5-Nitro-8-undecyn-2-one (**37**).—1-Nitro-4-heptyne (0.79 g, 5.62 mmol), diisopropylamine (0.3 ml), and methyl vinyl ketone (0.43 g, 6.1 mmol) in 6 ml of chloroform were stirred at 40° for 16 hr under nitrogen. The solution was then distilled to give 980 mg (83%) of product **37**: bp 110° (0.001 mm); ir (neat) 1715, 1545 cm^{-1}; nmr (CCl_4) δ 1.09 (t, 3 H, J = 7 Hz), 2.10 (s, 3 H), 4.6 (m, 1 H); mass spectrum m/e (rel intensity) 162 (P^+, 50), 147 (100). *Anal.* Calcd for $C_{11}H_{17}NO_3$: C, 62.53; H, 8.13. Found: C, 62.53; H, 8.10.

8-Undecyne-2,5-dione (**38**).—This compound was prepared by reduction of **37** with $TiCl_3$ according to procedure A above; an 85% yield was obtained after 18-hr reaction in dimethoxyethane as solvent.

Dehydrojasmone (**39**).—Diketone **38** (0.38 g, 2.1 mmol) was dissolved in 10 ml of 5% ethanolic KOH solution and the solution was refluxed for 2 hr under nitrogen. The solution was then poured into a separatory funnel, diluted with water, and extracted with ether. The extracts were washed with brine, dried ($MgSO_4$), concentrated, and distilled to yield dehydrojasmone (**39**, 0.34 g, 85%): bp 103–105° (0.1 mm); ir (neat) 1705, 1650 cm^{-1}; nmr (CCl_4) δ 1.13 (t, 3 H, J = 7 Hz), 2.15 (s, 3 H), 2.25 (m, 6 H), 2.95 (t, 2 H, J = 1.5 Hz); 2,4-DNP mp 165° (lit.[25] mp 166°).

(25) K. Sisido, Y. Kawasima, and T. Isida, *Perfum. Essent. Oil. Rec.*, **57**, 364 (1966).

cis-**Jasmone** (**40**).—Lindlar catalyst[16] (50 mg) in 2 ml of ethyl acetate was equilibrated under 1 atm of hydrogen for 12 hr and dehydrojasmone (0.050 g, 0.003 mol) in 1 ml of ethyl acetate was added. After 5 min, hydrogen uptake stopped, and the reaction was filtered free of catalyst and concentrated to yield *cis*-jasmone (**40**, 47 mg, 95%): ir 1705, 16.50 cm^{-1}; nmr (CCl_4) δ 0.97 (t, 3 H, J = 7.5 Hz), 2.02 (s, 3 H), 2.20 (m, 6 H), 2.84 (d, 2 H, J = 5 Hz), 5.22 (triplet of doublets, 2 H, J = 4, J' = 6 Hz); 2,4-DNP mp 116° (lit.[26] mp 117.5°).

Acknowledgment.—This work was supported by Grant GP28173 from the National Science Foundation.

Registry No.—**1**, 42397-25-1; **2**, 1703-51-1; **3**, 622-42-4; **5**, 1782-03-2; **7**, 16506-99-3; **9**, 42397-27-3; **10**, 646-14-0; **11**, 42397-28-4; **12**, 10312-37-5; **14**, 42397-30-8; **16**, 42397-31-9; **18**, 32863-04-0; **18** 2,4-DNP, 42397-33-1; **19**, 42397-34-2; **19** picrate 42397-12-6; **20**, 6125-24-2; **23**, 42397-13-7; **23** 2,4-DNP, 42397-14-8; **24**, 42397-15-9; **26**, 42397-16-0; **26** 2,4-DNP, 42397-17-1; **34**, 42441-83-8, and **35**, 18498-36-7 (Scheme I); **36**, 42397-19-3; **37**, 42397-20-6; **38**, 7051-43-6; **39**, 7051-37-8; **40**, 488-10-8; $TiCl_3$, 7705-07-9; 1-nitropropane, 108-03-2; methyl vinyl ketone, 78-94-4; 1-nitropropene, 3156-70-5; butadiene, 106-99-0; morpholinocyclohexene, 670-80-4; azoxy-*n*-hexane, 42441-84-9; 1-nitrocyclohexene, 2562-37-0; 4-heptyn-1-ol, 42397-24-0.

