316. *Aromatic Reactivity. Part X.* Relative Rates of Cleavage of Aryl–Silicon, –Tin, –Germanium, and –Lead Bonds by Aqueous-ethanolic Perchloric Acid.*

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We have measured the rates of cleavage of some $ArMR_3$ compounds, where M = Si, Ge, Sn, and Pb, by aqueous-ethanolic perchloric acid. The relative reactivities of $PhMEt_3$ compounds are approximately (M =) Si 1, Ge 36, Sn $3{\cdot}5 \times 10^5$, Pb 2×10^8, a reactivity sequence which appears to be unrelated to the electronegativities of the metals concerned. The predominant effects in the series (M =) Si, Ge, Sn, Pb may be increasing availability of *d*-orbitals in the valency shell and decreasing C–M bond strength. Possible mechanisms for the cleavage are discussed.

THE great majority of studies of electrophilic aromatic substitution have been concerned with hydrogen as the leaving group along with a large variety of entering groups. We now concentrate attention on the leaving group in a study of the acid-catalysed solvolysis of some $ArMR_3$ compounds, where M = Si, Ge, Sn or Pb:

$$ArMR_3 + YOH \xrightarrow{H^+} ArH + R_3M{\cdot}OH \quad (Y = H \text{ or } Et)$$

Applying the spectrophotometric technique used for aryltrimethylsilanes,[1] we have measured the rates of cleavage at 50·0° of the $ArMR_3$ compounds in ethanol containing 16·7 vol.-% of aqueous perchloric acid. From the pseudo-first-order rate constants listed in Table 1, relative reactivities listed in Table 2, section (i), have been calculated. Section (ii) of Table 2 lists some reactivity ratios available from other work, and section (iii) lists reactivity ratios derived by combining the figures of sections (i) and (ii), making some assumptions, implicit in the statements in parentheses in section (ii), which are not likely to introduce serious error. We thus arrive at the following approximate relative reactivities for $C_6H_5MEt_3$ compounds: † (M =) Si, 1; Ge, 36; Sn, $3{\cdot}5 \times 10^5$; Pb, 2×10^8.

TABLE 1. *Rates of cleavage of* $ArMR_3$ *compounds at* 50·0° *in ethanol containing* 16·7% *of aqueous perchloric acid.*

(i) Cleavage of p-$MeO{\cdot}C_6H_4{\cdot}MR_3$:

$[HClO_4]$ [a] (M)	MR_3	10^3k (min.$^{-1}$)	$[HClO_4]$ [a] (M)	MR_3	10^3k (min.$^{-1}$)
8·01	$SiEt_3$	26·3	4·10	$Ge(C_6H_{11})_3$	11·3
8·01	$Si(C_6H_{11})_3$	2·53	2·05	$SiEt_3$	0·74
8·01	$Ge(C_6H_{11})_3$	103	2·05	$GeEt_3$	11·9
4·10	$SiEt_3$	3·03	0·01	$SnEt_3$	19·6
4·10	$Si(C_6H_{11})_3$	0·28	0·01	$Sn(C_6H_{11})_3$	9·7
4·10	$GeEt_3$	46·7			

(ii) Cleavage of $ArMR_3$:

$[HClO_4]$ [a] (M)	Compound	10^3k (min.$^{-1}$)	$[HClO_4]$ [a] (M)	Compound	10^3k (min.$^{-1}$)
0·970	$C_6H_5.SnEt_3$	64·2	0·0057	p-$MeO{\cdot}C_6H_4{\cdot}SnEt_3$	10·6
0·970	$2,4,6$-$Me_3C_6H_2{\cdot}SiMe_3$	20·3	0·0057	$C_6H_5{\cdot}PbEt_3$	101

[a] Strength of acid, 1 vol. of which was added to 5 vol. of an ethanolic solution of $ArMR_3$.

The $ArMR_3 : ArM'R_3$ ratios depend on the nature of the aryl group, as shown, for example, by the fact that change from $C_6H_5{\cdot}MR_3$ to p-$MeO{\cdot}C_6H_4{\cdot}MR_3$ causes a 1500-fold increase in reactivity when $MR_3 = SiMe_3$ (in aqueous-methanolic perchloric acid) [1a] but

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* Part IX, *J.*, 1960, 1482.

