Intramolecular Assistance of Electron Transfer. Oxidative Cleavage of the Carbon−Tin Bond of Tetraalkylstannanes

Jun-ichi Yoshida* and Mitsuhiko Izawa

Contribution from the Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-01, Japan

Received March 21, 1997. Revised Manuscript Received July 26, 1997[⊗]

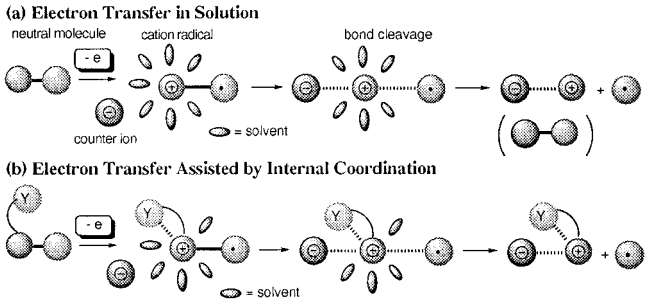
Abstract: Experimental and theoretical studies of intramolecular assistance by carbonyl groups and heteroatoms in the electron transfer driven cleavage of the carbon−tin bond of tetraalkylstannanes has been carried out. Carbonyl groups and heteroatoms (oxygen and nitrogen) in an appropriate position of tetraalkylstannane facilitate the electron transfer and selective cleavage of the carbon−tin bond. Although the coordination of the carbonyl groups and heteroatoms to tin was not detected in the neutral molecules, molecular orbital calculations indicate that the coordination of such groups to tin in the cation radical intermediate stabilizes the system and weakens the carbon−tin bond. These results offer striking examples of the intramolecular assistance of electron transfer driven reactions.

Introduction

Electron transfer in solution is generally assisted by the stabilization of the resulting cation radical or anion radical by the coordination of the solvent molecules or ions, and such coordination is usually very weak or not present before the electron transfer (Scheme 1a). So, if a substrate has a specific coordinating site to stabilize the developing ionic center, the electron transfer should be facilitated significantly (Scheme 1b). Such coordination is also expected to facilitate subsequent chemical processes such as fragmentation. However, only a limited number of papers have been published for such intramolecular assistance of an electron transfer driven reaction.[1] We report the importance of such intramolecular assistance in oxidative cleavage of the carbon−tin bond of tetraalkylstannanes.

The electron transfer driven cleavage of carbon−metal σ bonds[2] has received significant mechanistic study and is of demonstrated synthetic utility. For example, the initial one-electron oxidation gives the σ-cation radical intermediate and its subsequent fragmentation[3] gives products which are often synthetically useful.[4] In our study aimed at new methods for the activation of organometallic compounds toward electron transfer, we encountered an interesting observation indicating both the facilitation of electron transfer and the control of the subsequent fragmentation reaction by the intramolecular coordination. Such coordination was not detected in the starting neutral molecule. In this paper we describe experimental and theoretical studies of intramolecular assistance by dynamic coordination of carbonyl groups and heteroatoms to tin in the electron transfer driven reaction of tetraalkylstannanes.

Scheme 1



Results and Discussion

Electrochemical Study. We found that the oxidation potential of (3-oxobutyl)tributylstannane (**1**)[5] (E_d = 1.41 V vs Ag/AgCl) was less positive than that of tetrabutylstannane (E_d = 1.67 V) (Table 1) by 0.26 V, indicating that the electron transfer is facilitated by 6.0 kcal/mol. Although the activation of organometallic compounds toward electron transfer by extracoordination has been extensively studied,[6] in our case there is no indication of the coordination of the carbonyl group in the neutral molecule of **1** by IR spectroscopy (the carbonyl vibration band at 1717 cm^{-1}).[7] Usually the presence of electron-withdrawing groups on the metal is essential for such coordination, but there is no electron-withdrawing group on the tin atom in the present case. Therefore, the electron transfer seems to

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1997.

(1) (a) Sankararaman, S.; Lau, W.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1991**, 396−398. (b) Olabe, J. A.; Haim, A. *Inorg. Chem.* **1989**, *28*, 3277−3278.

(2) (a) Chanon, M.; Rajzmann, M.; Chanon, F. *Tetrahedron* **1990**, *46*, 6193−6299. (b) Kochi, J. K. In *Comprehensive Organic Synthesis* Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 7, Chapter 7.4, pp 849−889.

(3) (a) Shaik, S.; Reddy, A. C.; Ioffe, A.; Dinnocenzo, J. P.; Danovich, D.; Cho, J. K. *J. Am. Chem. Soc.* **1995**, *117*, 3205−3222. (b) Dinnocenzo, J. P.; Zuihof, H.; Lieberman, D. R.; Simpson, T. R.; MaKechney, M. W. *J. Am. Chem. Soc.* **1997**, *119*, 994−1004 and references and cited therein.

(4) Synthetic utility of electron transfer induced bond cleavage of group 14 metal compounds. For example, photoelectron transfer reactions: (a) Yoon, U. C.; Mariano, P. S. *Acc. Chem. Res.* **1992**, *25*, 233−240. (b) Mizuno, K.; Ikeda, M.; Toda, S.; Otsuji, Y. *J. Am. Chem. Soc.* **1988**, *110*, 1288−1290. Electrochemical reactions: (c) Yoshida, J. *Top. Current Chem.* **1994**, *170*, 40−81. (d) Yoshida, J.; Ishichi, Y.; Isoe, S. *J. Am. Chem. Soc.* **1992**, *114*, 7594−7595. Chemical electron transfer reactions: (e) Narasaka, K.; Kohno, Y. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3456−3463 and references cited therein.

