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Oxidative Cleavage of Tin–Tin Bonds in Hexaalkyldistannane with Several 1,4-Benzoquinones. Detection of the Semiquinone Radicals and 4-(Trialkylstannoxy)phenoxyl Radicals by ESR spectroscopy.

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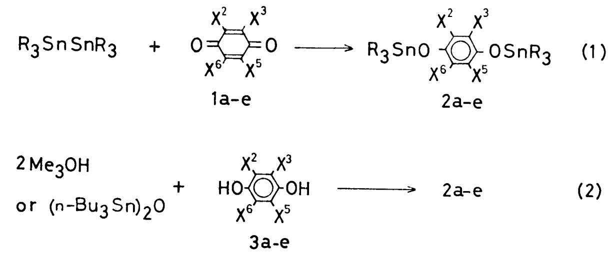
The mechanism of the oxidative cleavage of tin–tin bonds in hexamethyldistannane ($Me_3SnSnMe_3$) and hexabutyldistannane ($Bu_3SnSnBu_3$) with several 1,4-benzoquinones was investigated. Chlorine-substituted 1,4-benzoquinones exerted higher reactivity, implying that the electron-acceptability of quinone is a factor governing the reaction. Stoichiometric treatments of chloranil with the distannanes ruled out the alleged isolation of the free radical, 4-(trimethylstannoxy)phenoxyl radical, reported by Cornwell *et al.* The final products were not the free radical entity but normal compounds, 1,4-bis(trimethylstannoxy)benzenes. Measurements of ESR spectra revealed the formation of the semiquinone radical anions and the subsequent formation of 4-(tributylstannoxy)phenoxyl radicals as reactive intermediates in the reaction pathway.

Oxidative cleavage of the Sn–Sn bonds in hexaorganodistannanes ($R_3Sn–SnR_3$) with halogens, oxygen, and other oxidative materials has been widely investigated.[1–7] Recently, the ability of the σ(Sn–Sn) bond as an electron donor has been obviously demonstrated by the reaction of $R_3Sn–SnR_3$ with powerful π-electron acceptors such as tetracyanoethylene (TCNE),[8] and tetracyanoquinodimethane (TCNQ).[9] In these papers, formations of charge transfer complexes, $(R_3Sn–SnR_3)^+$ $(TCNE)^{\cdot}$[8] and $(Ph_3Sn–SnPh_3)^+$ $(TCNQ)^{\cdot}$,[9] were reported, referring also to the formations of free radicals, R_3Sn–TCNE·[8] and R_3Sn–TCNQ·.[9]

Concerning the reaction with less powerful π-electron acceptors, *viz.* 1,4-benzoquinones and its chlorinated compounds, quite limited information has ever been available. The anion radical of 1,4-benzoquinone was detected by an ESR spectroscopy in the photolytic reaction of $Bu_3Sn–SnBu_3$ in the presence of di-*t*-butyl peroxide and 1,4-benzoquinone.[10,11] A stable free radical, Me_3Sn–chloranil·, was reported to be isolated by simple mixing of $Me_3Sn–SnMe_3$ with chloranil in molar ratio of 1:2, however, no structural information except elemental analysis was presented.[9] Recent report on the ESR spectrum of Me_3Sn-9,10-phenanthrenequinone radical[12] prompted us to disclose our results of the oxidative cleavage of σ(Sn–Sn) bond of R_3SnSnR_3 with several 1,4-benzoquinones. We would like to show that the free radicals, R_3Sn-1,4-benzoquinone·, could be successfully detected by ESR spectroscopy in tetrahydrofuran at low temperature, but was too unstable to be isolated at room temperature. The reaction scheme is discussed on the basis of ESR and ^{1}H-NMR spectra.

