their reactivity towards alkenes and alkyl bromides was monitored by e.s.r. spectroscopy. Towards both reagents, the reactivity decreases as the number of chloro ligands increases, and it is tentatively suggested that this results from the reduced interaction of the SOMO of the radical and the LUMO of the alkene or alkyl bromide. All the radicals $Bu_nCl_{3-n}Sn^\bullet$ ($n = 0-3$) react with biacetyl to show the e.s.r. spectra of the tin derivatives of butane-2,3-semidione, $Bu_nCl_{3-n}SnOCMeCMeO^\bullet$, and these radicals have also been generated by a variety of other methods. Below about $+20^\circ C$, when $n = 0$ or 1, the adducts $Cl_3SnOCMeCMeO^\bullet$ and $BuCl_2SnOCMeCMeO^\bullet$ show hyperfine coupling by two non-equivalent methyl groups and one unique chlorine atom; above $+20^\circ C$, the methyl groups become magnetically equivalent, and coupling is by more than one chlorine atom.



This is interpreted to imply that the adducts have the structures (A) and (B) respectively, in which the ligands about the tin are approximately trigonal bipyramidal, and, at low temperatures, hyperfine coupling is by the apical chlorine atom; at higher temperatures, positional exchange between the ligands confers on the radicals C_{2v} symmetry on the e.s.r. time scale. When $n = 2$, the two methyl groups are non-equivalent from -50 to $0^\circ C$, with no hyperfine coupling from chlorine, probably implying the static monodentate structure (C). When $n = 3$, two radicals have been identified. The first, with a spectrum which is a regular binomial septet, is thought to be the rapidly fluxional *cis*-monodentate compound (D). The second, which displays a septet spectrum with a severe alternating line width effect, is thought to be the more slowly fluxional *trans*-compound (E).

WE have recently shown that cyclopentadienyltin(IV) compounds are readily photolysed by u.v. light, with homolysis of the cyclopentadienyl-tin bond [equation (1)].¹⁻⁴ If the reaction is carried out in the cavity of an e.s.r. spectrometer, the spectrum of the cyclopentadienyl radical can be observed, and this aspect of the work has recently been reported.⁴ These reactions also make it possible to study for the first time the effect of the ligands on the properties of tin-centred radicals, and this paper

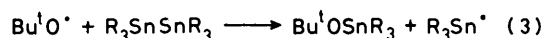


discusses this ligand-effect for other series of alkylchlorotin radicals R_nSnCl_{3-n} ($n = 0-3$).

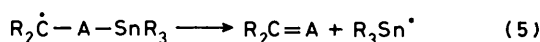
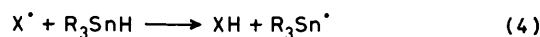
Within this series, only the trialkyltin radicals, R_3Sn^\bullet , have been prepared previously in solution.⁵ For e.s.r. studies, they are usually obtained by the photolysis of hexa-alkylditins alone [equation (2)] or in the presence of di-*t*-butyl peroxide as a source of *t*-butoxyl radicals, when reaction (3) also makes a contribution. Neumann⁶ has recently shown that some trialkyltin radicals with highly

sterically hindering alkyl groups can also be prepared by thermolysis of the corresponding ditins.

For reagents in chain reactions, trialkyltin radicals are



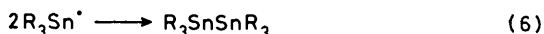
usually derived from trialkyltin hydrides [equation (4)],⁵ and a number of reactions which generate R_3Sn^\bullet radicals by a β -scission process [equation (5; $A = O$ or CR_2)] have also been developed.⁷⁻⁹



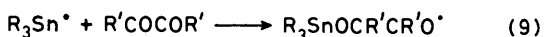
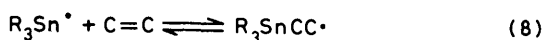
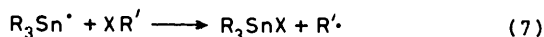
The e.s.r. spectra of a variety of organotin radicals have been observed in the solid state, and an increasing number now in fluid solution. The g factors are usually

high (*ca.* 2.015) and the lines are broad, and the large value of the hyperfine coupling with $^{117/119}\text{Sn}$ is taken to imply that the radicals are pyramidal rather than planar.

The reactions of the $\text{R}_3\text{Sn}^\cdot$ radicals in solution have received a lot of attention. When R is not a bulky group, the self-reactions of the radicals by equation (6) have the normal rate constants of *ca.* $2 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ for diffusion-controlled reactions.



The other most characteristic reactions of trialkyltin radicals are the abstraction of chlorine, bromine, or iodine from an alkyl halide [equation (7)],¹⁰ the addition to an alkene [equation (8)],¹¹ and the addition to carbonyl compounds, particularly 1,2-diones [equation (9)].¹²



All three reactions have been thoroughly investigated by e.s.r. spectroscopy, and the rate constants of a number of the halogen-abstraction process [equation (7)] have been measured. The spectra of many adducts of 1,2-diones¹²⁻¹⁵ (including *o*-quinones)¹⁶⁻¹⁸ [equation (9)] have been reported, but the precise structures of many of these adducts is uncertain. This point is discussed later on in this paper.

EXPERIMENTAL

The preparation of the compounds $\text{C}_5\text{H}_5\text{SnMe}_3$, $\text{C}_5\text{H}_5\text{SnBu}_3$, and $\text{C}_5\text{H}_5\text{SnCl}_3$ has already been reported.⁴

Dibutyl(cyclopentadienyl)tin Chloride.—Dibutyltin dichloride (6.08 g) in tetrahydrofuran (15 cm³; distilled from lithium aluminium hydride) was added dropwise under nitrogen over 0.5 h to a vigorously stirred suspension of cyclopentadienylsodium (1.76 g) in tetrahydrofuran at 0 °C. The mixture was stirred at room temperature for a further 1 h, then transferred to a centrifuge tube and spun for 3 h at 2 000 r.p.m.

The solution was decanted from the sodium chloride, then distilled yielding dibutyl(cyclopentadienyl)tin chloride as a light yellow oil, b.p. 78 °C at 0.05 mmHg, τ (CCl_4) 3.80 [5 H, s, C_5H_5 , $J(^{117/119}\text{Sn}-\text{H})$ 28 Hz] and 8.18—9.30 (18 H, C_4H_9).

Butyl(cyclopentadienyl)tin Dichloride.—By a similar procedure, butyltin trichloride (5.64 g) was caused to react with cyclopentadienylsodium (1.76 g), yielding butyl(cyclopentadienyl)tin dichloride as an oil, b.p. 69—71 °C at 0.05 mmHg, τ (CCl_4) 3.63 [5 H, s, C_5H_5 , $J(^{117/119}\text{Sn}-\text{H})$ 40 Hz] and 8.40—9.25 (9 H, C_4H_9).

