# Organic and Biological Chemistry

## Organometallic Electrochemistry. I. Derivatives of Group IV-B Elements

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**Abstract:** Organometallic derivatives of group IV elements have been studied *via* polarography, controlled potential electrolysis, and triangular voltammetry. Some subvalent organometals and anions have been generated and examined. In particular, the triphenylmetal radicals, $Ph_3M\cdot$ (where M = Si, Ge, Sn, Pb), have been shown to suffer quite dissimilar fates in dimethoxyethane. Abstraction (Si, Ge), coupling (Sn), and arylation of the Hg electrode (Pb) have been observed. Organometallic assemblies of the type $Ph_3M^-Bu_4N^+$ (where M = Ge, Sn) have been shown to serve as electron-transfer reagents in reactions with other group IV halides rather than as nucleophiles. Reduction of $R_2SnCl_2$ proceeds *via* ($R_2SnCl$), which rapidly dimerizes, providing a route to $R_2Sn(Cl)Sn(Cl)R_2$ species. Reduction of $Ph_2MX_2$ leads to $Ph_2MH_2$ (M = Si, Ge), or arylation (Pb).

Although the polarographic behavior of a large number of organic molecules has been investigated successfully, and the electrochemical behavior made use of in determining energy levels, or applied synthetically, no extensive study and only one intensive exploration of the electrochemistry of organometallic species have been made (*vide infra*).

Conceptually, one can envisage, for the reductive mode only, the addition of an electron or electrons to an organometallic assembly RmQ, where R is a $\sigma$- or $\pi$-bonded organic moiety, m is a metal and two of its valency positions, and Q is another R group, halo or oxyfunction. The fate of the affected assembly may be to exist for long time periods as the radical anion, or to lose the ligand Q as an anion, generating the subvalent organometal Rm. The fate of Rm might then take one of several courses: (1) ultimate decomposition to R· and m; (2) disproportionation, RmR + m, which may be concomitant with 1; (3) abstraction of H from the surroundings, yielding RmH; or (4) coupling to yield RmmR. Further reduction may yield Rm, which could decompose.

We have made an intensive study of the electrochemistry of organometallic compounds derived from the metals of group II, III, IV, V, and the transition series, in dimethoxyethane, using tetrabutylammonium perchlorate as a supporting electrolyte. High resistances in the H cell employed, where cathode and anode were separated by a glass frit, and low conductivity of the solution necessitated three electrode geometry.[1] A 0.001 *M* $AgClO_4$ (0.1 *M* $Bu_4NClO_4$)|Ag reference electrode was employed, along with a mercury pool anode, and either a dme, sheared dme, hanging Hg drop, or Hg pool cathode. Polarographic data were obtained with a Metrohm Polarecord, or with a unit based on standard operational amplifier circuitry. The latter unit was also equipped to apply slow-single or multiple-triangular voltage sweeps to a hanging drop or higher frequency single or multiple-triangular voltage sweeps to a sheared dme, during the last 100 to 1000 msec. of the drop's life. This latter technique allows the detection of short-lived species at the electrode by subsequent reoxidation to the normal valence state.[2] In the present system charging current problems set the lower limit on predecomposition lifetimes at 10–50 msec. The often high degree of electrochemical irreversibility (to be differentiated from chemical reversibility) led to the evaluation of *n* (number of electrons utilized at each polarographic step) *via* exhaustive controlled potential electrolysis. Where long-lived species seemed to be involved, such reduced solutions were electrochemically oxidized, often successfully, to regenerate the starting compound. Where stable intermediates or subvalent species were found, the chemistry of these species was explored, the course of the reaction being followed by polarography and ultraviolet spectroscopy. The present paper reports on systems derived from group IV metals.

### Experimental Section

**Equipment.** Polarographic and controlled potential electrolysis experiments were made in an H cell, the anodic and cathodic compartments being separated by a 25-mm. (medium) glass frit. The arms of the cell were as close as possible, and had flat bottoms, measuring 3 cm. in diameter. Ground-glass outer joints and O-ringed Teflon adapters permitted the insertion of degassing tubes, dropping mercury electrode (dme), or hanging drop accessories. The reference electrode, a 0.001 *M* $AgClO_4$ (0.1 *M* $Bu_4NClO_4$)|Ag wire, made electrical contact with the cathode environment *via* a tube separated into compartments by two glass frits, the terminal one being as close (1–2 mm.) as geometrical factors permitted. Normal cell resistances were $R_{T-R}$ = 10 kohms, $R_{T-C}$ = 10 kohms. Electrical contact with the anode pool, and the cathodic pool, if used, was made *via* Pt foil pinch sealed through the H cell arms, at the base of the cell. The dme was a rather fast, 3-sec. capillary, longer drop times leading to excessive maxima, and gross irregularities in *i*/*E* curves. The hanging drop assembly was a microsyringe mounted on a standard capillary.

Routine polarographs were made using a Metrohm Polarecord, in conjunction with a Sargent IR Compensator. Alternatively a

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[1] P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954.

[2] *Cf.* J. Rika in "Progress in Polarography," P. Zuman and I. M. Kolthoff, Ed., Interscience Publishers, Inc., New York, N. Y., 1962.

unit based on standard operational amplifier circuitry[3] could be employed, feeding into a Mosely 2D-2 X-Y plotter. The unit possessed an auxiliary input capable of accepting externally generated wave functions which then could be applied to the cell. Triangular voltammetry therefore was performed by external generation of a variable frequency square wave, *via* alternate saturation of two switching transistors. Integration of the square wave led to the triangular signal desired, which also was used as a feedback to the square wave generator section. Appropriate controls in this section permitted adjustment independently of cathodic and anodic limits of the triangular wave, and its midpotential. The anodic and cathodic duration of the square wave also could be altered, thus permitting generation of asymmetric triangular waves.[3] Connection directly to the bases of the switching transistors permitted gating of the generator by a monostable multivibrator.[4] The latter could be actuated manually, or by a suitable signal from an astable multivibrator, which also synchronized the gate with actuation of the shearing solenoid attached to the dme.[4] The former was used for hanging drop voltammetry, the latter for sheared drop. The readout devices were a Mosely 2D-2 recorder and a Tektronix Storage oscilloscope equipped with Polaroid camera.

