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STUDIES OF HOMOLYTIC ORGANOMETALLIC REACTIONS

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Summary

The author's work in the field of homolytic reactions of Main Group organometallic compounds is reviewed.

The autoxidation of organometallic compounds, RM, gives the peroxides, ROOM, as the principal products. The mechanism involves a radical chain reaction similar to that of the autoxidation of a hydrocarbon.

$$R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$$

$$ROO^{\cdot} + MR \rightarrow ROOM + R^{\cdot}$$

The key step, in which a radical brings about a bimolecular homolytic substitution (S_H2) at a metal centre, occurs with a wide variety of radicals (e.g. $RO^{\cdot}$, $RS^{\cdot}$, R_2CO^T) and metals (e.g. Mg, Zn, Cd, B, Al, P, Sb, Bi).

$$X^{\cdot} + MR \rightarrow XM + R^{\cdot}$$

The displaced radicals can be monitored by NMR spectroscopy, and the rate constants for many of these processes have been measured. The influence of steric and electronic factors can be observed which are often not apparent in the more familiar S_H2 processes at hydrogen centres.

Cyclopentadienyl derivatives of some metals (particularly Li, Hg, Sn, and Pb) undergo unimolecular photolysis by ultraviolet light.

$$C_5H_5M \xrightarrow{h\nu} C_5H_5^{\cdot} + M^{\cdot}$$

This enables the electronic effect of substituents, including organometallic substituents, on the π-electronic system of the cyclopentadienyl ring to be determined, and it also makes it possible to observe how the properties of the metal-centred radicals depend on the nature of the ligands about the metal.

Introduction

The development of organometallic chemistry has been interwoven remarkably closely with that of the concept of free radicals.

In 1842, Bunsen claimed to have isolated the first free radical ($Me_2As^\cdot$) from the reaction between dimethylchloroarsine and zinc.

$$2\ Me_2AsCl + Zn \rightarrow ZnCl_2 + 2\ Me_2As^\cdot$$

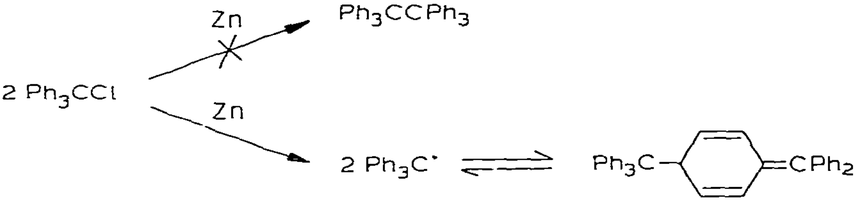
It was soon recognised however that the product was tetramethyldiarsine, which can claim to be the first organometallic compound of recognised structure.

Frankland, in 1850, thought that he had isolated ethyl radicals from a similar reaction.

$$2\ EtI + Zn \rightarrow ZnI_2 + 2\ Et^\cdot$$

Soon, again, it was shown that the principal product was the dimer, butane; but Frankland also isolated ethylzinc iodide and diethylzinc from these reactions, and his subsequent work with them and other organometallic compounds laid the foundation of organometallic chemistry.

Gomberg's reaction of triphenylmethyl chloride with metallic silver, mercury, or zinc (1900) is directly parallel to Frankland's, but whereas Frankland was aiming to make radicals and obtained covalent compounds, Gomberg was aiming to make a covalent compound (hexaphenylethane) and obtained instead the first authentic free radicals.



Again, Paneth and Hofeditz's elegant demonstration of the formation of the first simple alkyl radicals involved organometallic reactants. They showed that the pyrolysis of the alkyl derivatives of bismuth, zinc, antimony, tin, lead, and mercury, in the gas phase, gave rise to the corresponding free alkyl radicals, which would self-react to give hydrocarbons, or react with metal mirrors to regenerate organometallic compounds.

$$Me_4Pb \xrightarrow{450^\circ C} Pb + 4\ Me^\cdot$$

$$\begin{tikzcd}
 & Me_4Pb \\
Me^\cdot \arrow[ur, "Pb"] \arrow[dr] & \\
 & CH_4,\ C_2H_4,\ C_2H_6
\end{tikzcd}$$

Our introduction to free radicals similarly came out of organometallic chemistry, as accidentally as did Gomberg's.

Organometallic autoxidation

One of the most obvious characteristics of the alkyl derivatives of many main-group metals (e.g. Et_2Zn, Me_3B, Me_3Sb) is that they inflame in air. If the reaction is carried out in dilute solution, the inflammation can be avoided, and

TABLE 1

THE PREPARATION OF ORGANOMETALLIC PEROXIDES BY AUTOXIDATION

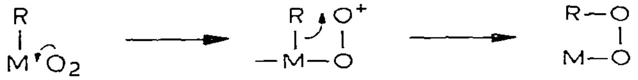
Reactants	Products
BuLi	BuOOLi
$C_5H_{11}MgBr$	$C_5H_{11}OOMgBr$
Et_2Zn	$Zn(OOEt)_2$
Me_2Cd	MeCdOOMe
$(PhCH_2)_3B$	$PhCH_2B(OOCH_2Ph)_2$
Et_3Tl	$Et_2TlOOEt$

high yields of the corresponding organoperoxymetallic compounds can be isolated.