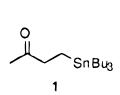
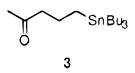
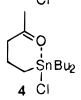
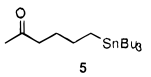
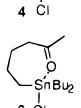
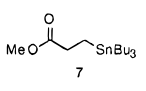
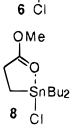
(5) The organotin compounds having a carbonyl group at the β-position are called tin homoenolates. See, for example, Kuwajima, I.; Nakamura, E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 2, Chapter 1.14, pp 441−454.

(6) (a) Corriu, R. J. P.; Young, J. C. In *The Chemistry of Organic Silicon Compound*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; Part 2, Chapter 20, pp 1241−1288. (b) Kumada, M.; Tamao, K.; Yoshida, J. *J. Organomet. Chem.* **1982**, *239*, 115−132 and references cited therein.

(7) It was reported that the carbonyl stretching frequencies of (3-oxobutyl)trimethylstannane and (3-oxobutyl)dimethylchlorostannane are 1710 and 1684 cm^{-1}, respectively: Kuivila, H. G.; Dixon, J. E.; Maxfield, P. L.; Scarpa, N. M.; Topka, T. M.; Tsai, K.-H.; Wursthorn, K. R. *J. Organomet. Chem.* **1975**, *86*, 89−107.

S0002-7863(97)00899-8 CCC: $14.00

Table 1. Electrochemical Oxidation of Ketoorganostannanes and Related Compounds

substrate	oxidation potential [a] (E_d V)	IR $\nu_{C=O}$ (cm^{-1})	preparative electrolysis [b] electricity (F/mol)	product	IR $\nu_{C=O}$ (cm^{-1})	yield (%) [c]	yield (%) of Bu_3SnCl [d]
 1	1.41	1717	2.0	 2	1686	57 (88)	(4)
 3	1.55	1719	2.0	 4	1692	56 (76)	(8)
 5	1.61	1721	2.0	 6	1705	39 (44) [d]	(14) [e]
 7	1.48	1740	2.0	 8	1690	63 (96)	trace
Bu_4Sn	1.67	—	2.0				51 (79)

[a] The oxidation potentials were determined by rotating disk electrode voltammetry in 0.1 M Bu_4NClO_4/CH_2Cl_2 by using a glassy carbon working electrode and a Ag/AgCl reference electrode. [b] The preparative electrochemical oxidation reactions were usually carried out with 0.25 mmol of the substrate with 0.75 mmol of 2,6-lutidine in 4.5 mL of 0.17 M Bu_4NClO_4/CH_2Cl_2 with use of a divided cell equipped with a carbon rod anode and a platinum plate cathode at 0 °C under constant current conditions. [c] Isolated yields. Yields in parentheses were determined by ^1H NMR with use of an internal standard. [d] Isolated yeild. Yields in parentheses were determined by GC analysis with use of an internal standard. [e] 32% of the starting material was recovered unchanged.

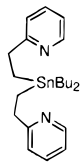
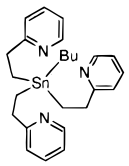
be facilitated by the coordination of the carbonyl group to tin in the cation radical intermediate.[8]

Preparative electrochemical oxidation of compound **1** in Bu_4NClO_4/CH_2Cl_2 followed by workup with aqueous NaCl gave rise to the selective cleavage of the butyl−tin bond and the addition of the chlorine atom to tin producing the pentacoordinate organotin compound (**2**) that exhibited the carbonyl vibration band at 1686 cm^{-1}.[7]

It is interesting that the oxidation potentials of organotin compounds having a carbonyl group at different positions (compound **3** and **5**) were found to be more positive than that of **1**. It is also noteworthy that the carbon−tin bond cleavage of **3** and **5** by the preparative anodic oxidation was not selective and that both the butyl−tin bond cleavage products (compounds **4** and **6**) and chlorotributylstannane were obtained. Therefore, the position of the carbonyl group seems to be crucial for both the promotion of electron transfer and the selective bond cleavage. This is consistent with the IR spectra of the products (**2**, **4**, and **6**); compound **2** exhibits the largest shift for the carbonyl vibration, indicating that the coordination to form the five-membered ring is more effective than those for the six- and seven-membered rings. The ester carbonyl group (compound **7**) was also effective.[9]

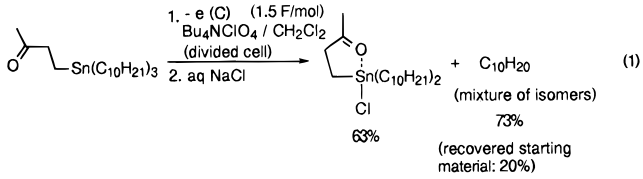
The formation of chlorostannanes (**2**, **4**, **6**, and **8**) may suggest that the fragmentation of the cation radical intermediate produces the tin cation stabilized by the carbonyl group, which reacts with chloride ion in the workup with aqueous NaCl. There is, however, another possibility to be considered. The fragmentation of the cation radical produces the tin radical,[10] which abstracts the chlorine atom from dichloromethane used as the solvent,[11] although it is well documented that the fragmentation of the organometallic cation radical usually affords a cationic metal and an organic free radical.[12] Such a possibility is denied by the fact that the workup without chloride did not give the chlorostannanes.

Table 2. Oxidation Potentials of Heteroatom-Substituted Tetraorganostannanes

substrate	oxidation potential (E_d, V)	substrate	oxidation potential (E_d, V)	substrate	oxidation potential (E_d, V)
	1.42		1.50	Bu_4Sn	1.67
	1.14		1.03		0.92

[a] The oxidation potentials were determined by rotating disk electrode voltammetry in 0.1 M Bu_4NClO_4/CH_2Cl_2 by using a glassy carbon working electrode and a Ag/AgCl reference electrode.

To examine the fate of the alkyl group, the anodic oxidation of the organotin compound having large decyl groups was carried out (eq 1). Decene was formed as a mixture of regioisomers suggesting the intermediacy of decyl cation.



