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Electrogeneration of Triphenyltin Radical, Anion, and Cation. Electrochemical Initiation of Tin Hydride-Promoted Radical Chain Reactions

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In our research of precursors of tin radicals able to initiate radical chain reactions under mild conditions, a series of triphenyltin derivatives Ph_3SnY (Y = H, I, Cl, OTf, OCHO, $SnPh_3$, SPh) is investigated by cyclic voltammetry. The results show that the tin radical $Ph_3Sn^\bullet$ is only produced from two compounds: by a one-electron oxidation of Ph_3SnH or by a one-electron reduction of Ph_3SnI. Therefore electrooxidation of Ph_3SnH generates $Ph_3Sn^\bullet$ which is able to initiate cyclization of haloalkynes. Reduction or oxidation of the other derivatives affords respectively the anion Ph_3Sn^- or the cation Ph_3Sn^+ because they are generated at potentials where the radical $Ph_3Sn^\bullet$ is either reduced or oxidized.

Introduction

Tin hydride-promoted radical chain reactions have met many important applications in modern organic synthesis.[1] The radical chain reactions are usually initiated by thermal decomposition of 2,2′-azobis(isobutyronitrile) (AIBN), benzoyl peroxide, and others.[2] Recently, new devices for the initiation of the radical chain reaction, *e.g.*, homolytic fission of Sn−H bond by ultrasonic irradiation,[3] trialkylborane-based radical- induced reaction[4] and others,[5] have been developed, which are characterized by extremely mild conditions allowing new synthetic applications. Since radicals can be produced after one-electron transfer, electrochemistry may be considered as an alternative procedure for such radical chain initiation under mild conditions. In order to delineate the possibilities of electrochemistry in this field, electrochemical properties of various tin derivatives have been investigated. This allowed us to define the precursor(s) and the experimental conditions prone to generate tin radicals able to initiate radical chain reactions. The key point is the ability to generate tin radicals at a potential where they could not be either oxidized or reduced.

Results and Discussion

Cyclic voltammetry on a series of triphenyltin derivatives ($Ph_3Sn{-}Y$) was investigated in THF or DMF using a gold or platinum disk electrode. The observed oxidation and reduction peak potentials $E^p{}_{ox}$ and $E^p{}_{red}$ are compiled in Table 1. They all refer to a saturated calomel reference electrode (SCE).

Table 1. Cyclic Voltammetry of Tin Derivatives ($Ph_3Sn{-}Y$)

$Ph_3Sn{-}Y$	solvent	$E^p{}_{ox}$/V vs SCE	$E^p{}_{red}$ /V vs SCE
Ph_3SnH	THF	+0.80[a] +1.15[a] +1.50[a]	−2.76[a] {−0.49}[a,b]
Ph_3SnI	THF	+1.03[a]	−0.80,[c] [−0.94[a]] −1.75,[c] [−1.37[a]]
Ph_3SnCl	THF		−2.48[a]
Ph_3SnOTf	THF		−1.42[a]
$Ph_3SnSnPh_3$	THF	+1.50[a]	−2.47[a]
Ph_3SnSPh	DMF	+1.22[d]	−2.30[a] −2.47[a]
$Ph_3SnOCHO$	DMF	+1.57[a]	−2.42[a]
$Ph_3SnSi(t\text{-}Bu)(Me)_2$	THF	+1.63[d]	−2.81[a]

[a] Determined at a steady gold disk electrode at the scan rate of 200 mV/s. [b] $E^p{}_{ox}$ corresponding to the oxidation of electrochemical product detected on the reverse scan. [c] $E_{1/2}$ determined at a rotating glassy carbon disk electrode ($\omega = 105$ r/s) at the scan rate of 20mV/s. [d] Determined at a steady platinum disk electrode at the scan rate of 200 mV/s.

Electrochemistry of Triphenyltin Hydride. The voltammetric oxidation of triphenyltin hydride Ph_3SnH gives rise to three oxidation peaks (E_{O1}, E_{O2}, E_{O3}) observed at +0.80, +1.15, +1.50 V vs SCE, respectively (Figure 1a). Its voltammetric reduction affords a reduction peak (E_{R1}) at −2.76 V associated with an oxidation peak (E_O) at −0.49 V observed on the reverse scan (Figure 1b).

On the other hand, the voltammetric oxidation of hexaphenylditin $Ph_3SnSnPh_3$ (Figure 2a) exhibits an oxidation peak at +1.50 V, which is identical to the third oxidation peak observed during oxidation of triphenyltin hydride (E_{O3}). On the cathodic scan (Figure 2b), a reduction peak (E_{R2}) is observed at −2.47 V and the reverse scan exhibits an oxidation peak at −0.49 V which is identical to that observed during the voltammetric reduction of triphenyltin hydride (E_O) (compare Figures 1b and 2b).

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1996.

(1) For reviews, see: (a) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, England, 1986. (b) Neumann, W. P. *Synthesis* **1987**, 665. (c) Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541. (d) Curran, D. P. *Synthesis* **1988**, 417, 489. (e) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 969.

(2) Cunan, D. P. In *Comprehensive Organic Synthesis*; Trost, B. M.; Flemming, I., Eds; Pergamon Press: Oxford, England, 1991; Vol. 4, pp 715−777.

(3) Nakamura, E.; Machii, D.; Inubushi, T. *J. Am. Chem. Soc.* **1989**, *111*, 6849.

(4) (a) Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987**, *109*, 2547. (b) Oshima, K.; Utimoto, K. *J. Synth. Org. Chem. Jpn.* **1989**, *47*, 40. (c) Nozaki, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1988**, *29*, 6127 and references cited therein.

(5) See, for example: Curran, D. P.; Chen, M. *J. Am. Chem. Soc.* **1987**, *109*, 6558.