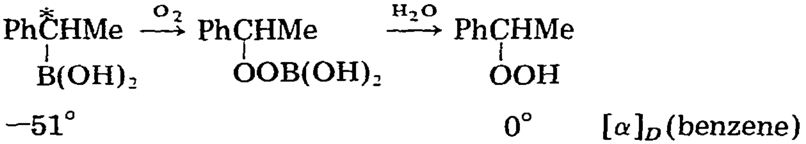
$RM + O_2 \rightarrow ROOM$

Some examples are shown in Table 1.

The reactions cannot be inhibited by simple phenols, and attempts by ESR spectroscopy to detect intermediate radicals were not successful, and it was suggested in 1955 that the insertion of oxygen into the metal—carbon bond involved coordination of dioxygen to the metal, accompanied or followed by a nucleophilic 1,3-rearrangement of the alkyl group from the metal to oxygen.



Matteson's resolution of 1-phenylethylboronic acid in 1965 made it possible to check the stereochemistry of this reaction.



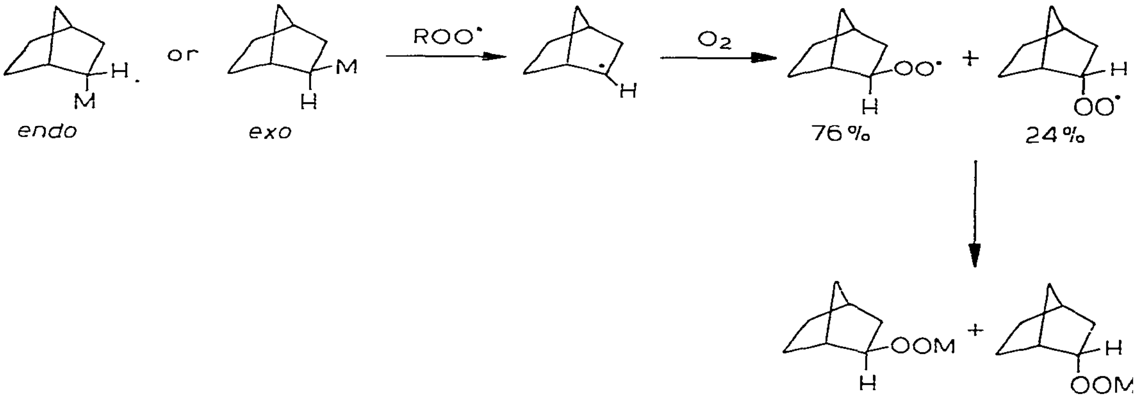
$$\underset{B(OH)_2}{Ph\overset{*}{C}HMe} \xrightarrow{O_2} \underset{OOB(OH)_2}{PhCHMe} \xrightarrow{H_2O} \underset{OOH}{PhCHMe}$$

$-51°$ $0°$ $[\alpha]_D$(benzene)

Whereas the rearrangement mechanism should involve retention of asymmetry, the hydroperoxide which is obtained after hydrolysis is completely racemic, and, further, the reaction can be inhibited by very powerful radical scavengers such as galvinoxyl. The reaction therefore appeared to be a radical chain process involving the intermediate free alkyl radicals, and this was later confirmed by a kinetic study. The autoxidation of alkyl derivatives of the Main Group metals is strictly parallel to the autoxidation of a hydrocarbon, and, as is so often observed, hydrogen behaves in the same way as does a main group metal in the same molecular environment.

Hydrocarbon Autoxidation	Organometallic Autoxidation
$R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$	$R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$
$ROO^{\cdot} + MR \rightarrow ROOM + R^{\cdot}$	$ROO^{\cdot} + HR \rightarrow ROOH + R^{\cdot}$

Similar stereochemical evidence is obtained from the autoxidation of the epimeric norborn-2-ylboranes and norborn-2-ylmagnesium halides. Whatever the epimeric composition of the reactant, the peroxide which is formed contains about 76% *exo* and 24% *endo* norbornyl—oxygen links, reflecting the stereoselectivity of the reaction of the norbornyl radical with oxygen.



The criterion of inhibition of the chain can be applied more generally, and gives positive results with a variety of alkyl derivatives of cadmium, zinc, boron, aluminium, antimony and bismuth. Indeed, there is no known exception to the rule that the alkyl derivatives of any Main Group metal are autoxidised by this radical chain process.

The form of the kinetic equation for the autoxidation of an organometallic compound, RM, is the same as that for a hydrocarbon (M = H).

