

## An Electron Spin Resonance Study of the Reactivity of Organotin and Organolead Radicals

By John Cooper, Andrew Hudson, and Richard A. Jackson,\* School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

Tri-*n*-butyltin radicals were prepared by photolysis of mixtures of *t*-butyl peroxide and hexa-*n*-butylditin. E.s.r. competition experiments gave activation energy differences for the abstraction of the halogen atom from 15 organic halides by the tri-*n*-butyltin radical. The results indicate that polar as well as enthalpy effects are important. Qualitative work on trimethyl-lead radicals, prepared by photolysis of hexamethyldilead, shows that ease of removal of halogen from organic halides by the trimethyl-lead radical decreases in the order allyl bromide > carbon tetrachloride > alkyl bromides > alkyl and allyl chlorides.  $S_H2$  Displacements by *t*-butoxyl radicals of an alkyl radical from trialkyltin bromides, chlorides, and acetates, but not the hydrides, were observed.

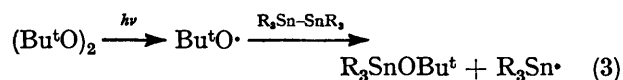
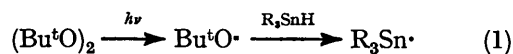
In an extension of our studies of reactions of trialkylsilyl radicals,<sup>1</sup> prepared by the abstraction of a hydrogen atom from  $R_3SiH$  by  $Bu^tO\cdot$ , we now report some reactions of organotin and organolead radicals, which show interesting differences in reactivity.

The e.s.r. spectral lines of organogermyl radicals are broader than those of organosilyl radicals,<sup>2</sup> probably due to the increased anisotropy of the  $g$  tensor coupled with the Brownian motion of the radicals: the lines in organotin and organolead radicals may be expected on these grounds to be broader still, thereby making these radicals more difficult to detect by e.s.r. In accordance with this, although the e.s.r. spectrum of the trimethyltin radical has recently been reported,<sup>3</sup> no other tin or lead centred radical has yet been observed in the liquid phase by e.s.r. spectroscopy. In the present work, the reactions of organotin and organolead radicals have been followed by observation of the organic radicals formed as products in these reactions.

### RESULTS AND DISCUSSION

*Reactions of Organotin Radicals.*—Two methods of formation of trialkyltin radicals were employed. (A) A mixture of *t*-butyl peroxide and the trialkyltin hydride was photolysed in the cavity of an e.s.r. spectrometer [reaction (1)].<sup>4</sup> Two disadvantages of this method, when used for kinetic studies of halogen atom abstractions, are

(i) the reactive alkyl radicals produced by reactions of type (4) may react with the organotin hydride, but at different rates, thus invalidating relationship (6) (see below), and (ii) if this method of making organotin radicals is used, trialkyltin halides rapidly accumulate in the system (by the sequence  $R_3Sn\cdot + R'Hal \rightarrow R_3SnHal + R'\cdot$ ;  $R'\cdot + R_3SnH \rightarrow R'H + R_3Sn\cdot$ ), which in turn gives rise to additional  $R\cdot$  radicals in the system by the  $S_H2$  process (11) discussed later, thus complicating the spectra. (B) These difficulties are avoided if photolysis of the hexa-alkylditin, either alone<sup>4</sup> (2) or with *t*-butyl peroxide<sup>3</sup> (3), is used as the source of trialkyltin radicals. The direct photolysis of hexa-alkylditin compounds alone was relatively unsatisfactory in terms of the radical concentration produced. Better results were obtained by photolysis of mixtures of the hexa-alkylditin and *t*-butyl peroxide: thus it appears that the  $S_H2$  reaction (3) is important (see also ref. 3).



<sup>2</sup> S. W. Bennett, C. Eaborn, A. Hudson, H. A. Hussain, and R. A. Jackson, *J. Organometallic Chem.*, 1969, **16**, P36.

<sup>3</sup> G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, 1972, **94**, 491.

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

<sup>1</sup> (a) A. Hudson and R. A. Jackson, *Chem. Comm.*, 1969, 1323; (b) A. J. Bowles, A. Hudson, and R. A. Jackson, *J. Chem. Soc. (B)*, 1971, 1947; (c) J. Cooper, A. Hudson, and R. A. Jackson, *Mol. Phys.*, 1972, **23**, 209 and papers cited therein.