(26) L. Crombie and S. H. Harper, *J. Chem. Soc.*, 869 (1952).

Synthesis of *N*-(2-Triphenylstannylethyl)amines and Their Reactivities

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The reactions of seven *N*-(2-triphenylstannylethyl)amines (**3a–g**), prepared from the corresponding 2-chloroethylamines (**1a–e,g**) and triphenyltinlithium (**2**), with methyl halides (MeX) or hydrogen halides (HX) were investigated. In the case of X = I or Br, the quaternary ammonium salts or the amine hydrohalides, produced from *N*-(2-triphenylstannylethyl)alkylamines (**3a** and **3b**), were unstable and were cleaved by nucleophilic attack of X^- at tin atom which resulted in the formation of triphenyltin halides and alkylamines with the loss of ethylene. On the contrary, **3a–c** hydrochlorides were stable, but the presence of excess hydrogen chloride led quantitatively to (2-alkylaminoethyl)phenyltin dichloride hydrochlorides (**8a–c**) by electrophilic attack of H^+ on the phenyl groups. However, the reaction of *N*-(2-triphenylstannylethyl)arylamines (**3d** and **3e**) with hydrogen chloride gave a mixture of triphenyltin chloride, diphenyltin dichloride, phenyltin trichloride, and *sec*-arylamines, as a result of the competition between the nucleophilic attack of Cl^- at tin atom and the electrophilic attack of H^+ on phenyl group.

Previous investigations of aminoalkyltin compounds have dealt with the chemistry of the α-[1] and γ-amino[2] derivatives. While a few of the β-aminoalkyltin compounds have been obtained by additions of triorganotin hydrides to vinylamines[2a,3] or by carbon–carbon insertion reaction into tin–nitrogen bonds,[4] little is known about their chemical properties. We now report the preparation of several new alkylamino- and arylaminoethyltriphenyltin compounds as well as some of the reactions that they undergo.

Seven *N*-(2-triphenylstannylethyl)amines (**3a–g**) were synthesized in 60–80% yields from reactions of the corresponding 2-chloroethylamines (**1a–e,g**) with triphenyltinlithium (**2**) in tetrahydrofuran (see Table I). Their structures were confirmed by elemental and ^1H nmr spectral analyses (see Table IV). *N*-(2-Triphenylstannylethyl)aniline (**3f**) was isolated in low yield from the reaction of *N*-(2-chloroethyl)acetanilide (**1g**) with **2**. Hydrolysis of *N*-(2-triphenylstannylethyl)acetanilide (**3g**) in alcoholic potassium hydroxide also gave **3f**. The reduction of **3g** with lithium aluminum hydride gave **3f** in high yield. No *N*-(2-triphenylstannylethyl)-*N*-ethylaniline was obtained. The acetylation of **3f** with acetic anhydride led to **3g**. However, the methylation of **3f** with an equimolar amount of methyl bromide or methyl iodide in ethanol did not produce *N*-(2-triphenylstannylethyl)-*N*-methylaniline (**3d**) as expected, but gave mixtures which consisted of *N*-methylaniline, triphenyltin bromide, or triphenyltin iodide, respectively, as major products, and aniline and *N*,*N*-dimethylaniline as minor products along with unreacted **3d**. These products are regarded as resulting from the following reactions (Scheme I).

The reaction of **3f** with MeX (X = Br, I) initially gives **3d** hydrohalide (**3d**-HX). Proton transfer from **3d**-HX to **3f** affords **3f** hydrohalide (**3f**-HX) and **3d**, which subsequent reacts with additional MeX to give *N*-(2-triphenylstannylethyl)-*N*,*N*-dimethyl-*N*-phenylammonium halide (**5d**). These three ammonium

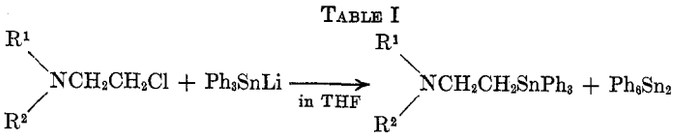
(1) D. J. Peterson, *J. Organometal. Chem.*, **21**, P63 (1970); *J. Amer. Chem. Soc.*, **93**, 4027 (1971). R. G. Kostyanovskii and A. K. Prokofev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 175 (1965).

