  Bull. Chem. Soc. Jpn., 60, 3299—3306 (1987)

Reactions of Trialkylstannane Anions R_3Sn^- with Arylstannanes $ArSnR'_3$

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(Received March 24, 1987)

The reactions of trialkylstannane anions R_3Sn^- with arylstannanes $ArSnR'_3$ have been investigated; trialkylstannane anions with arylstannanes at 50 °C gave substitution products $ArSnR_3$ in good yields. Most of these substitution products are diverted to reduction products ArH when *t*-butylamine for trapping free anionoids is present in the reaction mixture. These results are consistent with an initial tin–alkali metal exchange or an electron-transfer forming aryl anions and distannanes which subsequently react to the substitution products. Aryl radical intermediates by an electron-transfer process are also important in the reactions of trialkylstannane anions with electron-withdrawing groups-substituted arylstannanes, 1-naphthylstannanes, diphenylstannanes, and triphenylmethylstannane as good electron acceptor substrates.

The displacement of halides and other groups from alkyl and aryl substrates by alkali metal derivatives of organometal anions represents one of the most important methods for the formation of carbon–metal σ bonds.[1] This approach to the formation of carbon–metal σ bonds has been particularly useful in group 4B chemistry.

Arylstannanes can be synthesized by the reactions of triorganostannane anions with aryl halides.[2–12] This formal nucleophilic aromatic substitution by triorganostannane anions is of considerable interest both in synthetic chemistry and regarding reaction mechanisms. Recently, Kuivila and co-workers,[11] and Pereyre and co-workers[12] have reported on the reactions of trialkylstannane anions with aryl halides and discussed on the mechanism involving alkali metal exchange, electron-transfer, and benzyne process in detail. However, a study of nucleophilic aromatic substitution by triorganostannane anions has been limited to aryl halides as substrates.

In this paper, we describe other nucleophilic aromatic substitutions by trialkylstannane anions: that is, reactions of trialkylstannane anions with arylstannanes.

Results

Reactions of Trimethylstannane Anions with Phenyltrialkylsilane, -germane, and -stannane. Reactions of sodium, lithium, and potassium trimethylstannate, prepared from chlorotrimethylstannane or hexamethyldistannane and alkali metals with phenyltrialkylsilane, -germane, and -stannane were examined under various conditions. These results are

Table 1. Reactions of Trimethylstannane Anions with Phenyltrialkylsilane, -germane, and -stannane under Various Conditions

No.	Reactant/mmol		Condition[a]	Product, yield/%[b]				
	$PhMR_3$	Me_3SnM'		PhH	$PhSnMe_3$	$(Me_3Sn)_2$	$(R_3M)_2$	Me_3SnMR_3
1	$PhSiMe_3$ (1.74)	Li/THF (1.67)	A, B	0	0	50	0	0
2	$PhGeMe_3$ (1.22)	Li/THF (1.12)	A, B	0	0	49	0	0
3	$PhSnEt_3$ (1.22)	Li/THF (1.67)	A	0	0	49	0	1
4	$PhSnEt_3$ (1.12)	Li/THF (1.67)	B	<1	24	16	<1	18
5	$PhSnEt_3$ (1.12)	Li/DME (1.33)	B	<1	10	25	0	13
6	$PhSnEt_3$ (1.12)	Li/TG (1.42)	B	<1	8	43	0	7
7	$PhSnEt_3$ (1.12)	Li/HMPA (0.36)	A	0	22	11	—[c]	8
8	$PhSnEt_3$ (1.22)	Na/THF (1.08)	B	<1	26	13	4	18
9	$PhSnEt_3$ (1.22)	K/THF (1.78)	B	<1	24	22	2	25

a) A: at 24 °C for 1 h; B: at 50 °C for 30 min. b) Based on the concentration of Me_3SnM'. c) Yields of products could not be determined by GLC.

summarized in Table 1.

The reaction of lithium trimethylstannate with phenyltriethylstannane in tetrahydrofuran (THF) at 24 °C for 1 h gave no substitution products. Hexamethyldistannane was formed quantitatively and phenyltriethylstannane was nearly recovered. Lithium trimethylstannate reacted with phenyltriethylstanane at 50 °C for 30 min to give phenyltrimethylstannane, hexamethyldistannane, and trimethylstannane (No. 4). The reaction time and temperature effected the yields of products. At a constant temperature of 50 °C, the yield of phenyltrimethylstannane reached a maximum (ca. 30%) in 40—50 min and, then, gradually decreased. On the other hand, the yield of the product rose to ca. 40% as the temperature was increased to 60 °C for 30 min. However, it is known that lithium trimethylstannate reacts with THF to give ring-opening products at high temperatures and for a long reaction time.[13] Under the reaction conditions (50 °C and 30 min) employed here, the yield of phenyltrimethylstannane is better and side reactions occur only slightly.