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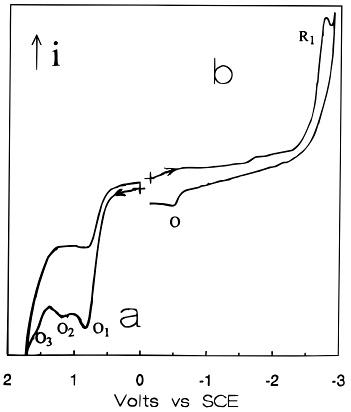


Figure 1. Cyclic voltammetry of Ph_3SnH (2 mM) in THF (0.3 M nBu_4NBF_4) at a gold disk electrode (∅ = 0.5 mm) with a scan rate of 0.2 V s^{-1}, 20 °C: (a) oxidation, (b) reduction.

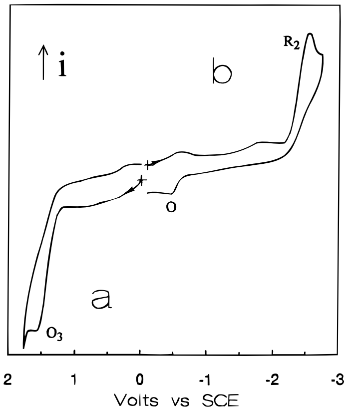


Figure 2. Cyclic voltammetry of $Ph_3SnSnPh_3$ (2 mM) in THF (0.3 M n-Bu_4NBF_4) at a gold disk electrode (∅ = 0.5 mm) with a scan rate of 0.2 V s^{-1}, 20 °C: (a) oxidation, (b) reduction.

On the basis of these observations, one can reasonably assume the following sequential reactions (eqs 1-1 − 1-6).[6] Thus, one-electron oxidation of triphenyltin hydride at E_{O1} affords triphenyltin radical (eq 1-1). Subsequent one-electron oxidation at E_{O2} is expected to afford the corresponding tin cation (eq 1-2). However the oxidation peak current of O_2 is considerably smaller than that of O_1 (Figure 1a). This means that the tin radical $Ph_3Sn^{\bullet}$ generated at E_{O1} partly undergoes dimerization (during the time required to scan the potential between O_1 and O_2)[7] to give hexaphenylditin attested by its oxidation peak at E_{O3} (eq 1-3) by comparison to that of an authentic sample. The reduction of both triphenyltin hydride and hexaphenylditin is expected to give the corresponding triphenyltin anion (eq 1-4, 1-6) whose oxidation peak was observed on the reverse scan at E_O for both compounds (eq 1-5). To support this attribution, reduction of hexaphenylditin was performed in the presence of trimethylsilyl chloride, Me_3SiCl. Under these conditions, the oxidation peak E_O at −0.49 V was no more observed on the reverse scan. Moreover, when the reduction scan was performed beyond the reduction of hexaphenylditin, a new reduction peak R_3 was observed at −2.71 V which might be ascribed to the reduction peak of $Ph_3SnSiMe_3$ (see the reduction potential of a similar compound: $Ph_3SnSi(t\text{-}Bu)(Me)_2$, in Table 1). These experiments prove that the reduction of Ph_3SnH and that of $Ph_3SnSnPh_3$ results in the formation of the anion Ph_3Sn^- which reacts with trimethylsilyl chloride to afford $Ph_3SnSiMe_3$ (eq 1-7).

Oxidation:

$$\mathrm{Ph_3SnH} \xrightarrow{O_1} \mathrm{Ph_3Sn^{\bullet}} + \mathrm{H^+} + 1e \qquad E_{O1} = +0.80\ \mathrm{V} \qquad (1\text{-}1)$$

$$\mathrm{Ph_3Sn^{\bullet}} \xrightarrow{O_2} \mathrm{Ph_3Sn^+} + 1e \qquad E_{O2} = +1.15\ \mathrm{V} \qquad (1\text{-}2a)$$

$$\mathrm{Ph_3Sn^{\bullet}} \longrightarrow {}^{1}\!/_{2}\mathrm{Ph_3SnSnPh_3} \qquad (1\text{-}2b)$$

$$\mathrm{Ph_3SnSnPh_3} \xrightarrow{O_3} 2\ \mathrm{Ph_3Sn^+} + 2e \qquad E_{O3} = +1.50\ \mathrm{V} \qquad (1\text{-}3)$$

Reduction:

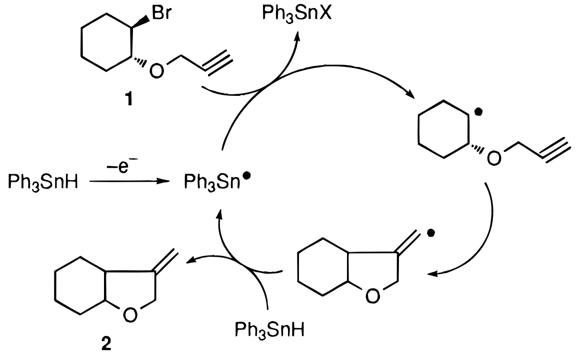
$$\mathrm{Ph_3SnH} + 1e \xrightarrow{R_1} \mathrm{Ph_3Sn^-} + \mathrm{H^{\bullet}} \qquad E_{R1} = -2.76\ \mathrm{V} \qquad (1\text{-}4)$$

$$\mathrm{Ph_3Sn^-} \xrightarrow{O} \mathrm{Ph_3Sn^{\bullet}} + 1e \qquad E_{O} = -0.49\ \mathrm{V} \qquad (1\text{-}5)$$

$$\mathrm{Ph_3SnSnPh_3} + 2e \xrightarrow{R_2} 2\ \mathrm{Ph_3Sn^-} \qquad E_{R2} = -2.47\ \mathrm{V} \qquad (1\text{-}6)$$

$$\mathrm{PhSn^-} + \mathrm{ClSiMe_3} \rightarrow \mathrm{Ph_3SnSiMe_3} + \mathrm{Cl^-} \qquad (1\text{-}7)$$

Scheme 1



Above all, these results suggest that the electrooxidation of triphenyltin hydride proceeds in a step-by-step manner, leading first to the radical and then to the cation. To the best of our knowledge, this is the first example where the oxidation peak of triphenyltin radical (E_{O2}) is observed. In order to confirm the generation of the triphenyltin radical, preparative electrolysis of triphenyltin hydride was carried out. A solution of triphenyltin hydride in THF containing n-Bu_4NClO_4 as the supporting electrolyte was oxidized in an undivided cell equipped with two platinum electrodes. Passage of 1.5 F/mol of electricity afforded hexaphenylditin in 83% yield. This fact strongly supports the generation of the tin radical ($Ph_3Sn^{\bullet}$) during the electrooxidation of triphenyltin hydride.