Results and Discussion

An equimolar solution of $Me_3SnSnMe_3$ and 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil, **1a**) in benzene was stirred at room temperature under ambient daylight in a nitrogen atmosphere. Gradual color change from the pale greenish yellow of **1a** into brown was observed. Grayish white solid began to appear in about 2 h, and precipitation almost completed within 30 h. The precipitates were identified as 1,4-bis(trimethylstannoxy)-2,3,5,6-tetrachlorobenzene (**2a**) by elemental analysis and by comparing the IR and ^{1}H-NMR spectra with those of the sample prepared by the dehydration method (Eq. 2 in Scheme 1).[13]



R = Me, or n-Bu
a: $X^2, X^3, X^5, X^6 = Cl$
b: $X^2, X^5 = Cl;\ X^3, X^6 = H$
c: $X^2, X^6 = Cl;\ X^3, X^5 = H$
d: $X^2, X^3, X^5, X^6 = H$
e: $X^2, X^3 = Cl;\ X^5, X^6 = CN$

Scheme 1.

Cornwell, Harrison, and Richards reported the isolation of pale creamy solid which they referred to a free radical, Me_3Sn–chloranil·, by the reaction of 1 mol of $Me_3SnSnMe_3$ with 2 mol of **1a** in benzene. Repetition of this reaction allowed us to obtain similar colorless crystals. This crystalline product, however, has now been identified as the normal compound **2a**. One mol of excess **1a** was recovered unchanged from the supernatant solution of the reaction mixture. The analogous reaction of 1 mol of $Me_3SnSnMe_3$ with each 2 mol of 2,5-dichloro-1,4-benzoquinone (**1b**), 2,6-dichloro-1,4-benzoquinone (**1c**), 1,4-benzoquinone (**1d**), and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (**1e**) were carried out to give the regular products **2b**—**e**, and 1 mol of each **1b**—**e** was recovered unchanged.

^{1}H-NMR studies on the reaction of 1 mol of Me_3Sn-$SnMe_3$ with 2 mol of these 1,4-benzoquinones (**1b**—**d**)

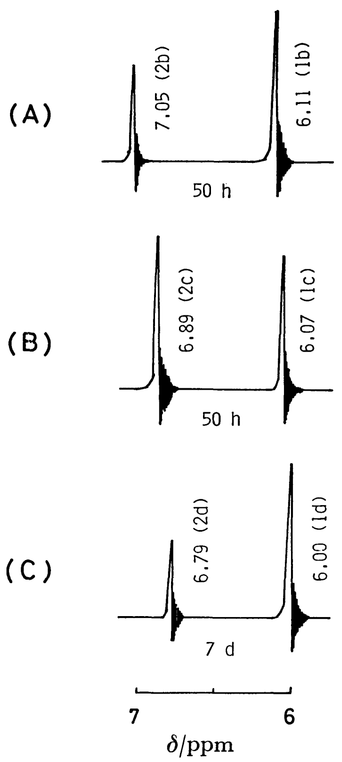


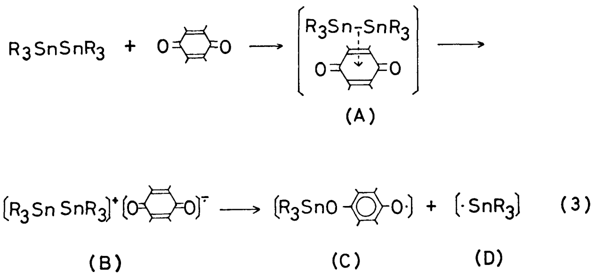
Fig. 1. ^{1}H-NMR spectra of the reaction mixtures of $Me_3SnSnMe_3$ (1 mol) with 1,4-benzoquinones (**1b**—**d**) (2 mol) in C_6D_6. (A): 2,5-Dichloro-1,4-benzoquinone, (B): 2,6-dichloro-1,4-benzoquinone, (C): 1,4-benzoquinone.

in C_6D_6 solution clearly showed that final products were not the free phenoxyl radicals but **2b**—**d**, and hence that 1 mol of the excess free 1,4-benzoquinones (**1b**—**d**) was always present in the solution (Fig. 1).

The electron affinity of the 1,4-benzoquinones is nicely correlated to the reaction times necessary for completing quantitative conversion in the reaction with **2e** (20 h), **2a** (1 d), **2b** (3 d), **2c** (3 d), and **2d** (a week). Particularly in the case of **2d**, the reaction was not induced in the dark even after 5 d at room temperature. These reactions were accelerated by heating and, more effectively, by UV irradiation. When the benzene solution was irradiated with a high pressure mercury lamp, the reaction was completed in less than 60 min.