The stability of lithium trimethylstannate was stable at 50 °C for 30 min (Fig. 1). A part of lithium trimethylstannate changed to hexamethyldistannane.

As shown in Table 1, a substitution product was also produced in the reactions of lithium trimethylstannate with phenyltriethylstannane in 1,2-dimethoxyethane (DME), tetraglyme (TG), and hexamethylphosphoric triamide (HMPA) (Nos. 5—7). The product was produced even at 24 °C in HMPA. The yield of a substitution product by lithium trimethylstannate in various solvents (Table 1) was variable and depended upon the polarity of the solvents employed.

Sodium and potassium trimethylstannate in THF also reacted with phenyltriethylstannane at 50 °C (Nos. 8 and 9). The yields of the substitution products were almost constant with experimental errors, despite counter ions.

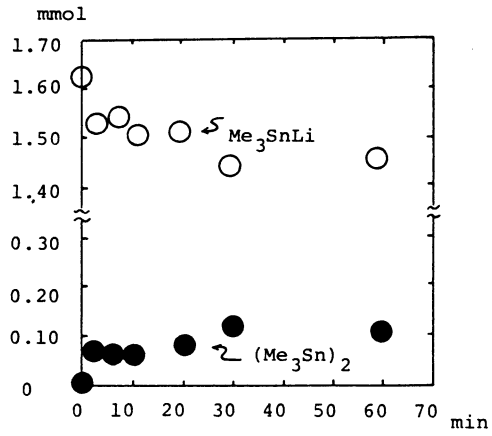


Fig. 1. The stability of lithium trimethylstannate (1.63 mmol) at 50 °C.

Through reactions of lithium trimethylstannate with phenyltrimethylsilane and -germane, the corresponding substitution products were not produced. Only hexamethyldistannane was formed (Nos. 1 and 2).

Reactions of Lithium Trimethylstannate with Arylstannanes. Reactions of lithium trimethylstannate with various arylstannanes in THF were examined. The results are summarized in Table 2.

Table 2 shows the effects of substituents of aryl groups on the yields of the substitution and reduction products in the reactions of lithium trimethylstannate and aryltriethylstannanes. The yields of substitution and reduction products increased as the substituents of aryl groups became electron-withdrawing: *m*-CF_3≫ *H*>*p*-CH_3≳*p*-OCH_3 (Nos. 4, 10, 11, and 12). With [*m*-(trifluoromethyl)phenyl]triethylstannane, α,α,α-trifluorotoluene was produced in 9% yield. Furthermore, the color of the solution of [*m*-(trifluoromethyl)phenyl]triethylstannane and lithium trimethylstannate changed to red, unlike other solutions. These facts probably suggest that the reaction of lithium trimethylstannate with [*m*-(trifluoromethyl)-phenyl]triethylstannane involves an electron transfer

Table 2. Reactions of Lithium Trimethylstannate with Arylstannanes

No.	Reactant/mmol		Condition[a]	Product, yield/%[b]	
	Ar_nSnR_{4-n}	Me_3SnLi		ArH	$ArSnMe_3$
10	MeO-C$_6$H$_4$-$SnEt_3$ (1.22)	Me_3SnLi (1.21)	B	<1	9
11	Me-C$_6$H$_4$-$SnEt_3$ (1.21)	Me_3SnLi (1.21)	B	<1	10
12	CF_3-C$_6$H$_4$-$SnEt_3$ (1.26)	Me_3SnLi (1.21)	B	9	64
13	$PhSnPr_3$ (1.23)	Me_3SnLi (1.98)	B	0	4
14	$PhSnBu_3$ (1.09)	Me_3SnLi (1.98)	B	0	4
15	Ph_2SnBu_2 (1.03)	Me_3SnLi (1.98)	A	0	4
16	Ph_2SnBu_2 (1.03)	Me_3SnLi (1.98)	B	4	32
17	Ph_3SnMe (0.83)	Me_3SnLi (1.98)	A	—[c]	4
18	Ph_3SnMe (0.83)	Me_3SnLi (1.98)	B	—[c]	99
19	1-NpSnEt$_3$ (1.17)	Me_3SnLi (1.67)	A	2	7
20	1-NpSnEt$_3$ (1.17)	Me_3SnLi (1.67)	B	4	31

a) A: at 24 °C for 1 h; B: at 50 °C for 30 min. b) Based on the concentration of Me_3SnLi. c) Yields of products could not be determined by GLC.