Controlled potential electrolysis was achieved at low current levels (10 ma.) *via* circuits based on conventional operational amplifier design. Higher levels (1000 ma.) were achieved with suitable master/slaving of Kepco CK-60-0.5 power supplies, the master being boot strapped to reduce drain on the reference electrode.[5]

**Chemicals.** Dimethoxyethane (Ansul 121) was purified by distillation through a 100-cm. packed column from $LiAlH_4$ under a nitrogen atmosphere. Careful attention to detail is necessary to prevent peroxide or water contamination.

Tetrabutylammonium perchlorate was prepared from the metathetical reaction between tetrabutylammonium iodide and silver perchlorate in hot ethanol. The silver iodide was filtered off, the solution cooled to $-80°$, or precipitated with water, and the perchlorate salt was filtered off and washed with water until freed from $Ag^+$ or $I^-$. Recrystallization from dimethoxyethane gave suitable material, with a window from approximately $+0.9$ to $-3.6$ with respect to reference. The material was dried in an Abderhalden pistol over $P_2O_5$, using boiling xylene, for a period of several hours at 0.1 mm. Samples from G. F. Smith and Matheson Coleman and Bell also proved satisfactory.

The organosilicon derivatives were kindly supplied by Dow Corning Corp. and were purified by standard methods of distillation or recrystallization.

Organogermanium, -tin, and -lead compounds were largely supplied from the Organic Chemical Institute, Utrecht, Holland, and M and T Chemical Co., Rahway, N. J.

Professor Max Schmidt of the Institute for Inorganic Chemistry of the University of Marburg very kindly supplied the compounds of the type $(C_6H_5)_3MM'M''(C_6H_5)_3$ where M = Sn; M′ = Sn, Te; and M″ = Sn, Ge.

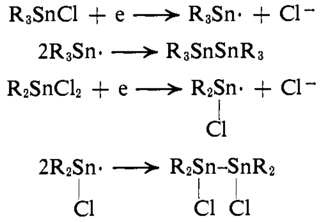
## Results and Discussion

Recent years have witnessed a renaissance of interest in the organic chemistry of group IV elements both on theoretical[6-9] and synthetic[10,11] grounds. Because of current interest in the area, certain group IV-B derived organometals were chosen first for electrochemical study.

Previous polarographic studies in this area have been few in number and restricted almost entirely to organotin compounds. The first recorded polarographic reduction of an organotin compound was that of diethyltin dichloride by Riccoboni and Peboff,[12] who claimed to have observed one two-electron reduction wave. The postulated product of this reduction was diethyltin, which was assumed to possess quite high stability under the conditions. Costa[13] studied a range of trialkyltin halides in 30% isopropyl alcohol and obtained three reduction waves. The first was thought to be the formation of hexaalkylditin. Doubt seemed to surround the origin of the latter two waves.

Toropova and Saikina,[14] studied similar compounds in 40% aqueous ethyl alcohol solutions at varying pH. The ease of reduction as a function of the organic radicals was in the order ethyl > propyl > butyl. The discharge of the methyl derivatives was sensitive to conditions, a not surprising observation considering the hydrolytic capabilities of the system. Employing oscillographic polarographic techniques, Saikina[15] obtained data on the reversibility of the above reductions, and found them to be highly irreversible.

Conceptually at least, the most thorough study of the polarographic behavior of organotin compounds must be credited to Allan[16] who, utilizing dimethylformamide as solvent and tetrabutylammonium perchlorate as supporting electrolyte, examined a variety of structural types. A plague of practical problems, however, arising from the presence of traces of water in the solvent, allowed none but most general of conclusions. $n$ values were estimated from $i_d$ values, using approximate diffusion coefficients. Allan could place confidence in data for only three compounds, tributyl-, triphenyl-, and trimethyltin halides. For compounds of the type $R_3SnX$ and $R_2SnX_2$, the first reduction wave was postulated to involve one electron as shown.



$$R_3SnCl + e \longrightarrow R_3Sn\cdot + Cl^-$$

$$2R_3Sn\cdot \longrightarrow R_3SnSnR_3$$

$$R_2SnCl_2 + e \longrightarrow \underset{\displaystyle Cl}{R_2\underset{|}{Sn}\cdot} + Cl^-$$

$$2\underset{\displaystyle Cl}{R_2\underset{|}{Sn}\cdot} \longrightarrow \underset{\displaystyle Cl\ \ Cl}{R_2Sn\text{–}SnR_2}$$

The second reduction waves were postulated to involve two electrons, the electrode reactions being

$$R_3SnCl + 2e \longrightarrow R_2Sn + R:^- + Cl^-$$

and

$$R_2SnCl_2 + 2e \longrightarrow R_2Sn + 2Cl^-$$

The present work will support some of this speculation.

Riccoboni[17] has reported on the polarographic behavior of triethyllead chloride in aqueous potassium chloride media. A one-electron reduction was claimed leading to triethyllead.

More recently, Curtis and Allred[18] have obtained data on compounds of the type $4\text{-}(CH_3)_3MC_6H_4C_6H_5$

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[3] C. Enke, Princeton University, personal communication.

[4] Electronics Design Shop, University of California, Los Angeles, California, personal communication.

[5] P. Birman, Kepco Inc., personal communication.

[6] A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 269 (1958).

[7] R. Drago, *ibid.*, **15**, 237 (1960).

[8] A. L. Allred and E. G. Rochow, *ibid.*, 20, 167 (1961).