2-Tributylstannyloxybutan-3-one.—Acetoin dimer (1.5 g, 0.017 mol) was heated under reflux in benzene (25 cm³) until the n.m.r. spectrum showed that formation of the monomer was complete (15 min). Bis(tributyltin) oxide (5.1 g, 0.008 5 mol) was then added and the solution was refluxed under a Dean and Stark water separator for 25 min. Benzene was removed under reduced pressure and the crude product (83%) was distilled under reduced pressure yielding

2-tributylstannyloxybutan-3-one, b.p. 84 °C at 0.01 mmHg, τ (CCl_4) 5.69 [1 H, q, CH, J (CH_3-CH) 7, $J(^{119}\text{Sn}-\text{H})$ 32 Hz], 7.94 (3 H, s, CH_3CO), 8.86 (3 H, d, CH_3CH), and 8.2—9.3 (27 H, Bu); ν_{max} (neat liquid) 1 720 cm⁻¹ (C=O); Mössbauer spectrum, δ 0.73 mm s⁻¹, ΔE_{q} 2.14 mm s⁻¹ (at 77 K with respect to SnO_2 at room temperature) (Found: C, 51.4; H, 9.2. $\text{C}_{16}\text{H}_{34}\text{O}_2\text{Sn}$ requires C, 51.6; H, 9.1%).

2-Trineophylstannyloxybutan-3-one.—2-Trineophylstannyloxybutan-3-one was prepared similarly by azeotropic dehydration of a mixture of acetoin (0.34 g) and trineophyltin hydroxide (2.09 g) in toluene (25 cm³). The solution was concentrated and used for photolytic experiments without further purification.

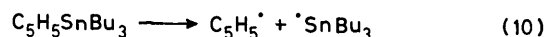
2-(Dibutylchlorostannyloxy)butan-3-one.—A mixture of acetoin (1.7 g) and dibutyltin methoxide chloride (6.3 g)^{19a} was stirred at room temperature for 90 min. Methanol was removed at 0.1 mmHg, leaving the product as a yellow oil (6.9 g); τ (CCl_4) 5.56 [1 H, q, CH; J (CH_3CH) 6 Hz], 7.76 (3 H, s, CH_3CO), 8.63 (3 H, d, CH_3CH), and 8.1—9.3 (27 H, m, Bu); Mössbauer spectrum, δ 1.24 mm s⁻¹, ΔE_{q} 3.29 mm s⁻¹.

2-(Butyldichlorostannyloxy)butan-3-one.—Acetoin (1.85 g, 0.021 mol) was added to a suspension of sodium methoxide in toluene (or benzene) in a centrifuge tube [prepared from sodium (0.50 g, 0.021 mol) and methanol (25 cm³) in toluene (25 cm³)]. Methanol was removed at the water pump, then butyltin trichloride (5.9 g, 0.021 mol) was added at 0 °C, and the mixture was stirred for 30 min. Sodium chloride was centrifuged off, and the solution was used directly for e.s.r. experiments, because the product decomposed when the solvent was removed, τ (C_6H_6) 6.13 [CH, q, J (CH_3-CH) 7 Hz], 7.84 (CH_3CO), and 8.3—9.3 (Bu and CH_3CH).

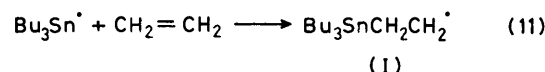
E.s.r. Experiments.—Samples, usually in toluene solvent, were sealed in Suprasil silica tubes, and photolysed in the cavity of a Varian E 4 e.s.r. spectrometer by the technique which has been described before.⁴

DISCUSSION

Reaction of the Radical $\text{R}_n\text{SnCl}_{3-n}$ with Alkenes and Alkyl Halides.—(i) $\text{Bu}_3\text{SnC}_5\text{H}_5$. Photolysis of tributylcyclopentadienyltin in cyclopropane showed a strong e.s.r. spectrum of the cyclopentadienyl radical.¹⁻⁴ Attempts to observe the spectrum of the $\text{Bu}_3\text{Sn}^\cdot$ radical under conditions of high microwave power were frustrated because the spectrum of the cyclopentadienyl radical could not be saturated, but the solutions showed the characteristic reactions of the $\text{Bu}_3\text{Sn}^\cdot$ radical, and there seems no reason to doubt that simple unimolecular photolysis occurs [equation (10)].



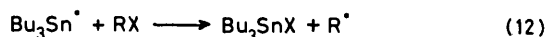
Thus, with ethylene as solvent, the spectrum of the adduct (I) was observed, with $a(2\text{H}_\alpha)$ 19.6 and $a(2\text{H}_\beta)$ 16.0 G at -90 °C (see Figure 1).



Photolysis in the presence of alkyl chlorides ($\text{Pr}^\text{t}\text{Cl}$, $\text{Bu}^\text{t}\text{Cl}$, $\text{ClCH}_2\text{COCH}_3$) showed only the spectrum of the cyclopentadienyl radical, but in the presence of alkyl bromides or iodides (*e.g.* $\text{Pr}^\text{t}\text{Br}$, $\text{Bu}^\text{t}\text{Br}$, MeI), strong

spectra of the corresponding alkyl radicals were observed [equation (12)].

In the presence of alkyl bromides or iodides, the e.s.r. spectrum of the cyclopentadienyl radical was broadened



to a degree depending on the concentration of the organic halide. This effect has been discussed in refs. 1 and 4. At high concentrations of the halide, the spectrum of the $\text{C}_5\text{H}_5^\bullet$ radical is broadened beyond detection and the spectrum of only the alkyl radical is observed.

Photolysis of tributylcyclopentadienyltin in the presence of carbon tetrachloride or bromotrichloromethane

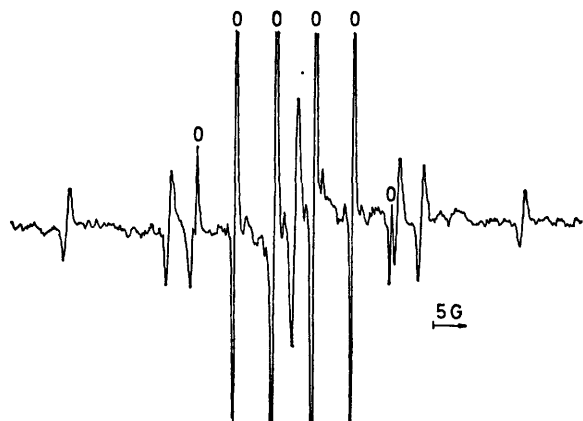
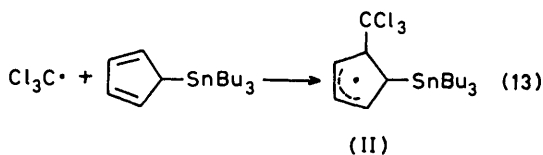


FIGURE 1 E.s.r. spectra of the radicals $\text{C}_5\text{H}_5^\bullet$ (marked 0) and $\text{Bu}_3\text{SnCH}_2\text{CH}_2^\bullet$ (I) from the photolysis of $\text{C}_5\text{H}_5\text{SnBu}_3$ in ethylene at -90°C

showed the spectrum of the adduct of the trichloromethyl radical with the parent tin compound (II).⁴ This suggests that the cyclopentadienyltin compounds may be useful reagents for the preparation of other derivatives of cyclopentadienes.



No adducts could be detected when the photolysis was carried out in the presence of acetone or chloroacetone, but 1,2-diones such as benzil or biacetyl showed strong spectra of the adducts with Bu_3Sn radicals. The adducts which biacetyl forms with the radicals $\text{Bu}_n\text{SnCl}_{3-n}$ are discussed below.