Two main types of reaction were studied: halogen abstraction by organotin radicals, and  $S_H2$  reactions at tin centres.

(i) *Halogen abstraction.* Photolysis of hexa-n-butyl-ditin with t-butyl peroxide was used as the source of tin radicals for quantitative work. This allowed e.s.r. spectra to be recorded in the region  $-50$  to  $0^\circ$ . The tributyltin radicals produced by reaction (3) react with alkyl halides by reactions of type (4): if two halides are present, superimposed spectra of the two alkyl radicals  $R\cdot$  and  $R'\cdot$  are seen. If the two alkyl radicals produced



are lost mainly by termination reactions (likely to be true here because our reaction mixtures do not contain compounds which react rapidly with alkyl radicals), and the rate constants for termination reactions are effectively independent of the nature of the radical,<sup>5,6</sup> the relative concentration of the two radicals depends only on their rates of formation [equation (6)] since termin-

$$[\text{R}\cdot]/[\text{R}'\cdot] = k_4[\text{RHal}]/k_5[\text{R'Hal}'] \quad (6)$$

ation is random and causes the disappearance of radicals in proportion to the amount of each present, thereby not altering the relative concentrations. (For a more rigorous mathematical derivation of this result for an analogous system see ref. 7). From the variation of  $[\text{R}\cdot]/[\text{R}'\cdot]$  with temperature, activation energy differences for pairs of reactions (4) and (5) were evaluated. The values listed in Table 1 are differences in activation

TABLE 1  
Activation energies for the reaction  
 $\text{Bu}_3\text{Sn}\cdot + \text{RHal} \longrightarrow \text{Bu}_3\text{SnHal} + \text{R}\cdot$

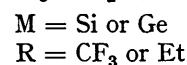
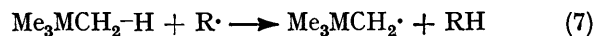
RHal	$E/kJ\ mol^{-1}$	RHal	$E/kJ\ mol^{-1}$
$\text{ICH}_2\text{CO}_2\text{Me}$	0.0 (assumed)	$\text{Bu}^t\text{Br}$	12.1
$\text{Me}_2\text{CBrCN}$	6.9	$\text{Pr}^t\text{Br}$	14.3
$\text{ClCH}_2\text{CN}$	7.2	cyclo- $\text{C}_6\text{H}_5\text{Br}$	14.4
$\text{Me}_3\text{SiCH}_2\text{Br}$	7.5	$\text{Me}_2\text{CCH}_2\text{Br}$	14.7
$\text{ClCH}_2\text{COMe}$	8.6	$\text{Pr}^n\text{Br}$	14.9
$\text{CH}_2=\text{CH}\cdot\text{CH}_2\text{Br}$	12.0	$\text{CH}_2=\text{CH}\cdot\text{CH}_2\text{Cl}$	19.5
$\text{MeCHBrCO}_2\text{Et}$	12.1	$\text{Bu}^t\text{Cl}$	34.9
		$\text{Pr}^t\text{Cl}$	40.8

energy for reactions of type (4) between the alkyl halide concerned and ethyl iodoacetate. The activation energy for the abstraction of I from  $\text{ICH}_2\text{CO}_2\text{Me}$  is probably effectively zero, on the basis of the following considerations. (a) The difference in activation energies for reactions of type (2) between  $\text{Pr}^t\text{Cl}$  and  $\text{Pr}^t\text{Br}$  is 27 kJ