[9] For a theoretical discussion see D. P. Craig and C. Zaul, *J. Chem. Phys.*, 37, 609 (1962).

[10] See H. Gilman, O. L. Marrs, and S. Y. Sim, *J. Org. Chem.*, **27**, 4232 (1962), for discussion and leading references.

[11] C. C. Tamborski, F. E. Ford, and E. J. Soloski, *ibid.*, **28**, 181 (1963).

[12] L. Riccoboni and P. Peboff, *Atti Ist. Veneto Sci.*, **107**, 123 (1949); *Chem. Abstr.*, **44**, 6752*a* (1950).

[13] G. Costa, *Gazz. Chim. Ital.*, 80, 42 (1950); *Chem. Abstr.*, **44**, 9926*d* (1950).

[14] V. F. Toropova and M. K. Saikina, *ibid.*, **48**, 12579 (1954).

[15] M. K. Saikina, *ibid.*, **51**, 7191*e* (1957).

[16] R. B. Allan, Dissertation, University of New Hampshire, 1959.

[17] L. Riccoboni, *Gazz. Chim. Ital.*, 72, 47 (1942).

[18] M. O. Curtis and A. L. Allred, Abstracts of Papers, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

and 4,4′-$(CH_3)_3MC_6H_4C_6H_4M(CH_3)_3$ where M = Si, Ge, Sn. Both polarographic and alkali metal reductions lead to the uninegative radical anions.

**$R_3MX$ Compounds.** The electrochemical behavior of this class of compounds (where R = $C_6H_5$) is seen in Chart I.

**Chart I.** Electrochemical Behavior of $Ph_3MX$ Compounds

$$Ph_3SiCl \xrightarrow[-3.1\text{ v.}]{e} Ph_3SiH$$

$$Ph_3GeCl \xrightarrow[-2.8\text{ v.}]{e} Ph_3GeH$$

$$Ph_3SnCl \xrightarrow[-1.6\text{ v.}]{e} 0.5Ph_3SnSnPh_3 \xrightarrow[-2.9\text{ v.}]{e} Ph_3Sn^-$$

$$Ph_3PbOAc \xrightarrow[-1.4\text{ v.}]{e} Ph_3Pb\cdot \xrightarrow{Hg} Ph_2Hg$$

$$\xrightarrow[-2.2\text{ v.}]{2e} Ph_3Pb{:}^-$$

The first detectable products resulting from the exhaustive electrolysis of solutions of the silicon and germanium compounds were shown to be corresponding silane and germane. The ultraviolet spectra of the solutions after electrolysis were identical with the spectra of authentic samples of triphenylsilane and -germane, respectively. These latter compounds were synthesized by lithium aluminum hydride reduction of the corresponding chlorides. Attempts to detect the presumed intermediates, triphenylsilyl and -germyl radicals by rapid triangular sweep voltammetry were unsuccessful. Hence, these fugitive triphenylmetal radicals have exceedingly short lifetimes in this system. The source of the abstracted hydrogen atom could conceivably be the tetrabutylammonium moiety or the glyme solvent, known to be a good hydrogen atom donor. Since both $Ph_3SiCl$ and $Ph_3GeCl$ discharge more cathodically than −2.6 v. (discharge potential of lithium ion), lithium perchlorate could not be substituted as a supporting electrolyte. However, similar abstraction behavior was observed with the diphenylsilicon and -germanium dichlorides (see later), in which cases substitution of lithium perchlorate for the tetraalkylammonium salt did not alter the product. Hence, it can be inferred that in the triphenylmetal cases solvent glyme is the source of hydrogen.

The reduction of triphenyltin chloride exhibits two well-defined waves. The reduction at −1.6 v., shown to require one electron per mole of triphenyltin chloride, yielded quantitatively (by polarography and ultraviolet spectroscopy) hexaphenylditin. The actual mechanism of this reaction cannot be determined from polarographic data alone. In addition to the sequence

$$Ph_3SnCl \xrightarrow{e} Ph_3Sn\cdot \xrightarrow{\text{coupling}} Ph_3SnSnPh_3$$

an initial two-electron uptake, producing $Ph_3Sn^-$, followed by rapid nucleophilic attack of this species on the residual $Ph_3SnCl$, is also possible.

$$Ph_3SnCl \longrightarrow Ph_3Sn^-$$

$$Ph_3Sn^- + Ph_3SnCl \longrightarrow Ph_3SnSnPh_3 + Cl^-$$

It will be shown (see later) that $Ph_3Sn^-$, produced by reduction of $Ph_3SnSnPh_3$, does indeed react extremely rapidly with $Ph_3SnCl$ to produce hexaphenylditin, but this does not establish the mechanism involved at the first wave.

The second reduction wave at −2.9 v. is identical with the single wave observed for hexaphenylditin. The second reduction wave of triphenyltin chloride could represent the uptake of two electrons per mole to lead directly to $Ph_3Sn^-$ without the intermediary of hexaphenylditin. This interpretation would demand that the identity in half-wave potentials of the second wave of $Ph_3SnCl$ and the single wave of $Ph_3SnSnPh_3$ was fortuitous. Unraveling of the possible reductive sequences in the $Ph_3Sn$ systems will be deferred until later when rapid cyclic voltammetric results will be presented.

Attempts to examine solutions of triphenyllead chloride were thwarted by a rapid reaction with metallic mercury. Further inquiries into the nature of the reaction quickly revealed it to involve the arylation of mercury. Diphenyllead dichloride exhibited similar behavior. A glyme solution of diphenyllead dichloride was shaken with pure metallic mercury for 4 hr., and filtered into a large stirred volume of water. A white flocculence appeared and this material, without further purification, melted at 124°. (Diphenylmercury melts at 124°.) The identity of the product was further substantiated by its polarographic half-wave potential ($E_{1/2} = -3.3$ v.) and its ultraviolet spectrum.