Electrooxidative Initiation of Triphenyltin Hydride-Promoted Radical Chain Reaction.[8] The above observations resulting from cyclic voltammetry performed on triphenyltin hydride prompted us to investigate the tin hydride-promoted cyclization of haloalkynes under electrochemical conditions (Scheme 1, Table 2).

Electrolysis was carried out in a divided cell fitted with two platinum electrodes. The anodic compartment was charged with a mixture of bromoalkyne **1** (0.30 mmol)

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(6) We write here global electrochemical reactions (e.g., eq 1-1) for simplifying the presentation. However, this does not imply that we do not retain the possible existence of transient ion radicals (e.g., $Ph_3SnH^{\bullet+}$ in eq 1-1). For an extended discussion on the mechanism of the first electron transfer (inner sphere or outer sphere contribution), see: Klingler, R.; J.; Kochi, J.; K. *J. Am. Chem. Soc.* **1981**, *103*, 5839.

(7) *Vide infra* for steady state voltammetry of reduction of Ph_3SnI.

(8) Tanaka, H.; Suga, H.; Ogawa, H.; Abdul Hai, A. K. M.; Torii, S.; Jutand, A.; Amatore, C. *Tetrahedron Lett.* **1992**, *33*, 6495.

Table 2. Electrooxidative Cycloaddition of Haloalkynes 1

entry	substrate **1**	electricity, F/mol	compartment[a]	product **2** yield (isolated), %
1	X = Br	0.5	anode	69
2	X = Br	2.0	cathode	—[b]
3	X = Br	2.0	anode/cathode[c]	65
4[d]	X = Br	2.0	anode	—[e]
5	X = I	0.2	anode	72

[a] Carried out in a divided cell unless otherwise noted. [b] Recovery of **1** (83%). [c] Carried out in an undivided cell. [d] Without addition of Ph_3SnH. [e] Recovery of **1** (89%).

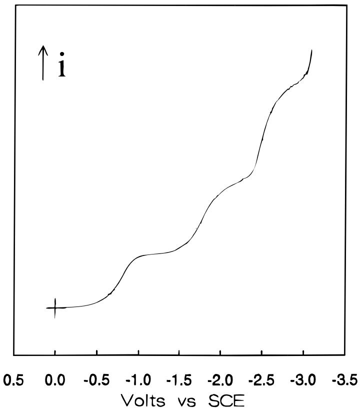


Figure 3. Reduction of Ph_3SnI (2 mM) in THF (0.3 M n-Bu_4NBF_4) at a rotating glassy carbon disk electrode (Ø = 2 mm; $v = 0.02$ V s^{-1}; $\omega = 105$ rad s^{-1}), 20 °C.

and triphenyltin hydride (0.36 mmol) in THF (8 mL) containing Bu_4NClO_4 (7.5 mM). The cathodic compartment was charged with the same solvent. Direct current (10 mA/cm^2) was supplied at ambient temperature. After passage of 0.5 F/mol of electricity, most of **1** was consumed. Usual workup of the anolyte afforded cyclized product **2** (69%) (Table 2, entry 1).

We observed that the cyclization reaction can be performed in the anodic compartment (entries 1–3, and 5) but not in the cathodic compartment (entry 2). In the latter case, the reduction of the triphenyltin hydride should generate the anion Ph_3Sn^- that could react with compound **1** via a nucleophilic substitution. However, compound **1** was recovered in 83% yield, and the substitution product could not be identified. Other reactions, *e.g.*, protonation of the anion might compete with the nucleophilic substitution. In the absence of triphenyltin hydride, no appreciable amount of the cyclization product **2** was obtained (entry 4). These facts indicate that the radical chain reaction is initiated by one-electron oxidation of triphenyltin hydride at the anode, leading to a tin radical (Scheme 1). In other words, the electrochemical oxidation of triphenyltin hydride provides a new promising alternative for initiation of radical chain reactions under mild conditions.

Electrochemistry of Triphenyltin Halides. The cyclic voltammetry of triphenyltin iodide, Ph_3SnI, performed at a rotating carbon disk electrode shows two one-electron reduction waves at $E_{1/2} = -0.80$ and -1.75 V (Figure 3), suggesting that the electroreduction of triphenyltin iodide proceeds in a stepwise manner, leading first to the tin radical $Ph_3Sn^{\bullet}$ and then to the tin anion Ph_3Sn^-.

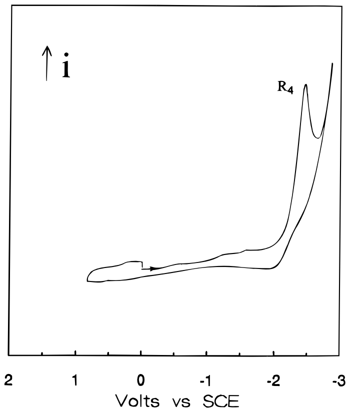
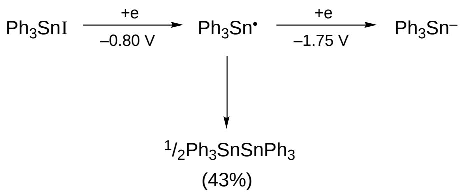


Figure 4. Voltammetric reduction of Ph_3SnCl (2 mM) in THF (0.3 M n-Bu_4NBF_4) at a gold disk electrode (Ø = 0.5 mm) with a scan rate of 0.2 V s^{-1}, 20 °C.