† It should be noted that the $Et_3Si{\cdot}C_6H_5 : Et_3Ge{\cdot}C_6H_5$ ratio refers to cleavage by aqueous-methanolic perchloric acid.

[1] (*a*) Eaborn, *J.*, 1956, 4858; (*b*) Deans and Eaborn, *J.*, 1959, 2299.

TABLE 2. *Relative rates of cleavage of* $ArMR_3$ *compounds.*

(i) Observed relative rates:

p-MeO·C_6H_4·$GeEt_3$: p-MeO·C_6H_4·$SiEt_3$ = 15·5 (15·4 with 4·1M-acid; ~16·1 with 2·05M-acid).
p-MeO·C_6H_4·Ge$(C_6H_{11})_3$: p-MeO·C_6H_4·Si$(C_6H_{11})_3$ = 40·5 (40·7 with 8·0M-acid; 40·2 with 4·1M-acid).
p-MeO·C_6H_4·$SiEt_3$: p-MeO·C_6H_4·Si$(C_6H_{11})_3$ = 10·6
p-MeO·C_6H_4·$GeEt_3$: p-MeO·C_6H_4·Ge$(C_6H_{11})_3$ = 4·1
p-MeO·C_6H_4·$SnEt_3$: p-MeO·C_6H_4·Sn$(C_6H_{11})_3$ = 2·0
C_6H_5·$SnEt_3$: 2,4,6-$Me_3C_6H_2$·$SiMe_3$ = 3·15
C_6H_5·$PbEt_3$: p-MeO·C_6H_4·$SnEt_3$ = 9·5

(ii) Other relative rates used:

C_6H_5·$GeEt_3$: C_6H_5·$SiEt_3$ = 35·6 (in aqueous-methanolic perchloric acid).
2,4,6-$Me_3C_6H_2$·$SiMe_3$: C_6H_5·$SiMe_3$ = 53,600 (in aqueous-methanolic perchloric acid [a]).
C_6H_5·$SiMe_3$: C_6H_5·$SiEt_3$ = 2·1 (actually ratio for p-MeO compounds in aqueous-methanolic perchloric acid [b]).
p-MeO·C_6H_4·SnR_3 : C_6H_5·SnR_3 = 63 (for R = C_6H_{11} in ethanol containing 3·8 vol.-% of aqueous perchloric acid [c]).

(iii) Derived relative rates:

C_6H_5·$SnEt_3$: C_6H_5·$SiEt_3$ = $3{\cdot}15 \times 2{\cdot}1 \times 53{,}600 = 3{\cdot}5 \times 10^5$.
C_6H_5·$PbEt_3$: C_6H_5·$SnEt_3$ = $63 \times 9{\cdot}5 = 598$.

[a] Ref. 1*a*. [b] Unpublished work by Miss P. M. Greasley. Ref. 2.

only a 60-fold increase when $MR_3 = Sn(C_6H_{11})_3$ (in aqueous-ethanolic perchloric acid).[2] (The change in R and in the medium contribute very little to this difference.) Again, the C_6H_5·$GeEt_3$: C_6H_5·$SiEt_3$ ratio is 35·6 (in aqueous-methanolic acid) but the p-MeO·C_6H_4·$GeEt_3$: p-MeO·C_6H_4·$SiEt_3$ ratio is only 15 (in aqueous-ethanolic acid).

An $ArMR_3$: $ArM'R_3$ ratio also depends on the nature of R. In particular, large R groups hinder reaction more the smaller is M, as shown by the p-MeO·C_6H_4·MEt_3 : p-MeO·C_6H_4·M$(C_6H_{11})_3$ ratios in Table 2(i).

It is interesting to include Ar–CR_3 and Ar–H bonds in the reactivity comparisons, even though the figures for them can only be approximations. De-deuteration of monodeuterobenzene in 79·2 wt.-% sulphuric acid has a rate constant of $4{\cdot}53 \times 10^{-5}$ sec.$^{-1}$ at 25°.[3] Cleavage of the compound p-NO_2·C_6H_4·$SiMe_3$ in this acid has a rate constant of of $2{\cdot}2 \times 10^{-3}$ sec.$^{-1}$ at 35°,[4] and thus (using the temperature coefficient of 2·9/10° measured in sulphuric acid–acetic acid–water [1b]) of *ca.* 8×10^{-4} at 25°. The ratio p-NO_2·C_6H_4·$SiMe_3$: C_6H_5D is thus *ca.* 18. Using the ratio C_6H_5·$SiMe_3$: p-NO_2·C_6H_4·$SiMe_3$ of *ca.* $0{\cdot}8 \times 10^4$ observed in sulphuric acid–acetic acid–water,[1b] and assuming a C_6H_5·H : C_6H_5D ratio of *ca.* 4 * we arrive at a C_6H_5·$SiMe_3$: C_6H_5·H ratio of *ca.* 4×10^4.