(1)

It should be emphasized that intramolecular assistance for the electron transfer is also effected by other groups containing heteroatoms such as oxygen and nitrogen (Table 2).[13] The effect of the pyridyl group is remarkable.[14] Although ^{119}Sn NMR indicates that the pyridyl group does not coordinate to tin at the neutral stage (−12.15 ppm in $CDCl_3$)[16] the introduction of a pyridyl group resulted in a dramatic decrease of the oxidation potential ($\Delta E_d = 0.53$ V), suggesting the coordination to tin in the cation radical intermediate.[17] It is also noteworthy that the oxidation potential decreases with the increase of the number of the pyridyl groups. In the case of tris [2-(2-pyridyl)ethyl]-butylstannane, the simultaneous coordination of three pyridyl groups to tin seems to be difficult, if we assume that the maximum coordination number of tin is six. Probably the entropic factor plays some role.

(8) Facilitation of electrophilic reactions of tetraorganostannane by the carbonyl coordination has been reported. See ref 7 and: Podesta, J. C.; Chopa, A. B.; Koll, L. C. *J. Chem. Res. (S)* **1986**, 308−309.

(9) Nagao and Ochiai reported the effective intramolecular coordination of acetal oxygen to tin although an electronegative chlorine atom is present on the tin: Ochiai, M.; Iwaki, S.; Ukita, T.; Matsuura, Y.; Shiro, M.; Nagao, Y. *J. Am. Chem. Soc.* **1988**, *110*, 4606−4610.

(10) It has been reported that the oxidative cleavage of the carbon−tin bond gives the carbocation and the tin radical if the electron donating group is attached on the carbon. Eaton, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 3278−3281.

(11) The abstract of halogen atom from organic halides by tin radicals is well-known. For example, see: Curran, D. P.; Jasperse, C. P.; Totleben, M. J. *J. Org. Chem.* **1991**, *56*, 7169−7172. See also ref 9.

(12) For example, Eaton, D. F. *Pure Appl. Chem.* **1984**, *56*, 1191−1202.

(13) Intramolecular coordination of a nitrogen atom at tin promoting the C−Sn bond cleavage has been reported. For example: (a) Vedejs, E.; Haight, A. R.; Moss, W. O. *J. Am. Chem. Soc.* **1992**, *114*, 6556−6558. (b) Jousseaume, B.; Villeneuve, P. *J. Chem. Soc., Chem. Commun.* **1987**, 513−514.

(14) [2-(2-Pyridyl)ethyl]tributyltin was prepared by hydrostannylation of 2-vinylpyridine.[15]

(15) Mahon, M. F.; Molloy, K. C.; Waterfield, P. C. *Organometallics* **1993**, *12*, 769−774.

(16) Davies, A. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 2, Chapter 11, pp 519−628.

(17) The coordination of the pyridyl group to tin in [2-(2-pyridyl)ethyl]-diphenyltin halides has been reported. See ref 17.

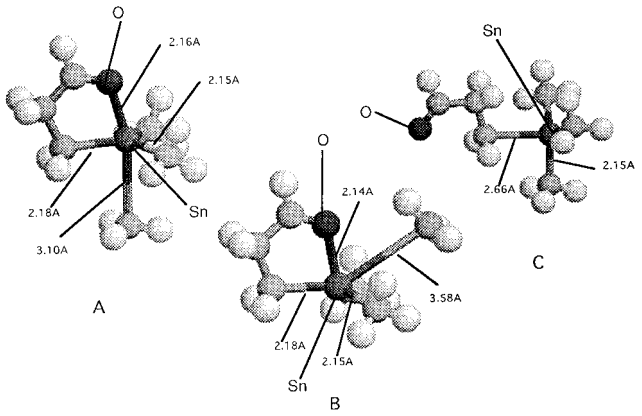
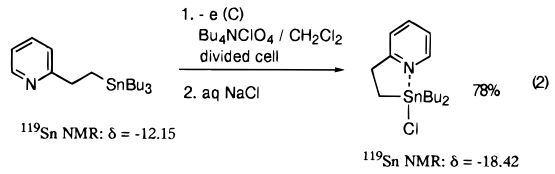


Figure 1. Optimized structures of the cation radical of (3-oxopropyl)-trimethylstannane obtained by *ab initio* MO calculations (HF/3-21G*).

The preparative electrochemical oxidation of [2-(2-pyridyl)-ethyl]tributylstannane in Bu_4NClO_4/CH_2Cl_2 followed by workup with aqueous NaCl gave rise to the selective cleavage of the butyl−tin bond and addition of the chlorine atom to tin producing the pentacoordinate organotin compound. Therefore, the pyridyl group is also effective for the selective cleavage of the carbon−tin bond.



Another important point is that a benzene ring is also effective for the facilitation of the electron transfer, although its magnitude is not so large. Presumably, π-coordination[1b] to the tin atom stabilizes the developing cation radical intermediate.

Computational Studies. To get a deeper insight into the intramolecular assistance for the electron transfer and the subsequent fragmentation, we carried out a computational study using *ab initio* molecular orbital calculations.[18] (3-Oxopropyl)-tributylstannane was chosen as a model compound. The geometry optimization at the HF/3-21G* level gave three structures (**A**, **B**, and **C** in Figure 1). In **A** the carbonyl group coordinates tin to form the trigonal bipyramidal structure. In **B** the carbonyl group also coordinates tin, but the structure of **B** is quite different from that of **A**. In **C** there is no coordination of the carbonyl group to tin. One of the C−Sn bonds in **A** and **B** is remarkably lengthened by 44−67% relative to the other C−Sn bonds,[19] implying that such a bond is selectively weakened by the coordination. In **A** the C−Sn bond *trans* to the carbonyl oxygen is elongated whereas in **B** the C−Sn bond *cis* to the carbonyl oxygen is much longer than usual. In **C** four C−Sn bonds have similar lengths, although one of them is slightly longer than the others. The optimization at HF/LANL2DZ also gave similar structures.