Initiation $\xrightarrow{R_i} R^\cdot$

Propagation $R^\cdot + O_2 \rightarrow ROO^\cdot$

$ROO^\cdot + RM \xrightarrow{k_p} ROOM + R^\cdot$

Termination $2\,ROO^\cdot \xrightarrow{2k_t}$ products

By the steady state approximation

$$R_i = 2k_t[ROO^\cdot]^2$$

therefore

$$\frac{-d[O_2]}{dt} = k_p[ROO^\cdot][RM]$$

$$= k_p[RM]\left(\frac{R_i}{2k_t}\right)^{1/2}$$

Values of k_p for various organoboranes are given in Table 2.

The relative reactivity $(n\text{-}C_4H_9)_3B$ and $(s\text{-}C_4H_9)_3B$ indicates the presence of a steric effect, and the reactivity of $(PhCH_2BO)_3$ compared with $(n\text{-}C_4H_9BO)_3$ shows the effect of resonance stabilisation in the displaced radical. The general lower reactivity of the boroxines compared with boranes probably reflects the fact that in the former compounds the p_π—p_π bond between oxygen and boron has to be broken during the attack of the radical at the metal to form the 4-coordinated transition state or intermediate.

TABLE 2

RATE CONSTANTS AT 30°C FOR THE REACTION $ROO^{\cdot} + MR_n \rightarrow ROOMR_{n-1} + R^{\cdot}$

MR_n	k_p/l mol^{-1} s^{-1}
$(n\text{-}C_4H_9)_3B$	2×10^6
$(i\text{-}C_4H_9)_3B$	8×10^4
$(s\text{-}C_4H_9)_3B$	5×10^6
$(n\text{-}C_4H_9BO)_3$	1×10^3
$(s\text{-}C_4H_9BO)_3$	1×10^4
$(t\text{-}C_4H_9BO)_3$	3×10^4
$(PhCH_3BO)_3$	1×10^6

An alkylperoxyl radical therefore reacts at boron in a trialkylborane some 10^7 times faster than it does at hydrogen in the same molecular environment. It seemed likely that other electronegative radicals should react rapidly at metallic centres, and this indeed was soon established.

S_H2 Reactions at metallic centres

The most direct test for bimolecular homolytic substitution at a metal centre is the observation by ESR spectroscopy of the radical which is displaced.

Thus, if di-t-butyl peroxide is photolysed in the presence of tri-n-butylborane in an inert solvent, a strong ESR spectrum of the n-butyl radical is observed.

$$\text{t-BuOO-t-Bu} \xrightarrow{h\nu} 2\ \text{t-BuO}^{\cdot}$$

$$\text{t-BuO}^{\cdot} + BBu_3 \rightarrow \text{tBuOBBu}_2 + Bu^{\cdot}$$

The same elementary reaction can occur as one component in a chain sequence. If t-butyl hypochlorite is used as the reagent, the butyl radical abstracts chlorine from the hypochlorite, and butyl chloride and dibutyl-t-butoxyborane is formed by the following reactions,

$$\text{t-BuO}^{\cdot} + Bu_3B \rightarrow \text{t-BuOBBu}_2 + Bu^{\cdot}$$

$$Bu^{\cdot} + \text{t-BuOCl} \rightarrow BuCl + \text{t-BuO}^{\cdot}$$

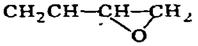
Chain and non-chain reactions analogous to these have been established for a wide variety of radical reagents and of metals. The metals have included organic derivatives of lithium, beryllium, magnesium, zinc, cadmium, mercury, boron, aluminum, thallium, tin, lead, phosphorus, arsenic, antimony, and bismuth. Relatively little work has been carried out on derivatives of transition metals, although a few isolated examples of the S_H2 process at these metals are known. The principal radical reactants which have been studied, and their source and mode (chain or non-chain) of reaction, are listed in Table 3. Typical examples of the reactants and products of the chain reactions are shown in the following equations.

$$(CH_2CO)_2NCl + Bu_4Sn \rightarrow Bu_3SnN(COCH_2)_2 + BuCl$$

$$2\ PhSH + Me_3Sb \rightarrow MeSb(SPh)_2 + 2\ MeH$$

TABLE 3

S_H2 REACTIONS AT METAL CENTRES:
$X^\cdot + MR_n \rightarrow XMR_{n-1} + R^\cdot$