The arylation was shown to be quantitative in the case of diphenyllead dichloride (ultraviolet spectra) and triphenyllead chloride (ultraviolet spectra and polarography). At the completion of the reactions, controlled potential electrolyses indicated that 2 equiv. of reducible mercury species were produced per mole of initial diphenyllead dichloride, and 1 equiv. per mole of initial triphenyllead chloride.

Hence the observations are consistent with the overall stoichiometry.

$$Ph_2PbCl_2 + 3Hg \longrightarrow Ph_2Hg + Pb + 2hgCl$$

$$2Ph_3PbCl + 5Hg \longrightarrow 3Ph_2Hg + 2Pb + 2hgCl$$

The alkylating and arylating capabilities of organolead compounds have been explored considerably. The arylation of mercuric acetate with diphenyllead diacetate is the best known route to the elusive monophenyllead derivatives.[19] The counterpart of this reaction is the arylation of lead tetraacetate with diphenylmercury.[20]

The corresponding acetates did not arylate mercury under the same conditions as did the chlorides, and satisfactory electrochemical data could be obtained. Diphenyllead diacetate is reduced in two one-electron steps at the dropping mercury electrode (see Chart II), which most reasonably correspond to

$$Ph_2Pb(OAc)_2 \xrightarrow[-1.1\text{v.}]{e} Ph_2Pb\cdot(OAc) + OAc^- \xrightarrow[-1.6\text{ v.}]{e} Ph_2Pb + OAc^-$$

Controlled potential electrolysis at a potential (−2.1 v.), slightly more cathodic than the second step, results in a quantitative yield of diphenylmercury (ultraviolet spectra and polarograph). Similar observations were made in the case of triphenyllead acetate. Electrolysis at a potential corresponding to the first step $Ph_3PbOAc \xrightarrow{e} Ph_3Pb\cdot + OAc^-$ again yields diphenylmercury quantitatively.

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(19) E. M. Panov and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, **85**, 1037 (1952); *Chem. Abstr.*, 47, 6365*i* (1953).

(20) R. Criegee, P. Dimroth, and R. Schempf, *Chem. Ber.*, 90, 1337 (1957).

Hence arylation by the $Ph_3Pb\cdot$ species occurs faster than coupling to produce hexaphenyldilead. There appears little question, then, that subvalent organoleads are highly active arylating agents. The reactions of di- and triphenyllead halides may be rewritten with subvalent organolead intermediates. Metallic mercury acts as a reducing agent to produce the subvalent organolead. These reductions are reminiscent of the action of mercury on triphenylmethyl chloride to produce triphenylmethyl.[21]

$$Ph_2PbCl_2 + 2Hg \longrightarrow Ph_2Pb + 2HgCl$$

$$Ph_2Pb + Hg \longrightarrow Ph_2Hg + Pb$$

$$Ph_3PbCl + Hg \longrightarrow Ph_3Pb\cdot + HgCl$$

$$2Ph_3Pb\cdot + 3Hg \longrightarrow 3Ph_2Hg + 2Pb$$

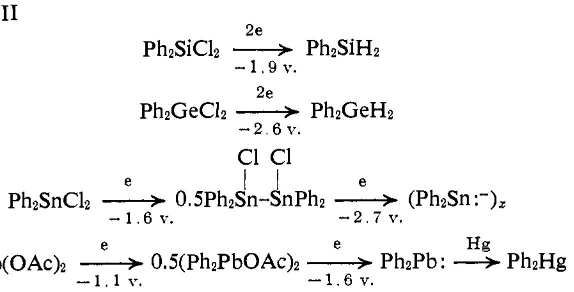
The lack of reaction of the acetates under these conditions may be ascribed in part to the lessened affinity of mercury for the acetate ligand. Agents such as ferrocene and titanous salts are known to reduce alkyllead derivatives. Thus, Wang[22] has observed that triethyllead acetate undergoes reduction at room temperature to form triethyllead, which further fragments to diethyllead and ethyl radical, which abstracts a hydrogen atom to yield ethane. The fragmentation of triphenyllead must be more restricted in nature, since no benzene is formed. The formation of a triphenylleadmercury intermediate, which suffers intramolecular collapse and aryl migration, would explain the present specificity.

It is apparent from Chart I that as one progresses the series, Si, Ge, Sn, and Pb, reduction becomes more facile. A difference of 1.7 v. separates the extreme members of the sequence. Also the final product of reduction differs greatly as one descends the series. Abstraction ($Ph_3Si\cdot$, $Ph_3Ge\cdot$), coupling ($Ph_3Sn\cdot$), and arylation ($Ph_3Pb\cdot$) have been observed.

It is possible that interaction between triphenylgermyl and -silyl radicals and the mercury electrode may be so weak that the high activity of such radicals is not reduced, thus favoring abstraction. In the tin case, polarisability interactions with the electrode may trap $Ph_3Sn\cdot$ on the mercury envelope, resulting in a weakly bonded [$Ph_3Sn$–Hg] complex. On meeting its own kind, coupling occurs to produce $Ph_3SnSnPh_3$. Presumably the same idea may be valid in the lead case, except that the relative stabilities of the Ph–Pb and Ph–Hg linkages render the existence of [$Ph_3Pb$–Hg] so unfavorable that arylation occurs before collision and coupling.