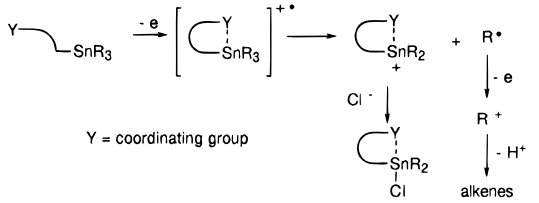
The total energies calculated at several levels indicated that the carbonyl-coordinated conformers (**A** and **B**) are much more stable than the noncoordinated conformer **C** (Table 3), and that **A** is slightly more stable than **B** irrespective of the level of the calcuation. Thus, the molecular orbital calculations indicated that the cation radical intermediate is stabilized by the intramolecular coordination. Such stabilization favors the electron transfer to decrease the oxidation potential. It is also noteworthy that in **A** and **B** one of the carbon−tin bonds is selectively elongated. Therefore, the intramolecular coordination is also responsible for the selective cleavage of the C−Sn bond.

Table 3. Relative Energies of Cation Radicals Obtained by *ab Initio* MO Calculations[a]

	relative total energies (eV)			
structure	HF/3-21G*// HF/3-21G*	MP2/3-21G*// HF/3-21G*	B3LYP/3-21G*// HF/3-21G*	HF/LANL2DZ// HF/HFLANL2DZ
A	−1.44	−1.34	−1.03	−1.84
B	−1.30	−1.15	−0.82	−1.72
C	0	0	0	0

[a] Calculations were carried out with use of G94W.

Scheme 2



Reaction Mechanism. On the basis of the experimental results and computational study, we propose a reaction mechanism involving the coordination of a carbonyl group or a heteroatom in an appropriate position to tin stabilizing the cation radical intermediate. Such nucleophilic assistance also facilitates the selective cleavage of the carbon−tin bond (Scheme 2).

The picture emerging from the existence of pre-coordination in the neutral molecule might also explain the present results. Since such pre-coordination was not detected by the IR and NMR studies, the population of the pre-coordinated complexes is very small even if they exist. The pre-coordinated species are, however, expected to have lower oxidation potentials. Therefore, even if their population is very small, there is a possibility that the electron transfer might selectively take place from such species. However, it seems to be difficult to distinguish such a mechanism from the mechanism based on the stabilization of the cation radical intermediate. At some point in the reaction coordinate, the geometry changes to achieve the intramolecular coordination to facilitate the electron transfer. If such a geometry change occurs in a very early stage, it is regarded as the pre-coordination. If the coordination takes place in a very late stage, it is regarded as the stabilization of the cation radical. There is another possibility that involves the initial partial geometry change to decrease the oxidation potential followed by the ionization and subsequent geometry change to stabilize the resulting cation radical. Some part of the facilitation of the electron transfer might also be attributed to a rapid follow up chemical reaction, because the coordination facilitates the subsequent bond cleavage. Therefore, we must consider "dynamic coordination" instead of "static coordination" to account for the intramolecular assistance of electron transfer.

Conclusions

The findings of the present study offer striking examples of the intramolecular assistance of electron transfer driven reactions. The dynamic intramolecular coordination facilitates the electron transfer and controls the subsequent fragmentation reactions. Such dynamic coordination provides a new method for the activation of substrate molecules toward electron transfer and the control of the subsequent reaction of the cation radical intermediate. Various types of electron transfer driven reactions

(18) The *ab initio* MO calculations were carried out with the Gaussian 94W program. All the optimized structures (UHF/3-21G*) were local minima according to the vibration analysis. The calculations from ECP (HF/LANL2DZ) also gave similar optimized structures.

(19) MNDO calculations of tetraalkyltin cation radical indicated that the bond to the apical alkyl group is lengthened by ca. 13%. Dewar, M. J. S.; Grady, G. L.; Kuhn, D. R. *Organometallics* **1985**, *4*, 1041−1044.

will hopefully be developed on the basis of this concept and widely utilized in organic synthesis.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were measured on a Varian Gemini 2000 spectrometer with Me_4Si as an internal standard. ^{119}Sn NMR spectra were measured on a JEOL JNM-A400 spectrometer with Me_4Sn as an internal standard. $CDCl_3$ was used as the solvent unless stated otherwise. IR spectra were measured with a Shimazu FTIR-8100 spectrophotometer. Mass spectra were obtained with a JEOL IMS-300 spectrometer. Thin-layer chromatography (TLC) was carried out by using Merck precoated silica gel F_{254} plates (thickness 0.25 mm), and silica gel used for flash chromatography was Wakogel C300. Gel permeation chromatography (GPC) was carried out with a Japan Analytical Industry LC 908 with $CHCl_3$ as the eluent.

Diethyl ether and tetrahydrofuran was distilled from benzophenone ketyl. Dichloromethane was washed with water and distilled from P_2O_5, then removal of the trace of acid was carried out by distillation from dried K_2CO_3 and distillate was stored over molecular sieves 4A. Olefins were distilled under appropriate pressure before the hydrostannylation reaction.

All reactions were carried out under Ar atmosphere unless otherwise noted.

Voltammetry. The oxidation potentials were measured by rotating disk electrode voltammetry, which was carried out with a Bioanalytical Systems BAS 100B and a Nikko Keisoku RRDE-1 with a glassy carbon working electrode, platinum wire counter electrode, and Ag/AgCl (saturated aq KCl) reference electrode in 0.1 M Bu_4ClO_4/CH_2Cl_2 at 1000 rpm. The sweep rate was 10 mV/s. Cyclic voltammetry was also carried out with a BAS 100B with a glassy carbon working electrode. All the organotin compounds showed irreversible oxidation waves, and the peak potentials shifted with the sweep rate.