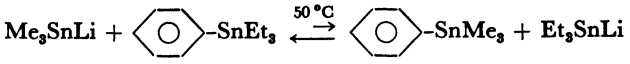
followed by a free radical process, rather than a simple bimolecular nucleophilic reaction.

Table 2 also shows the effects of aryl groups on the yields of substitution and reduction products in the reactions of lithium trimethylstannate with arylstannanes. Lithium trimethylstannate reacted with phenyltripropylstannane and phenyltributylstannane with difficulty to produce phenyltrimethylstannane, (Nos. 13 and 14, respectively). However, with diphenyldibutylstannane, triphenylmethylstannane, and 1-naphthyltriethylstannane, lithium trimethylstannate reacted at 24 °C to give substitution products, although the yields of the products were very low. Especially, triphenylmethylstannane was very reactive toward lithium trimethylstannate and the substitution product by the reaction of lithium trimethylstannate with triphenylmethylstannane at 50 °C was formed quantitatively (No. 18).

The formation of reduction products was fairly well observed in the reactions of lithium trimethylstannate with [*m*-(trifluoromethyl)phenyl]triethylstannane, diphenyldibutylstannane, and 1-naphthyltriethylstannane. These arylstannanes are known to be good electron acceptor substrates.

Reactions of Lithium Trialkylstannates with Phenyltrimethylstannane. The effect of modest changes in the steric bulk at the tin atom were estimated by examining the reactions of lithium triethylstannate, tripropylstannate, and tributylstannate with respect to the yields of substitution products. These results are summarized in Table 3. The reaction of lithium triethylstannate with phenyltrimethylstannane occurred with great facility to give a substitution product, phenyltriethylstannane, in high yield. Benzene was formed in low yield (No. 21). However, lithium tripropylstannate or tributylstannate did not react with phenyltrimethylstannane. Hexaalkyldistannanes were detected in both reactions. It is clear that the difference of reactivities of lithium trialkylstannates may be due to either the steric bulk at the tin atom or the degree of associations of lithium trialkylstannates.

By taking the results in Tables 1 and 3 into consideration, the reaction of lithium trimethylstannate with phenyltriethylstannane at 50 °C is reversible. Equilibrium of this reaction leans to the reverse direction.



On the other hand, the reactions of lithium trimethylstannate with phenyltripropylstannane and phenyltributylstannane are irreversible.

Reactions of Lithium Trimethylstannate with Aryltriethylstannanes in the Presence of Trapping Reagents. Recently, Kuivila and co-workers have reported that *t*-butylamine is a very effective trapping reagent for free anionoids.[14] In order to obtain further information on the mechanism of the reactions of trialkylstannane anions with arylstannanes, the reactions of lithium trimethylstannate with phenyltriethylstannane, [*m*-(trifluoromethyl)phenyl]triethylstannane, and 1-naphthyltriethylstannane in the presence of *t*-butylamine for aryl anions and cumene

Table 3. Reactions of Lithium Trialkylstannates with Phenyltrimethylstannane at 50 °C for 30 min

No.	Reactant/mmol		Product, yield/%[a]	
	$PhSnMe_3$	R_3SnLi	PhH	$PhSnR_3$
21	$PhSnMe_3$ (1.74)	Et_3SnLi (1.32)	2	82
22	$PhSnMe_3$ (1.74)	*n*-Pr_3SnLi (1.55)	0	0
23	$PhSnMe_3$ (1.74)	*n*-Bu_3SnLi (1.17)	0	0

a) Based on the concentrations of R_3SnLi.

Table 4. Reactions of Lithium Trimethylstannate wtih Aryltriethylstannanes in the Presence of Trapping Reagents at 50 °C for 30 min

No.	Reactants/mmol			PhH	Product, yield/%[a]			
	$ArSnEt_3$	Me_3SnLi	Trap		$PhSnMe_3$	$(Me_3Sn)_2$	$Me_3SnSnEt_3$	$(Et_3Sn)_2$
24	Ph (1.12)	Me_3SnLi (1.28)	TBA[b] (1.43)	10	2	44	19	0
25	Ph (1.12)	Me_3SnLi (1.28)	Cumene (1.44)	0	12	42	11	0
26	*m*-$CF_3C_6H_4$ (1.26)	Me_3SnLi (1.36)	TBA (1.43)	54	17	25	62	11
27	*m*-$CF_3C_6H_4$ (1.26)	Me_3SnLi (1.36)	Cumene (2.16)	3	45	9	33	8
28	1-Np (1.17)	Me_3SnLi (1.97)	TBA (1.90)	19	14	31	26	—[c]
29	1-Np (1.17)	Me_3SnLi (1.36)	Cumene (2.16)	1	10	15	14	—[c]

a) Based on the concentration of Me_3SnLi. b) *t*-Butylamine. c) Yields of products could not be determined by GLC.

for free aryl radicals were examined. These results are summarized in Table 4.

t-Butylamine reacted more rapidly with the carbanion intermediates to give the corresponding alkanes than with lithium trimethylstannate under these conditions. The stability of lithium trimethylstannate in the presence of *t*-butylamine was examined at 50 °C. Lithium trimethylstannate is susceptible to form hexamethyldistannane. However, the concentration of lithium trimethylstannate is sufficiently large to react with aryltriethylstannanes under these conditions (Fig 2).