The trialkylcyclopentadienyltin compounds therefore provide a valuable new source of $\text{R}_3\text{Sn}^\bullet$ radicals for e.s.r. studies, and perhaps may also find applications in organic synthesis.

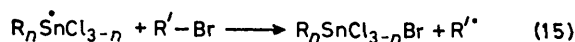
(ii) $\text{Bu}_2(\text{C}_5\text{H}_5)\text{SnCl}$. The introduction of one chlorine ligand reduced the reactivity of the tin radicals towards alkyl halides and alkenes. Both tin compounds showed strong spectra of the cyclopentadienyl radical on photolysis. In the presence of ethyl bromide, dibutylcyclopentadienyltin chloride showed a weak spectrum of the

ethyl radical, but no adduct could be detected when ethylene or di-*t*-butylethylene were added.

The adduct which the radical Bu_2SnCl forms with biacetyl is discussed below.

(iii) $\text{Bu}(\text{C}_5\text{H}_5)\text{SnCl}_2$ and $\text{C}_5\text{H}_5\text{SnCl}_3$. The presence of two or three chloro-ligands on the tin radicals which are formed on photolysis reduced the reactivity of these radicals to such a degree that the only reactions which could be detected by e.s.r. spectroscopy were the additions to 1,2-diones, which are discussed below. Photolysis of butyl(cyclopentadienyl)tin dichloride or of cyclopentadienyltin trichloride in the presence of ethylene, propylene, *t*-butylethylene, or methyl methacrylate showed only the spectrum of the cyclopentadienyl radicals, and in the presence of alkyl bromides (*e.g.* *t*-butyl bromide) only the bromide-broadened spectrum of the radical could be observed.

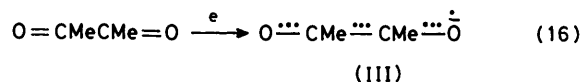
(iv) *The relative reactivities of the radicals $\text{Bu}_n\text{SnCl}_{3-n}$.* The principal conclusion from the above studies is that the reactivity of the radicals $\text{R}_n\text{SnCl}_{3-n}$ towards ethylene and alkyl bromides by equations (14) and (15) decreases as *n* decreases.



It should be borne in mind that the addition of tin-centred radicals to alkenes is usually reversible,⁹ and that the intensities of the spectra of the olefin adducts in equation (14) provide a measure of the overall affinity of the various tin radicals for the alkene rather than of the relative rates for the forward reactions. No such ambiguity applies to the abstraction of halogen by equation (15). These relative reactivities can be rationalised if it is assumed that in both reaction (14) and (15), the principal interaction is between the singly occupied molecular orbital (SOMO) of the radical and the lowest unoccupied molecular orbital (LUMO) rather than the highest occupied molecular orbital (HOMO) of the alkene or alkyl halide.

The HOMO and LUMO energies of ethylene are -10.5 and $+1.5$ eV, respectively, and the trialkyltin radicals have a high SOMO energy ($\text{Me}_3\text{Sn}^\bullet$, -7.1 eV).^{19b} If the interaction is principally between the SOMO and LUMO, the $\text{R}_3\text{Sn}^\bullet$ radical behaves as a nucleophilic species, donating an electron into the vacant π^* -orbital. In valence bond terms, this implies that the polar canonical form $\text{R}_3\text{Sn}^+\text{CH}_2^-\dot{\text{C}}\text{H}_2$ makes a significant contribution to the structure of the transition state. No measurement of the SOMO energies of the chlorotin radicals $\text{R}_n\text{SnCl}_{3-n}$ ($n = 0-2$) appears to be available, but there is qualitative evidence that they decrease with the introduction of chloro ligands: Cl_3SnH is a strong acid which gives stable salts $\text{Cl}_3\text{Sn}^-\text{M}^+$, whereas R_3SnH is a relatively weak acid. As the SOMO energy decreases, the orbital will interact less effectively with the LUMO, and, in valence bond terms, the structure $\text{Cl}_3\text{Sn}^+\text{CH}_2^-\dot{\text{C}}\text{H}_2$ will have little to contribute to the stability of the transition state.

Similar reasoning can be applied to the reaction with alkyl bromides. If the principal interaction of the SOMO is with the LUMO of the bromide, this places an electron in the antibonding σ^* orbital of the CBr bond of the bromide, and the transition state will be polar in the sense $R_3Sn^+Br^-R$. Again, this polar structure would



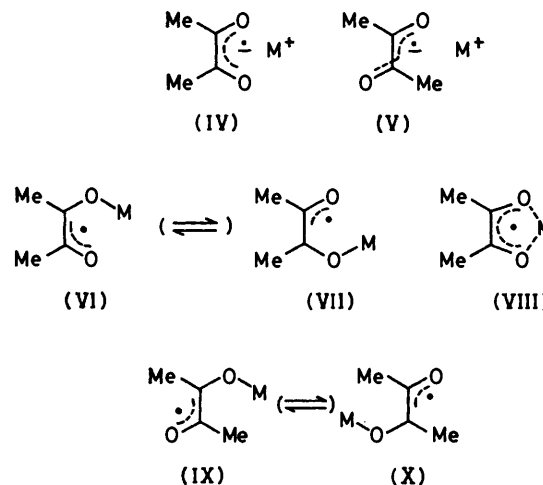
become less stable as chloro ligands replace alkyl groups, and the reactivity would drop.

The low reactivity of the Cl_3Sn radical towards alkenes is relevant to the possible synthesis of alkyltin trichlorides by the homolytic addition of trichlorotin hydride to olefins. Recent work has shown that $HSnCl_3$ can readily be prepared by the reaction between HCl and $SnCl_2^{20,*}$ and if this could be caused to add readily to simpler alkenes † it would provide a valuable industrial route to organotin compounds. The present work suggests why such a reaction may not be possible.

Reactions of the Radicals $Bu_nSn^{\cdot}Cl_{3-n}$ with Biacetyl.—A great deal of work has been reported on radicals derived from biacetyl and similar 1,2-diones. Frequently, the biacetyl has been reduced in aqueous or other polar solutions to the semidione radical ion (III). If the cation is derived from a strongly electropositive metal (M), the ionic or ion-pair *cis* or *trans* structures (IV) and (V) can be identified, but such structures are unlikely to be important for derivatives of tin(IV) in non-polar solvents. ‡

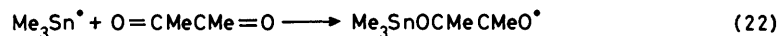
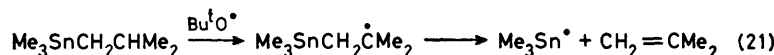
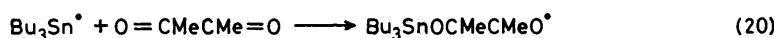
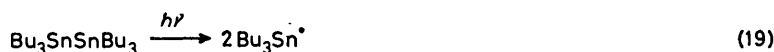
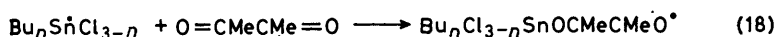
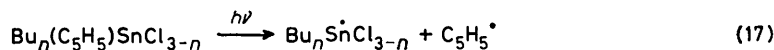
rate, this would impose an alternating linewidth effect on the e.s.r. spectrum, until it rendered the two methyl groups equivalent on the e.s.r. time scale. It is normally considered that this would cause the spectrum to be indistinguishable from that of the structure (VIII) in which the biacetyl acts as a symmetrical bidentate ligand, but, as we show below, this is not necessarily so.