(2) (a) G. J. M. van der Kerk and J. G. Noltes, *J. Appl. Chem.*, **9**, 106 (1959); (b) *ibid.*, **9**, 176 (1959).

(3) G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.*, **7**, 356 (1957); W. P. Neumann, H. Niermann, and R. Sommer, *Justus Liebigs Ann. Chem.*, **659**, 27 (1962).

(4) G. Chandra, T. A. George, and M. F. Lappert, *Chem. Commun.*, 116 (1967).

TABLE I



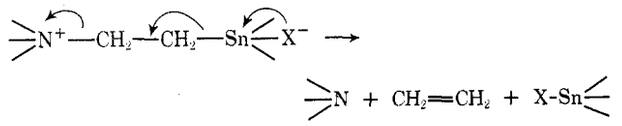
1a–e,g 2 3a–g 4

Compd	R1	R2	Reaction conditions: Temp	Reaction conditions: Time, hr	3: Mp, °C	3: Yield, %	4, Yield, %
a	CH_3	CH_3	Room	7	81–83	85.3	5
b	C_2H_5	C_2H_5	Room	18	48.5–49.5	63.5	5
			Reflux	2			
c	$(-CH_2CH_2)_2O$		Room	18	125–126	56.1	7
			Reflux	2			
d	CH_3	C_6H_5	Room	20	59.5–60.0	62.4	5
			Reflux	2			
e	C_6H_5	C_6H_5	Room	19	98–100	78.5	5
			Reflux	3			
f	H	C_6H_5			91–92.5	*a*	
g	CH_3CO	C_6H_5	Room	18	106–108	65.0	9
			Reflux	2			

[a] **3f** was isolated from the reaction of **1g** with **2** as a by-product in 4% yield.

halides, **3d**-HX, **3f**-HX, and **5d**, are cleaved by nucleophilic attack of the X^- at the tin atom to give the amines, triphenyltin halide, and ethylene (path a, b, and c). Evidence in support of these three postulated reaction paths is found in the following experimental results. The addition of an equimolar solution of hydrogen bromide in ether to **3d** afforded *N*-methylaniline and triphenyltin bromide, accompanied by a small amount of **3d** hydrobromide (**3d**-HBr). Similarly, the addition of an equimolar amount of hydrogen bromide to **3f** gave **3f** hydrobromide (**3f**-HBr) quantitatively, which was readily cleaved to aniline and triphenyltin bromide by heating in ethanol. The reaction of **3d** with an equimolar amount of methyl iodide gave *N*,*N*-dimethylaniline, triphenyltin iodide, and no **5d**.

The other β-aminoethyltin compounds, *N*-(2-triphenylstannylethyl)dimethylamine (**3a**) and *N*-(2-triphenylstannylethyl)diethylamine (**3b**), gave, upon reaction with excess methyl bromide, the corresponding amine methobromides (**6a** and **6b**) and triphenyltin bromide, respectively. Attempts to isolate quaternary ammonium bromides from any of the reactions were unsuccessful. *N*-(2-Triphenylstannylethyl)diphenylamine (**3e**) and **3g** did not react with the methyl halide to form quaternary ammonium salts. There is no doubt from these results that the cleavage of *N*-(2-triphenylstannylethyl)amines by methyl halides proceeds *via* the quaternary ammonium salts.



Early observations in organosilicon chemistry indicated that substituted organosilanes, $R_3SiCH_2CH(R')X$ (X = halogen or hydroxyl, R′ = H or alkyl), react rapidly with acid, base, and a variety of other reagents to generate the corresponding alkene and R_3SiX.[5] Davis, *et al.*,[6] recognized that β-triphenylstannyl alcohols readily undergo an acid-catalyzed deoxymetalation reaction in an acidic medium.

$$Ph_3SnCH_2CH_2OH \xrightarrow{H^+} Ph_3SnCH_2CH_2O^+H_2 \xrightarrow{MeOH-H_2O} Ph_3SnOH + CH_2{=}CH_2 + H_2O + H^+$$