Lithium trimethylstannate reacted with phenyltriethylstannane in THF at 50 °C to produce <1% benzene, 24% phenyltrimethylstannane, 16% hexamethyldistannane, and 17% 1,1,1-trimethyl-2,2,2-triethyldistannane (No. 4). When *t*-butylamine was present in the initial reaction mixture, the yields of benzene, hexamethyldistannane, and 1,1,1-trimethyl-2,2,2-triethyldistannane increased upon increasing the concentration of *t*-butylamine, and that of phenyltrimethylstannane deccreased correspondingly (Fig. 3). Lithium trimethylstannate reacted with phenyltriethylstannane at higher *t*-butylamine concentrations to give 10% benzene, 2% phenyltrimethylstannane, 44% hexamethyldistannane, and 19% 1,1,1-trimethyl-2,2,2-triethyldistannane. Similarly, the effects of the *t*-butylamine concentration on the yields of products in the reactions of lithium trimethylstannate with [*m*-(trifluoromethyl)phenyl]triethylstannane and 1-naphthyltriethylstannane were examined. The yields of reduction products, hexamethyldistannane, and 1,1,1-trimethyl-2,2,2-triethyldistannane increased with the concentration of *t*-butylamine, and the substitution products decreased correspondingly. The yields of substitution products at the higher *t*-butylamine concentrations decreased in order: [*m*-(trifluoromethyl)phenyl]triethylstannane>1-naphthyltriethylstannane>phenyltriethylstannane. In contrast with the results of [*m*-(trifluoromethyl)phenyl]triethylstannane (Nos. 12 and 26) and 1-naphthyltriethylstannane (Nos. 20 and 28), a total amount of increased reduction product and decreased substitution product in the reaction of lithium trimethylstannate with phenyltriethylstannane in the presence of *t*-butylamine is not consistent with that of reduction and substitution products in the initial reaction (Nos. 4 and 24). This inconsistency may be explained by the fact that lithium trimethylstannate in part changes to hexamethyldistannane before a nucleophilic reaction by trimethylstannane anion in the presence of *t*-butylamine; then, the concentration of lithium trimethylstannate decreases.

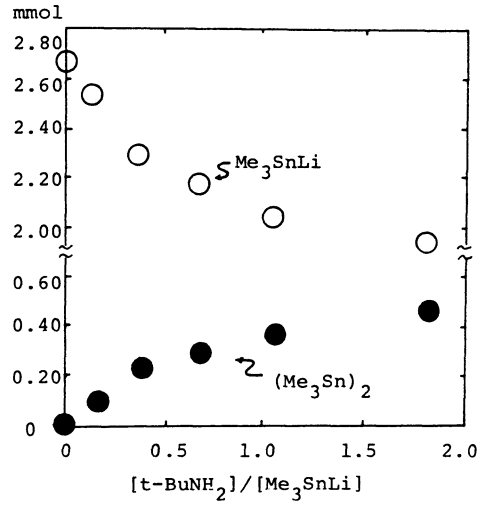


Fig. 2. The stability of lithium trimethylstannate (2.66 mmol) in the presence of *t*-butylamine at 50 °C for 30 min.

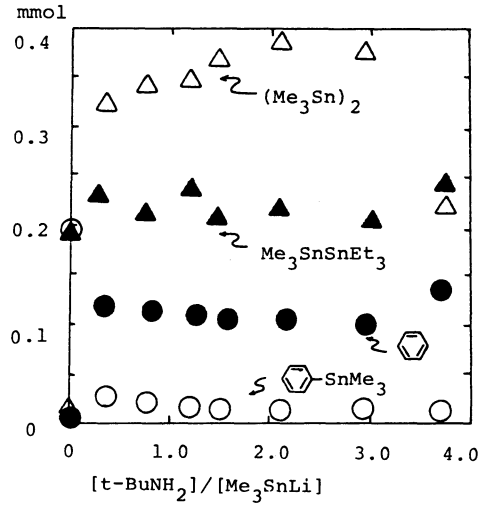


Fig. 3. Effects of TBA concentration on yields of products in the reaction of lithium trimethylstannate (1.28 mmol) with phenyltrimethylstannane (1.12 mmol) at 50 °C for 30 min.