In bromination by Br^+ or $BrOH_2^+$, the C_6H_5–CMe_3 bond is broken 1·4 times as readily as a C_6H_5–H bond,[6] and a factor of the same order of magnitude is likely to apply when the electrophilic reagent is oxonium ion and the displaced group is CEt_3. We can thus write the complete series of relative reactivities of Ar–X compounds towards acid very roughly as follows:

X = ...	H	CEt_3	$SiEt_3$	$GeEt_3$	$SnEt_3$	$PbEt_3$
Rel. reactivity	1	(1)	10^4	10^6	10^{10}	10^{13}

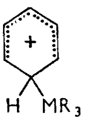
The main factors which might be expected to influence the relative reactivities of $ArMR_3$ compounds in the series M = Si, Ge, Sn, and Pb are (i) the electronegativity of M, (ii) the strength of the Ar–M bond, (iii) the accessibility of *d*-orbitals in the valency shell of M (which increases with increasing atomic number), and (iv) the size of M. The information available on factors (i) and (ii) requires discussion.

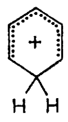
The question of the electronegativities of the Group IVB metals, which is in dispute,

* Compare the [$^2H_1$]benzene : [$^3H_1$]benzene ratio of 1·5.[5]

[2] Eaborn and Waters, unpublished work.
[3] Gold and Satchell, *J.*, 1955, 3619.
[4] Deans and Eaborn, unpublished work.
[5] Melander and Olsson, *Acta Chem. Scand.*, 1956, **10**, 879.
[6] de la Mare and Harvey, *J.*, 1957, 131.

has been reviewed by Allred and Rochow.[7] From thermochemical data, the values on the Pauling scale [8] (extended by Haissinky [9] to include Pb^{IV}) are: Si, 1·8; Ge, 1·7; Sn, 1·7; Pb, 2·4 (C, 2·5; H, 2·1), and on the Huggins [10] scale: Si, 1·9; Ge, 1·9; Sn, 1·9 (C, 2·60; H, 2·2). From nuclear quadrupole resonance studies, Gordy [11] obtains: Si, 1·99; Ge, 2·03; Sn, 1·92 (C, 2·54). On the basis of Sanderson's " stability ratio," [12] the values are Si, 1·74; Ge, 2·31; Sn, 2·02; Pb, 2·37 (C, 2·47; H, 2·31).[12] Pritchard and Skinner [13] select " best values " of Si, 1·8—1·9; Ge, 1·8—1·9; Sn, 1·8—1·9; Pb, 1·8 (C, 2·5—2·6; H, 1·8—1·9). Values obtained by Allred and Rochow [7] from nuclear magnetic resonance studies of Me_4M compounds (assuming values of 2·60 for C and 1·90 for Si) are: Ge, 2·00; Sn, 1·93; Pb, 2·45. These last values, which have been shown to be consistent with many physical and chemical properties,[7] are derived from a direct measure of electron-release from a Me_3M group to the carbon atom of a CH_3 group, and thus appear to be most suitable for our purposes, since we are concerned with the ability of R_3M groups to release electrons to a carbon atom [which is mainly of the *sp*^{3}-bonded type in the intermediate (I) and transition states close to it]. All the measures of electronegativity show little difference between silicon and tin, and, where figures are available, show lead to have a distinctly higher electronegativity than either.


(I)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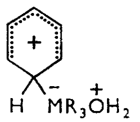
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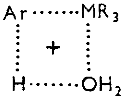
(IV)

Cottrell [14] lists the following C–M average bond-energies (in kcal. mole^{-1}, determined with Et_4M compounds): (M =) Si, 60; Sn, 54; Pb, 31 (cf. 82·6 for M = C). While these figures may not be very accurate it seems clear that the C–M bond energy decreases in the series (M =) Si, Sn, Pb.