Similar treatment of an equimolar solution of $Bu_3SnSnBu_3$ with 1,4-benzoquinones in benzene gave brownish (**2a**—**d**) and reddish oily products (**2e**).

The following scheme (Scheme 2) delineates a possible pathway. This is analogous to the proposed mechanism for the similar reaction of $Me_3SnSnMe_3$ with 9,10-phenanthrenequinone:[10] The electron-donating σ(Sn–Sn) bond of R_3SnSnR_3 might interact with the electron defficient 1,4-benzoquinones (acceptor) to form (σ-π) charge transfer complexes (**A**) at the initial step. The transient appearance of the dark brown color in the reaction mixture could be attributed to the formation of **A**. Then, one electron transfer from the Sn–Sn bond into the 1,4-benzoquinone to produce the semiquinone radical anion along with the radical cation of the distannane (**B**). The succeeding cleavage of the Sn–Sn bond of the cation radical in **B** affords both 4-(trialkylstannoxy)phenoxyl radical (**C**) and trialkylstannyl radical (**D**).

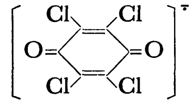
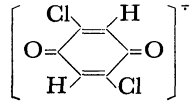
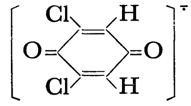
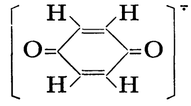
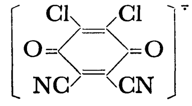


Scheme 2.

ESR measurements have supported the above reaction scheme. The intermediary formation of the semiquinone radical anions (**B**) and the subsequent phenoxyl radicals (**C**) has been clearly demonstrated.

The ESR spectrum of a solution of $Me_3SnSnMe_3$ and **1b** in benzene measured at room temperature displayed a triplet signal (1: 2: 1, a_H=1.98 G) assignable to the radical anion of **1b**.[14] The intensity of the signals gradually increased to reach a maximum in 24 h, and then began to decrease, and became finally undetectable after 3 d. Analogous semiquinone radical anion of **1c** has been observed (Table 1). In the case of **1d**, feeble signal of the semiquinone radical was detected with difficulty.

Table 1. ESR data of the semiquinone radicals observed in the reaction of $Me_3SnSnMe_3$ or $Bu_3SnSnBu_3$ with 1,4-benzoquinones

Radicals	$(Me_3Sn)_2$	$(Bu_3Sn)_2$
		g=2.0061 singlet
	g=2.0055 triplet (1: 2: 1) a_H=1.98 G	g=2.0055 weak and complicated
	g=2.0053 triplet (1: 2: 1) a_H=2.38 G	g=2.0053 weak and complicated
	very weak	g=2.0050 quintet (1: 4: 6: 4: 1) a_H=2.32 G
		g=2.0052 quintet (1: 2: 3: 2: 1) a_N=0.61 G

By contrast, in the ESR spectra of $Bu_3SnSnBu_3$–1,4-benzoquinones systems, stronger and more clearly detectable quintet signal of the semiquinone radical of **1d** (Table 1) was observed, when a benzene solution of **1d** and $Bu_3SnSnBu_3$ was warmed up from a liquid nitrogen temperature and was kept at room temperature for 1 h. The ESR spectra of the benzene solution of $Bu_3SnSnBu_3$ with **1b** or **1c** displayed broad and weak signals. The concentration of **B** from **1b** or **1c** was too low to be detected by ESR spectra, since **B**, if formed, could be comparatively labile and readily converted into the corresponding **C**. These different results of $Bu_3SnSnBu_3$ from those of $Me_3SnSnMe_3$ could be interpreted by taking account of the more electron donating ability of $Bu_3SnSnBu_3$ than that of $Me_3SnSnMe_3$.[7]

When the ESR spectroscopy was carried out in toluene at lower temperature, mixtures of **1b** or **1c** with $Bu_3SnSnBu_3$ afforded complicated spectra consisting of the mixed signals of **B** and **C**. The ESR spectra of the $Bu_3SnSnBu_3$–**1d** and –**1e** systems in toluene displayed strong quintet signals of the corresponding semiquinone radical anions.