The distinction between the monodentate structures (VI) and (VII), and the bidentate structure (VIII) may



be blurred if some attractive interaction occurs in (VI) and (VII) between the free acyl oxygen and the metal.

Structures (IX) and (X) represent the *trans*-equivalents of the structures (VI) and (VII). Again, if the



Paramagnetic species have also been prepared by generating the R_3Si^{\cdot} ,¹² R_3Ge^{\cdot} ,¹² or R_3Sn^{\cdot} ,^{12,13} radicals in the presence of biacetyl in non-polar solvents, and the structures (VI)—(X) have been considered for the adducts which are formed.

Structures (VI) and (VII) represent biacetyl as a monodentate ligand, in which the hyperfine coupling constants in the e.s.r. spectrum by the two methyl groups would be non-equivalent. If migration of the group M between the two oxygen atoms occurred at a sufficient

group M does not migrate rapidly, the methyl groups will be magnetically non-equivalent, and if rapid migration does occur, the spectrum will reduce to a binomial septet.

We have generated the radicals $Bu_nCl_{3-n}OCMeCMeO^{\cdot}$ ($n = 0-3$) by photolysis in the presence of biacetyl of the appropriate cyclopentadienyltin compounds, $Bu_n(C_5H_5)SnCl_{3-n}$ [equations (17) and (18)], and, when $n = 3$, by the similar reaction of hexabutylditin [equations (19) and (20)]. The radical $Me_3SnOCMeCMeO^{\cdot}$ has also been

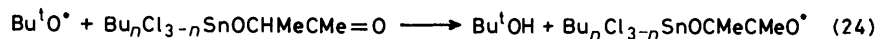
* There is evidence that the composition of the product may be H_2SnCl_4 rather than $HSnCl_3$.²¹

† Rapid nucleophilic addition does occur to electronegatively substituted alkenes such as acrylic esters.

‡ The conjugate acid of (III) has a pK_a value of ca. 4.²² The organotin derivatives of even strong acids like perchloric acid do not ionise in non-polar solvents, though they frequently form oligomers containing five- or six-co-ordinate tin.

generated by the photolysis of di-*t*-butyl peroxide in the presence of trimethylisobutyltin and biacetyl [equations (21) and (22)] (*cf.* ref. 9).

The radicals $\text{Bu}_n\text{Cl}_{3-n}\text{SnOCMeCMeO}^\bullet$ ($n = 0-3$) have also been generated by the fundamentally different route of abstraction of hydrogen from the corresponding



organotin derivative of acetoin [equations (23) and (24)].

Details of the e.s.r. spectra which are observed are given in the Table.

(i) $\text{Cl}_3\text{SnOCMeCMeO}^\bullet$ and $\text{BuCl}_2\text{SnOCMeCMeO}^\bullet$. The spectrum of the radical $\text{Cl}_3\text{SnOCMeCMeO}^\bullet$, superimposed on that of the cyclopentadienyl radical, which is observed when cyclopentadienyltin trichloride is photolysed in the presence of biacetyl [equations (17) and (18) ($n = 0$)] at -17°C is shown in Figure 2a; it can be simulated on the

that of the Cl_3Sn derivative, and could be simulated using the parameters $a(3\text{H})$ 9.98, $a(3\text{H})$ 9.10, $a(1\text{Cl})$ 0.88, ΔH_{pp} 0.65 G.

In both these radicals, one chlorine must occupy a unique position at low temperature, and the two methyl groups are nearly but not quite equivalent. We con-

clude that the unique chlorine atom is the apical ligand at approximately trigonal bipyramidal tin in the bidentate *cis*-complexes (XI) and (XII).

As the temperature is raised above *ca.* 0°C , the spectra of both (XI) and (XII) change. At $+20^\circ\text{C}$ the spectrum of (XII) appeared as a septet of septets (see Figure 3). This would result if rapid positional exchange of the ligands about the tin rendered the two chlorine atoms magnetically equivalent; the hyperfine coupling by ^{35}Cl

Tin(IV) derivatives of butane-2,3-semidione, and related radicals

Reagent	Radical	Solvent	$T/^\circ\text{C}$	Hyperfine coupling constants (G)			g
$\text{Cl}_3\text{SnC}_6\text{H}_5 + \text{OCMeCMeO}$	$\text{Cl}_3\text{SnOCMeCMeO}^\bullet$ ^a	PhMe	$\begin{cases} -20 \\ +10 \end{cases}$	9.98 (3 H)	9.10 (3 H)	0.88 (1Cl)	2.0030
$\text{BuCl}_2\text{SnC}_6\text{H}_5 + \text{OCMeCMeO}$	$\text{BuCl}_2\text{SnOCMeCMeO}^\bullet$ ^a	PhMe	$\begin{cases} -20 \\ +10 \end{cases}$	9.98 (3 H)	9.10 (3 H)	0.88 (1 Cl)	2.0028
$\text{BuCl}_2\text{SnOCHMeCMeO} + \text{Bu}^t\text{OOBu}^t$	$\text{BuCl}_2\text{SnOCMeCMeO}^\bullet$	C_6H_6	$\begin{cases} -5 \\ +10 \end{cases}$	9.98 (3 H)	9.10 (3 H)	0.88 (1 Cl)	
$\text{Bu}_2\text{ClSnC}_6\text{H}_5 + \text{OCMeCMeO}$	$\text{Bu}_2\text{ClSnOCMeCMeO}^\bullet$	PhMe	$\begin{cases} -50 \\ 0 \end{cases}$	10.8 (3 H)	7.4 (3 H)		2.0039
$\text{Bu}_2\text{ClSnOCHMeCMeO} + \text{Bu}^t\text{OOBu}^t$	$\text{Bu}_2\text{ClSnOCMeCMeO}^\bullet$	PhMe	$\begin{cases} -65 \\ -40 \end{cases}$	10.6 (3 H)	7.5 (3 H)		
$\text{Bu}_3\text{SnC}_6\text{H}_5 + \text{OCMeCMeO}$	$\text{Bu}_3\text{SnOCMeCMeO}^\bullet$ ^a	PhMe	$\begin{cases} -50 \\ +60 \end{cases}$	$\begin{cases} 8.5 (6 \text{ H}) \\ 7.5 (6 \text{ H}) \end{cases}$ ^c			2.0040 2.0045 2.0040
$\text{Bu}_3\text{SnOCHMeCMeO} + \text{Bu}^t\text{OOBu}^t$	$\text{Bu}_3\text{SnOCMeCMeO}^\bullet$	C_6H_6	$\begin{cases} -110 \\ +19 \end{cases}$	8.5 (6 H)	10.9 (^{119}Sn)		
$\text{Bu}_3\text{SnSnBu}_3 + \text{OCMeCMeO}$	$\text{Bu}_3\text{SnOCMeCMeO}^\bullet$	PhMe	$\begin{cases} -20 \\ +95 \end{cases}$	7.2 (6 H) ^c	8.5 (^{119}Sn)		
$\text{Me}_3\text{SnSnMe}_3 + \text{OCMeCMeO}$	$\text{Me}_3\text{SnOCMeCMeO}^\bullet$	PhMe	$\begin{cases} -50 \\ +80 \end{cases}$	7.2 (6 H) ^c	8.5 (^{119}Sn)		2.0040
$\text{Me}_3\text{SnCH}_2\text{CHMe}_2 + \text{Bu}^t\text{OOBu}^t + \text{OCMeCMeO}$	$\text{Me}_3\text{SnOCMeCMeO}^\bullet$	PhMe	$\begin{cases} -37 \\ -12 \end{cases}$	$\begin{cases} 7.5 (6 \text{ H}) \\ 8.6 (6 \text{ H}) \end{cases}$ ^c			2.0043
$\text{Nph}_3\text{SnOCHMeCMeO} + \text{Bu}^t\text{OOBu}^t$ ^d	$\text{Nph}_3\text{SnOCMeCMeO}^\bullet$ $\text{Nph}_3\text{SnO}\dot{\text{C}}\text{HCH}_3$	PhMe	$\begin{cases} -20 \\ +90 \end{cases}$	21.5 (3 H)	14.7 (1 H)		2.0030 2.0041
HOCHMeCMeO	$\text{HO}\dot{\text{C}}\text{HMe}$	PhMe	$\begin{cases} -80 \\ -40 \end{cases}$	8.5 (6 H)	15.00 (^{119}Sn)		
$\text{HOCHMeCMeO} + \text{Bu}^t\text{OOBu}^t$	$\text{HO}\dot{\text{C}}\text{MeCMeO}$	PhMe	$\begin{cases} -40 \\ +17 \end{cases}$	23.5 (3 H)	16.0 (1 H)	1.25 (1 H)	
$\text{Me}_3\text{SiOCHMeCMeO} + \text{Bu}^t\text{OOBu}^t$	$\text{Me}_3\text{SiO}\dot{\text{C}}\text{HMe}$	PhMe	$\begin{cases} -93 \\ -20 \end{cases}$	13.4 (3 H)	2.6 (3 H)	2.1 (1 H)	
$\text{Me}_3\text{SiOCH}_2\text{Me} + \text{Bu}^t\text{OOBu}^t$	$\text{Me}_3\text{SiO}\dot{\text{C}}\text{HMe}$	C_6H_6	$\begin{cases} 0 \\ +15 \end{cases}$	22.8 (3 H)	16.5 (1 H)		2.0027