Steady state voltammetry was preferred instead of cyclic voltammetry to enhance the reduction wave of the radical $Ph_3Sn^{\bullet}$. Indeed, in cyclic voltammetry, owing to the transient character of the radical $Ph_3Sn^{\bullet}$, the reduction peak of $Ph_3Sn^{\bullet}$ is minor, because most of the radicals produced at the first peak dimerize while the potential is scanned in the range between the two peaks. In the steady state method, the events occurring at the first wave do not interfere with the second reduction step.[9] Thus, the second wave corresponds to an overall two-electron reduction. This also implies that the reaction of Ph_3Sn^- with Ph_3SnI does not take place significantly, because this would lead to an overall one-electron process at the second wave.[9] Thus the third reduction wave observed on the voltammogram (Figure 3) corresponds to reduction of Ph_3SnH formed by protonation of Ph_3Sn^- by water.[10] The preparative electroreduction of triphenyltin iodide provided hexaphenylditin in 43% yield. This demonstrates that the formation of the hexaphenylditin proceeds through tin radical generated by reduction at the first step as illustrated in eq 2.



(2)

It is worth noting that the quantitative formation of triphenyltin radical is expected during a potential controlled electroreduction of triphenyltin iodide, performed at the first reduction peak. On the basis of this observation, it should be possible to initiate radical chain reactions (such as in Scheme 1) by electroreduction of Ph_3SnI. However, after the radical chain initiation and the cyclization, a stoichiometric amount of hydrogen radical source, viz. Ph_3SnH, is necessary to close the cycle. Therefore if we want to synthesize compound **2** from compound **1** by initiating the chain by $Ph_3Sn^{\bullet}$ resulting from the reduction of Ph_3SnI, we need a catalytic amount of Ph_3SnI and also a stoichiometric amount of Ph_3SnH. Moreover, if the cyclization is performed from compound **1** where X = I (Scheme 1), Ph_3SnI will build up while the cycle proceeds, resulting in

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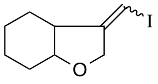
[9] Amatore, C.; Bayachou, M.; Boutejengout, F.; Verpeaux, J. N. *Bull. Soc. Chim. Fr.* **1993**, *130*, 371.

[10] In order to distinguish between a radicalar or an anionic mechanism, water was purposely added to the THF.

an increasing rate of production of $Ph_3Sn^\bullet$ radicals. This is expected to introduce significant changes in the initiation/termination rates and therefore will result in difficulties in controlling the rate of propagation of the radical chain.[11] Therefore this process is expected to be more difficult to operate at preparative levels in contrast with the process described above, which involves only Ph_3SnH, this species playing a double role: source of $Ph_3Sn^\bullet$ and source of hydrogen radical. Were Ph_3SnI used in stoichiometric amount, another compound, **3**, would be formed instead of compound **2** as similarly reported in ref 12, where the catalytic cycle was initiated by the cleavage of $Bu_3SnSnBu_3$ to $Bu_3Sn^\bullet$ under ultraviolet irradiation.



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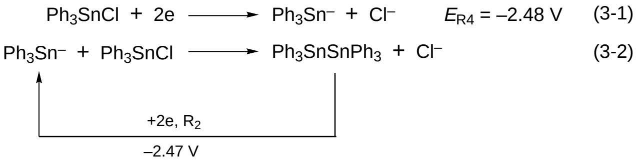
The cyclic voltammogram of triphenyltin chloride (Figure 4) performed at a steady electrode exhibits only a single reduction peak (E_{R4}) at −2.48 V. Since the reduction takes place at a potential more negative than the reduction potential of the triphenyltin radical (see above), the radical is produced at a potential where it is reduced to the anion. This suggests that the reduction of triphenyltin chloride involves two electrons and gives the triphenyltin anion (eq 3-1). However, the oxidation peak (E_O) of Ph_3Sn^- is not observed on the reverse scan at low scan rate (200 mV/s) but becomes observable at higher scan rate (>2 V/s). This proves that the triphenyltin anion undergoes a fast reaction. Since preparative electroreduction of triphenyltin chloride in DMF afforded the hexaphenylditin as the major product (73% yield), the fast reaction is ascribed to the reaction of the triphenyltin anion with triphenyltin chloride (eq 3-2).



It is worth noting that the yield of the dimer obtained in the electrolysis is a dynamic yield since the hexaphenylditin is reducible ($E_{R2} = -2.47$ V) at a slightly less negative potential than that of triphenyltin chloride. This means that the reduction of hexaphenylditin would also proceed in the electroreductive media, at least in part, to generate the Ph_3Sn^- anion (eq 1−3) which slowly gives back the dimer (eq 3-2) provided the parent substrate Ph_3SnCl is still present in the catholyte. After 2 F/mol has been consumed, no Ph_3SnCl reactant is present in the medium and reduction of the dimer proceeds to the anion Ph_3Sn^- (eq 1−6). From these results we see that Ph_3SnCl cannot be a convenient source of the radical $Ph_3Sn^\bullet$ since this latter is produced at a potential where it is reduced to the corresponding anion. Similar results were found for the reduction of Ph_3SnOTf. This compound is reduced at −1.42 V at a gold electrode, *i.e.*, at a potential more negative than the reduction potential of $Ph_3Sn^\bullet$ (−1.37 V at a gold electrode; see Table 1). Moreover a second reduction peak was detected at −2.47 V, demonstrating that $Ph_3SnSnPh_3$ was formed by reaction of the electrogenerated anion Ph_3Sn^- with the parent substrate Ph_3SnOTf.