Cumene is known to be an effective reagent for trapping free aryl radicals. Lithium trimethylstannate reacted with phenyltriethylstannane in the presence of cumene to produce <1% benzene, 12% phenyltrimethylstannane, 42% hexamethyldistannane, and 1,1,1-trimethyl-2,2,2-triethyldistannane (No. 25). Similarly, the effects of cumene on the yields of products in the reactions of lithium trimethylstannate with [*m*-(trifluoromethyl)phenyl]triethylstannane and 1-naphthyltriethylstannane were also examined. The yields of the reduction products, substitution products, 1,1,1-trimethyl-2,2,2-triethyldistannane, and hexaethyldistannane decreased, and hexamethyldistannane increased in both reactions in the presence of cumene (Nos. 27 and 29). By taking into consideration that lithium trimethylstannate is susceptible to form hexamethyldistannane in the presence of cumene at 50 °C, the decreased yields of products,

except for hexamethyldistannane, may be due to the low concentration of lithium trimethylstannate. Thus, cumene may not be an effective trapping reagent for free aryl radical intermediates under these reaction conditions. The results of reactions of lithium trimethylstannate with arylstannanes in the presence of trapping reagents are summarized in Table 4.

ESR Studies. In addition to the chemical evidence, ESR studies on the reactions of lithium trimethylstannate with phenyltriethylstannane and [*m*-(trifluoromethyl)phenyl]triethylstannane were examined. No ESR signals in the reaction of lithium trimethylstannate with phenyltriethylstannane in THF were observed. On the other hand, a very complexed ESR spectra attributed to carbon centered radicals (judging from the *g* factor) were observed in the case of [*m*-(trifluoromethyl)phenyl]triethylstannane. However, the ESR spectra could not be analyzed.

Discussion

The results summarized in Tables 1—3 demonstrate that trimethylstannane and triethylstannane anions react with arylstannanes to give substitution products, aryltrimethylstannane and aryltriethylstannane, respectively. The reactions of trialkylstannane anions with aryltriethylstannanes are endothermic. The yields of reduction and substitution products are highly variable, depending on the arylstannanes employed. In general, the yields of reduction products increased in the reactions of trialkylstannane anions with electron-withdrawing groups-substituted aryltriethylstannanes, 1-naphthyltriethylstannane, diphenyldibutylstannane, and triphenylmethylstannane as good electron acceptor substrates.

Recently, Kuivila and co-workers have demonstrated that *t*-butylamine is an effective reagent for trapping free anionoids.[14] The results in Table 4 show that the yields of reduction products increase in the presence of *t*-butylamine. These facts strongly imply that aryl anions are imporatnt intermediates in these reactions by trialkylstannyl anions. The formation of aryl anions can be explained by tin–alkali metal exchange or electron-transfer process. By the results of tin–alkali metal exchange in the reactions of trialkylstannyl anions with arylstannanes, aryl anions and distannanes are formed in the cage. Continuously, aryl anions react with distannanes to form substitution products (arylstannanes) and the corresponding stannane anions. Furthermore, the reactions of stannane anions, thus prepared, with the substitution products (arylstannanes) occur if circumstance requires. When *t*-butylamine is present in the reaction mixture, escaped aryl anions from the cage are trapped to give reduction products. As a result, the yields of reduction products and unattacked distannanes by aryl anions increase and those of substitution products decrease.

On the other hand, in light of trialkylstannane anions to act as one electron reducing reagents toward suitable substrates, the formation of aryl anions may also be explained by an electron-transfer process.[15] The first step is an electron-transfer from trialkylstannane anions to arylstannanes that leads to arylstannane anion radicals and trialkylstannane radicals in a cage. Subsequently, aryl anions and stannane radicals are formed from unstable arylstannane anion radicals. Distannanes are formed by a cage combination of stannane radicals from unstable arylstannane anion radicals and trialkylstannane radicals. The property of the formation of aryl anions by electron-transfer is discussed later. The attack on either tin atoms of the formed distannanes by aryl anions depends on the nature of the aryl anions and the stannane compounds. The mechansim for aryl anion intermediates in the reactions of trialkylstannane anions with arylstannanes is proposed in the following (Scheme 1).

The reaction of lithium trimethylstannate with phenyltriethylstannane at 50 °C is reversible. Equilibrium of this reaction shifts to the reverse direction. This shift may be due to either the difference of nucleophilicity or the degree of association of trimethylstannane and triethylstannane anions. On the other hand, the reactions of lithium trimethylstannate with phenyltripropylstannane and phenyltributylstannane at 50 °C are irreversible, respectively. This irreversibility of the reaction may result from either the steric hindrance or degree of association of tributylstannane and tripropylstannane anions.