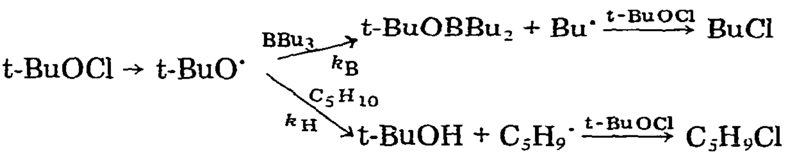
$X^\cdot$	Source of $X^\cdot$	
	Non-chain	Chain
$ROO^\cdot$		O_2
$RO^\cdot$	t-BuOOt-Bu t-BuON=NO-t-Bu	t-BuOCl $CH_2=O$ $CH_2=CH—CH=O$  $\mathrm{CH_2CH{-}\underbrace{CH{-}CH_2}_{O}}$
$R_3SiO^\cdot$	$Me_3SiOOSiMe_3$	
RCO_2	PhCOOOCOPh	
$RS^\cdot$	t-BuSS-t-Bu PhSSPh	MeSSMe PhSSMe BuSH
$R_2N^\cdot$	$Me_2NN=NNMe_2$	Me_2NCl $CH_2=CH—C\equiv N$
$(Me_3Si)_2N^\cdot$	$(Me_3Si)_2NN(SiMe_3)_2$	$(Me_3Si)_2NBr$
$(CH_2CO)_2N^\cdot$		$(CH_2CO)_2NX$
$R^{F\cdot}$	$R^FI + Me_3Sn^\cdot$	
$Me_3Si^\cdot$		$(Me_3Si)_2Hg$
R_2CO^T	$Me_2CO + h\nu$	

$$Me_2NCl + Bu_3B \rightarrow Bu_2BNMe_2 + BuCl$$

$$CH_2=CH—CH=O + Et_3B \rightarrow EtCH_2CH=CH—OBEt_2$$

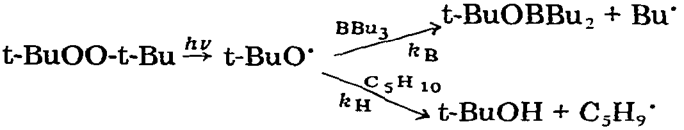
$$t\text{-}BuOCl + Pr_3SnCl \rightarrow Pr_2Sn(O\text{-}t\text{-}Bu)Cl + PrCl$$

Rate constants for many of these reactions have been measured, usually by causing the organometallic compound to compete with another compound, of known reactivity, for reaction with the radical. The ratio of the products derived from the two reactants is then a function of the ratio of the rate constants for the two processes, and if one of them is known, the second can be derived. For example, in the scheme below, k_B is obtained in terms of k_H for cyclopentane as the reference standard.



$$\frac{k_B}{k_H} = \frac{[BuCl][C_5H_{10}]}{[C_5H_9Cl]BBu_3]}$$

Alternatively, as the rate constants for the removal of simple alkyl radicals from solution fall within a narrow range (ca. 2×10^9 l mol^{-1} s^{-1}), the relative concentrations of the two displaced radicals can be measured under steady-state conditions by ESR spectroscopy, and related similarly to the rate constants of the reactions in which they are formed.



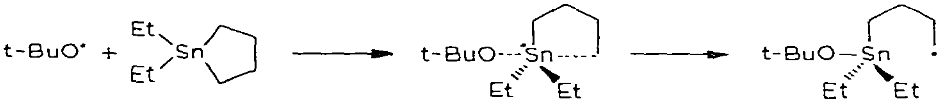
$$\text{t-BuOO-t-Bu} \xrightarrow{h\nu} \text{t-BuO}^{\cdot} \begin{cases} \xrightarrow[k_B]{BBu_3} \text{t-BuOBBu}_2 + \text{Bu}^{\cdot} \\ \xrightarrow[k_H]{C_5H_{10}} \text{t-BuOH} + C_5H_9^{\cdot} \end{cases}$$

$$\frac{k_B}{k_H} = \frac{[Bu^{\cdot}][C_5H_{10}]}{[C_5H_9^{\cdot}][BBu_3]}$$

The results generally endorse and extend those quoted above for the alkylperoxydealkylation of organoboranes, but some of the reactions need special comment.

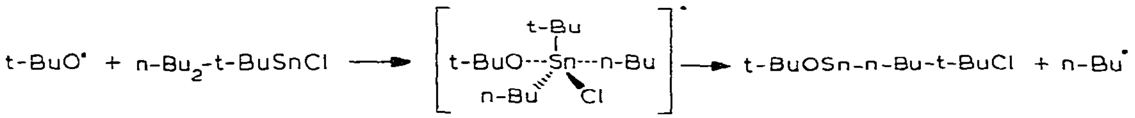
Succinimidyl radicals react with tetraalkyltin compounds by an S_H2 reaction at the tin centre, and the reactivities are dominated by steric factors ($Me_4Sn > Et_4Sn > n\text{-}Bu_4Sn > s\text{-}Bu_4Sn$). Alkoxyl radicals on the other hand react with acyclic tetraalkyltins by abstraction of hydrogen from the α or β position of an alkyl group, but they react with 1,1-dialkylstannacyclopentanes and 1,1-dialkylstannacyclohexanes by again S_H2 displacement at the tin centre, with opening of the ring.