**$Ph_2MX_2$ Compounds.** The electrochemical behavior of this group of compounds is presented in Chart II.

Chart II



$$Ph_2SiCl_2 \xrightarrow[-1.9\text{ v.}]{2e} Ph_2SiH_2$$

$$Ph_2GeCl_2 \xrightarrow[-2.6\text{ v.}]{2e} Ph_2GeH_2$$

$$Ph_2SnCl_2 \xrightarrow[-1.6\text{ v.}]{e} 0.5Ph_2\overset{Cl}{\overset{|}{Sn}}-\overset{Cl}{\overset{|}{Sn}}Ph_2 \xrightarrow[-2.7\text{ v.}]{e} (Ph_2Sn{:}^-)_x$$

$$Ph_2Pb(OAc)_2 \xrightarrow[-1.1\text{ v.}]{e} 0.5(Ph_2PbOAc)_2 \xrightarrow[-1.6\text{ v.}]{e} Ph_2Pb{:} \xrightarrow{Hg} Ph_2Hg$$

The first detectable product of the reduction of dichlorodiphenylsilane was shown to be diphenylsilane by ultraviolet spectroscopy. By analogy with the alkali-metal reduction of dichlorodiphenylsilane, other possible products appeared to be octaphenylcyclotetrasilane and decaphenylcyclopentasilane, resulting from coupling of the presumed diphenylsilene intermediate. However, these derivatives exhibit ultraviolet absorption spectra inconsistent with that observed in the electrochemical reduction.[23]

Reduction of diphenyltin dichloride exhibits two steps, the first of which involves one electron and produces tetraphenyldichloroditin, a particularly elusive species when more formal synthetic routes are employed.[24] Thus electrolysis at the first wave, followed by addition of the calculated amount of silver benzoate yielded a solution whose polarogram was superimposable on that of authentic dibenzoatotetraphenylditin.[25] The second reduction wave of diphenyltin dichloride involves two electrons; and the product, an orange-red species, is formally $Ph_2S\dot{n}{:}^-$, although its state of aggregation in solution has yet to be established. The same species can be generated from the benzoato analog. Synthetic studies with this reagent are currently being conducted and results available support its formulation as $Ph_2\overline{Sn}-\overline{Sn}Ph_2$, as does its lack of paramagnetic properties. Dibutyltin dichloride shows a similar electrochemical behavior.

As previously described in detail, diphenyllead dichloride reacts with metallic mercury to yield diphenylmercury. Consequently, the acetato analog was employed. Two one-electron reductions are observed, the product of the first being concluded to be diacetatotetraphenyldilead. However, electrolysis at the first wave results in some diphenylmercury formation and hence the radical $Ph_2PbOAc$ possesses some arylating capability. Arylation and coupling presumably have comparable rate constants. As already stated, electrolysis at the second wave involves two electrons and results in quantitative formation of diphenylmercury, almost certainly *via* diphenyllead.

**$Ph_3MM'Ph_3$ Compounds.** The electrochemical behavior of this class of compounds is collected in Chart III.

Although the lithium metal cleavage of hexaphenyldisilane to produce triphenylsilyllithium is well known, electrochemical cleavage could not be effected in this system.

The reduction of the $Ph_3MM'Ph_3$ compounds suggests that in homometal compounds, anion production is the usual consequence if reduction can be achieved. In heterometal compounds, the most easily reduced moiety yields an anion, the remaining part of the molecule being extruded as a radical, which abstracts, if reduction of its homometal parent is more cathodic.

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[21] M. Gomberg, *J. Am. Chem. Soc.*, **22**, 757 (1900).

[22] C. H. Wang, P. L. Levins, and H. G. Pars, *Tetrahedron Letters*, **No. 12**, 687 (1964).

[23] The ultraviolet spectra of octaphenylcyclotetrasilane and decaphenylcyclopentasilane were kindly supplied by Professor Henry Gilman, Department of Chemistry, Iowa State University, Ames, Iowa.

[24] Attempts to prepare 1,1,2,2-tetraphenyl-1,2-dichloroditin by controlled chemical reduction of dichlorodiphenyltin resulted only in formation of bis(diphenylchlorotin) oxide. The hydrazine reduction of dichlorodiphenyltin, once claimed to lead to 1,1,2,2-tetraphenyl-1,2-dichloroditin (*cf.* O. H. Johnson, H. E. Fritz, D. O. Halvorson, and R. L. Evans, *J. Am. Chem. Soc.*, **77**, 5857 (1955)) was subsequently shown to produce bis(diphenylchlorotin) oxide (A. J. Gibbons, A. K. Sawyer, and A. Ross, *J. Org. Chem.*, **26**, 2304 (1961)).

[25] The authors are indebted to Professor C. R. Dillard of the Brooklyn College of City University of New York for a sample of this compound.

**Chart III**

| | Structure proof |
|---|---|
| $Ph_3SiSiPh_3 \longrightarrow$ no reduction | |
| $Ph_3GeGePh_3 \xrightarrow[-3.5\text{ v.}]{2e} 2Ph_3Ge\!:^-$ | $(+\ Ph_3GeCl \longrightarrow 2\ Ph_3GeH)$ |
| $Ph_3SnSnPh_3 \xrightarrow[-2.9\text{ v.}]{2e} 2Ph_3Sn^-$ | $(+\ Ph_3SnCl \longrightarrow Ph_3SnSnPh_3)$ |
| $Ph_3GeSiPh_3 \longrightarrow$ no reduction | |
| $Ph_3SnSiPh_3 \xrightarrow[-3.1\text{ v.}]{e} Ph_3Sn\!:^- + Ph_3SiH$ | $(+\ Ph_3SnCl \longrightarrow Ph_3SnSnPh_3)$ |
| $Ph_3PbPbPh_3 \xrightarrow[-2.0\text{ v.}]{2e} 2Ph_3Pb\!:^-$ | $(+\ CpFe(CO)_2I \longrightarrow Ph_3PbFe(CO)_2Cp)$ |

An alternative to electrolytic metal–metal bond cleavage is storage of the electrons in $\pi^*$ orbitals of the phenyl rings. Reaction with water and dilute acid would not be anticipated to result in M–M bond scission in such radicals. The products obtained (see later) would demand this.