$\text{mol}^{-1}$ , between  $\text{ClCH}_2\text{CN}$  and  $\text{Me}_2\text{CBrCN} < 1\ \text{kJ}\ \text{mol}^{-1}$ ; likewise  $E_{\text{Pr}^t\text{Cl}} - E_{\text{Bu}^t\text{Cl}} = 6\ \text{kJ}\ \text{mol}^{-1}$ ,  $E_{\text{Pr}^t\text{Br}} - E_{\text{Bu}^t\text{Br}} = 2\ \text{kJ}\ \text{mol}^{-1}$ . The lower differences between the second pairs in each group indicate that these reactions probably have low activation energies, such that differences in structure can have little effect. (b) If  $E_2$  ( $\text{RHal} = \text{ICH}_2\text{CO}_2\text{Et}$ ) = 0, we can calculate  $A$  factors for the corresponding reactions with t-butyl chloride and bromide as  $10^{10.32}$  and  $10^{10.05}\ \text{l}\ \text{mol}^{-1}\ \text{s}^{-1}$  respectively, from our activation energy differences combined with the absolute rate constant determinations made at  $25^\circ$  by Carlsson and Ingold.<sup>5</sup> These  $A$  factors appear somewhat high for radical transfer reactions (values within the range  $10^8$ – $10^9$  are normal in the gas phase<sup>8</sup>); if  $E_4$  ( $\text{RHal} = \text{ICH}_2\text{CO}_2\text{Et}$ ) is significantly greater than zero, the  $A$  factors would have to be still higher, which would be implausible.

*Trends.* Two well established trends in reactivity of organotin radicals with alkyl halides<sup>9,10</sup> are that rates increase in the order primary < secondary < tertiary for different alkyl groups in the alkyl halide, and the ease of abstraction of halogens increases in the order  $\text{Cl} < \text{Br} < \text{I}$ . The data in Table 1 indicate that activation energy differences are important in determining these reactivity trends. The difference between primary and tertiary halides may be rationalized in terms of the stability of the radical produced, and thus an increase in the exothermicity of the reaction, but other factors must be important for the differences between chlorides, bromides, and iodides, since the exothermicities of the halogen abstraction reactions are apparently quite similar for all three groups of compound.<sup>5,10</sup>

The increased reactivity of  $\text{Me}_3\text{SiCH}_2\text{Br}$  compared with  $\text{Me}_3\text{CCH}_2\text{Br}$  towards attack by tributyltin radicals may partly reflect stabilization in the  $\text{Me}_3\text{SiCH}_2\cdot$  radical due to delocalization of the unpaired electron into a silicon  $d$  orbital,<sup>11</sup> but polar effects are probably also important since the corresponding hydrogen abstraction reactions from  $\text{Me}_4\text{M}$  by trifluoromethyl<sup>12</sup> and ethyl<sup>13</sup> radicals (7) show smaller activation energy differences even though the overall activation energies are higher. It is probable that polar contributions involving negative rather than



positive charge on the methylene group are more important in stabilizing the transition state, *i.e.*  $[\text{Me}_3\text{SiCH}_2\text{-Br}\cdot + \text{SnBu}_3]$  is more important in reaction (4) than  $[\text{Me}_3\text{SiCH}_2\text{+H}\cdot\text{-CF}_3]$  is in reaction (7), since in

<sup>5</sup> D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, 1968, **90**, 7047.

<sup>6</sup> D. J. Carlsson, K. U. Ingold, and L. C. Bray, *Internat. J. Chem. Kinetics*, 1969, **1**, 315.

<sup>7</sup> A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc. (B)*, 1971, 1823.

<sup>8</sup> S. W. Benson, 'Thermochemical Kinetics,' Wiley, New York, 1968.

<sup>9</sup> H. G. Kuivila, *Adv. Organometallic Chem.*, 1964, **1**, 47; *Accounts Chem. Res.*, 1968, **1**, 299.

<sup>10</sup> R. A. Jackson, *Adv. Free Radical Chem.*, 1969, **3**, 231; *Chem. Soc. Special Publ. No. 24*, 1970, 295.

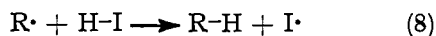
<sup>11</sup> J. H. Mackey and D. E. Wood, *Mol. Phys.*, 1970, **18**, 783; T. Kawamura and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 648.

<sup>12</sup> T. N. Bell and A. E. Platt, *Internat. J. Chem. Kinetics*, 1970, **2**, 299.

<sup>13</sup> P. J. Boddy and E. W. R. Steacie, *Canad. J. Chem.*, 1960, **38**, 1576.

$\text{Me}_3\text{SiCH}_2^-$  the negative charge can be delocalized into the  $d$  orbitals of the silicon atom, but in  $\text{Me}_3\text{SiCH}_2^+$  there is no possibility of such stabilization.