Table 3. Electrolysis of Triphenyltin Benzenethiolate

entry	conditions[a]	compartment[b]	electricity, F/mol	yield, % isolated	
				$Ph_3SnSnPh_3$	PhSSPh
1	A	anode	4		45
2	B	anode	1.2		97
3	A	cathode	4	21	
4	A	undivided	4	69	7

[a] A: DMA/n-Bu_4NClO_4, 6.6 mA/cm^2. B: CH_2Cl_2/n-Bu_4NBF_4, 1.6 mA/cm^2. [b] Carried out in a divided cell.

Electrochemistry of Triphenyltin Benzenethiolate. The voltammetric oxidation of triphenyltin benzenethiolate Ph_3SnSPh exhibits an oxidation peak at +1.22 V in DMF, and its reduction involves two reduction peaks, one at −2.30 V and the second one at −2.47 V, which is the reduction peak of $Ph_3SnSnPh_3$. On the reverse scan an oxidation peak is detected at +0.06 V, characteristic of the oxidation of PhS^- (the same oxidation peak was observed on the reverse scan after reduction of PhSH at −1.75 V).

Therefore the reduction of Ph_3SnSPh generates $Ph_3SnSnPh_3$ and thiolate ion (PhS^-). The presence of the reduction peak of $Ph_3SnSnPh_3$ and the absence of the oxidation peak (E_O) of Ph_3Sn^- on the reverse scan demonstrate that the latter species (generated by reduction of Ph_3SnSPh) reacts with Ph_3SnSPh to form $Ph_3SnSnPh_3$ and PhS^-. Recently, Nokami et al. have reported that the electrolysis of triphenyltin benzenethiolate in an undivided cell afforded hexaphenylditin in 73−85% yields.[13] We have reinvestigated electrolysis of triphenyltin benzenethiolate, in either cathodic or anodic compartments in a divided cell, to clarify the mechanism of the oxidation and reduction of Ph_3SnSPh (Table 3).

When the electrolysis was carried out in the anodic compartment, diphenyl disulfide PhSSPh, was obtained in 45−97% yields (entries 1 and 2). Notably, the passage of 1.2 F/mol of electricity gave diphenyl disulfide in 97% yield (entry 2), suggesting that one-electron oxidation of triphenyltin benzenethiolate generates the radical $PhS^\bullet$ along with triphenyltin cation. When the electrolysis of triphenyltin benzenethiolate was performed in an undivided cell, hexaphenylditin was obtained in 69% yield (Table 3, entry 4), whereas the electrolysis of triphenyltin benzenethiolate in the cathodic compartment of a divided cell afforded hexaphenylditin in only 21% yield (entry 3). The difference in the yields of hexaphenylditin between entries 3 and 4 can be explained by assuming the following two reaction pathways (Scheme 2).

One involves a two-electron reduction of triphenyltin benzenethiolate leading to triphenyltin anion (Ph_3Sn^-) and subsequent reaction with the residual triphenyltin benzenethiolate. Another involves anodic and cathodic processes; firstly, electrooxidation of triphenyltin benzenethiolate affording triphenyltin cation (Ph_3Sn^+) together with diphenyl disulfide, and secondly, cathodic reduction of the triphenyltin cation leading to the corre-

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[11] Amatore, C.; Pinson, J.; Thiebault, A.; Saveant, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 6930.

[12] Curran, D. P.; Chen, M. H.; Kim, D. *J. Am. Chem. Soc.* **1986**, *108*, 2489.

[13] Nokami, J.; Nose, H.; Okawara, R. *J. Organomet. Chem.* **1981**, *212*, 325.

[14] In Scheme 4, the electron transfers at the first wave are only considered. This means that when two electron are transferred, they are transferred at the potential of the first wave. The further step of oxidation (or reduction) of the radical $Ph_3Sn^\bullet$ is not mentioned for simplification.

Scheme 2

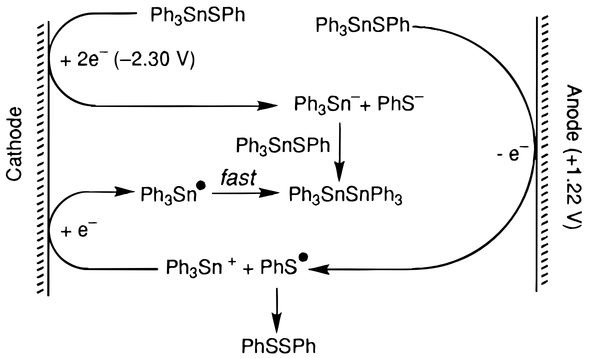


Table 4. Electrolysis of Triphenyltin Formate

entry	compartment	electricity, F/mol	$Ph_3SnSnPh_3$ yield, % (isolated)
1	undivided cell	1.2	23
2	cathode[a]	1.2	
3	anode[a]	1.2	
4	anode/cathode[a,b]	1.25 × 2[b]	12
5	cathode/anode[a,b]	1.25 × 2[b]	

[a] Divided cell. [b] Polarities of electrodes were exchanged (anode → cathode, cathode → anode) after passage of 1.25 F/mol of electricity (see text).

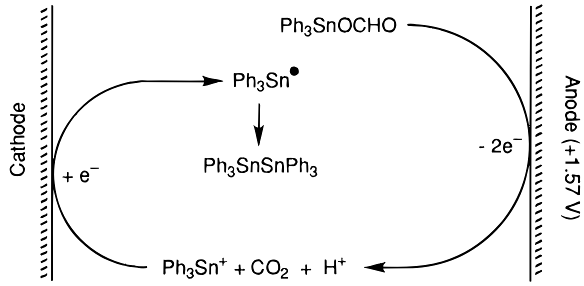
sponding tin radical and subsequent homocoupling, yielding the hexaphenylditin.

Thus, it is not possible to generate $Ph_3Sn^•$ either by direct oxidation or by reduction of Ph_3SnSPh. $Ph_3Sn^•$ could only be generated in a second step by reduction of Ph_3Sn^+ produced by oxidation of Ph_3SnSPh. However this supposes that the anode and cathode are located not too far to prevent secondary reactions of Ph_3Sn^+ (such as reaction with water, etc.).