(3-Oxobutyl)tributylstannane (1). To methylmagnesium iodide prepared from 2.38 g (17.0 mmol) of MeI and 472 mg (19.4 mmol) of Mg in 40 mL of diethyl ether was added dropwise 2.73 g (7.93 mmol) of (2-cyanoethyl)tributylstannane. The mixture was stirred overnight at room temperature, then 4 mL of aqueous NH_4Cl was added carefully at 0 °C. The resulting mixture was filtered, and the solvent was removed under reduced pressure. Purification of the crude product via flash chromatography (silica gel, hexane:ethyl acetate = 100:1) followed by distillation (bulb-to-bulb, 170 °C/1 mmHg) afforded 1.70 g (4.71 mmol, 59%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.80−0.85 (m, 8H), 0.89 (s, 9H, J = 7.2 Hz), 1.30 (sextet, 6H, J = 7.3 Hz), 1.42−1.55 (m, 6H), 2.14 (s, 3H), 2.60 (t, 2H, J = 8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 1.91, 8.89, 13.56, 27.26, 28.90, 29.06, 40.85, 210.72; IR (neat) 2957 (s), 2924 (s), 1717 (s), 1375 (w), 1360 (m), 1177 (m), 1136 (w), 1072 (w), 961 (w), 689 (m) cm^{-1}; MS (EI) *m*/*e* (%) 305 (M^+ − Bu, 100), 249 (7), 191 ($SnCH_2CH_2COCH_3$, 16), 121 (4); HRMS calcd for $C_{12}H_{25}OSn$ (M^+ − Bu) 305.0927, found 305.0925.

(3-Oxobutyl)tridecylstannane. To a solution of trichloro(3-oxobutyl)stannane[20] (2.96 g, 10.0 mmol) in THF (30 mL) was added decyl magnesium bromide (prepared from 6.70 g (30.3 mmol) of decyl bromide and 946 mg (38.9 mmol) of Mg in 30 mL of THF) at −78 °C for 1 h. THF (30 mL) was added and the mixture was stirred at −78 °C for 4.5 h. The precipitate was removed by a short column (silica gel, hexane:ethyl acetate = 3:1) and the eluent was washed with brine and dried with $MgSO_4$. After removal of the solvent, the crude product was purified via flash chromatography (hexane:ethyl acetate = 50:1) to obtain the title compound (3.53 g, 5.75 mmol, 58%). The product was further purified with GPC: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.79−0.92 (m, 17H), 1.26 (br s, 42H), 1.48 (br, 6H), 2.14 (s, 3H), 2.59 (t, 2H, J = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 1.97, 9.26, 14.00, 22.59, 26.81, 28.93, 29.18, 29.27, 29.59, 31.85, 34.37, 40.91, 210.81; IR (neat) 2924 (s), 2853 (s), 1719 (s), 1358 (m), 1175 (m), 1136 (w), 722 (w), 689 (w) cm^{-1}; MS (FAB) *m*/*e* 473 (M^+ − $C_{10}H_{21}$, 100), 331 (10), 261 (13), 191 ($SnCH_2CH_2COCH_3$, 48); HRMS calcd for $C_{24}H_{49}SnO$ (M^+ − $C_{10}H_{21}$) 473.2805, found 473.2831.

(4-Oxopentyl)tributylstannane (3). This compound was prepared in 55% yield from (3-cyanopropyl)tributylstannane according to a similar procedure for the preparaiton of **1**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.73−0.79 (m, 2H), 0.80−0.85 (m, 6H), 0.89 (t, 9H, J = 7.2 Hz), 1.24−1.35 (m, 6H), 1.42−1.52 (m, 6H), 1.71−1.82 (m, 2H), 2.13 (s, 3H), 2.44 (t, 2H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.35, 8.36, 13.56, 21.63, 27.26, 29.10, 29.80, 48.43, 209.45; IR (neat) 2957 (s), 2924 (s), 1719 (s), 1458 (m), 1358 (m), 1171 (m), 1071 (w), 596 (w) cm^{-1}; MS (EI) *m*/*e* (%) 319 (M^+ − Bu, 100), 291 (12), 235 (7), 205 ($SnCH_2CH_2CH_2COCH_3$, 5), 177 (SnBu, 23), 121 (6); HRMS calcd for $C_{13}H_{27}OSn$ (M^+ − Bu) 319.1084, found 319.1078.

(5-Oxohexyl)tributylstannane (7). To a solution of NaOH (453 mg, 18.9 mmol) in H_2O (4 mL)/MeOH (4 mL) was added (5-oxo-4-methoxycarbonylhexyl)tributylstannane (417 mg, 0.933 mmol). The reaction mixture was refluxed for 20 min, and then 1.2 mL (21 mmol) of acetic acid was added. The mixture was extracted with ether, and the organic phase was washed with saturated aqueous $NaHCO_3$ and brine and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified via flash chromatography (hexane:ethyl acetate = 30:1) to obtain 316 mg (0.812 mmol, 87%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.75−0.84 (m, 8H), 0.89 (t, 9H, J = 7.2 Hz), 1.29 (t, 6H, J = 7.3 Hz), 1.41−1.61 (m, 10H), 2.13 (s, 3H), 2.43 (t, 2H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.44, 8.56, 13.56, 26.57, 27.25, 28.48, 29.12, 29.68, 43.30, 209.45; IR (neat) 2957 (s), 2926 (s), 1721 (s), 1464 (m), 1481 (w), 1358 (m), 1169 (m), 1071 (w), 961 (w), 691 (m); MS (EI) *m*/*e* 333 (M − Bu, 100), 277 (10), 235 (6), 177 (SnBu, 19), 121 (7). Anal. Calcd for $C_{18}H_{38}OSn$: C, 55.55; H, 9.84. Found: C, 55.85; H, 10.12.