In order to obtain the more detectable ESR spectra of less stable phenoxyl radical (**C**) at low temperature, tetrahydrofuran (THF) was used as a solvent. It could be expected that THF could accelerate both the electron transfer from the Sn–Sn bond and the heterolytic cleavage of Sn–Sn bond to readily convert **B** into **C**, then the concentration of **C** increased in the sample. The ESR signals of the unstable phenoxyl radicals (**C**) have now been observed at low temperature, as described below.

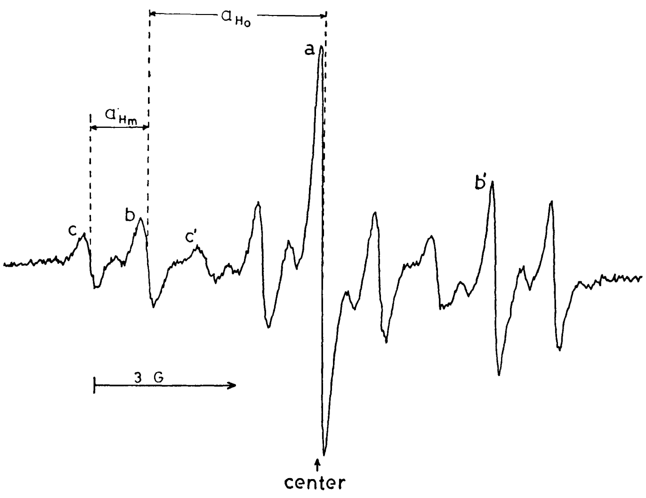
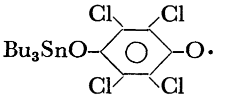
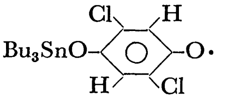
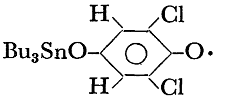
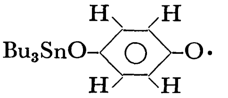
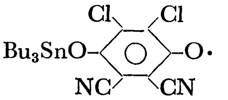


Fig. 2. The ESR spectrum of a THF solution of $Bu_3SnSnBu_3$ and 1,4-benzoquinone at −80 °C.

When a freshly prepared THF solution of $Bu_3SnSnBu_3$ and **1d** was warmed from liquid nitrogen temperature up to about 50 °C for 1 min, and was subjected to the ESR measurement at −80 °C, there were obtained ESR signals (Fig. 2). The triplet (1: 2: 1) of triplet (1: 2: 1) pattern of the signal is clearly different from that of **B** which displays the quintet, but is consistent with that of the 4-(tributylstannoxy)phenoxyl radical (**C**) (Table 2), as compared with those of the other phenoxyl radicals.[15] As the temperature of the cavity was raised from −80 °C, the ESR signals collapsed to become broad, and completely disappeared at about −20 °C. This could be due to the unstability of **C** above −20 °C. When the cavity was cooled back to −80 °C, the same spectral pattern reappeared. A short time irradiation by UV light of the solution kept in the cavity at −80 °C resulted in the increase of these ESR signals. When the reaction had been completed by 20 min irradiation with UV light in the cavity, ESR signal was no longer observed.

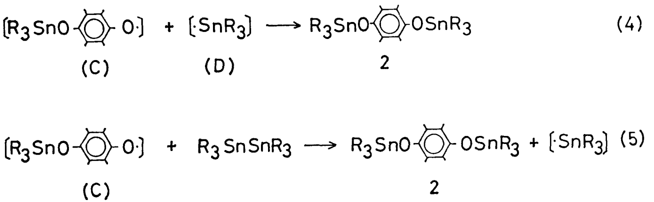
Table 2. Hyperfine splitting constants in 4-(tributylstannoxy)phenoxyl radicals

Radicals	g	a_{H_o}/G	a_{H_m}/G	$a_{^{119}Sn}$/G $a_{^{117}Sn}$/G	Pattern
	2.0050	—	—	2.21 2.11	singlet
	2.0054	3.12	1.04	1.94 1.85	doublet of doublet
	2.0053	—	1.28	1.35 1.29	triplet
	2.0047	3.67	1.22	1.36 1.30	triplet of triplet
	not detected				

Every reaction mixture of the other 1,4-benzoquinones (**1a**—**c**) with $Bu_3SnSnBu_3$, gave ESR signals possessing splitting patterns, coupling constants and g-values which deserved the corresponding free phenoxyl radical (**C**) (Table 2).