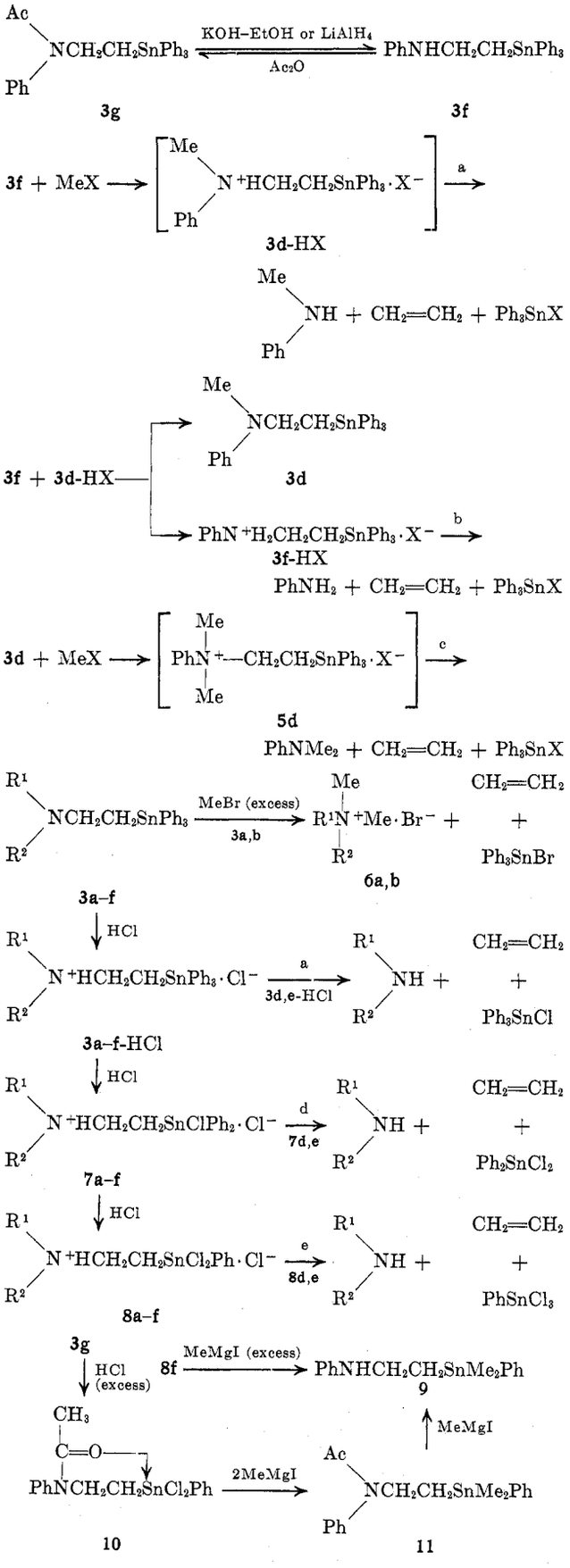
Addition of an equimolar amount of ethereal hydrogen bromide to **3a** gave a mixture of **3a** hydrobromide (**3a**-HBr), dimethylamine, and triphenyltin bromide, whereas stable crystals of **3a** hydrochloride (**3a**-HCl) were formed upon treatment of **3a** with an equimolar amount of ethereal hydrogen chloride (Table II). Two equivalents of hydrogen chloride and **3a** in ether gave quantitatively (2-dimethylaminoethyl)diphenyltin chloride hydrochloride (**7a**). When further excess hydrogen chloride in ether was treated with **3a**, (2-dimethylaminoethyl)phenyltin dichloride hydrochloride (**8a**) only was isolated quantitatively. These results suggest that the phenyl–tin bonds are cleaved stepwise by electrophilic attack of H^+ to give **7a** from **3a**-HCl, then **8a** from **7a**, but one phenyl–tin bond remains. These three amine hydrochlorides are stable and the nucleophilic attack of Cl^- at the tin atom is not observed. The same results were also obtained in the other (2-triphenylstannylethyl)amines: **3b**, *N*-(2-triphenylstannylethyl)morpholine (**3c**) and **3f** to give (2-diethylaminoethyl)phenyltin dichloride hydrochloride (**8b**), (2-morpholinoethyl)phenyltin dichloride hydrochloride (**8c**), and (2-anilinoethyl)phenyltin dichloride hydrochloride (**8f**) in a quantitative yield, respectively.