^a Plus $\text{C}_6\text{H}_5^\bullet$. ^b See text. ^c With alternating linewidth effect. ^d Nph = neophyl.

basis that the two methyl groups are non-equivalent, $a(3\text{H})$ 9.98, $a(3\text{H})$ 9.10, ΔH_{pp} 0.3 G, and only one chlorine (I ^{35}Cl 3/2) couples, $a(1^{35}\text{Cl})$ 0.88 G.

The radical $\text{BuCl}_2\text{SnOCMeCMeO}^\bullet$ could be obtained both by photolysis of butyl(cyclopentadienyl)tin dichloride in the presence of biacetyl [equations (17) and (18) ($n = 1$)], and of di-*t*-butyl peroxide in the presence of the acetoin derivative $\text{BuCl}_2\text{SnOCHMeCMe=O}$ [equations (23) and (24) ($n = 1$)]. Apart from an increased linewidth, the spectra of the radicals from both routes at low temperature (Figure 3) were the same as

and ^{37}Cl would then give rise to a rough septet pattern with approximate intensities 1 : 2 : 3 : 4 : 3 : 2 : 1. If exchange between the two methyl groups is also involved, equal hyperfine coupling by the six protons would give rise to a septet of relative intensities 1 : 6 : 15 : 20 : 15 : 6 : 1.

Similarly the Cl_3Sn adduct (XI) showed more complicated groups of multiplets at $+20^\circ\text{C}$. These were too weak to interpret in detail, but they would be compatible with the septet of approximate decets which would be obtained from hyperfine coupling by two equivalent

methyl groups and three equivalent chlorine atoms. Again, it seems likely that rapid positional exchange renders equivalent the three chlorine ligands, and the two methyl groups, on the e.s.r. time scale.

These five-co-ordinate structures for (XI) and (XII) are reasonable in view of the known tendency for organotin dichlorides and trichlorides to form trigonal bipyramidal complexes in which chloro ligands are more apicophilic

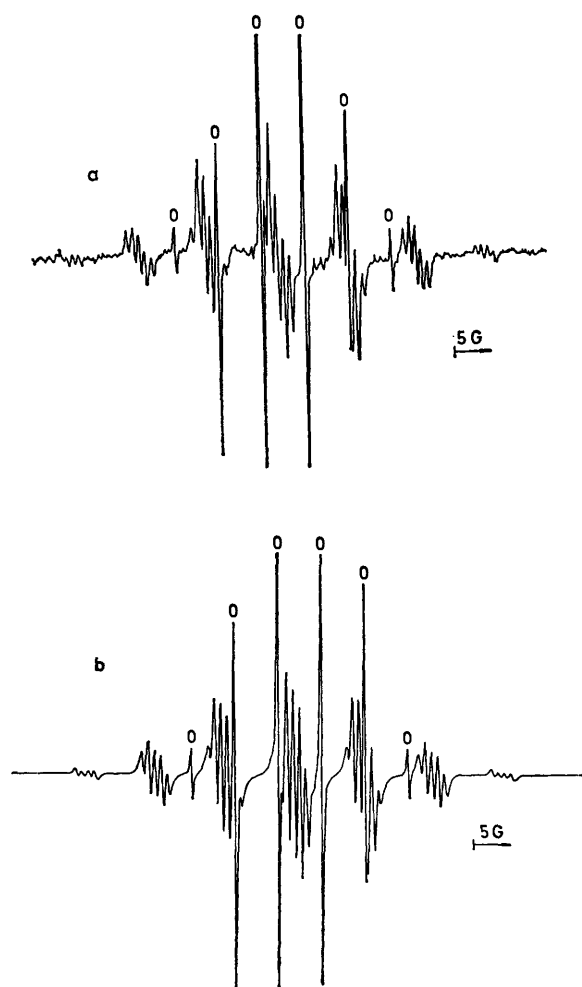


FIGURE 2 a, E.s.r. spectrum of the radical $\text{Cl}_3\text{SnOCMeMeO}^\bullet$ (XI) from the photolysis of $\text{C}_6\text{H}_5\text{SnCl}_3$ in the presence of biacetyl in toluene at -17°C . The signals of the $\text{C}_6\text{H}_5^\bullet$ radical are marked 0. b, Simulation, using the parameters $a(3\text{H})$ 9.975, $a(3\text{H})$ 9.100, $a(^{135}\text{Cl})$ 0.875, ΔH_{pp} 0.3 G

than alkyl ligands, and a 1,4- or 1,5-bidentate ligand tends to bridge apical and equatorial sites. For example, an X-ray diffraction study of 2-methoxycarbonyl-ethyltin trichloride showed it to have the structure (XIII) with one apical chloro and one equatorial alkyl group, and the bidentate ligand bridging equatorial and apical positions.²³

(ii) $\text{Bu}_2\text{ClSnOCMeMeO}^\bullet$. The spectrum of the radical $\text{Bu}_2\text{ClSnOCMeMeO}^\bullet$ could be obtained from the photolysis of dibutyl(cyclopentadienyl)tin chloride in the presence of biacetyl [reactions (17) and (18) ($n = 2$)], or of di-*t*-butyl peroxide in the presence of the acetoin