The activation energy  $E_2$  falls in the series  $\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl} > \text{MeCOCH}_2\text{Cl} > \text{ClCH}_2\text{CN}$ . This is inconsistent with the stabilization of the intermediate radical being of dominant importance since there should be greater stabilization in the allyl than in the acetylonyl or  $\cdot\text{CH}_2\text{CN}$  radical because of the symmetrical nature of the  $\pi$  system in the allyl radical. The extent of stabilization of the acetylonyl radical is uncertain. The barrier to rotation about the  $\text{CH}_2-\text{CO}$  bond in the acetylonyl radical has been measured in aqueous solution<sup>14</sup> as  $39.5 \text{ kJ mol}^{-1}$ , indicating a stabilization energy in this region (the stabilization energy of the allyl radical in the gas phase is believed<sup>15</sup> to be *ca.*  $40 \text{ kJ mol}^{-1}$ ). On the other hand Solly *et al.*<sup>16</sup> have suggested that the stabilization energy of the acetylonyl radical is effectively zero. However, this low value depends on the generalization that the activation energies for reactions of type (8) are  $4 \pm 4 \text{ kJ mol}^{-1}$ , which may break down for  $\text{R} = \text{acetylonyl}$  because of the lack of favourable polar contributions to the transition state (contributions of the type  $[\text{R}^+ \text{H} \cdot \text{I}^-]$  may be important for  $\text{R} = \text{alkyl}$ , but are not likely to contribute significantly for  $\text{R} = \text{acetylonyl}$ ).

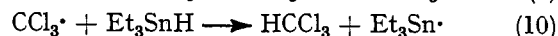
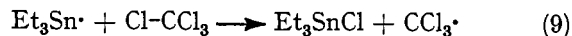


Thus the observed reactivity in the halogen abstraction (4) of  $\text{MeCOCH}_2\text{Cl}$  and  $\text{ClCH}_2\text{CN}$  is probably due to favourable polar contributions in the transition state when these compounds react with an electropositive radical (*e.g.* contributions of the type  $[\text{MeCOCH}_2^- \text{Cl} \cdot^+ \text{SnBu}_3]$ ). [An extreme example of the influence of such polar effects is probably shown by the reaction of sodium atoms with organic chlorides:<sup>17</sup> although the drop in activation energy on going from isopropyl chloride to allyl chloride ( $11 \text{ kJ mol}^{-1}$ ) is less than for the corresponding reactions of tributyltin radicals ( $21 \text{ kJ mol}^{-1}$ ), the drop on going from allyl chloride to chloroacetone is almost twice as great for the sodium atom reactions (18 as opposed to  $11 \text{ kJ mol}^{-1}$ ).]

The extreme reactivity of ethyl iodoacetate is probably due to a combination of polar effects of this sort, together with the greater ease of abstraction of iodine compared with the other halogens.

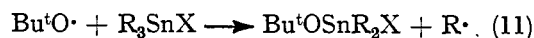
A vigorous exothermic reaction takes place when triethyltin hydride and carbon tetrachloride are mixed at room temperature (*cf.* ref. 5). We find that the reaction is inhibited by galvinoxyl, which indicates that the reaction is a free radical chain process, probably with the two propagation steps (9) and (10) which are normal for this type of reaction. A low value for the activation energy and a high value for the rate constant of (9)

would accord with the polar effects discussed above



(carbon tetrachloride is more than twice as reactive as allyl bromide towards tributyltin radicals<sup>18</sup> at  $45^\circ$ ), and the rapidity of the reaction may cause heat to be liberated too fast for thermal equilibrium to be maintained.

(ii)  $S_{\text{H}2}$  Reactions. When mixtures of *t*-butyl peroxide with trimethyltin bromide, triethyltin bromide, triethyltin acetate, or tri-*n*-butyltin chloride were photolysed, *e.s.r.* spectra of methyl, ethyl, ethyl, or *n*-butyl radicals respectively were observed, confirming the recent, similar observations by Davies and his co-workers.<sup>19</sup> Thus it appears that *t*-butoxyl radicals undergo  $S_{\text{H}2}$  attack at the tin atom in these compounds with the displacement of an alkyl radical [reaction (11)]. This type of reaction is not observed with the corresponding silicon compounds, which accords with other evidence



that  $S_{\text{H}2}$  attack at tin is more ready than at silicon, nor do  $S_{\text{H}2}$  reactions appear to occur when *t*-butoxyl radicals react with trialkyltin hydride alone. It appears (as is reasonable) that the  $S_{\text{H}2}$  reaction cannot compete with hydrogen abstraction from the M-H group.