However, by judging from the results of the formation of reduction products at the higher *t*-butylamine concentrations, aryl radical intermediates are also formed in the reactions of trialkylstannane anions with arylstannanes. The formation of aryl radicals may be explained by an electron-transfer process. The first step is an electron-transfer from trialkylstannane anions to arylstannanes that leads to

$$R_3Sn^-M^+ + ArSnR_3' \longrightarrow \begin{array}{l} \overline{Ar^-M^+\ R_3SnSnR_3'} \\ \text{or} \\ \overline{R_3Sn\cdot\ M^+\ [ArSnR_3']^{\pm}} \longrightarrow \overline{Ar^-M^+\ R_3Sn\cdot\ \cdot SnR_3'} \\ \longrightarrow \text{products} \end{array}$$

Scheme 1. The mechanism for aryl anion intermediates.

$$R_3Sn\text{-}M^+ + ArSnR_3' \longrightarrow \overline{R_3Sn\cdot\ M^+\ [ArSnR_3']^{\pm}}$$
$$\longrightarrow \overline{R_3Sn\cdot\ \cdot Ar\ M^+SnR_3'^-}$$
$$\longrightarrow \text{products}$$

Scheme 2. The mechanism for aryl radical intermediates.

arylstannane anion radicals and trialkylstannane radicals in the cage. Subsequent dissociation of aryl radicals produced from unstable arylstannane anion radicals followed by cage combination with trialkylstannane radicals and by proton abstraction from solvents employed would provide substitution products, aryltrialkylstannanes, and reduction products, respectively. According to this scheme, the formations of reduction and substitution products can be observed despite of *t*-butylamine (Scheme 2).

In fact, the formation of reduction products in the absence of *t*-butylamine and substitution products at the higher *t*-butylamine concentrations were observed in the reactions of trialkylstannane anions with [*m*-(trifluoromethyl)phenyl]triethylstannane, 1-napthyltriethylstannane, diphenyldibutylstannane, and triphenylmethylstannane. These facts imply that aryl radical intermediates are also involved in the reactions of trialkylstannane anions with good electron acceptors such as the above arylstannanes.

A pattern of cleavage of the aryl–tin bond for arylstannane anion radicals may be shown in the following.

$$[ArSnR_3]^{\pm} \begin{cases} \longrightarrow Ar^- + \cdot SnR_3 \\ \longrightarrow Ar\cdot + {}^-SnR_3 \end{cases}$$

A pattern of cleavage of the aryl–tin bond for arylstannane anion radicals may depend on the nature of the aryl group (Ar) and the alkyl group (R).

In conclusion, the reactions of trialkylstannane anions with arylstannanes proceed via two different key intermediates: aryl anions and aryl radicals. Aryl anion intermediates formed by tin–alkali metal exchange or electron-transfer are most important in the reactions of trialkylstannane anions with arylstannanes. However, aryl radical intermediates formed by an electron-transfer is also important in the reactions of trialkylstannane anions with [*m*-(trifluoromethyl)phenyl]triethylstannene, 1-naphthyltriethylstannane, diphenyldibutylstannane, and triphenylmethylstannane as good electron acceptor substrates.

Experimental

^{1}H NMR spectra were recorded on a Varian FT 80A, with tetramethylsilane as internal standard. GC-Mass spectra were obtained with JEOL JMS-DX 303 mass spectrometer. Infrared spectra were recorded on a Hitachi 260-10 spectrometer. Gas chromatography was performed on a Shimadzu GC-6A and -8A with 2 m 20% SE-30 and 2 m 30% Apiezon L columns.