When the reaction of $Bu_3SnSnBu_3$ with **1e** was carried out in THF, the ESR spectrum exhibited a clearly detectable quintet of **B** at −30 °C—−80 °C, but no signal of **C** even at −80 °C. Warming up the solution at 50 °C for 2 min resulted in collapse of the quintet signals. This result might be attributed to the rapid conversion of the phenoxyl radical into the final product (**2e**).

The transient free phenoxyl radical (**C**), assigned by ESR spectroscopy in THF, could be converted into the product (**2**) either by the coupling with the radical (**D**), or by the reaction of **C** with R_3SnSnR_3 (Eqs. 4 and 5 in Scheme 3).



Scheme 3.

In all cases of $Me_3SnSnMe_3$ with **1b**—**e**, no definite ESR spectrum for the free phenoxyl radical was obtained even in THF solution at low temperature. This could be attributed to the more rapid consumption of **C** (R=Me) with $Me_3Sn\cdot$ or $Me_3SnSnMe_3$ than that of **C** (R=Bu) with $Bu_3Sn\cdot$ or $Bu_3SnSnBu_3$, probably because $Me_3Sn\cdot$ group or $Me_3SnSnMe_3$ has much less steric hindrance than $Bu_3Sn\cdot$ or $Bu_3SnSnBu_3$.

Experimental

All reactions were carried out in a nitrogen atmosphere. 1,4-Benzoquinones (**1a**—**e**) were purified either by vacuum sublimation or recrystallization immediately before use. The ^{1}H-NMR spectra were measured with JEOL-C60HL spectrometer operating at a resonance frequency of 60 MHz. The ^{13}C-NMR spectra were recorded in the pulse Fourier transform mode using a JEOL-FX60 spectrometer operating at a resonance frequency of 15.03 MHz. Chemical shifts were referred to tetramethylsilane.

The ESR measurements were made using a JEOL X-band spectrometer (Model ME-3) equipped with 100 kHz field modulation. The magnetic field was calibrated by the hyperfine splittings of Mn^{2+} doped in MgO and of ^{14}N of the peroxylaminedisulfonate ion.

The samples for the ESR measurements were prepared as follows. To a mixture of R_3SnSnR_3 and 1,4-benzoquinones in a quartz tube attached to a high vacuum line, anhydrous benzene, toluene, or THF was transferred. The solution was degassed at least four times. The sealed benzene solution was kept at room temperature under ambient diffused light. The ESR spectra of the benzene solution were measured at room temperature. The sealed THF solution was kept in a liquid nitrogen bath. Just before the measurement, the solution was taken out from the cold bath and warmed up at 50°C. After the solution was kept at 50 °C for several minutes in a water bath, it was cooled to −80 °C in a cavity.

Reaction of ***1a*** *with* $Me_3SnSnMe_3$. An equimolar mixture of $Me_3SnSnMe_3$ (0.800 g, 0.24 mmol) and **1a** (0.053 g, 0.22 mmol) in benzene (10 ml) was kept at room temperature under ambient daylight. The color of the solution gradually darkened and became dark brown in 2 h. Colorless crystals began to appear in 3 h, and were completely precipitated in 1 d. After 2 d, the crystals were collected and washed twice with benzene, and dried *in vacuo* to give colorless hexagonal plates (0.111 g), which was identified as 1,4-bis(trimethylstannoxy)-2,3,5,6-tetrachlorobenzene (**2a**). This compound (**2a**) was also prepared by the dehydration method[13] from trimethyltin hydroxide and 2,3,5,6-tetrachloro-1,4-benzenediol (**3a**) (Eq. 2 in Scheme 1). Both samples displayed the same IR and ^{1}H-NMR spectra (Table 3). Benzene of the supernatant solution was evaporated off to give brown solid (0.034 g), which was rinsed with benzene to afford **2a** (0.021 g). Total yield of **2a** was 0.132 g (94%).