Presumably this high reactivity reflects the relief of angle strain in the 5-coordinate transition state (or intermediate), and also perhaps the fact that steric hindrance is less severe than in the acyclic compounds.



(k = 2 1 × 10^6 l mol^{-1} s^{-1} at -30 °C)

In contrast to the acyclic tetraalkyltins, the trialkyltin chlorides do undergo S_H2 alkoxydealkylation at tin. The stability of different alkyl radicals follows the sequence $R^p < R^s < R^t$, but di-n-butyl-t-butyltin chloride reacts with t-butoxyl radicals with the predominant displacement of the less thermodynamic-stable n-butyl radicals. This anomalous selectivity may be rationalised on the grounds that, in the 5-coordinate transition state, the t-butyl group will occupy the less sterically demanding equatorial position, leaving an n-butyl ligand in the apical position, and that, as in the phosphoranyl radicals ($^{\cdot}PX_5$), it is the apically-directed bond which cleaves.



(k = 4 5 × 10^5 l mol^{-1} s^{-1} at -60 °C, for $n\text{-}Bu_3SnCl$, k = 2 1 × 10^6 l mol^{-1} s^{-1} at -60 °C)

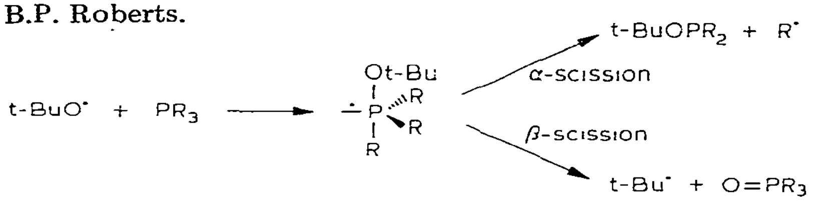
Ketone triplets imitate the behaviour of alkoxyl radicals in inducing homolytic substitution at metal centres, such as boron or tin, and photochemical techniques can now be used to investigate the mechanisms of the reactions. The rate constants which are observed are broadly parallel to those obtained for alkoxyl radicals, and it appears that the ketone triplets form a complex with the organoboron or organotin compound, which can decompose by loss of an alkyl radical or can revert to the parent organometallic compound and ground-state ketone, e.g.:

$Me_2CO^T + Bu_3B \rightleftharpoons Me_2COBBu_3 \rightarrow Me_2COBBu_2 + t\text{-}Bu^{\cdot}$

($k = 7 \times 10^6$ l mol^{-1} s^{-1} at 20°C; for t-BuO$^{\cdot}$, $k = 3 \times 10^7$ l mol^{-1} s^{-1} at 20°C).

The evidence for the existence of an intermediate in the S_H2 reactions of organoboranes and organotins is persuasive, but not compelling. On the other hand, the evidence for an intermediate in the reactions of organophosphines (and organoarsines) in incontrovertible, as the species $^{\cdot}PX_4$ (and $^{\cdot}AsX_4$) can be detected directly by ESR spectroscopy.

The phosphoranyl radicals usually have an approximately trigonal bipyramidal structure, with the unpaired electron occupying an equatorial site as a "phantom ligand". They show a large hyperfine coupling to phosphorus, e.g. t-BuOP$^{\cdot}$(OMe)$_3$, a (^{31}P) = 891 G, (t-BuO)$_2$PEt$_2$, a (^{31}P) = 705 G, with smaller coupling to the ligands, and positional exchange between the ligands can be observed with suitable examples. The phosphoranyl radicals may decompose by either α-scission or β-scission resulting in oxidation to a P^V compound, and the selectivity of these reactions for the apical or equatorial sites has been thoroughly investigated. Most of the work in this field has been carried out by Dr. B.P. Roberts.



β-Scission reactions

β-Scission processes such as those exhibited by some alkoxyphosphoranyl radicals, and generalised in the following equation, are common in free radical chemistry.

$X{-}A{-}B^{\cdot} \rightarrow X^{\cdot} + A{=}B$

An interesting example occurs in the reactions of organosilicon and organogermanium peroxides.

These compounds can readily be prepared by treating trialkylchlorosilanes or -germanes with the hydrogen peroxide complex of diazabicyclooctane.

$$4\ R_3SiCl + N(CH_2CH_2)_3N,\ 2\ H_2O_2 + N(CH_2CH_2)_3N \rightarrow 2\ R_3SiOOSiR_3 + 2[N(CH_2CH_2)_3N,\ 2\ HCl]$$

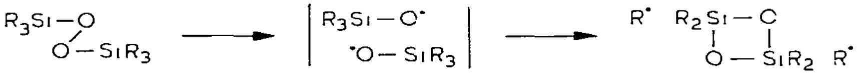
When bis(trimethylsilyl) peroxide is photolysed in solution, it gives the trimethylsiloxyl radical, Me$_3$SiO$^{\cdot}$, which is a useful alternative to the t-butoxyl radical, Me$_3$CO$^{\cdot}$, in free radical studies. Photolysis of the higher trialkylsilyl and trialkylgermyl peroxides at low temperature however shows the ESR spectra of the appropriate alkyl radicals $R^{\cdot}$. This is formally analogous to the familiar β-scission of t-alkoxyl radicals.