These  $S_{\text{H}2}$  reactions at tin may be synchronous, or may involve a penta-co-ordinate intermediate  $\text{R}_3\text{SnX}(\text{OBu}^t)$ . We have not been able to observe such an intermediate by *e.s.r.* spectroscopy.

The occurrence of these  $S_{\text{H}2}$  reactions is one of two reasons (see beginning of paper) why the reaction between  $\text{Bu}^t\text{O} \cdot$  and  $\text{R}_3\text{SnSnR}_3$  was preferred as a source of  $\text{R}_3\text{Sn} \cdot$  radicals for kinetic studies on halogen abstraction reactions.

*Addition to unsaturated compounds.* Photolysis of a mixture of hexa-*n*-butylditin and acetone resulted in an *e.s.r.* spectrum identified as  $\text{Me}_2\dot{\text{C}}\text{OSnBu}_3$  ( $a_{\text{H}} = 19.1 \text{ G}$ ). On the other hand, addition to methyl formate could not be observed (contrast triethylsilyl radicals, which give adduct radicals with formates<sup>1b</sup> but not with acetates<sup>1b,20</sup>).

*Lead Radicals.*—Photolysis of hexamethyldilead in pentane (with or without *t*-butyl peroxide) gave a lead mirror on the wall of the tube but no spectrum attributable to the trimethyl-lead radical; presumably the same factors which make tin radicals difficult to see are even more important for lead.

The intermediacy of trimethyl-lead radicals in this photolysis may be inferred from the observation that when reactive organic halides such as allyl bromide are present, the lead mirror is not formed, but is replaced by

<sup>14</sup> G. Golde, K. Möbius, and W. Kaminski, *Z. Naturforsch.*, 1969, **24a**, 1214.

<sup>15</sup> D. M. Golden, N. A. Gac, and S. W. Benson, *J. Amer. Chem. Soc.*, 1969, **91**, 2136.

<sup>16</sup> R. K. Solly, D. M. Golden, and S. W. Benson, *Internat. J. Chem. Kinetics*, 1970, **2**, 11.

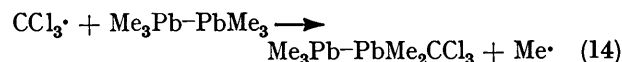
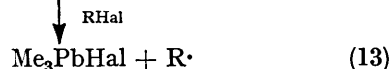
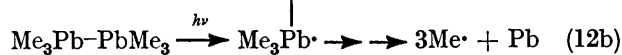
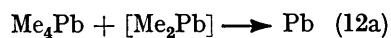
<sup>17</sup> E. Warhurst, *Quart. Rev.*, 1951, **5**, 44.

<sup>18</sup> L. W. Menapace and H. G. Kuivila, *J. Amer. Chem. Soc.*, 1964, **86**, 3047.

<sup>19</sup> A. G. Davies, B. P. Roberts, and J. C. Scaiano, *J. Organometallic Chem.*, 1972, **89**, C55.

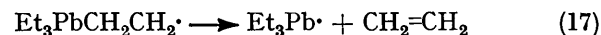
<sup>20</sup> J. Cooper, A. Hudson, and R. A. Jackson, unpublished work.

a white precipitate, presumably of impure trimethyl-lead halide, and the spectrum of the appropriate organic radical is observed (Table 2). Thus for reactive halides,



it appears that the abstraction reaction (13) can compete with the decomposition of the trimethyl-lead radical (12). For *t*-butyl bromide, reactions (12) and (13) seem well balanced, since a lead mirror is formed along with a

of *t*-butyl peroxide. The absence of a signal attributable to  $\text{Et}_3\text{Pb}\dot{\text{C}}\text{HCH}_3$  implies that abstraction of the  $\alpha$ -hydrogen atom is not so significant as in the analogous reaction with tetraethyltin.<sup>21</sup> It is possible that  $\beta$ -hydrogen abstraction by the *t*-butoxyl radical so produced would be expected on thermochemical grounds to fragment rapidly into a triethyl-lead radical and ethylene<sup>10</sup> [reaction (17)], and therefore would not be expected to give rise to an observable e.s.r. spectrum.