A solution of $Me_3SnSnMe_3$ (0.073 g, 0.22 mmol) and **1a** (0.096 g, 0.39 mmol) in benzene (30 ml) was kept at room temperature. The reaction proceeded in the same process as the equimolar reaction. After 2 d, the crystals (**2a**, 0.109 g) were collected by decantation. Benzene of the yellowish brown supernatant solution was evaporated off *in vacuo* to give yellow crystals (0.078 g), which was dissolved in benzene (5 ml). The insoluble **2a** (0.004 g) was separated [total yield of **2a** was 0.113 g (85%)]. The benzene solution was subjected to column chromatography (silica gel, benzene) to recover the excess amount of analytically pure **1a** (0.048 g).

Reaction of ***1b*** *with* $Me_3SnSnMe_3$. An equimolar mixture of $Me_3SnSnMe_3$ (0.072 g, 0.22 mmol) and **1b** (0.035 g, 0.20 mmol) in benzene (10 ml) was kept at room temperature. The color of the solution darkened gradually from yellow to brown, and finally reddish brown. After 4 d, the solvent was evaporated off *in vacuo* to give pale brown solid (0.110 g) of **2b** identified by IR and ^{1}H-NMR spectra (Table 3).

A solution of $Me_3SnSnMe_3$ (0.061 g, 0.19 mmol) and **1b** (0.058 g, 0.31 mmol) in benzene (10 ml) was kept at room temperature. After 4 d, the solvent was evaporated off *in vacuo* to give pale brown solid (0.122 g). This solid was rinsed with a mixed solvent of cyclohexane (4 ml) and benzene (2 ml), and was recrystallized from benzene to give pale brown crystals (**2b**, 0.063 g). The solvent of the supernatant solution was evaporated off and the residue was redissolved in the mixed solvent to give the insoluble solid (**2b**, 0.010 g). The solvent of the rinsed solution was evaporated off to give brown solid (0.040 g), whose ^{1}H-NMR spectrum ($CDCl_3$) had two singlets; the one (+6.00 ppm) was assigned to **1b**, the other (+0.63 ppm) was assigned to Me_3SnOH.

Reaction of ***1c*** *with* $Me_3SnSnMe_3$. An equimolar solution of $Me_3SnSnMe_3$ (0.154 g, 0.47 mmol) and **1c** (0.083 g, 0.47 mmol) in benzene (15 ml) was kept at room temperature. The color of the solution darkened gradually from yellow to brown, and finally dark brown. After 4 d, the solvent was evaporated off *in vacuo* to give dark violet solid (0.230 g) identified as **2c** by IR and ^{1}H-NMR (Table 3). ^{13}C-NMR ($CDCl_3$): δ −2.3 (methyl carbons), +119.5 (3,5-carbons), +126.3 (2,6-carbons).

A solution of $Me_3SnSnMe_3$ (0.097 g, 0.30 mmol) and **1c** (0.092 g, 0.52 mmol) in benzene (10 ml) was kept at room temperature. After 4 d, the solvent was evaporated off *in vacuo* to give brown solid (0.187 g). Mixed solvent of cyclohexane (2.5 ml) and benzene (1.5 ml) was added to the brown solid and insoluble solid was collected, rinsed with benzene to give pale brown solid (**2c**, 0.077 g). The solvent of the supernatant solution was evaporated off to give brown solid, which was rinsed with the mixed solvent, and further with benzene to afford **2c** (0.013 g) [total yield of **2c** was 0.090 g (63%)]. The solvent was evaporated off from the rinsed solution to give brown solid (0.091 g), whose ^{1}H-NMR ($CDCl_3$) showed two singlets; the one (+6.05 ppm) was assigned to **1c**, the other (+0.58 ppm) was assigned to Me_3SnOH.