N-(2-Triphenylstannylethyl)acetanilide (**3g**) also reacted quantitatively with excess hydrogen chloride in ether to give the crystals, mp 149–150°, whose elemental analysis, molecular weight determination, and nmr spectrum showed reasonable agreement with (2-acetylphenylaminoethyl)phenyltin dichloride (**10**). The carbonyl absorption of **10** shifted extremely to low frequency, at 1565 and 1575 cm^{-1} in carbon tetrachloride. The carbonyl band of *N*-(2-dimethylphenylstannylethyl)acetanilide (**11**), derived by the reaction of **10** with 2 equiv of methylmagnesium iodide, was observed again at 1660 cm^{-1} in the same region as **3g**. Therefore it seems reasonable to assume that the low-frequency shift of the carbonyl stretching vibration of

(5) C. Eaborn and R. W. Bott in A. G. MacDiarmid, Ed., "Organometallic Compounds of the Group IV Elements, Vol. 1: The Bond to Carbon," Part 1, Marcel Dekker, New York, N. Y., 1968, pp 378–391, and references cited therein.

(6) D. D. Davis and C. E. Gray, *J. Org. Chem.*, **35**, 1303 (1970).

SCHEME I



10 is due to the formation of an intramolecular six-membered ring by the coordination of the carbonyl oxygen to the tin atom, which acidity was enhanced by the two chlorine atoms. A similar intramolecular cyclization has been reported on [2,3-bis(ethoxycarbonyl)propyl]-*n*-butyltin dibromide by Matsuda and coworkers.[7]

Two organic groups in a tetraorganotin compound can be replaced stepwise by free halogen under appropriate condition to give diorganotin dihalides;[8] however, the cleavage of the tin–carbon bonds of alkyltriphenyltin derivatives by hydrogen halides has not been studied in detail. From the results mentioned above, it seems general that alkyltriphenyltin compounds will give the corresponding alkylphenyltin dichlorides by excess ethereal hydrogen chloride. The following experiments are performed on this point of view. When six alkyltriphenyltin compounds (**12a–f**) were treated with excess hydrogen chloride in ether at room temperature, the corresponding alkylphenyltin dichlorides (**13a–f**) were given quantitatively as shown in Table III. This procedure provides an excellent method to prepare alkylphenyltin dichlorides.

The reaction of either **3d** or **3e** with 3 mol of hydrogen chloride[9] in ether led to a mixture, whose nmr spectra showed the absence of N–CH_2CH_2Sn linkage. Glc analysis of each reaction mixture suggested the presence of phenyltin chlorides and secondary amine instead of (2-methylphenylaminoethyl)phenyltin dichloride hydrochloride (**8d**) or (2-diphenylaminoethyl)-phenyltin dichloride hydrochloride (**8e**), expected from the results described above. In order to obtain a more definite conclusion, each reaction mixture was methylated by an excess of methylmagnesium bromide. Separation of the products gave the following compounds: methyltriphenyltin (56%), dimethyldiphenyltin (31%), trimethylphenyltin (4%), and *N*-methylaniline (78%) from the reactant of **3d**; methyltriphenyltin (56%), dimethyldiphenyltin (34%), trimethylphenyltin (1%), and diphenylamine (85%) from the reactant of **3e**. The ratios of these tin compounds were apparently consistent with the original ratios of phenyltin chlorides.

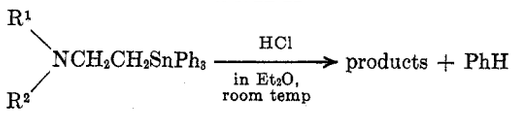
Each of the reactions probably takes place in the following stages. At first, nearly half of the **3d** hydrochloride (**3d**-HCl) or **3e** hydrochloride (**3e**-HCl) is cleaved to form triphenyltin chloride and secondary amine with the loss of ethylene by nucleophilic attack of Cl^- on the triphenyltin moiety (path a). (In fact, independent **3d**-HCl, prepared from **3d** and 1 equiv of hydrogen chloride, was unstable at room temperature decomposing readily to triphenyltin chloride and *N*-methylaniline.) On another half, electrophilic attack of H^+ on the phenyl group results in the formation of (2-methylphenylaminoethyl)diphenyltin chloride hydrochloride (**7d**) or (2-diphenylaminoethyl)diphenyltin chloride hydrochloride (**7e**). At the second stage, a part of **7d** or **7e** is cleaved to give diphenyltin dichloride, secondary amine and ethylene (path d). A few remaining parts lead to **8d** or **8e**. **8d** or **8e** cleavage then gives phenyltin trichloride, secondary

(7) I. Omae, S. Onishi, and S. Matsuda, *J. Organometal. Chem.*, **22**, 623 (1970).