(3-Methoxypropyl)tributylstannane. To a solution of sodium methoxide (6.7 mmol) in THF (5 mL)/MeOH (10 mL) was added 2.27 g (5.5 mmol) of (3-bromopropyl)tributylstannane. The mixture was refluxed overnight, and then 0.10 mL (1.8 mmol) of acetic acid was added. The reaction mixture was extracted with ether, and the organic phase was washed with water and dried over $MgSO_4$. After the solvent was evaporated, the crude product was purified with flash chromatography (hexane:ethyl ether = 50:1) to obtain 1.28 g (0.352 mmol, 64%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.73−0.85 (m, 8H), 0.89 (t, 9H, J = 7.1 Hz), 1.24−1.36 (m, 6H), 1.42−1.53 (m, 6H), 1.71−1.81 (m, 2H), 3.32 (t, 2H, J = 6.9 Hz), 3.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 4.43, 8.68, 13.57, 26.79, 27.31, 29.13, 58.45, 76.34; IR (neat) 2957 (s), 2924 (s), 1420 (w), 1307 (m), 1340 (w), 1201 (m), 1119 (s), 693 (m) cm^{-1}; MS (EI) *m*/*e* (%) 307 (M^+ − Bu, 100), 193 ($SnCH_2CH_2CH_2OCH_3$, 11), 177 (SnBu, 30); HRMS calcd for $C_{12}H_{27}OSn$ (M^+ − Bu) 307.1084, found 307.1070.

[2-(2-Pyridyl)ethyl]tributylstannane. A mixture of Bu_3SnH (828 mg, 2.84 mmol), AIBN (25 mg, 0.15 mmol), and 2-vinylpyridine (376 mg, 3.58 mmol) was stirred at 60 °C for 3 h. Flash chromatography (hexane:ethyl acetate = 20:1) of the crude product afforded 707 mg (1.78 mmol, 63%) of the title compound. ^{1}H NMR (300 MHz) δ 0.78−0.84 (m, 6H), 0.88 (t, 9H, J = 7.2 Hz), 1.16−1.21 (m, 2H), 1.29 (sextet, 6H, J = 7.3 Hz), 1.40−1.51 (m, 6H), 2.95−3.01 (m, 2H), 7.06−7.11 (m, 1H), 7.16−7.18 (m, 1H), 7.56−7.62 (m, 1H), 8.50−8.52 (m, 1H); ^{13}C NMR (75 MHz) δ 8.73, 8.80, 13.60, 27.31, 29.12, 35.31, 120.85, 122.00, 136.41, 149.24, 165.12; IR (neat) 3007 (w), 2955 (s), 2922 (s), 1591, (s), 1568 (m), 1464 (m), 1433 (s), 1375 (m), 749 (s) cm^{-1}; MS (EI) *m*/*e* (%) 340 (M^+ − Bu, 100), 226 ($SnCH_2CH_2C_5H_4N$, 26). Anal. Calcd for $C_{19}H_{35}SnN$: C, 57.60; H, 8.90; N, 3.54. Found: C, 57.34; H, 9.04, N, 3.43.

Bis[2-(2-pyridyl)ethyl]dibutylstannane. To a solution of [2-(2-pyridyl)ethyl]tributylstannane (260 mg, 0.656 mmol) in THF (1 mL) was added BuLi (1.57 M in hexane, 0.46 mL, 0.72 mmol) at −78 °C within 2 min. The resulting deep red solution was stirred for 33 min at −78 °C, and a solution of Bu_2SnCl_2 (90 mg, 0.30 mmol) in THF (1 mL) was added within 3 min. THF (1 mL) was added and the mixture was stirred for 10 min at −78 °C, warmed to room temperature, and stirred at this temperature for 1 h. The reaction mixture was poured into 10 mL of 1 N HCl, and the mixture was washed with 10 mL of hexane. The aqueous phase was separated, and KOH was added until the pH of the solution became 10. The mixture was extracted with 20 mL of ether, and the organic phase was separated and dried over $MgSO_4$. The removal of the solvent under reduced pressure afforded 96 mg of crude product. Flash chromatography (hexane:ethyl acetate = 3:1) gave 77 mg (0.17 mmol, 57%) of the title compound: ^{1}H NMR (300 MHz) δ 0.77−0.87 (m, 10H), 1.17−1.33 (m, 8H), 1.38−1.46 (m, 4H), 2.95−3.01 (m, 4H), 7.05−7.10 (m, 2H), 7.14−7.17 (m, 2H), 7.56−7.61 (m, 2H), 8.49−8.52 (m, 2H); ^{13}C NMR (75 MHz) δ 8.88, 9.11, 13.54, 27.26, 29.00, 35.10, 120.82, 122.00, 136.35, 149.14, 164.87;

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IR (neat) 3067 (w), 3007 (w), 2955 (s), 2923 (s), 1592 (s), 1563 (m), 1473 (s), 1433 (s), 1375 (w), 1150 (m), 1049 (m), 749 (s); MS (EI) *m*/*e* (%) 389 ($M^+ - Bu$, 100), 340 ($M - CH_2CH_2C_5H_4N$, 65) 226 ($SnCH_2CH_2C_5H_4N$, 52). Anal. Calcd for $C_{22}H_{34}SnN_2$: C, 59.35; H, 7.70; N, 6.29. Found: C, 59.52; H, 7.94; N, 6.10.