**Electron Transfer and Other Reactions of $Ph_3MX$.** Attention in this section will be focused mainly on the reactions of the two-electron reduction product of hexaphenylditin, *viz.*, $Ph_3Sn^-Bu_4N^+$. Since contrasting behavior with $Ph_3SnLi$ will soon be apparent, the status of this latter reagent will be discussed briefly and factors affecting the reactivity of the triphenyltin moiety will be evaluated.

The preparation of triphenyltinlithium has been discussed by several workers and the available preparative methods have been well summarized by Tamborski.[11] Dependent on the method of preparation, $Ph_3SnLi$ may lead to quite different products and yields. Most pronounced differences in behavior are exhibited by $Ph_3SnLi$ generated by the following routes.

$$3PhLi + SnCl_2 \longrightarrow Ph_3SnLi + 2LiCl \qquad (a)$$

$$Ph_3SnCl + 2Li \longrightarrow Ph_3SnLi + LiCl \qquad (b)$$

$$Ph_3SnLi + Ph_3SnCl \longrightarrow Ph_3SnSnPh_3 + LiCl$$

$$Ph_3SnSnPh_3 + 2Li \longrightarrow 2Ph_3SnLi$$

For example the product from route a is alleged to give a negative color test,[26] while that from route b yields a positive test.[11] A consideration of the available data suggests that the product from route b is indeed $Ph_3SnLi$ while incomplete reaction in method a may account for certain irregularities. However, the most pertinent general observations concerning $Ph_3SnLi$ is that it reacts *almost exclusively* as a nucleophile in displacement reactions.

Variations in covalent and electrostatic contributions to bonding in organometals are expected to be sensitive functions of counterion structure. Not only cation size, but also actual steric shielding of the site of cation charge are to be considered. The relatively small lithium ion is capable of quite close approach to the stannanion thus maximizing covalent character in the bond. In this way, the extent of free stannanion character is reduced. On the other hand, the positive charge in the tetrabutylammonium ion is located on the nitrogen, which is effectively screened by butyl groups. Thus, the positive and negative centers, for steric reasons, cannot approach, and covalent interaction is minimized. Thus the free stannanion character is enhanced.[27] Consequently, the systems with tetrabutylammonium and lithium counterions are expected to exhibit quite different behavior (see Table I).

Table I

| Reagent | System | Substrate | Product(s)[a] |
|---|---|---|---|
| $Ph_3Sn\!:^-$ | 1 | $Ph_3SiCl$ | $Ph_3SnSnPh_3 + Ph_3SiH$ |
| | 2 | $Ph_3GeCl$ | $Ph_3SnSnPh_3 + Ph_3GeH$ |
| | 3 | $Ph_3SnCl$ | $Ph_3SnSnPh_3$ |
| | 4 | $PhHgCl$ | $Ph_3SnSnPh_3 + Ph_2Hg$ |
| | 5 | $CO_2$ | $Ph_3SnSnPh_3 + {}^-O_2CCO_2{}^-$ |
| | 6 | $AgClO_4$ | $Ph_3SnAg$ (red solution, stable) |
| | 7 | $H_2O$ | $Ph_3SnOH$ |
| | 8 | $HClO_4$-$H_2O$ | $Ph_3SnSnPh_3$ |
| | 9 | $HCl$ | $Ph_3SnH$ |
| $Ph_3Ge\!:^-$ | 10 | $Ph_3SiCl$ | $Ph_3GeH + Ph_3SiH$ |
| | 11 | $Ph_3GeCl$ | $Ph_3GeH$ |
| | 12 | $Ph_3SnCl$ | $Ph_3GeH + Ph_3SnSnPh_3$ |
| | 13 | $AgClO_4$ | $Ph_3GeAg$ (pink solution, unstable) |
| $Ph_3Pb\!:^-$ | 14 | $Ph_3SnCl$ | $Ph_3SnPbPh_3$ (unstable) |
| | 15 | $AgClO_4$ | $Ph_3PbAg$ (green solution, unstable) |

[a] Products established by ultraviolet spectroscopy and polarography on final solutions and comparison with authentic samples, except in the case of $Ph_3MAg$ compounds.

$Ph_3Sn\!:^-$ has the capability to act as an electron source or as a nucleophile. Consideration of reaction scheme 1 indicates that nucleophilic displacement on silicon cannot be the relevant process, since $Ph_3SnSiPh_3$, a known stable compound,[28] would be the expected product. The products actually observed (ultraviolet spectra and polarography) can arise only from an *electron transfer process.*

$$\begin{tikzcd}
Ph_3Sn^- + Ph_3SiCl \arrow[r] & Ph_3Sn\cdot \arrow[d, "coupling"] & + & Ph_3Si\cdot \arrow[d, "abstraction"] & + Cl^- \\
& Ph_3SnSnPh_3 & & Ph_3SiH &
\end{tikzcd}$$

Thus, systems 1, 2, and 5 must involve electron transfer. System 3 could involve nucleophilic displacement, while system 4 could involve redistribution subsequent to nucleophilic attack.

The reaction between $Ph_3Sn^-$ and $AgClO_4$ is instantaneous and produces a red compound which is stable under an argon blanket. Electrolysis of this solution ($n = 1$) gradually discharges the red color and produces a metallic silver deposit. Addition of $Ph_3SnCl$ in the calculated amount to the resulting solution produces $Ph_3SnSnPh_3$.

There seems little doubt then that the original red color is indeed due to $(Ph_3SnAg)_x$.

$$Ph_3Sn^- + Ag^+ClO_4 \longrightarrow (Ph_3SnAg)_x \text{ (red)}$$

$$Ph_2SnAg \longrightarrow Ph_3Sn^- + Ag^0$$

$$Ph_3Sn^- + Ph_3SnCl \longrightarrow Ph_3SnSnPh_3 + Cl^-$$

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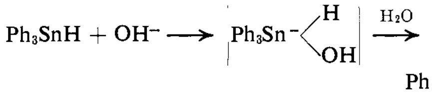
(26) H. Gilman and S. D. Rosenburg, *J. Org. Chem.*, **18**, 680 (1953).