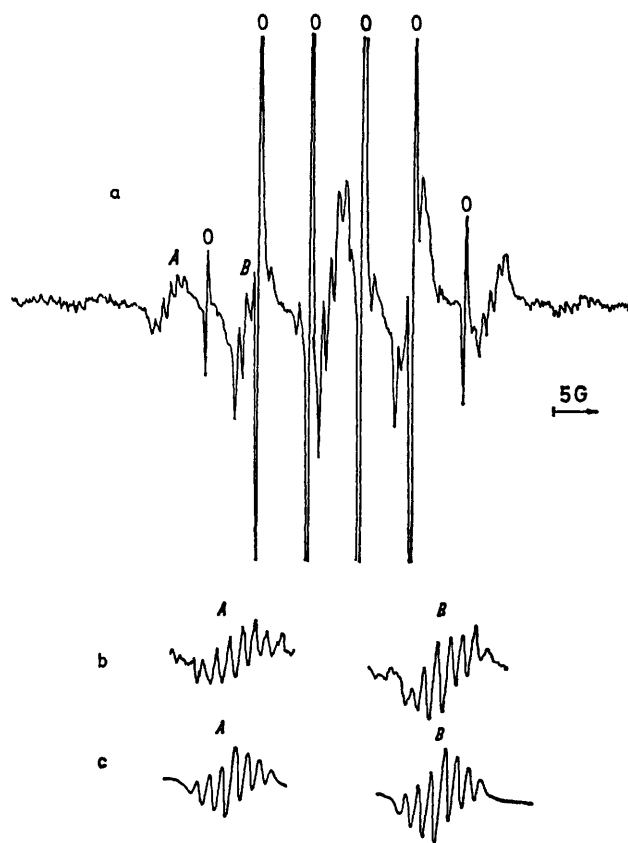
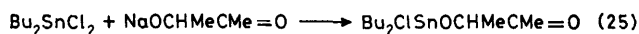
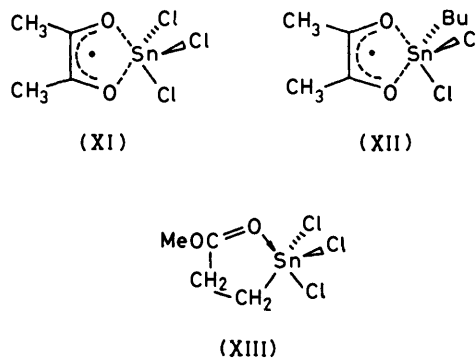


FIGURE 3 a, E.s.r. spectrum of the radical $\text{Cl}_2\text{BuSnOCMeMeO}^\bullet$ (XII) from the photolysis of $\text{C}_6\text{H}_5\text{SnBuCl}_2$ in the presence of biacetyl in toluene at -13°C . The signals of the $\text{C}_6\text{H}_5^\bullet$ radical are marked 0. Expansion of the multiplets A and B at $+20^\circ\text{C}$ showing the septet splitting from two non-equivalent chlorine atoms. At this temperature, the spectrum of the $\text{C}_6\text{H}_5^\bullet$ radical is weak or undetectable. c, Simulation of the multiplets A and B at 20°C using the parameters $a(2\text{Cl})$ 0.56, ΔH_{pp} 0.3 G

derivative $\text{Bu}_2\text{ClSnCHMeMe=O}$ [equations (23) and (24) ($n = 2$)], which was prepared by reaction (25).



The spectrum from this latter route is shown in Figure 4, and it shows quite different characteristics from the corresponding radicals containing trichlorotin and butyldichlorotin groups. Over the whole range of



temperature (-50 to 0°C) which could be studied, the two methyl groups were non-equivalent, $a(3\text{H})$ 7.4, $a(3\text{H}')$ 10.90 G, and no chlorine coupling could be detected.

This would be compatible with either a five-co-ordinate

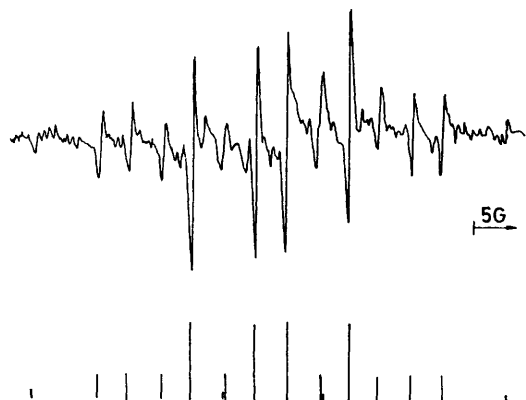
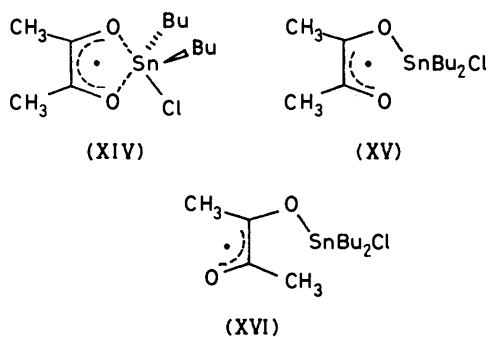


FIGURE 4 E.s.r. spectrum of the radical $\text{ClBu}_3\text{SnOCMeCMeO}\cdot$ (XV) from the photolysis of Bu^tOOBu^t in the presence of $\text{ClBu}_3\text{SnOCHMeCMeO}$ in toluene at -49°C ; the stick spectrum illustrates the splitting into a quartet of quartets

structure in which the two methyl groups are rendered non-equivalent by the trigonal bipyramidal configuration at tin (XIV), or with a four-co-ordinate *cis*- or *trans*-non-fluxional structure (XV) or (XVI).

A confident choice between these alternatives does not appear possible, but we favour the *cis*-monodentate structure (XV). By comparison with the Cl_3Sn and BuCl_2Sn derivatives (XI) and (XII), the absence of any chlorine coupling, and the larger difference between the coupling constants of the two methyl groups seems to argue against the bidentate structure (XIV). On the other hand, the difference between $a(3\text{H})$ and $a(3\text{H}')$ seems too small for the *trans*-monodentate structure (XVI), as the *trans*-protio compound shows $a(3\text{H})$ 12.8 and $a(3\text{H}')$ 3.8 G.^{22,*}

A decreased tendency to five-co-ordination would be



compatible with the established behaviour of dialkyl-(alkoxy)tin chlorides. For example, dimethyl(methoxy)-tin chloride in concentrated solution exists as the five-co-

* Only the equilibrating *cis*-protio compound is known, $a(6\text{H})$ 9.6 G; the alternating line width effect could be detected, but the region of slow exchange could not be reached.²² The Me_3Si derivative [$a(3\text{H})$ 15.5, $a(3\text{H}')$ 0.45 G], and the Me_3Ge derivative [$a(3\text{H})$ 14.3, $a(3\text{H}')$ 2.0 G], have been suggested to have the *trans*-structure.¹²

ordinated dimer, but it is monomeric four-co-ordinate in dilute solution.²⁴

(iii) $\text{Bu}_3\text{SnOCMeCMeO}\cdot$. The reaction of trialkyltin radicals with biacetyl has been investigated previously. Cooper *et al.*¹² photolysed hexabutylditin and di-*t*-butyl peroxide in the presence of biacetyl, and observed from -40 to $+55^\circ\text{C}$ an e.s.r. spectrum with $a(6\text{H})$ 7.2 G. They ascribed this to the rapidly equilibrating *trans*-monodentate structure (IX) \rightleftharpoons (X) but the fluxional *cis*-structure (VI) \rightleftharpoons (VII), could not be ruled out. Further evidence for a fluxional structure came from parallel studies on the adducts of acenaphthoquinone.¹⁴ Schroeder *et al.*¹³ photolysed a mixture of hexamethylditin and biacetyl, and observed a spectrum consisting of a binomial septet, $a(6\text{H})$ 7.87 G, and preferred the interpretation of a *cis*-chelated structure (VIII).