Tris[2-(2-pyridyl)ethyl]butylstannane. To a solution of [2-(2-pyridyl)ethyl]tributylstannane (438 mg, 1.55 mmol) in THF (10 mL) was added BuLi (1.57 M in hexane, 3.8 mL, 6.0 mmol) at −76 °C within 2 min. The resulting deep red solution was stirred for 1 h at −73 °C, then 438 mg (1.55 mmol) of $BuSnCl_3$ was added at −73 °C. The solution was stirred for 20 min at −73 °C, then stirred for 90 min at 0 °C. To the reaction mixture was added 10 mL of 1 N HCl and 30 mL of hexane. The organic phase was separated and washed with 10 mL of 1 N HCl. The aqueous phase and the washing was combined, and NaOH was added until the pH of the solution became 10. The mixture was extracted twice with 50 mL of ether. The combined organic phase was dried over $MgSO_4$, and the solvent was removed under reduced pressure. Flash chromatography (ethyl acetate) of the crude product gave 458 mg (0.927 mmol, 60%) of the title compound. This product was further purified with GPC ($CHCl_3$) (50% yield): ^{1}H NMR (300 MHz) δ 0.75−0.86 (m, 5H), 1.08−1.30 (m, 8H), 1.34−1.42 (m, 2H), 2.94−3.00 (m, 6H), 7.05−7.09 (m, 3H), 7.13−7.15 (m, 3H), 7.54−7.60 (m, 3H), 8.49−8.51 (m, 3H); ^{13}C NMR (75 MHz) δ 9.23, 9.64, 13.51, 27.25, 28.89, 34.93, 120.75, 121.98, 136.27, 149.05, 164.75; IR (neat) 3065 (m), 3007 (m), 2951 (s), 2919 (s), 1591 (s), 1568 (m), 1473 (s), 1433 (s), 1150 (m), 994 (m), 750 (s) cm^{-1}; MS (FAB) *m*/*e* (%) 438 ($M^+ - Bu$, 9), 389 ($M^+ - C_2H_4C_5H_4N$, 100), 269 (Bu_2SnCl, 18), 177 (BuSn, 17), 155 (SnCl, 19). Anal. Calcd for $C_{25}H_{33}SnN_3$: C, 60.75; H, 6.73; N, 8.50. Found: C, 61.01; H, 6.73; N, 8.46.

(2-Phenylethyl)tributylstannane. To Grignard reagent prepared from 650 mg (3.53 mmol) of phenylethyl bromide and 105 mg (4.32 mmol) of Mg in 5 mL of diethyl ether was added 952 mg (2.92 mmol) of Bu_3SnCl dropwise. The mixture was stirred overnight at ambient temperature. To the reaction mixture was added 0.65 mL of aqueous NH_4Cl carefully with stirring. The resulting mixture was filtered, and the filtrate was dried over $MgSO_4$. After removal of the solvent the crude product was purified via flash chromatography (hexane) followed by bulb-to-bulb distillation (190 °C/2 mm Hg) to obtain the title compound (2.40 mmol, 950 mg, 82%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.76−0.80 (m, 6H), 0.82−0.91 (m, 9H), 1.10−1.16 (m, 2H), 1.22−1.34 (m, 6H), 1.39−1.51 (m, 6H), 2.78−2.83 (m, 2H), 7.16−7.30 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.67, 10.66, 13.60, 27.30, 29.13, 32.94, 125.63, 127.80, 128.41, 146.06; IR (neat) 3063 (w), 3027 (w), 2957 (s), 2924 (s), 1603 (w), 1495 (m), 1454 (m), 1375 (m), 1071 (w), 747 (m), 698 (s) cm^{-1}; MS (EI) *m*/*e* 339 ($M^+ - Bu$, 100); HRMS calcd for $C_{16}H_{27}Sn$ ($M^+ - Bu$) 339.1135, found 339.1134.

General Procedure for the Anodic Oxidation of Organotin Compounds. The anodic oxidation reactions were carried out in a divided cell equipped with a carbon rod anode (15 mm × ϕ 6 mm) and a platinum plate cathode (15 mm × 10 mm). In the anodic chamber were placed an organotin compound (0.25 mmol), 0.17 M Bu_4NClO_4/CH_2Cl_2 (4.5 mL), 2,6-lutidine (0.75 mmol), and molecular sieves 4A (300 mg). In the cathodic chamber were placed 0.17 M Bu_4NClO_4/CH_2Cl_2 (4.5 mL) and molecular sieves 4A (300 mg). The constant current electrolysis (5 mA) was carried out at 0 °C with magnetic stirring until 2.0 F/mol of electricity was consumed. After completion of the reaction, saturated aqueous NaCl (2 mL) was added to the anodic chamber and the mixture was stirred for several minutes at 0 °C, and then warmed to room temperature. The mixture in the anodic chamber was collected. After the addition of saturated aqueous NaCl (3 mL), the mixture was stirred at room temperature for several min. The volatile materials were removed under reduced pressure. Ether (15 mL) was added, and the mixture was stirred vigorously. After removal of the insoluble materials by filtration, the organic phase was separated, and the aqueous phase was extracted with ether. The combined organic phase was dried over $MgSO_4$. After removal of the solvent the crude product was purified by using preparative TLC (Merck precoated silica gel F-254 plates (thickness 0.25 mm) or GPC (Jaigel 1H, 2H, $CHCl_3$)).

Chloro(3-oxobutyl)dibutylstannane (2) was purified with PTLC (hexane:ethyl acetate = 10:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, 6H, J = 7.2 Hz), 1.18 (t, 2H, J = 7.1 Hz), 1.26−1.42 (m, 8H), 1.57−1.67 (m, 4H), 2.27 (s, 3H), 2.98 (t, 2H, J = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.17, 13.94, 19.22, 27.04, 28.31, 29.24, 40.64, 217.52; IR (neat) 2957 (s), 2924 (s), 1686 (s), 1420 (w), 1366 (m), 1335 (w), 1183 (m), 1125 (w), 1076 (w), 702 (w) cm^{-1}; MS (EI) *m*/*e* (%) 305 ($M^+ - Cl$, 20), 283 ($M^+ - Bu$, 100), 191 ($M^+ - 2Bu$, 36); HRMS calcd for $C_8H_{16}ClOSn$ ($M^+ - Bu$) 282.9912, found 282.9905.