When a solution of tetraethyl-lead and allyl bromide in *n*-pentane was photolysed, the spectrum of the allyl radical was observed. A lead mirror was not formed, but a precipitate of triethyl-lead bromide appeared.

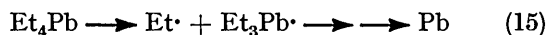
TABLE 2  
Photolysis of hexamethyldilead in the presence of organic halides

Halide	Temp. range (°C)	Solvent	Radical observed	Lead mirror	White precipitate observed
None	-50	Pentane	Me· (weak)	Yes	
EtBr	-80 to +10	Pentane	Et·	Yes	
Pr <sup>i</sup> Br	-90 to -70	Pentane	Pr <sup>i</sup> ·	Yes	
Bu <sup>t</sup> Br	-50 to 0	Pentane	Bu <sup>t</sup> ·	Yes	Yes
CH <sub>2</sub> =CH·CH <sub>2</sub> Br	-50	Pentane	CH <sub>2</sub> =CH·CH <sub>2</sub> ·	No	Yes
Bu <sup>n</sup> Cl	-60 to 0	Pentane		Yes	
Pr <sup>i</sup> Cl	-60 to 0	Pentane		Yes	
Bu <sup>t</sup> Cl	-50 to 0	Pentane		Yes	
CH <sub>2</sub> =CH·CH <sub>2</sub> Cl	-60	Pentane	[Weak Me·]	Yes	
CCl <sub>4</sub>	-50	Pentane or CCl <sub>4</sub>	Me· + CCl <sub>3</sub> ·	No	Yes
CH <sub>2</sub> =CH·CH <sub>2</sub> Br	-50	CCl <sub>4</sub>	CH <sub>2</sub> =CH·CH <sub>2</sub> ·	No	Yes

white precipitate. Less reactive bromides give a mirror but no appreciable white precipitate. The spectrum of ethyl from ethyl bromide was less intense at -80° than at higher temperatures, indicating that the abstraction reaction (13; RHal = EtBr) must have a significant activation energy. Alkyl and allyl chlorides are too unreactive for reaction (13) to occur. Due to the formation of the lead mirror, it was not possible to carry out competition experiments: however a general reactivity order allyl bromide > CCl<sub>4</sub> > alkyl bromides > allyl and alkyl chlorides was established. This order is similar to that found for the corresponding reactions of tri-*n*-butyltin radicals, but the positions of allyl bromide and carbon tetrachloride are reversed.

When hexamethyldilead was photolysed in the presence of carbon tetrachloride, the spectra of both trichloromethyl and methyl radicals were seen. This indicates that the trichloromethyl radical may attack at a lead centre in the hexamethyldilead [reaction (14)].

When tetraethyl-lead was photolysed in pentane at -50°, a lead mirror was formed and the spectrum of the ethyl radical was observed, suggesting the homolytic sequence (15). The intensity of the ethyl radical



spectrum was not noticeably affected by the presence

This indicates that the triethyl-lead radicals formed during the photolysis will abstract a bromine atom from the allyl bromine in confirmation of the observations made with hexamethyldilead and allyl bromide [reaction (13)].

*Addition of lead radicals to multiple bonds.* Although trialkyltin radicals add to ethylene and other olefins, it has been predicted on thermochemical grounds that trialkyl-lead radicals should not add to simple olefins [see reaction (17)].<sup>10</sup> In support of this, we did not observe the  $\text{Me}_3\text{PbCH}_2\text{CH}_2\cdot$  radical when hexamethyldilead was photolysed in pentane in the presence of ethylene. We were also unsuccessful in adding  $\text{Me}_3\text{Pb}\cdot$  to buta-1,3-diene (a reaction which should be less thermodynamically unfavourable than the addition to ethylene) or to benzophenone.

#### EXPERIMENTAL

*Materials.*—*t*-Butyl peroxide was purified by treatment with acidic potassium iodide solution, followed by filtration through activated alumina. Hexamethyldilead was a gift from Dr. F. Waugh. Hexa-*n*-butylditin was from B.D.H. Tri-*n*-butyltin hydride was prepared from the chloride

<sup>21</sup> P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1969, **91**, 6161.