We have generated the radicals $\text{R}_3\text{SnOCMeCMeO}\cdot$ by the four routes shown in equations (17)–(24), and have identified not one but *two* septet spectra, characterised by different hyperfine coupling constants (*ca.* 7.3 and 8.5 G respectively), *g* values, and tendency to an alternating linewidth effect.

The septet with the larger hyperfine splitting is the



FIGURE 5 E.s.r. spectrum of the radical $\text{Bu}_3\text{SnOCMeCMeO}\cdot$ (XVII) \rightleftharpoons (XVIII) [$a(6\text{H})$ 8.5 G] from the photolysis of di-*t*-butyl peroxide in the presence of $\text{Bu}_3\text{SnOCHMeCMeO}$ in cyclopropane at -109°

only spectrum which is observed when di-*t*-butyl peroxide is photolysed in the presence of the tributyltin derivative of acetoin [equations (23) and (24); see Figure 5], and shows $a(6\text{H})$ 8.54, $a(^{119}\text{Sn})$ 11.0 G at -108°C , $a(6\text{H})$ 8.42, $a(^{119}\text{Sn})$ 8.5 G at $+19^\circ\text{C}$. At no temperature was there any evidence for an alternating linewidth effect.

The same species provided the principal spectrum from the systems hexabutylditin and biacetyl [reactions (19) and (20)] and tributyl(cyclopentadienyl)tin and biacetyl [reactions (17) and (18)] above 50°C ; any contamination by the septet $a(6\text{H})$ 7.3 G could be removed by shuttering the light, when this latter spectrum rapidly decayed, and the former one persisted.

The spectrum $a(6\text{H})$ 7.3 G is best observed at low temperature; it is the principal species which is observed

up to *ca.* +50 °C when hexabutylditin is photolysed in the presence of biacetyl (Figure 6) [equations (19) and (20)] and a similar spectrum is observed up to -10 °C when di-*t*-butyl peroxide is photolysed in the presence of trimethylisobutyltin and biacetyl [equations (21) and (22)]. Photolysis of tributyl(cyclopentadienyl)tin in the presence of biacetyl [equations (17) and (18)] gave up to *ca.* 20% of the species with $a(6H)$ 7.3 G below +50 °C, but thereafter the wider spaced multiplet was the main product.

The spectrum with $a(6H)$ 7.3 G (g 2.004 5 at -64 °C) was centred *ca.* 0.5 G downfield of the other septet (g 2.004 0 at -6 °C), and showed an alternating linewidth effect which was so severe that the spectrum often appeared as a doublet with a separation of *ca.* 15 G. This type of alternating linewidth effect has been discussed by Norman and Pritchett²² for hydrogen migration in the radical *trans*-HOCMeCMeO[•]: when the migration is fast, the spectrum appears as a binomial septet, and when it is slow, the two non-equivalent methyl



FIGURE 6 E.s.r. spectrum of the radical $Bu_3SnOCMeCMeO^{\bullet}$ (IX) \rightleftharpoons (X) ($R = Bu_3Sn$) [$a(6H)$ 7.2 G], with an alternating linewidth effect, from the photolysis of a mixture of hexabutylditin, di-*t*-butyl peroxide, and biacetyl in toluene at -1 °C

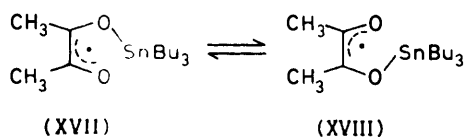
groups give rise to a quartet of quartets, but at intermediate rates the second, fourth, and sixth lines of the septet are broadened beyond detection, and the intensities of the third and fifth lines are reduced to 9/15 of their original intensity.

These two different septet spectra must presumably correspond to two of the three possibilities: *cis*-fluxional

trans-monodentate pair (IX) and (X). We suggest that this is the spectrum $a(6H)$ 7.3 G which shows the strong alternating linewidth effect: the exchange (IX) \rightleftharpoons (X) would be expected to be slower than that between (VI) \rightleftharpoons (VII) as is observed when $M = H$,²² and the bidentate structure (VIII) should show no alternating line width effect (or at most only a small one if the two methyl groups are rendered slightly non-equivalent by a trigonal bipyramidal structure at tin).

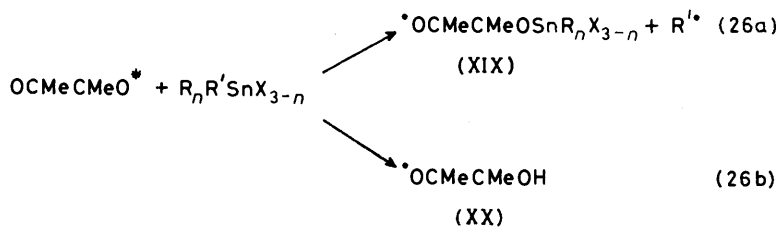
The septet with $a(6H)$ *ca.* 8.5 G with no detectable alternating linewidth effect is therefore to be assigned to either the rapidly fluxional *cis*-monodentate pair (VI) \rightleftharpoons (VII), or the bidentate structure (VIII).

The evidence is inconclusive, but we feel it is more consistent with rapidly equilibrating monodentate structures, as shown in (XVII) and (XVIII). The



Bu_3Sn group is less susceptible to increase its co-ordination number than the Bu_2ClSn group, which we have suggested to be four-co-ordinate in the structure (XV). The pronounced negative temperature coefficient of $a(Sn)$ seems unlikely for the cyclic structure (VII), even if the ring were non-planar, but it could be compatible with the structures (XVII) \rightleftharpoons (XVIII) in which rotation could occur about the O-Sn bond. The larger value of $a(^{119}Sn)$ in the trineophylltin derivative could similarly be accounted for in terms of a different conformation imposed by the steric demands of the bulky alkyl group in an acyclic structure.