Reaction of ***1d*** *with* $Me_3SnSnMe_3$. An equimolar solution of $Me_3SnSnMe_3$ (0.165 g, 0.50 mmol) and **1d** (0.055 g, 0.51

Table 3. Melting points, analytical and ^{1}H-NMR (THF) data of **2a**—**e** (R=Me)

Compound	Mp/°C	Found (%)			Calcd (%)			Sn-CH_3		CH
		C	H	N	C	H	N	δ/ppm	J_{Sn-CH_3}/Hz	δ/ppm
2a	173—174	25.03	3.37		25.12	3.14		0.56	66.0	—
2b	172—173	28.86	3.94		28.57	4.00		0.41	64.5	6.55
2c	193—194	29.93	3.79[a]		28.57	4.00		0.48	63.9	6.63
2d[b]	190—191[c]							0.42[18]	62.0	6.42[18]
2e	190—200[d]	30.46	3.40	5.08	30.30	3.27	5.05	0.62	68.0	—

a) Elemental analyses did not give satisfactory results in spite of efforts of repeated preparations and analysis. The deviation found in the elemental analyses might be due to the partial hydrolysis of the sample during recrystallization procedures.[16] b) **2d** was partially hydrolyzed during repeated recrystallizations to give analytically pure 4-(trimethylstannoxy)phenol, dp 200 °C—215 °C.[18] c) Lit, 187 °C.[17] d) Dp.

mmol) in benzene (10 ml) was kept at room temperature. The solution darkened slightly in a week. After 2 weeks the solvent was evaporated off to give pale brown solid (0.210 g). This was rinsed with cyclohexane to give pale brown solid (0.168 g, 77%) identified as **2d** by ^{1}H-NMR (Table 3) and IR spectra.[17]

*Reaction of **1e** with $Me_3SnSnMe_3$.* An equimolar solution of $Me_3SnSnMe_3$ (0.070 g, 0.21 mmol) and **1e** (0.046 g, 0.20 mmol) in benzene (10 ml) was kept at room temperature. The solution gradually turned brown in 15 min and reddish yellow crystals began to precipitate. The solution turned yellow in 3 h. When the mixture was kept for 20 h, the reaction was completed. The crystals were separated and recrystallized with benzene to give orange yellow needles (0.109 g, 98%) identified as **2e** (Table 3).

A solution of $Me_3SnSnMe_3$ (0.067 g, 0.20 mmol) and **1e** (0.092 g, 0.40 mmol) in benzene (10 ml) was kept at room temperature. After 2 d, crystalline **2e** (0.100 g, 90%) was collected. Benzene of the reddish brown supernatant solution was evaporated off *in vacuo* to recover the excess amount of **1e** (0.052 g).

*Reaction of **1a—d** with $Me_3SnSnMe_3$ under Irradiation.* An equimolar solution of **1a** (0.049 g, 0.20 mmol) and $Me_3SnSnMe_3$ (0.075 g, 0.23 mmol) in benzene (10 ml) in a sealed Pyrex glass tube was irradiated externally with a high pressure mercury lamp (450 W) at 20 °C. After 10 min irradiation, colorless solid precipitated and the solution turned almost colorless. After 20 min, the precipitates were collected by decantation, rinsed with benzene and dried *in vacuo* to give pure **2a** (0.083 g, 73%). The solvent of the supernatant solution was evaporated off and washed with benzene to give **2a** (0.030 g, 26%).

The reactions of **1b—d** with $Me_3SnSnMe_3$ were carried out analogously as described above: The reactions were completed within 1 h to obtain **2b**, **2c**, and **2d** in the yields of 86%, 82%, 74%, respectively.

*Reaction of $Bu_3SnSnBu_3$ with **1a—e**.* A solution of $Bu_3SnSnBu_3$ (0.18 mmol) and **1a** (0.17 mmol) in benzene (10 ml) was stirred at room temperature being exposed to ambient diffused light. Almost quantitative yield of a brown viscous liquid, **2a** also was obtained in 25 h.