The order of reactivity of the $ArMR_3$ compounds, *viz.*, (M =) Si $<$ Ge $\ll$ Sn $\ll$ Pb, conforms to the generalisation that the reactivity of a C–M bond increases with increasing atomic number of M within a sub-group of the Periodic Table,[15] but conflicts with the reasonable proposal that such increase in reactivity results mainly from decreasing electronegativity of M, *i.e.*, from increasing polarity of the C–M bond.[16] The order of reactivity, including the very sharp rise from Ge to Sn, is that expected from increasing metallic character of M as revealed by the electrical properties of the solid elements, but not from the variation of metallic character as revealed in chemical properties of the quadrivalent compounds and in various measures of electronegativity.[7] In particular, the great reactivity increase on going from the Ar–SiR_3 to the Ar–SnR_3 bond, and the very high reactivity of Ar–PbR_3 compounds, are completely out of keeping with electronegativity values on any scale.

It is interesting to consider possible mechanisms for the cleavage in terms of the observed reactivities. Since the reactions are, by definition, electrophilic aromatic

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[7] Allred and Rochow, *J. Inorg. Nuclear Chem.*, 1958, **5**, 269.

[8] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, Ithica, N.Y., 2nd edn., 1940, p. 64.

[9] Haissinky, *J. Phys. Radium*, 1946, **7**, 7; Wells, " Structural Inorganic Chemistry," Oxford Univ. Press, 1950, p. 36.

[10] Huggins, *J. Amer. Chem. Soc.*, 1953, **75**, 4123.

[11] Gordy, *Discuss. Faraday Soc.*, 1955, **19**, 14.

[12] Sanderson, *J. Chem. Phys.*, 1955, **23**, 2467.

[13] Pritchard and Skinner, *Chem. Rev.*, 1955, **55**, 745.

[14] Cottrell, " The Strengths of Chemical Bonds," Butterworths Scientific Publications, London, 1958, pp. 275—278.

[15] Gilman, " Organic Chemistry," Wiley and Sons, New York, 2nd edn., Vol. I, p. 520.

[16] Rochow, Hurd, and Lewis, " The Chemistry of Organometallic Compounds," Wiley and Sons, New York, 1957, pp. 21—25.

substitutions, it is reasonable to postulate intermediates of type (I).[17] We can, however, rule this out in the case of the lead compounds for the following reasons: (i) The ease of forming the intermediates of type (I) should increase with increasing base-strength of the $\mathrm{ArMR_3}$ compounds, and so with the electron-releasing ability of $\mathrm{MR_3}$; if the intermediate were formed in the slow step we should expect the lead compounds to be less reactive than the silicon and germanium compounds; (ii) in acid-catalysed aromatic hydrogen exchange, the rate of formation of the intermediate (II) approximates (within one power of 10) to the rate of reaction, and thus, when $\mathrm{M} = \mathrm{Pb}$, formation of the intermediate (I) would (irrespective of whether it were a fast or slow step) have to occur at least 10^{12} times as fast as formation of the ion (II). The fact that $\mathrm{Pb^{IV}}$ is reported to be more electronegative (and thus less electron-releasing) than hydrogen seems to exclude such rapid formation of the ion (I) when $\mathrm{M} = \mathrm{Pb}$,* even after allowance for the large polarisability of the lead atom and for uncertainty in the electronegativity values.