Electrochemistry of Triphenyltin Formate. The voltammetric oxidation and reduction of triphenyltin formate, $Ph_3SnOCHO$, exhibits oxidation and reduction peaks at +1.57 and −2.42 V, respectively. Both peaks are rationalized by assuming two-electron oxidation generating a triphenyltin cation Ph_3Sn^+ (because occurring at a potential more positive than the oxidation potential of $Ph_3Sn^•$) and two-electron reduction generating a triphenyltin anion Ph_3Sn^- (because occurring at a potential more negative than the reduction potential of $Ph_3Sn^•$). To confirm this, preparative electrolysis of triphenyltin formate was carried out in both divided and undivided cells (Table 4). The hexaphenylditin was not produced in the cathodic or anodic compartments in a divided cell (entries 2 and 3) which confirms that neither reduction nor oxidation of $Ph_3SnOCHO$ produce the radical $Ph_3Sn^•$. Hexaphenylditin was only obtained in an undivided cell (entry 1). This fact indicates that the homocoupling reaction of triphenyltin formate involves both anodic and cathodic processes. In entries 4 and 5, the current direction was changed after 1.25 F/mol of electricity passed. First oxidation and then reduction gave hexaphenylditin (entry 4), whereas first reduction then oxidation gave no appreciable amount of hexaphenylditin. These results led us to propose the following reaction sequence (Scheme 3).

Thus, anodic oxidation of triphenyltin formate affords a tin cation, Ph_3Sn^+, and $HCO_2^•$ (which affords CO_2 and $H^•$ further oxidized to H^+). Ph_3Sn^+ in turn, undergoes one-electron reduction at the cathode and affords hexaphenylditin through a tin radical ($Ph_3Sn^•$) as proposed in the case of Ph_3SnSPh (see above).

Scheme 3



Conclusion

In search of routes for production of tin radicals, the electrochemical properties of a broad series of tin derivatives have been investigated by cyclic voltammetry analyses and preparative electrosyntheses. The mechanisms of oxidation and reduction of several triphenyltin derivatives have been proposed. The corresponding results are summarized in Figure 5 together with the corresponding potentials.

The reduction potentials of the triphenyltin derivatives examined so far, except for triphenyltin iodide, are more negative than the reduction potential of the triphenyltin radical. The triphenyltin compounds, therefore, undergo reduction to generate the corresponding tin anion. On the other hand, the oxidation potentials of the triphenyltin derivatives examined so far, except for triphenyltin hydride, are more positive than the potential of the

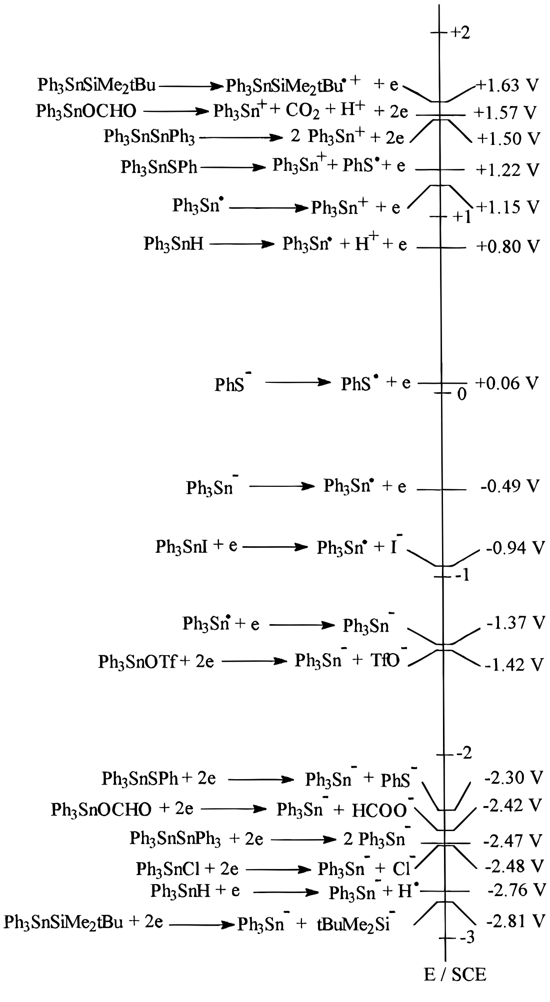
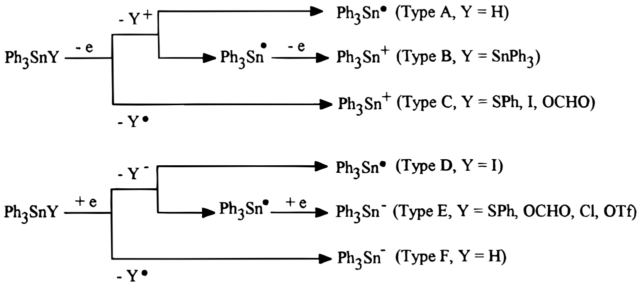


Figure 5. Oxidation and reduction of Ph_3SnY derivatives.

Scheme 4



triphenyltin radical. The triphenyltin compounds, therefore, undergo oxidation to generate the corresponding tin cation. These results shows that only electrooxidation of triphenyltin hydride and electroreduction of triphenyltin iodide can generate tin radical ($Ph_3Sn^{\bullet}$) in the electrolysis media.

Therefore, reaction modes of the triphenyltin derivatives are highly dependent on the nature of the substituents (Y). The reaction modes of the triphenyltin derivatives are divided into six categories as illustrated in Scheme 4.

The electrogenerated species, e.g., tin radical, tin anion, and tin cation, are of great interest from synthetic points of view. The present work was mainly focused on the production of tin radical. We believe that the two other electrogenerated species (cation and anion) may also find interesting applications in organic synthesis.