This picture of a rapidly mobile R_3Sn group and a less mobile R_2ClSn group would be consistent with recent work on the derivatives of 3,6-di-*t*-butyl-1,2-semiquinone.^{16-18,25} The relative values of a and of g in *cis*- and *trans*- $R_3SnOCMeCMeO^{\bullet}$ would also be in line with the corresponding parameters for the radical anion and for the protic derivative: *cis*- $\ddot{O}CMeCMeO^{\bullet}$, $a(6H)$ 7.0 G, g 2.004 83, *trans*- $\ddot{O}CMeCMeO^{\bullet}$, $a(6H)$ 5.6 G, g 2.004 97 (in DMSO),²⁶ and *cis*-HOCMeCMeO[•], $a(6H)$ 9.6 G, *trans*-HOCMeCMeO[•], 8.3 G (in H_2O).²²



(VI) \rightleftharpoons (VII), *cis*-bidentate (VIII), or *trans*-fluxional (IX) \rightleftharpoons (X). It seems unlikely that the monodentate species (VI) or (VII) could exist alongside the *cis*-bidentate species (VIII), therefore one of the spectra which is observed presumably relates to the fluxional

The isomeric radicals $R_3SnOCMeCMeO^{\bullet}$, which we believe to be *cis*- and *trans*-isomers, are observed in different concentrations from the different preparations and they do not equilibrate during their lifetimes in the cavity, at least below room temperature. The reactions

involving biacetyl apparently therefore cannot all involve simple addition of the R_3Sn^{\cdot} radical by equation (9). It seems unlikely that biacetyl would form a complex with the tetra-alkyltins, but some of the variation may result from an S_H2 reaction by photoexcited biacetyl at tin [equation (26a)]: 27,* an S_H2 reaction by $n \rightarrow \pi^*$ excited biacetyl at tin in hexa-alkylditin [equation (26a; $X = R, R' = SnR_3$)] is very reasonable, and Sakurai has established the reaction of ketone triplets with cyclopentadienyltin(IV) compounds [cf. equation (26a; $X = R, R' = C_5H_5$),³⁰ but tetra-alkyltin compounds such as trimethylisobutyltin would be expected to undergo abstraction of hydrogen [equation (26b)].⁹

The alkyltin chlorides on the other hand usually react with alkoxy radicals and ketone triplets by an S_H2 reaction at the tin centre,²⁷ and it seemed possible that the alkylchlorotin derivatives of butane-2,3-semidione (XIX) might be formed by the photolysis of biacetyl in the presence of alkyltin chlorides by equation (26a; $R' = R, X = Cl$), but under these conditions, tributyltin chloride, dibutyltin dichloride, and butyltin trichloride still reacted by equation (26b), and the only spectrum which was observed was that of the protonated semidione (XX).

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[0/124 Received, 23rd January, 1980]

* Biacetyl exists almost wholly in the *s-trans* form,^{28,29} with a calculated barrier to rotation of 4.87 kcal mol⁻¹.²⁹ The dihedral angle in the $n \rightarrow \pi^*$ triplet appears not to be known.

REFERENCES

- 1 A. G. Davies and M.-W. Tse, *J.C.S. Chem. Comm.*, 1978, 353.
- 2 P. J. Barker, A. G. Davies, and J. D. Fisher, *J.C.S. Chem. Comm.*, 1979, 587.
- 3 P. J. Barker and A. G. Davies, *J.C.S. Chem. Comm.*, 1979, 815.
- 4 P. J. Barker, A. G. Davies, and M.-W. Tse, *J.C.S. Perkin II*, 1980, 946.
- 5 Reviewed by A. G. Davies, 'Organotin Compounds: New Chemistry and Applications,' American Chemical Society, Washington, 1976.
- 6 H. A. Buschhaus, M. Lehnig, and W. P. Neumann, *J.C.S. Chem. Comm.*, 1978, 129; H. A. Buschhaus and W. P. Neumann, *Angew. Chem. Internat. Edn.*, 1978, 17, 59.
- 7 H. Hillgartner, W. P. Neumann, and B. Schroeder, *Annalen*, 1975, 586.
- 8 W. P. Neumann, B. Schroeder, and M. Ziebarth, *Annalen*, 1975, 2279.
- 9 A. G. Davies, B. P. Roberts, and M.-W. Tse, *J.C.S. Perkin II*, 1978, 145 and references cited therein.
- 10 J. Cooper, A. Hudson, and R. A. Jackson, *J.C.S. Perkin II*, 1973, 1056.
- 11 P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1969, 91, 6161; 1971, 93, 846.
- 12 J. Cooper, A. Hudson, and R. A. Jackson, *J.C.S. Perkin II*, 1973, 1933.
- 13 B. Schroeder, W. P. Neumann, and H. Hillgartner, *Chem. Ber.*, 1974, 107, 3494.
- 14 A. Alberti and A. Hudson, *J.C.S. Perkin II*, 1978, 1098.
- 15 K. S. Chen and J. K. S. Wan, *J. Amer. Chem. Soc.*, 1978, 100, 6051.
- 16 S. G. Kukes, A. N. Prokof'ev, N. N. Bubnov, C. P. Solodovnikov, E. D. Korniets, D. H. Kravtsov, and M. I. Kabachnik, *Doklady Akad. Nauk. S.S.S.R.*, 1976, 229, 877.
- 17 A. I. Prokof'ev, T. I. Prokof'eva, N. N. Bubnov, S. P. Solodovnikov, I. S. Belostotskaya, V. V. Ershov, and M. I. Kabachnik, *Doklady Akad. Nauk S.S.S.R.*, 1978, 239, 1367.
- 18 G. A. Razuvaev, V. A. Tsarjapkin, L. V. Gorbunova, V. K. Cherkasov, G. A. Abakumov, and E. S. Klimov, *J. Organometallic Chem.*, 1979, 174, 47.
- 19 (a) A. G. Davies and P. G. Harrison, *J. Chem. Soc. (C)*, 1967, 298; (b) I. Fleming, 'Frontier Orbitals and Organic Chemical Reactions,' Wiley, London, 1976, p. 118; *J. Phys. Chem. Reference Data*, 1977, 6, Suppl. 1, 604.
- 20 R. E. Hutton and V. Oakes, 'Organotin Compounds: New Chemistry and Applications,' ed. J. J. Zuckerman, Amer. Chem. Soc. Adv. in Chem. Series, 1976, 157, 123; J. W. Burley, R. E. Hutton, and V. Oakes, *J.C.S. Chem. Comm.*, 1976, 665.
- 21 E. J. Bulten and J. W. G. van den Hurk, *J. Organometallic Chem.*, 1978, 162, 161.
- 22 R. O. C. Norman and R. J. Pritchett, *J. Chem. Soc. (B)*, 1967, 378.
- 23 P. G. Harrison, T. J. King, and M. A. Healy, *J. Organometallic Chem.*, 1979, 182, 17.
- 24 A. C. Chapman, A. G. Davies, P. G. Harrison, and W. McFarlane, *J. Chem. Soc. (C)*, 1970, 821.
- 25 A. G. Davies and J. A.-A. Hawari, unpublished work.
- 26 G. A. Russell and R. D. Stephens, *J. Phys. Chem.*, 1966, 70, 1320; G. A. Russell, 'Aspects of Mechanism and Organometallic Chemistry,' ed. J. H. Brewster, Plenum Press, New York, 1978, p. 59.
- 27 A. G. Davies and J. C. Scaiano, *J.C.S. Perkin II*, 1973, 1777.
- 28 D. D. Danielson and K. Hedberg, *J. Amer. Chem. Soc.*, 1979, 101, 3730.
- 29 J. Tyrrell, *J. Amer. Chem. Soc.*, 1979, 101, 3766.
- 30 M. Kira, M. Watanabe, and H. Sakurai, *Chemistry Letters*, 1979, 973.