Materials. *t*-$BuNH_2$ and cumene are commercially available and purified prior to use. Me_3SnCl, bp 152—154 °C,[16] Et_3SnCl, bp 109—110 °C/20 mmHg†,[17] Pr_3SnCl, bp 123 °C/13 mmHg,[18] Bu_3SnCl, bp 145—147 °C/5 mmHg,[19] $Me_3SnSnMe_3$, bp 182 °C,[20] $Et_3SnSnEt_3$, bp 160 °C/23 mmHg,[20] $Pr_3SnSnPr_3$, bp 142 °C/15 mmHg,[21] $Bu_3SnSnBu_3$, bp 156—160 °C/0.03 mmHg,[20] $Me_3SnSnEt_3$, bp 105 °C/6 mmHg,[20] Me_3SnH, bp 59 °C,[22] Et_3SnH, bp 79—81 °C/92 mmHg,[23] $PhSiMe_3$, bp 72 °C/27 mmHg,[24] $PhGeMe_3$, bp 80 °C/27 mmHg,[25] $PhSnMe_3$, bp 91 °C/30 mmHg,[27] *p*-$MeC_6H_4SnMe_3$, bp 105 °C/3 mmHg,[27] *p*-$MeOC_6H_4SnMe_3$, bp 115 °C/3 mmHg,[28] *m*-$CF_3C_6H_4SnMe_3$, bp 78—81 °C/14 mmHg,[28] 1-$NpSnMe_3$, bp 120 °C/1 mmHg,[27] $PhSnEt_3$, bp 113—114 °C/6 mmHg,[29] *p*-$MeC_6H_4SnEt_3$, bp 91 °C/1 mmHg,[29] *p*-$MeOC_6H_4SnEt_3$, bp 138 °C/5 mmHg,[29] *m*-$CF_3C_6H_4SnEt_3$, bp 105 °C/3 mmHg,[30] $PhSnPr_3$, bp 150 °C/15 mmHg,[31] $PhSnBu_3$, bp 139 °C/0.6 mmHg,[31] Ph_2SnBu_2, bp 137 °C/0.2 mmHg,[31] and Ph_3SnMe, mp 61 °C were prepared as cited literatures.

Preparation of 1-Naphthyltriethylstannane. A Grignard reagent was prepared from 1-bromonaphthalene (11.0 g, 0.05 mol) and magnesium (1.2 g, 0.05 g atom) in a mixture solvent of THF (50 cm^3), benzene (30 cm^3), and ether (20 cm^3). To this Grignard reagent was added chlorotriethylstannane (12.0 g, 0.05 mol) in a mixture solvent of THF (20 cm^3), benzene (10 cm^3), and ether (5 cm^3). The reaction mixture was stirred with reflux for 5 h. After hydrolysis with water, the organic layer was extracted with ether and dried over sodium sulfate. The solvent was removed and then fractional distillation gave 1-naphthyltriethylstannane (10 g, 0.03 mol, 60% yield), bp 142—145 °C/3 mmHg; ^{1}H NMR ($CDCl_3$) δ=1.30 (s, 15H), 7.25—8.00 (m, 7H); n^{20} 1.5957. Found: C, 57.48; H, 6.72%. Calcd for $C_{16}H_{22}Sn$: C, 57.70; H, 6.66%.

Preparation of Lithium Trimethylstannate. Lithium trimethylstannate was prepared from hexamethyldistannane or chlorotrimethylstannane and lithium metal in THF, DME, TG, or HMPA in an atmosphere of nitrogen for 4—5 h. Yields were determined by treatment with bromobenzene or *p*-tolyl bromide and the amounts of phenyltrimethylstannane or *p*-tolyltrimethylstannane produced, respectively, by GLC with an internal standard method. Yields were 80—85%.

Preparation of Sodium Trimethylstannate. Sodium trimethylstannate was prepared from hexamethyldistannane and sodium metal as described above for lithium trimethylstannate. Yields were 80—90%.

Preparation of Potassium Trimethylstannate. Potassium trimethylstannate was prepared as described above lithium trimethylstannate. Yields were 85—90%.

Preparation of Lithium Triethylstannate, Tripropylstannate, and Tributylstannate. Lithium triethylstannate, tripropylstannate, and tributylstannate were prepared from the corresponding chlorides and lithium metal in THF in an atmosphere of nitrogen for 4—5 h. Yields were determined by treatment with an excess of bromobenzene or *p*-tolyl bromide and by the amounts of the corresponding tin compounds formed.

Stability of Lithium Trimethylstannate at 50 °C. Li-

† 1 mmHg=133.322 Pa.

thium trimethylstannate in THF was heated at 50 °C. Yields of lithium trimethylstannate were determined by the reaction of excess of bromobenzene or *p*-tolyl bromide at constant time and the amounts of phenyltrimethylstannane or *p*-tolyltrimethylstannane, respectively, and hexamethyldistannane produced.

Stability of Lithium Trimethylstannate in the Presence of *t*-Butylamine at 50 °C. A mixture of lithium trimethylstannate and *t*-butylamine in THF was heated at 50 °C. Yields of lithium trimethylstannate were determined as described above for the stability of lithium trimethylstannate at 50 °C.

Stability of Lithium Trimethylstannate in the Presence of Cumene. A mixture of lithium trimethylstannate and cumene in THF was heated at 50 °C. Yields of lithium trimethylstannate were determined as described above of the stability of lithium trimethylstannate at 50 °C.