We suggest that the jump in reactivity from germanium to tin corresponds with a change in mechanism, and that this occurs at the point at which increased size and readier accessibility of *d*-orbitals lead to a marked increase in the co-ordinating ability of the metal atom. When $\mathrm{M} = \mathrm{Si}$ or Ge, intermediates of type (I) could be concerned, either formed or destroyed in the rate-determining step. (The latter possibility, involving rate-determining nucleophilic attack by solvent at M, seems more likely, since steric effects from big R groups on silicon can cause large reductions in the rate of cleavage.[18]) Where $\mathrm{M} = \mathrm{Sn}$ or Pb, initial co-ordination of solvent might occur rapidly to give complexes of the type $\mathrm{Ar}\overset{-}{\mathrm{M}}\mathrm{R_3} \longleftarrow \overset{+}{\mathrm{O}}\mathrm{H_2}$, which would then be destroyed by attack of oxonium ion at carbon, *via* intermediates of the type (III). (Intermediates of the type $\mathrm{Ar}\overset{-}{\mathrm{M}}\mathrm{R_3} \longleftarrow \overset{+}{\mathrm{O}}\mathrm{H_2}$ would not be expected to form very rapidly where $\mathrm{M} = \mathrm{Si}$.[19] The most convincing single item of evidence in support of this is that oxygen exchange between triphenylsilanol and $\mathrm{H_2{}^{18}O}$ is slow in neutral aqueous dioxan,[20] although in this case co-ordination of water to silicon would effectively constitute reaction, subsequent proton-transfer being rapid in the medium used.) This mechanism is consistent with the relatively small effect of ring substituents when $\mathrm{M} = \mathrm{Sn}$ or Pb. An electron-releasing substituent, for example, would hinder formation of the complex $\mathrm{Ar}\overset{-}{\mathrm{M}}\mathrm{R_3} \longleftarrow \overset{+}{\mathrm{O}}\mathrm{H_2}$ but facilitate subsequent electrophilic attack on this complex, and overall a small effect would be observed.

A possibility which cannot be discounted is that reaction occurs through a four-centre transition state such as (IV) (another solvent molecule possibly being needed to accept a released proton), the emphasis on the forming of the M–O bond and breaking of the C–M bond increasing in the series Si, Ge, Sn, Pb. The fraction of positive charge on the metal atom in the transition state would increase in the same order, and the effects of ring substituents thus decrease. At present, however, there is no reason to believe that the cleavages involve a process so fundamentally different from familiar aromatic substitutions in which C–H bonds are broken.

EXPERIMENTAL

Triethyl-p-*methoxyphenylgermane*.—Triethylgermanium bromide (7 g.) and the Grignard reagent from *p*-bromoanisole (11 g.) and magnesium (1·5 g.) in ether (120 ml.) were boiled together for 8 hr. Addition of aqueous acid followed by separation, washing, drying ($\mathrm{Na_2SO_4}$),

* Hyperconjugation from the C–H bonds is important in stabilising the ion (II) (Muller, Pickett, and Mulliken, *J. Amer. Chem. Soc.*, 1954, **76**, 4770). Hyperconjugation from the $\mathrm{C{-}PbEt_3}$ bond in the ion (I) should certainly not be more effective than that from a C–H bond.

[17] Ingold, " Structure and Mechanism in Organic Chemistry," Bell and Sons, Ltd., London, 1953, Chap. VI.

[18] Unpublished work by Miss P. M. Greasley.

[19] Eaborn, " Organosilicon Compounds," Butterworths Scientific Publications, London, 1960, pp. 107—110.

[20] Allen and Modena, *J.*, 1957, 3671.

and fractionation of the ethereal layer gave *triethyl-*p*-methoxyphenylgermane* (6 g., 79%), b. p. 141°/10 mm., 118°/3 mm., n_D^{20} 1·5217. The product was refractionated and the middle fraction (2 g.) was used (Found: C, 58·9; H, 8·3. $C_{13}H_{22}OGe$ requires C, 58·5; H, 8·3%).

*Triethyl-*p*-methoxyphenylstannane.*—This *compound* was made from triethyltin bromide by the method used for the corresponding germanium derivative, except that 5% aqueous ammonium chloride solution was used in the hydrolysis. The fraction (52%) of b. p. 157—158°/12 mm., 139°/5 mm., n_D^{20} 1·5410, was used (Found: C, 50·2; H, 6·9. $C_{13}H_{22}OSn$ requires C, 49·9; H, 7·1%).

Triethylphenylstannane.—When this compound was prepared from triethyltin chloride and phenylmagnesium bromide it could not be freed from traces of biphenyl.

Triethyltin chloride (20 g. mole) was boiled for 1½ hr. with phenyl-lithium made from bromobenzene (0·08 mole) and *n*-butyl-lithium (0·08 mole) in ether. Addition of water followed by separation, drying, and fractionation of the ethereal layer gave triethylphenyltin (18 g., 77%), b. p. 128·5°/12·5 mm., n_D^{20} 1·5349 (lit.,[21] b. p. 128·5°/12 mm.). The ultraviolet absorption spectrum showed it to be free from biphenyl.