Experimental Section

General. ^{1}H NMR (200 MHz) and ^{13}C NMR spectra (50 MHz) were recorded on a Varian VXR-200 spectrometer, and chemical shifts are reported in part per million (δ) downfield from TMS. IR spectra were obtained on a JEOL RFX-3002 grating infrared spectrophotometer. Column chromatography was carried out on a Merck silica gel 60, 230−400 mesh ASTM. All preparative electrolyses were carried out twice under a nitrogen atmosphere. Cyclic voltammetry was performed under an argon atmosphere.

Electrochemical Setup and Electrochemical Procedure for Cyclic Voltammetry. Cyclic voltammetry was performed with a homemade potentiostat[15] and a wave-form generator, PAR Model 175. The cyclic voltammograms were recorded with a Nicolet 3091 digital oscilloscope. Experiments were carried out in a three-electrode cell connected to a Schlenck line. The counter electrode was a platinum wire of ca. 1 cm^2 apparent surface area; the reference was a saturated calomel electrode (Tacussel) separated from the solution by a bridge (3 mL) filled with a 0.3 M n-Bu_4NBF_4 solution of THF. Then, 12 mL of THF containing 0.3 M n-Bu_4NBF_4, was poured into the cell followed by 0.024 mmol of the tin derivative (2×10^{-3} M). The cyclic voltammetry was performed at a disk electrode (a gold or platinum disk made from cross section of wire ($\varnothing = 0.5$ mm) sealed into glass) with a scan rate of 0.2 V s^{-1}. In the case of Ph_3SnI, the cyclic voltammetry was performed at a rotating disk electrode (a glassy carbon disk ($\varnothing = 2$ mm) inserted into a Teflon holder, Tacussel EDI 65109) with a scan rate of 0.02 V s^{-1} and an angular velocity of 105 rad s^{-1} (Tacussel controvit). The same reference electrode (SCE) was used for cyclic voltammetry performed in DMF. In this case the filling solution was 3 mL of DMF containing n-Bu_4NBF_4 (0.3 M).

With this series of experiments on triphenyltin derivatives, we did not have to meet with problems of coating and passivation of the electrodes which usually occur with tin derivatives. It might be due to the presence of the phenyl groups on the tin atom.

Materials. The following solvents were purified by distillation: tetrahydrofuran (THF) from sodium benzophenone; dichloromethane (CH_2Cl_2) from P_2O_5; *N*,*N*-dimethylformamide (DMF) from CaH_2; *N*,*N*-dimethylacetamide (DMA) from CaH_2. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Triphenyltin hydride,[16] triphenyltin iodide,[17] triphenyltin benzenethiolate,[18] (*tert*-butyldimethylsilyl)triphenyltin,[19] and triphenyltin triflate[20] were prepared according to reported procedures.

Electrooxidation of Triphenyltin Hydride. A mixture of triphenyltin hydride (100 mg, 0.28 mmol) and Bu_4NClO_4 (50 mg, 0.146 mmol) in THF (7 mL) was placed in a beaker-type undivided cell fitted with two platinum electrodes (1.5×2 cm^2). A constant current (5 mA/cm^2) was supplied at room temperature for 46 min (1.5 F/mol). The reaction mixture was concentrated under diminished pressure, and the residue was diluted with hexane/CH_2Cl_2 (1/1). The solution was washed with brine, dried (Na_2SO_4), and concentrated in vacuum. The residue was recrystallized from hexane to afford $Ph_3SnSnPh_3$ (83 mg, 83%): IR (KBr) 3066, 3012,1481, 1429, 1073, 1021, 998, 727, 698 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.25−7.42, 7.44−7.54, 7.59−7.65 (m, 30H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 128.66, 128.78, 137.44, 139.07. ^{1}H-NMR and ^{13}C-NMR spectra are identical with those of the authentic sample.[13]

Electroreduction of Triphenyltin Chloride. Electrolysis was carried out in an H-type divided cell fitted with platinum anode (1.5×2 cm^2) and lead cathode (1.5×2 cm^2). Triphenyltin chloride (300 mg, 0.78 mmol) was placed in the cathodic compartment, and a DMF solution of Et_4NOTs (250 mg, 0.83 mmol/7 mL, each) was charged in both the anodic and cathodic compartments. The mixture was electrolyzed under a constant current density (3.3 mA/cm^2) with stirring at room temperature. After passage of 1.5 F/mol of electricity (188 min), the catholytes were poured into cold aqueous 5% HCl and extracted with hexane/CH_2Cl_2 (1/1). The combined extracts were washed with aqueous $NaHCO_3$ and brine and dried (Na_2SO_4). After removal of the solvents, the residue was recrystallized from hexane to afford $Ph_3SnSnPh_3$ (142 mg, 73%) whose IR and ^{1}H-NMR spectra are identical with those described above.

Electroreduction of Triphenyltin Iodide. Electrolysis was carried out in an H-type divided cell fitted with a platinum anode (1.5×2 cm^2) and a lead cathode (1.5×2 cm^2). Triphenyltin iodide (100 mg, 0.21 mmol) was placed in the cathodic compartment, and a DMF solution of Et_4NOTs (250 mg, 0.83 mmol/7 mL, each) was charged in both the anodic and cathodic compartments. The mixture was electrolyzed under a constant current density (3.3 mA/cm^2) with stirring at room temperature. After passage of 1.2 F/mol of electricity (39 min), the catholytes were poured into water and the mixture was extracted with a mixed solution of hexane/CH_2Cl_2 (1/1). The combined extracts were washed with brine and dried (Na_2SO_4). After removal of the solvents, the residue was chromatographed on a silica gel column with hexane to give $Ph_3SnSnPh_3$ (31 mg, 43%) whose IR and ^{1}H-NMR spectra are fully identical with those described above.