Chloro(4-oxopentyl)dibutylstannane (4) was purified with PTLC (hexane:ethyl acetate = 10:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, 6H, J = 7.2 Hz), 1.21−1.44 (m, 10H), 1.61−1.72 (m, 4H), 1.89−1.97 (m, 2H), 2.20 (s, 3H), 2.60 (t, 2H, J = 5.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.54, 18.25, 18.79, 20.10, 26.67, 27.87, 30.33, 40.66, 215.29; IR (neat) 2957 (s), 2923 (s), 1694 (s), 1377 (m), 1184 (m), 1076 (w), 720 (w), 673 (w), 594 (w), 523 (w) cm^{-1}; MS (EI) *m*/*e* 319 ($M^+ - Cl$, 9), 297 ($M^+ - Bu$, 100), 269 (Bu_2SnCl, 18), 177 (BuSn, 17), 155 (SnCl, 19). Anal. Calcd for $C_{13}H_{27}ClOSn$: C, 44.17; H, 7.70. Found: C, 44.45; H, 7.73.

Chloro(5-oxyhexyl)dibutylstannane (6) was purified with PTLC (hexane:ethyl acetate = 10:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, 6H, J = 7.2 Hz), 1.24−1.42 (m, 10H), 1.59−1.67 (m, 8H), 2.15 (s, 3H), 2.47 (t, 2H, J = 6.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.46, 17.36, 17.55, 25.20, 26.33, 26.72, 27.32, 27.70, 42.98, 209.26; IR (neat) 2957 (s), 2924 (s), 1707 (s), 1418 (m), 1360 (m), 1173 (w), 1076 (w), 700 (w), 675 (w) cm^{-1}; MS (EI) *m*/*e* 333 ($M^+ - Cl$, 6) 311 ($M^+ - Bu$, 100), 269 (Bu_2SnCl, 13), 177 (BuSn, 9), 155 (SnCl, 15). Anal. Calcd for $C_{14}H_{29}ClOSn$: C, 45.75; H, 7.95. Found: C, 45.46; H, 7.91.

Chloro[2-(2-pyridyl)ethyl]dibutylstannane was purified with PTLC (hexane:ethyl acetate = 3:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (t, 6H, J = 7.2 Hz), 1.26−1.39 (m, 8H), 1.53−1.67 (m, 6H), 3.42 (t, 2H, J = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.30, 13.51, 19.78, 26.72, 28.11, 32.27, 122.77, 124.41, 138.85, 145.59, 162.00; IR (neat) 3060 (w), 3023 (w), 2955 (s), 2923 (s), 1603 (s), 1439 (s), 1289 (m), 1186 (m), 1013 (s), 762 (s); MS (EI) *m*/*e* 340 ($M^+ - Cl$, 23), 318 ($M^+ - Bu$, 100), 285 (17), 224 (37), 155 (SnCl, 15). Anal. Calcd for $C_{15}H_{26}ClNSn$: C, 48.11; H, 7.00; N, 3.74. Found: C, 48.39; H, 6.87; N, 3.59.

Chloro(2-methoxycarbonylethyl)dibutylstannane (3) was purified with PTLC (hexane:ethyl acetate = 10:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, 6H, J = 7.4 Hz), 1.28−1.44 (m, 10H), 1.59−1.68 (m, 4H), 2.77 (t, 2H, J = 7.5 Hz), 3.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.66, 13.51, 18.76, 26.58, 27.84, 29.71, 53.36, 181.52; IR (neat) 2957 (s), 2924 (s), 1690 (s), 1443 (s), 1358 (s), 1184 (m), 1128 (m), 681 (m) cm^{-1}; MS (EI) *m*/*e* (%) 321 ($M^+ - Cl$, 23), 299 ($M^+ - Bu$, 100), 207 ($M^+ - 2Bu$, 19); HRMS calcd for $C_8H_{16}ClO_2Sn$ ($M^+ - Bu$) 298.9861, found 298.9869.

Chloro(3-oxybutyl)didecylstannane was purified with GPC ($CHCl_3$): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 6H, J = 6.6 Hz), 1.17 (t, 2H, J = 7.4 Hz), 1.26−1.30 (m, 32H), 1.60−1.68 (m, 4H), 2.26 (s, 3H), 2.97 (t, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.79, 13.98, 19.13, 22.56, 25.72, 28.80, 29.09, 29.22, 29.51, 29.54, 31.82, 33.64, 40.21, 217.37; IR (neat) 2924 (s), 1688 (s), 1466 (m), 1366 (s), 1335 (m), 1181 (m), 1125 (w); MS (FAB) *m*/*e* 473 ($M^+ - Cl$, 100), 367 ($M^+ - C_{10}H_{21}$, 24), 331 (9), 191 (28); HRMS calcd for $C_{14}H_{28}ClOSn$ ($M^+ - C_{10}H_{21}$) 367.0851, found 367.0838. Anal. Calcd for $C_{24}H_{49}ClOSn$: C, 56.77; H, 9.73. Found: C, 56.79; H, 9.72.

Acknowledgment. This work was partially supported by Grant-in-Aid for Scientific Research on Priority Areas (No. 283, Innovative Synthetic Reactions) from Monbusho. We thank Mr. Haruo Fujita of our department for the measurement of the ^{119}Sn NMR spectra, Dr. Shigeru Yamago for valuable discussion, and Mr. Mitsuru Watanabe and Mr. Takao Manabe for the assistance of the electrochemical measurements. We dedicate this paper to Professor Hans Schäfer in honor of this 60th birthday.

Supporting Information Available: Listings of geometries of cation radicals obtained by MO calculations (3 pages). See any current masthead page for ordering and Internet access instructions.

JA970899T