$R_3CO^{\cdot} \rightarrow R^{\cdot} + R_2CO$

A similar simple β-scission of trialkylsiloxyl radicals to give silanones can hardly be accepted because it would be strongly endothermic.

$R_3SiO^{\cdot} \rightarrow R^{\cdot} + R_2SiO$

It seems likely that the alkyl radicals are generated in a process that leads directly to the formation of two Si—O single bonds rather than one Si=O double bond, and this might occur in a cyclic process or between a caged pair of radicals, e.g.



No such ambiguity applies to the formation of trialkyltin radicals by β-scission processes. The $R_3Sn^{\cdot}$ radicals are important reagents particularly for the abstraction of halogen atoms from alkyl halides, and for adding to the double bond of alkenes. They are usually generated from the hydrides R_3SnH or the ditins R_3SnSnR_3, but these compounds are very reactive reducing agents, and alternative sources of the $R_3Sn^{\cdot}$ radicals would be useful.

If di-t-butyl peroxide is photolysed in the presence of acyclic tetraalkyltins, they undergo abstraction of hydrogen to give the α-stannylalkyl and β-stannylalkyl radicals, e.g.

$Et_4Sn + t\text{-}BuO^{\cdot} \rightarrow Et_3Sn\dot{C}HCH_3 + Et_3SnCH_2\dot{C}H_2$

The β-stannylalkyl radicals can then undergo β-scission to give a tin radical and an alkene, and by this process, trimethylisobutyltin serves as a useful source of tin radicals.

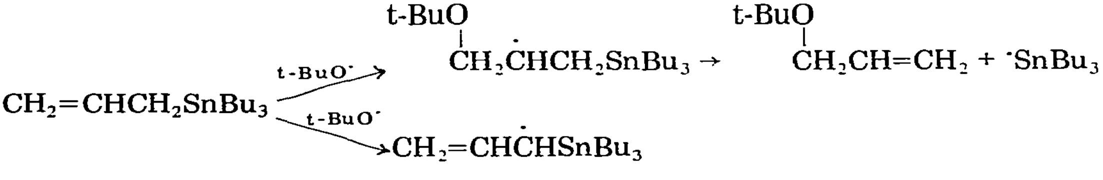
$t\text{-}BuO^{\cdot} + Me_3SnCH_2CHMe_2 \rightarrow Me_3SnCH_2\dot{C}Me_2 \rightarrow Me_3Sn^{\cdot} + CH_2{=}CMe_2$

Trialkyltin isopropoxides can be used in the same way:

$t\text{-}BuO^{\cdot} + Bu_3SnOCHMe_2 \rightarrow Bu_3SnO\dot{C}Me_2 \rightarrow Bu_3Sn^{\cdot} + O{=}CMe_2$

Photolysis of cyclopentadienylmetallic compounds

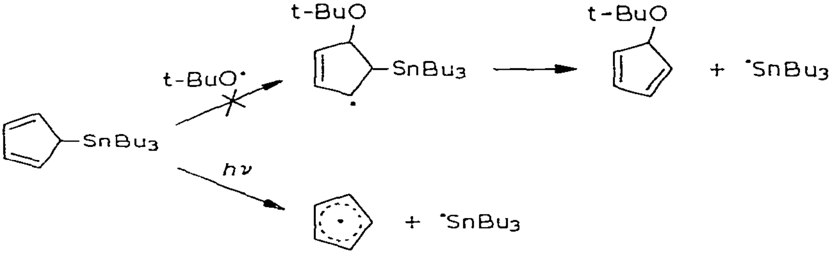
It was a search for further routes to trialkyltin radicals which led us into the field of the photolysis of cyclopentadienylmetallic compounds. One possibility seemed to be to generate a β-stannylalkyl radical by addition rather than by abstraction of hydrogen, but, not surprisingly, allyltributyltin reacted with t-butoxyl radicals to give the stannylallylic radical.



$$CH_2{=}CHCH_2SnBu_3 \xrightarrow{t\text{-}BuO^{\cdot}} \underset{t\text{-}BuO}{C}H_2\dot{C}HCH_2SnBu_3 \rightarrow \underset{t\text{-}BuO}{C}H_2CH{=}CH_2 + {}^{\cdot}SnBu_3$$

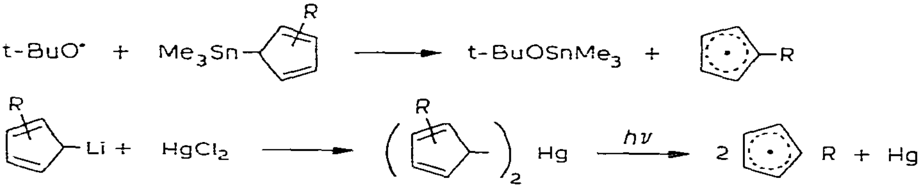
$$CH_2{=}CHCH_2SnBu_3 \xrightarrow{t\text{-}BuO^{\cdot}} CH_2{=}CH\dot{C}HSnBu_3$$

Dienes usually undergo homolytic addition more readily than monoenes, so tributylcyclopentadienyltin was subjected to the same reaction.