Triethylphenyl-plumbane.—This compound, b. p. 126—130°/5—6 mm., n_D^{20} 1·5732, was obtained from triethyl-lead chloride by the method described in the previous paragraph. Some decomposition occurs during fractionation. Previously recorded [22] physical constants are: b. p. 135°/12 mm., n_D^{20} 1·5762; b. p. 137—140°/13 mm., n_D^{20} 1·5532; b. p. 137—140°/13 mm., n_D^{20} 1·5752.

*Tricyclohexyl-*p*-methoxyphenylsilane.*—Tricyclohexylsilyl fluoride (5 g.) was added to *p*-methoxyphenyl-lithium made from *p*-bromoanisole (31 g.) and lithium (2·5 g.) in ether (80 ml.). The ether was replaced by benzene (100 ml.), and the mixture was boiled for 2 hr. Excess of lithium was filtered off and dilute hydrochloric acid was added to the solution. Separation of the organic layer, followed by removal of the solvent and recrystallisation of the residue from ethanol, gave *tricyclohexyl-*p*-methoxyphenylsilane* (3·6 g., 52%), m. p. 150° (Found: C, 78·05; H, 10·2. $C_{25}H_{40}OSi$ requires C, 78·05; H, 10·5).

*Preparation of Tricyclohexyl-*p*-methoxyphenylgermane.*—This *compound*, m. p. 132·5° (Found: C, 69·95; H, 9·3. $C_{25}H_{40}OGe$ requires C, 69·96; H, 9·4%), was prepared in 84% yield from tricyclohexylgermanium chloride by the method described in the previous paragraph.

Rate Measurements.—The general method has been described.[1] The reaction mixture was made up by adding 1 vol. of aqueous perchloric acid to 5 vol. of an ethanolic solution of the $ArMR_3$ compound of concentration shown in Table 3. The change in absorption was recorded at the wavelengths shown in Table 3.

TABLE 3.

Compound	$10^4 \times$ Concn. (M)	λ (mμ)	Compound	$10^4 \times$ Concn. (M)	λ (mμ)
p-$MeO{\cdot}C_6H_4{\cdot}SiEt_3$	14	284	*p*-$MeO{\cdot}C_6H_4{\cdot}Sn(C_6H_{11})_3$	7	284
p-$MeO{\cdot}C_6H_4{\cdot}Si(C_6H_{11})_3$ ...	8	284	$C_6H_5{\cdot}SnEt_3$	17	259
p-$MeO{\cdot}C_6H_4{\cdot}GeEt_3$	13	284	$C_6H_5{\cdot}PbEt_3$	4	295
p-$MeO{\cdot}C_6H_4{\cdot}Ge(C_6H_{11})_3$...	13	284, 285	2,4,6-$Me_3C_6H_2{\cdot}SiMe_3$ ...	37	259
p-$MeO{\cdot}C_6H_4{\cdot}SnEt_3$	14	288			

In the case of *p*-$MeO{\cdot}C_6H_4{\cdot}SnEt_3$ with added 0·0057M-perchloric acid, rate constants fell off in the later stages of the reaction because the concentration of the organotin compound was comparable with that of the acid and triethyltin hydroxide is sufficiently basic to remove a significant amount of the acid. In this case the rate constant quoted in Table 1 was derived from the first 40% of reaction. In all other cases satisfactorily constant first-order rate coefficients were observed for more than 70% of reaction.

It should be noted that for M = Si, Ge, and Sn, the ultraviolet absorption utilised arises mainly from the aryl groups, the absorption of which is modified by the attached MR_3 groups. With $C_6H_5{\cdot}PbEt_3$ the absorption arises from the lead atom, and is much greater than that of benzene in the same region. The final absorption on cleavage of this compound agreed

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[21] Luijten and van der Kerk, " Investigations in the Field of Organotin Chemistry," Tin Research Institute, Greenford, 1958, p. 114.

[22] Calingaert and Shapiro, U.S.Pat. 2,535,190 (1950); *Chem. Abstracts*, 1951, **45**, 3864; Gilman and Bindschadler, *J. Org. Chem.*, 1953, **18**, 1675.

(within 5% over the range 250—257 mμ and within 1% over the range 257—280 mμ) with that obtained when an equivalent amount of triethyl-lead chloride was dissolved in the same medium.

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