(27) However, for an alternative viewpoint see T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **87**, 669 (1965).

(28) H. Gilman and S. O. Rosenburg, *ibid.*, **74**, 531 (1952).

Reaction with water (system 8) leads to $Ph_3SnOH$, presumably involving the sequence[29]

$$\mathrm{Ph_3Sn^- + HOH \longrightarrow Ph_3SnH + OH^-}$$



$$\mathrm{Ph_3SnH + OH^- \longrightarrow \left|\, Ph_3Sn^- \begin{smallmatrix} H \\ OH \end{smallmatrix} \right| \xrightarrow{H_2O} Ph_3SnOH + H_2 + OH^-}$$

Dry HCl gas (system 10) leads initially to $Ph_3SnH$ (ultraviolet spectra) which on exposure to air overnight is converted to $Ph_3SnSnPh_3$.[30] Dilute perchloric acid (system 9) results in the immediate production of $Ph_3SnSnPh_3$, undoubtedly, involving $Ph_3SnH$ which is rapidly oxidized by the excess $HClO_4$.

Systems 10, 11, and 12 (Table I) appear to find a rationale only in terms of electron transfer. The pink species produced in system 13 is presumed to be $Ph_3GeAg$ by analogy with the findings from system 6. Rapid decomposition to $Ph_3GeH$ and Ag prevented further studies. System 14 seems to proceed by way of nucleophilic displacement on tin to yield an unstable entity, presumed to be $Ph_3SnPbPh_3$.[31] On standing under the argon blanket, decomposition occurs with the production of $Ph_3SnSnPh_3$. This change can be monitored by noting the gradual disappearance of the wave ($E_{1/2}$ = −2.4 v.) assigned to the Pb–Sn compound and the appearance of the $Ph_3SnSnPh_3$ wave.

Although $Ph_3PbAg$ has been suggested to account for the green color produced in the reaction

$$\mathrm{Ph_3PbPbPh_3 \xrightarrow[-80^\circ]{Ag^+} Ph_3PbAg}$$

no corroborative evidence was advanced.[32] The production of a green color in system 16 and extrapolation from system 7 seem to support this postulate.

In the cases cited, the $Bu_4N^+$ counterion confers a different and often enhanced reactivity on the $Ph_3Sn$ moiety in comparison to $Li^+$. One case investigated, however, seems to exhibit the opposite tendency. $Ph_3SnLi$ is known to react with bromobenzene to give good yields to tetraphenyltin.[6] $Ph_3Sn^-Bu_4N^+$ in the presence of bromobenzene either failed to react, or at best was exceedingly sluggish. Since $Bu_4N^+$ would be a poor assistor for leaving group ($Br^-$) departure, it may be concluded that bond breaking (assisted by $Li^+$) is important in this reaction.

In addition to studies of systems containing a M–M′ bond, extension to systems containing the M′M′–M′′ arrangement seemed worthwhile. The hexaphenyl derivatives of Sn–Se–Sn and Sn–Se–Ge were amenable to study.

The symmetrical compound, $Ph_3SnSeSnPh_3$ is reduced in two one-electron steps as indicated.

$$\mathrm{Ph_3SnSeSnPh_3}\begin{array}{l} \xrightarrow[-2.4\ \mathrm{v.}]{e} \mathrm{Ph_3Sn\cdot + Ph_3SnSe^-} \\ \xrightarrow[-2.9\ \mathrm{v.}]{2e} \mathrm{Ph_3SnSe^- + Ph_3Sn^-} \end{array}$$

Exhaustive electrolysis at the first wave, involving one electron, produced hexaphenylditin (*via* coupling of $Ph_3Sn\cdot$) and $Ph_3SnSe^-$, identified by its reaction with $Ph_3SnCl$ to yield the starting material.[33] Hence it appears that selenium can accommodate the negative charge better than tin, a not unexpected state of affairs.

The unsymmetrical material, $Ph_3SnSeGePh_3$ is also reduced in two one-electron steps.

$$\mathrm{Ph_3SnSeGePh_3}\begin{array}{l} \xrightarrow[-2.4\ \mathrm{v.}]{2e} \mathrm{Ph_3SnSe^- + Ph_3Ge\cdot} \\ \qquad\qquad\qquad\qquad\qquad\ \downarrow \\ \qquad\qquad\qquad\qquad\quad \mathrm{Ph_3GeH} \\ \xrightarrow[-2.9\ \mathrm{v.}]{e} \mathrm{Ph_3SnSe^- + Ph_3Ge^-} \end{array}$$

Electrolysis at the first wave did not lead to hexaphenylditin, indicating preferential rupture of the Ge–Se linkage. The addition of $Ph_3SnCl$ to this solution yielded $Ph_3SnSeSnPh_3$ as would be expected. Further characterization of the presumed $Ph_3SnSe^-$ species was attempted by reaction with silver ion. The addition of the calculated amount of silver ion to the solution produced by electrolysis at the first wave yielded an exceedingly intense purple-black coloration. Under the argon blanket, decomposition set in, resulting in decoloration and metallic deposits. By analogy with the more established example of $Ph_3SnAg$, it is suggested that the species initially formed is $Ph_3SnSeAg$.

**Cyclic Voltammetric Studies in Organotin Systems.** The very short preabstraction lifetimes of organosilicon and organogermanium radicals made direct detection of such species impossible with the present apparatus. However, studies in the organotin area have been more rewarding and strong circumstantial evidence for the existence of $Ph_3Sn\cdot$, a metal analog of triphenylmethyl, has been obtained. The findings on several triphenyltin systems are discussed below.