Surprisingly, the reaction showed a strong ESR spectrum of the cyclopentadienyl radical. We had carried out the right experiment for the wrong reason, and found a route to cyclopentadienyl radicals and to various metallic radicals, which had not previously been accessible. It is remarkable that, at the same time, Sakurai in Japan was carrying out the same reaction with a different but equally misguided aim. He had showed that cyclopentadienylsilanes underwent abstraction of hydrogen from the ring to give silylcyclopentadienyl radicals, $R_3SiC_5H_4^\cdot$, and by a similar reaction he hoped to obtain stannylcyclopentadienyl radicals, $Me_3SnC_5H_4^\cdot$. Our publications on this new route to cyclopentadienyl radicals appeared almost simultaneously.

Both radical fragments which are formed are important. The cyclopentadienyl radicals are the simplest π-annulene radicals which are known, and their ESR spectra would provide a way of investigating the interaction of substituents with the π-electron system but there was previously no route to the alkylcyclopentadienyl radicals because the cyclopentadienes underwent homolytic addition to the diene system rather than abstraction of hydrogens. Sakurai obtained these radicals by the S_H2 reaction of t-butoxyl radicals with alkylcyclopentadienyltrimethyltin compounds, and we obtained them by the unimolecular photolysis of alkylcyclopentadienylmercury compounds.



The stannyl radicals which are formed are important because previous studies were limited to the trialkyltin radicals, $R_3Sn^\cdot$. Photolysis of cyclopentadienyltin compounds $C_5H_5SnR_nX_{3-n}$ gave access for the first time to a variety of radicals $^\cdot SnR_nX_{3-n}$ (e.g. $X = Cl$, $n = 1$—3, or $X = CH_3CO_2$, $n = 3$), enabling the effect of the ligands on the properties of the radicals to be studied. The lead radicals $R_nX_{3-n}Pb^\cdot$ are also accessible from a similar route.

The spectra of the substituted cyclopentadienyl radicals can be interpreted in terms of the interaction of the substituent with the degenerate ψ_S and ψ_A molecular orbitals as shown in Figure 1. An electron-releasing substituent at C1 will destabilise the ψ_S MO which has a high coefficient at C1, but will not affect the ψ_A MO which has a node through this position. The unpaired electron will

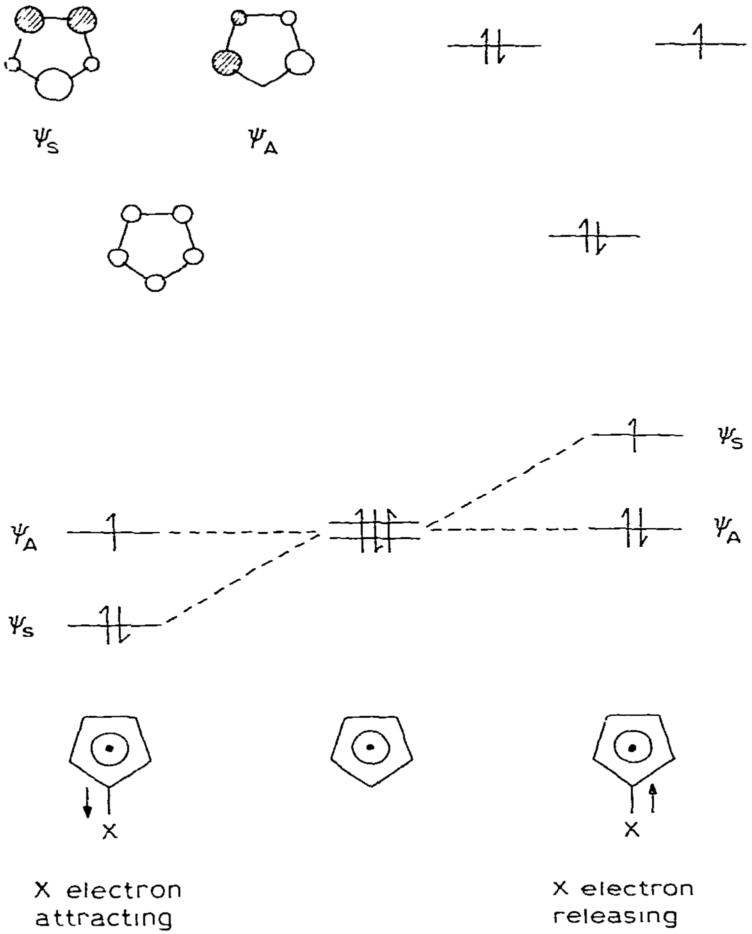


Fig. 1. Splitting of degenerate Hückel MOs of the cyclopentadienyl radical by electron attracting and electron releasing substitutents.