The reactions of $Bu_3SnSnBu_3$ with **1b—e** were carried out in the same manners as mentioned above. The reactions were completed in 66, 63, 140, and 24 h, respectively. Brown oily products were identified as **2b—e**, by comparing the IR and ^{13}C-NMR spectra with those of the samples prepared by Eq. 2 in Scheme 1.[13]

*Reaction of $Bu_3SnSnBu_3$ with **1a** under Irradiation.* A solution of $Bu_3SnSnBu_3$ (0.37 mmol) and **1a** (0.37 mmol) in benzene (15 ml) was irradiated. After 10 min irradiation, the color of the solution changed from pale greenish yellow to brown, and $\nu_{C=O}$ absorption of **1a** (1690 cm^{-1}) in the IR spectrum disappeard completely. Removal of the solvent *in vacuo* gave almost quantitative yield of **2a**.

*Thermal Reaction of $Bu_3SnSnBu_3$ with **1a**.* An equimolar mixture of $Bu_3SnSnBu_3$ (0.31 mmol) and **1a** (0.27 mmol) in benzene was heated under reflux for 1.5 h. The $\nu_{C=O}$ absorption in the IR spectrum was absent, and the solvent was evaporated off to give **2a** quantitatively.

References

1) G. Tagliavini, S. Faleschini, G. Pilloni, and G. Plazzogna, *J. Organomet. Chem.*, **5**, 136 (1966).

2) H. H. Anderson, *Inorg. Chem.*, **3**, 108 (1964).

3) P. Bamberg, B. Ekström, and B. Sjöberg, *Acta Chem. Scand.*, **22**, 367 (1968).

4) G. Tagliavini and L. Doretti, *Chem. Commun.*, **1966**, 562.

5) L. Doretti and G. Tagliavini, *J. Organomet. Chem.*, **12**, 203 (1968).

6) N. A. D. Carey and H. C. Clark, *Can. J. Chem.*, **46**, 643 (1968).

7) A. Peloso, *J. Organomet. Chem.*, **67**, 423 (1974); **74**, 59 (1974).

8) P. J. Krusic, H. Stoklosa, L. E. Manzer, and P. Meakin, *J. Am. Chem. Soc.*, **97**, 667 (1975); V. F. Traven and R. West, *ibid.*, **95**, 6824 (1973); *Zh. Obshch. Khim.*, **44**, 1837 (1974); O. A. Reutov, V. I. Rozenberg, G. V. Gavrilova, and V. A. Nikanorov, *J. Organomet. Chem.*, **177**, 101 (1979).

9) A. B. Cornwell, P. G. Harrison, and J. A. Richards, *J. Organomet. Chem.*, **140**, 273 (1977).

10) J. Cooper, A. Hudson, and R. A. Jackson, *J. Chem. Soc., Perkin Trons. 2*, **1973**, 1933.

11) K. S. Chen, T. Foster and J. K. S. Wan, *J. Chem. Soc., Perkin Trans, 2*, **1979**, 1288.

12) K. Mochida, J. K. Kochi, K. S. Chen, and J. K. S. Wan, *J. Am. Chem. Soc.*, **100**, 2927 (1978).

13) G. Weissenberger, U. S. Patent 3129236 (Cl. 260—429.7), Apr. 14, (1964); Swiss Appl. Dec. 31, (1960), 6 pp; *Chem. Abstr.*, **61**, 686 e, (1964).

14) W. E. Geiger, Jr., and W. M. Gulik, Jr., *J. Am. Chem. Soc.*, **91**, 4657 (1969).

15) T. J. Stone and W. A. Waters, *J. Chem. Soc.*, **1964**, 213; H. B. Stegmann and K. Scheffler, *Tetrahedron Lett.*, **1964**, 3387.

16) The elemental analyses always showed the intermediate values between the calulated ones of **2c** and those of 4-trimethylstannoxy-3,5-dichlorophenol (Calcd for $C_9H_{12}O_2Cl_2Sn$: C, 31.67; H, 3.52%).

17) N. Wiberg and M. Veith, *Chem. Ber.*, **104**, 3191 (1971).

18) ^{1}H-NMR (THF): δ 0.43 (s, 9H, J_{Sn-CH_3}=60.0 Hz), 6.40 (d, 2H, 2,6-protons, J=9 Hz), 6.50 (d, 2H, 3,5-protons). Found: C, 39.84; H, 5.33%. Calcd for $C_9H_{14}O_2Sn$: C, 39.61; H, 5.17%.