**$Ph_3SnSnPh_3$.** When a solution of $Ph_3SnSnPh_3$ is subjected to triangular voltammetry, at oscilloscopic sweep rates, with initial anodic hold, the first observable cathodic process is that which corresponds to the polarographic step, with $n = 2$, ascribed previously to production of $Ph_3Sn{:}^-$. Sweep reversal at this cathodic limit shows no evidence for electrochemical reversibility of the step, but two oxidative peak currents appear at more anodic potentials, and the second cathodic sweep of a multiple oscillopolarogram, with symmetrical 100-v./sec. wave forms, shows two *new* reductive peak currents anodic with respect to the still present $Ph_3SnSnPh_3$ reduction, and linked to the oxidative peak currents.[34] The entire set of four peaks is linked to the reduction of $Ph_3SnSnPh_3$.

**$Ph_3Sn{:}^-$.** If a solution of $Ph_3SnSnPh_3$ is controlled potential electrolyzed and subjected to triangular voltammetry, with cathodic hold, a set of two oxidative peak currents and linked reductive peak currents on first reversal are noted, at potentials identical with the set of four noted in the case above.

**$Ph_3Sn^+$.** Solutions containing $Ph_3Sn^+ClO_4^-$ can be prepared by either metathetical reaction of $Ph_3SnCl$ +

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(29) J. G. Noltes and G. J. M. Van der Kerk, "Functionally Substituted Organotin Compounds," Tin Research Institute, Greenford, Middlesex, England, 1958, p. 69.

(30) Reference 24, p. 48.

(31) Compounds containing a Sn–Ph bond have recently been reported: see L. C. Willemsens and G. J. M. van der Kirk, *J. Organometal. Chem.*, 2, 260 (1964).

(32) E. Krause and A. von Grosse, "Die Chemie der Metallorganischen verbindungen," Bortraeger, Berlin, 1937, p. 378.

(33) The preparation and reactions of an analogous species, $Ph_3GeSNa$ have been discussed previously: M. C. Henry and W. F. Davidson, *Can. J. Chem.*, **41**, 1276 (1963).

(34) Peaks are said to be linked, when the oxidative process must precede the observance of the reductive peak current, or *vice versa*. This is tested by alteration of the cathodic and anodic limits, or the midpotential, of the sweeps, thus altering the effective size or position of the viewing window.

$AgClO_4$, or by the oxidation–reduction reaction, $Ph_3SnSnPh_3 + 2AgClO_4 \rightarrow 2Ag + 2Ph_3Sn^+ClO_4^-$. Both proceed quantitatively and rapidly to completion, even at $10^{-3}$ *M* concentrations, as evidenced by polarographic studies. The polarography of such solutions shows two steps, the first somewhat more anodic than the first step of $Ph_3SnCl$ reduction (−1.6 v.), the second being identical with $Ph_3SnSnPh_3$. Triangular voltammetry of these solutions, with *anodic hold*, shows on first cathodic sweep two reductive peak currents; and first anodic reversal, at potentials well anodic to the reduction of $Ph_3SnSnPh_3$, shows two linked oxidative peak currents. Again, the set of four occurs at potentials identical with the sets already described.

It seems justified then to assign the set of four linked peaks to those electrochemical processes shown in Figure 1.

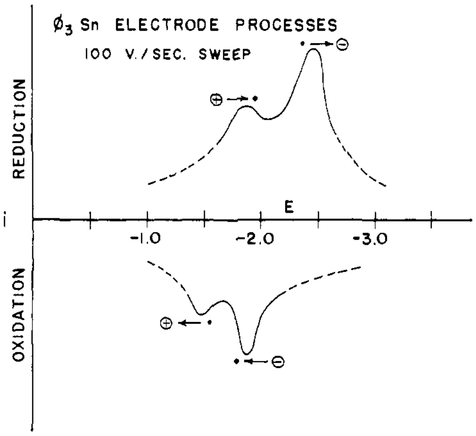

Figure 1.

Asymmetric triangular voltammetry, with lower charging rates in one leg than the other, shows that the radical species has a precoupling lifetime of about 50 msec.

Some additional studies of $Ph_3Sn$ systems were conducted with $Ph_3SnOH$ and $(Ph_3Sn)_2O$. The former undergoes a one-electron reduction at −2.9 v., the product of which reacts with $Ph_3SnCl$ in equimolar concentration to yield a species which also reduces at −2.9 v. This compound was shown by ultraviolet spectroscopy to be exclusively $(Ph_3Sn)_2O$ and not a mixture of $Ph_3SnOH$ and $Ph_3SnSnPh_3$. Thus the sequence described above may be summarized as

$$Ph_3SnOH \xrightarrow{e} Ph_3SnO^- + H \qquad (c)$$

$$Ph_3SnO^- + Ph_3SnCl \longrightarrow (Ph_3Sn)_2O \qquad (d)$$

Cyclic voltammetric evidence for these processes was obtained. With cathodic hold before sweep, an oxidative peak current linked with a reductive peak on first reversal was clearly discernible. This latter signal disappeared at slower sweep rates (25 v./sec. instead of the usual 100 v./sec.) when asymmetric techniques were employed. The observations seem consistent with the scheme

$$Ph_3SnO^- \longrightarrow Ph_3SnO\cdot$$

$$Ph_3SnO\cdot \longrightarrow Ph_3SnO^-$$

$(Ph_3Sn_2)O$ undergoes a two-electron reduction at −2.9 v. to yield, *via* Sn–O fission, $Ph_3SnO^-$ and $Ph_3Sn^-$. The addition of 2 equiv. of $Ph_3SnCl$ to such a solution yielded a mixture of $(Ph_3Sn)_2O$ and $Ph_3SnSnPh_3$ (polarographically and ultraviolet spectra).

Since the oxidation potentials of $Ph_3Sn^-$ and $Ph_3SnO^-$ occur in close proximity, only one anodic signal was observed in the oscillopolarogram of $(Ph_3Sn)_2O$ with cathodic hold before sweep.

Further studies on transient organometal species are being conducted and the synthetic applications of more stable entities are being explored.

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