Electrolysis of Triphenyltin Benzenethiolate. Procedure A. Electrolyses were carried out in an H-type divided cell fitted with two platinum electrodes (1.5×2 cm^2). A solution of triphenyltin benzenethiolate (400 mg, 0.87 mmol) and Bu_4NClO_4 (1 g, 2.92 mmol) in DMA (7 mL) was placed in the anodic compartment, and the same solution was placed in the cathodic compartment. A constant current density (6.7 mA/cm^2) was supplied under stirring at room temperature. After passage of 4 F/mol of electricity (280 min), the catholyte was filtered and washed with MeOH and ether to afford Ph_3-

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SnSnPh$_3$ (64 mg, 21%) as crystals. The IR and ^{1}H-NMR spectra of Ph$_3$SnSnPh$_3$ are identical with those described above. On the other hand, the anolyte was poured into water and extracted with hexane. The extracts were washed with brine, dried (Na$_2$SO$_4$), and concentrated in vacuum. The residue was chromatographed on a silica gel column with hexane to give diphenyl disulfide (43 mg, 45%): ^{1}H-NMR (200 MHz, CDCl$_3$) δ 7.16−7.34 (m, 4H), 7.45−7.53 (m, 6H); ^{13}C-NMR (50 MHz, CDCl$_3$) δ 127.12, 127.50, 129.03, 137.01.

Procedure B. Electrolysis was carried out in the same cell as described above. Triphenyltin benzenethiolate **5** (200 mg, 0.436 mmol) was placed in the anodic compartment, and both the anodic and cathodic compartments were charged with a CH$_2$Cl$_2$ solution of *n*-Bu$_4$NClO$_4$ (1.52 mmol/7 mL). A constant current density (1.7 mA/cm^2) was supplied with stirring at room temperature. After passage of 1.2 F/mol of electricity (168 min), the anolytes were poured into water and the mixture was extracted with CH$_2$Cl$_2$/hexane (1/1). The combined extracts were washed with water and brine and dried (Na$_2$SO$_4$). After removal of the solvents in vacuum, the residue was chromatographed on a silica gel column with hexane/EtOAc (50/1) to give diphenyl disulfide (46 mg, 97%) whose ^{1}H-NMR and ^{13}C-NMR spectra are identical with those described above in procedure A.

Procedure C. A mixture of triphenyltin benzenethiolate (400 mg, 0.87 mmol) and nBu$_4$NClO$_4$ (30 mg, 0.088 mmol) in DMA (7 mL) was placed in a beaker-type undivided cell fitted two platinum electrodes (1.5 × 2 cm^2). A constant current density (6.7 mA/cm^2) was supplied at room temperature for 280 min (4 F/mol). The reaction mixture was filtered and the solids were washed with MeOH and diethyl ether to afford Ph$_3$SnSnPh$_3$ (211 mg, 69%). The filtrate and the washings were poured into water, and the mixture was extracted with a mixed solution of CH$_2$Cl$_2$/hexane (1/1). The combined extracts were washed with water and brine, and dried (Na$_2$SO$_4$). After removal of the solvents in vacuum, the residue was chromatographed on a silica gel column with hexane to give diphenyl disulfide (7 mg, 7%). The IR and ^{1}H-NMR spectra of Ph$_3$SnSnPh$_3$ and PhSSPh are identical with those described above.

Synthesis of Triphenyltin Formate.[21] A mixture of triphenyltin hydride (1.2 mL, 4.7 mmol) and formic acid (0.18 mL, 4.7 mmol) in heptane (20 mL) was heated under reflux for 12 h. After being cooled to room temperature, the reaction mixture was filtered and washed with hexane to afford triphenyltin formate (529 mg, 28%): IR (KBr) 3050, 2852, 1580, 1562, 1433, 1383, 1363, 1079, 729, 696 cm^{-1}; ^{1}H-NMR (200 MHz, CDCl$_3$) δ 7.41−7.62 (m, 9H), 7.68−7.91 (m, 6H), 8.37 (s, 1H); ^{13}C-NMR (50 MHz, CDCl$_3$) δ 129.01, 130.38, 136.80, 137.30, 166.77.

Electrolysis of Triphenyltin Formate. Procedure A. A mixture of triphenyltin formate (100 mg, 0.25 mmol) and Bu$_4$NClO$_4$ (30 mg, 0.088 mmol) in DMA (7 mL) was placed in a beaker-type undivided cell fitted two platinum electrodes (1.5 × 2 cm^2). A constant current density (3.3 mA/cm^2) was supplied at room temperature for 49 min (1.2 F/mol). The reaction mixture was poured into water, and the mixture was extracted with EtOAc. The combined extracts were washed with water and brine and dried (Na$_2$SO$_4$). After removal of the solvents in vacuum, the residue was chromatographed on a silica gel column with hexane/EtOAc (50/1) to give hexaphenylditin (21 mg, 23%) whose IR and ^{1}H-NMR spectra are identical with those described above.

Procedure B. Electrolysis was carried out in an H-type divided cell fitted with two platinum electrodes (1.5 × 2 cm^2). Triphenyltin formate (100 mg, 0.25 mmol) was placed in the anodic compartment, and a DMA solution of Bu$_4$NClO$_4$ (1.46 mmol) was charged into both the anodic and cathodic compartments (7 mL each). The mixture was electrolyzed under a constant current density (1.6 mA/cm^2). After passage of 1.25 F/mol of electricity (102 min), the current direction was changed and the electrolysis was continued under a constant current density (1.6 mA/cm^2). After passage of additional 1.25 F/mol of electricity, the mixture was poured into water and extracted with CH$_2$Cl$_2$/hexane (1/1). The combined extracts were washed with water and brine and dried (Na$_2$SO$_4$). After removal of the solvents *in vacuum*, the residue was chromatographed on a silica gel column with hexane/EtOAc (20/1) to give hexaphenylditin (11 mg, 12%).

Yields reported in Tables 2−4 were sometimes modest. However, appreciable amounts of the starting material were not recovered. An additional complex mixture was formed which was much more polar than the product(s) indicated in the tables. HPLC (or TLC) analysis of the complex mixtures, however, did not show the presence of particular major products which could be isolated and identified.

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