Reaction of Lithium Trimethylstannate with Phenyltrimethylsilane. Lithium trimethylstannate (1.67 mmol) was added to phenyltrimethylsilane (1.74 mol) in THF (2 cm^3) and stirred at 24 °C for 1 h or 50 °C for 30 min. After hydrolysis with water, the organic layer was extracted with ether. The ether solution was dried over sodium sulfate. Phenyltrimethylsilane (1.74 mmol) and hexamethyldistannane (0.86 mmol) were determined by an internal standard method by GLC. Each product was isolated by preparative GLC and structures were verified by comparing their GC-Mass, IR, and NMR retention times on GLC of authentic samples.

Reaction of Lithium Trimethylstannate with Phenyltrimethylgermane. Lithium trimethylstannate (1.12 mmol) was added to phenyltrimethylgermane (1.22 mmol) in THF (2 cm^3) and stirred at 24 °C for 1 h or at 50 °C for 30 min. After hydrolysis with water, the organic layer was extracted with ether. The ether solution was dried over sodium sulfate. Phenyltrimethylgermane (1.20 mmol) was recovered and hexamethyldistannane (0.53 mmol) was produced. Each product was isolated by preparative GLC and the structures were identified by comparing their GC-Mass, IR, and NMR spectra, and retention times on GLC with those of authentic samples.

Reaction of Lithium Trimethylstannate with Phenyltriethylstannane at 24 °C. Lithium trimethylstannate (1.67 mmol) was added to phenyltriethylstannane (1.2 mmol) in THF (2 cm^3) and stirred at 24 °C for 1 h. After hydrolysis with water, the organic layer was dried over sodium sulfate. Phenyltriethylstannane (1.18 mmol) was recovered and hexamethyldistannane (0.61 mmol), and 1,1,1-trimethyl-2,2,2-triethyldistannane (0.01 mmol) were formed. Each product was isolated by preparative GLC and the structures were identified by comparing their GC-Mass, IR, NMR, and retention times on GLC with those of authentic samples.

Reaction of Lithium Trimethylstannate with Phenyltriethylstannane at 50 °C. Lithium trimethylstannate (1.67 mmol) was added to phenyltriethylstannane (1.12 mmol) in THF (2 cm^3) and stirred at 50 °C for 30 min. After hydrolysis with water, the solution was extracted with ether. The organic layer was dried over sodium sulfate. Yields of benzene (trace), phenyltrimethylstannane (0.40 mmol), phenyltriethylstannane (0.68 mmol), hexamethyldistannane (0.27 mmol), 1,1,1-trimethyl-2,2,2-triethyldistannane (0.30 mmol), and hexaethyldistannane (trace) were determined by an internal standard method by GLC.

Reactions of Trialkylstannane Anions with Arylstannanes. Reactions of trialkylstannane anions with arylstannanes were carried out as described above for the reaction of lithium trimethylstannate with phenyltriethylstannane. Yields of the reaction products were determined in the same manner as those of the reaction of lithium trimethylstannate with phenyltriethylstannane.

Reaction of Lithium Trimethylstannate with Aryltriethylstannanes in the Presence of *t*-Butylamine. A typical example for the reactions of lithium trimethylstannate with aryltriethylstannanes in the presence of *t*-butylamine is described. Lithium trimethylstannate (1.28 mmol) was added to a mixture of phenyltriethylstannane (1.12 mmol) and *t*-butylamine (1.43 mmol) in THF (2 cm^3) and stirred at 50 °C for 30 min. After hydrolysis with water, the solution was extracted with ether. The organic layer was dried over sodium sulfate. Yields of benzene (0.12 mmol), phenyltrimethylstannane (0.03 mmol), hexamethyldistannane (0.56 mmol), and 1,1,1-trimethyl-2,2,2-triethyldistannane (0.24 mmol) were formed.

Reactions of Lithium Trimethylstannate with Aryltriethylstannanes in the Presence of Cumene. A typical example for the reactions of lithium trimethylstannate with aryltriethylstannanes in the presence of cumene is described. Lithium trimethylstannate (1.28 mmol) was added to a mixture of phenyltriethylstannane (1.12 mmol) and cumene (1.44 mmol) in THF (2 cm^3) and stirred at 50 °C for 30 min. After hydrolysis with water, the solution was extracted with ether. The organic layer was dried over sodium sulfate. Yields of phenyltrimethylstannane (0.15 mmol), hexamethyldistannane (0.53 mmol), and 1,1,1-trimethyl-2,2,2-triethyldistannane (0.14 mmol) were formed.

ESR Studies on the Reactions of Lithium Trimethylstannate with Aryltriethylstannanes. In a typical example, a solution of lithium trimethylstannate in THF was added using a hypodermic syringe to a small amount of phenyltriethylstannane contained THF in a glass tube constructed with a 6×60 mm upper portion and 2×80 mm lower portion. The tube was then sealed off after freeze-pump-thaw cycles on a vacuum line.

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