(B.D.H.) by reduction with lithium aluminium hydride.<sup>22</sup> The other tin compounds were available in the laboratory. Methyl iodoacetate was prepared by esterification of the acid.  $\alpha$ -Bromoisobutyronitrile was prepared by the method of Stevens.<sup>23</sup> Other halides were of the purest commercial grade available, and were distilled before use.

*E.s.r. Competition Experiments.*—A stock solution of *ca.* 75% *t*-butyl peroxide, 15% hexa-*n*-butylditin, and 10% of a mixture of the two halides was made up. The mixtures of halides were made upon a trial and error basis until a ratio of weights of halides was found which gave e.s.r. signals due to the two radicals which were of comparable intensity. Samples of the stock solution were degassed in the sample tubes by freezing and thawing under vacuum. Ratios of radical concentrations were obtained to within a scale factor by rapid scanning over single peaks, followed by comparison of peak heights. In the case of the cyanomethyl radical it was necessary to make allowance for the effect of temperature on the line width<sup>24</sup> by comparing peak heights with integrals obtained by the second moment method. For each pair of halides, 10–13 points were obtained in the temperature range  $-60$  to  $0^\circ$ . The results were treated by the least-squares method. Selective depletion of one of the halides, with a consequent need to extrapolate results back to zero time, was not a problem with most of the halide mixtures used.

Because of the difficulty caused by overlapping of peaks, only a limited number of cross-checks could be carried out. The activation energy difference for  $\text{Bu}^t\text{Br} - \text{Pr}^n\text{Br}$  was measured as  $3.3 \pm 0.4$  kJ mol<sup>-1</sup> by direct comparison, whereas indirect comparison *via*  $\text{Pr}^i\text{Br}$  indicated  $2.0 \pm 0.5$ .

<sup>22</sup> H. G. Kuivila and O. F. Beumel, jun., *J. Amer. Chem. Soc.*, 1961, **83**, 1246.

<sup>23</sup> C. L. Stevens, *J. Amer. Chem. Soc.*, 1948, **70**, 165.

For  $\text{Bu}^t\text{Cl}$  and  $\text{Pr}^n\text{Br}$  the difference was  $22.1 \pm 3.3$  (direct) and  $19.5 \pm 1.5$  kJ mol<sup>-1</sup> (indirect, *via* allyl chloride). (Error limits were determined from least-squares analysis of the Arrhenius plots.) The random error associated with the difference between  $\text{Pr}^i\text{Cl}$  and  $\text{ICH}_2\text{CO}_2\text{Me}$  (*via* *t*-butyl chloride, *n*-propyl bromide, and allyl bromide) is 2.9 kJ mol<sup>-1</sup>, though systematic errors may be greater than this.

*Reaction of Hexamethyldilead with Carbon Tetrachloride.*—Photolysis of a solution of hexamethyldilead in carbon tetrachloride at  $-40^\circ$ , followed by addition of pentane gave a white solid of indefinite m.p. (some sublimation at *ca.*  $180^\circ$  was observed). Extraction of the solid with acetone left most of the solid undissolved, but evaporation of the extract yielded a small amount of white solid, the mass spectrum of which showed it to be a mixture. An intense series of peaks in the region of *m/e* 288 in the mass spectrum showed the correct pattern for  $\text{Me}_3\text{PbCl}$ .

*Reaction of Tetraethyl-lead with Allyl Bromide.*—A solution of allyl bromide (2.4 g) and tetraethyl-lead (7 g) in pentane (100 ml) was photolysed at  $0^\circ$  for 15 h using a 250 W tungsten lamp. A small amount of pale yellow solid was filtered off, and the filtrate was evaporated to a third of its volume, when white crystals (*ca.* 500 mg) were deposited, m.p.  $101-103^\circ$  (lit.,<sup>25</sup> for  $\text{Et}_3\text{PbBr}$ ,  $103-104^\circ$ ) (Found: C, 19.5; H, 4.25. Calc. for  $\text{C}_6\text{H}_{15}\text{BrPb}$ : C, 19.35; H, 4.05%).

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<sup>24</sup> H. G. Benson, A. J. Bowles, A. Hudson, and R. A. Jackson, *Mol. Phys.*, 1971, **20**, 713.

<sup>25</sup> R. W. Leeper, L. Summers, and H. Gilman, *Chem. Rev.*, 1954, **54**, 101.