therefore occupy principally or wholly the ψ_S MO, and the ESR spectrum will reflect the spin density distribution in ψ_S. Conversely, an electron attracting substituent will stabilise ψ_S, and the ESR spectrum will reflect the spin density distribution in ψ_A. The predicted hyperfine coupling constants derived from the Hückel coefficients of ψ_S and ψ_A, and the observed coupling constants in some substituted cyclopentadienes are shown in Table 4.

In $Me_3CC_5H_4^{\cdot}$, the Me_3C group releases electrons causing the paired electron to occupy the destabilised ψ_S MO. Conversely, in $Me_3SiC_5H_4^{\cdot}$, the Cl_3Si group attracts electrons, stabilising the ψ_S MO, leaving the unpaired electron in the ψ_A MO. The Me_3Si group is less strongly electron attracting, and the configuration of the radical $Me_3SiC_5H_4^{\cdot}$ is approximately $\psi_S^{0.3}\psi_A^{0.7}$. Clearly this technique should be widely applicable for determining the electronic effects of other metallic and non-metallic substituents.

As yet, studies on the effect of the ligands on the properties of tin radicals have been carried out on alkyl, cyclopentadienyl, chloro, and acetoxy ligands,

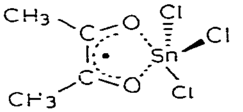
TABLE 4

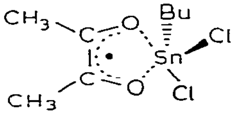
CALCULATED AND OBSERVED HYPERFINE COUPLING CONSTANTS IN SUBSTITUTED CYCLOPENTADIENES

	$a^{\star}$(H1)	a(H2,5)	a(H3,4)
Calcd. for ψ_S	(12.00)	1.1	7.8
Found for $MeC_5H_4^{\cdot}$	(12.69)	0.90	7.65
$Me_3CC_5H_4$	(12.78)	1.20	7.40
Calcd. for ψ_A	0.00	10.8	4.1
Found for $Cl_3SiC_5H_4^{\cdot}$	(—1.00)	11.60	3.85
Calcd. for 0.3 ψ_S: 0.7 ψ_A	3.60	7.85	5.26
Found for $Me_3SiC_5H_4^{\cdot}$	(3.94)	7.78	5.29

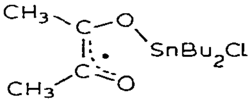
Replacing one or more alkyl groups in the radical $R_3Sn^{\cdot}$ by one of the other three more electronegative groups severely reduces the reactivity of the radicals in abstracting bromine from alkyl bromides or in adding to alkenes, but all the radicals still form adducts with 1,2-diketones, orthoquinones, and nitro compounds. In the adducts which the alkylchlorotin radicals form with biacetyl, hyperfine coupling by the chloro ligands has enabled the structures of the adducts to be interpreted in greater detail then before.

The adducts formed by the radicals $Cl_3Sn^{\cdot}$ and $BuCl_2Sn^{\cdot}$ show coupling by one unique chlorine atom and two slightly non-equivalent methyl groups at low temperature, but above about 10°C the methyl groups and the two or three chlorine atoms are apparently rendered equivalent. This is interpreted as implying chelated 5-coordinate tin in which trigonal bipyramidal structure causes the two methyl groups to be non-equivalent and allows only the apically positioned chlorine to couple. At higher temperatures, rapid positional permutation of the ligands about the tin removes the non-equivalence.

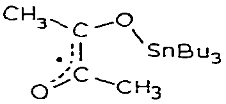


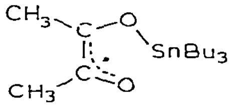


The adduct formed by the Bu_2SnCl radical on the other hand shows no coupling to chlorine, and two severely non-equivalent methyl groups over the whole range of temperature which can be studied. This probably implies a monodentate structure which is not fluxional on the ESR time scale.



Finally the $Bu_3Sn^{\cdot}$ radical shows the formation of two adduct radicals. The first, which is best observed at low temperatures, shows a low proton hyperfine coupling constant and a strong alternating line-width effect in the ESR spectrum and is assigned to the *trans* monodentate structure which is slowly fluxional. The second predominates at higher temperatures. The ESR spectrum is a binomial septet with a larger value of *a* (6 H) and with no alternating line width effect, and is thought to be the corresponding rapidly fluxional *cis*-radical.





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