(8) G. P. Van Der Kelen, E. V. Van Den Berghe, and L. Verdonck in A. K. Sawyer, Ed., "Organotin Compounds," Vol. 1, Marcel Dekker, New York, N. Y., 1971, pp 58–88.

(9) This amount is a theoretical mole for the preparation of **8d** or **8e**. When excess hydrogen chloride is employed, initially produced triphenyltin chloride is converted to diphenyltin dichloride.

TABLE II

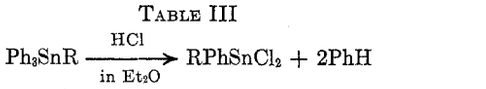


3a–g

3	Reaction conditions: HCl, mol	Time, hr	Products	Mp, °C	Yield, %	
a	1	4	$Me_2N^+HCH_2CH_2SnPh_3 \cdot Cl^-$	106–107.5	100	**3a**-HCl
a	2	4	$Me_2N^+HCH_2CH_2SnClPh_2 \cdot Cl^-$	156–157	100	**7a**
a	Excess	4	$Me_2N^+HCH_2CH_2SnCl_2Ph \cdot Cl^-$	177–180	100	**8a**
b	Excess	17	$Et_2N^+HCH_2CH_2SnCl_2Ph \cdot Cl^-$	177–178	100	**8b**
c	Excess	14	$OCH_2CH_2N^+HCH_2CH_2SnCl_2Ph \cdot Cl^-$ (CH_2CH_2)	201–203	100	**8c**
d	3	27	Ph_3SnCl		56[a]	
			Ph_2SnCl_2		31[a]	
			$PhSnCl_3$		4[a]	
			$PhMeN^+H_2 \cdot Cl^-$		78	
			$CH_2=CH_2$			
e	3	14	Ph_3SnCl		56[a]	
			Ph_2SnCl_2		34[a]	
			$PhSnCl_3$		1[a]	
			$Ph_2N^+H_2 \cdot Cl^-$		84	
			$CH_2=CH_2$			
f	Excess	20	$PhN^+H_2CH_2CH_2SnCl_2Ph \cdot Cl^-$ (Ac)	95–100 dec	100	**8f**
g	Excess	5	$NCH_2CH_2SnCl_2Ph$ (Ph)	149–150	100	**10**

[a] These compounds were isolated from the mixture as the corresponding methylphenyltin derivatives.

TABLE III



12a–f **13a–f**

	R	Reaction conditions: Temp	Time, hr		Products (13a–f)[a]: Mp or bp, °C (mm)	Yield, %
a	Me	Room	5	$MePhSnCl_2$	41–43	100
b	Et	Room	4	$EtPhSnCl_2$	54.5–60	100
c	*n*-Pr	Room	4	*n*-$PrPhSnCl_2$	35–37	100
d	*i*-Pr	Room	2	*i*-$PrPhSnCl_2$	153–157 (10)	100
e	*n*-Bu	Room	3.5	*n*-$BuPhSnCl_2$	43.5–45	100
f	Bz	Room	2	$BzPhSnCl_2$	82–84	100

[a] Satisfactory analytical data (±0.4% for C, H) were reported for all new compounds listed in the table: Ed.

amine, and ethylene (path e). Thus the competition between the electrophilic aromatic substitution and the nucleophilic cleavage reaction occurs by *N*-(2-triphenylstannylethyl)arylamines. If redistribution reactions were slow enough among the phenyltin chlorides produced *via* paths a, d, and e, the contribution of these paths could be estimated as 56%, path a; 31–34%, d; and 1–4%, e.

Experimental Section

Nuclear magnetic resonance spectra were recorded using a JNM-MH-60 (JOEL) spectrometer employing tetramethylsilane as an internal standard. Infrared spectra were obtained using an IR-A-2 (JASCO) spectrophotometer. Gas–liquid chromatographic analyses were performed on JGC-750 and JGC-1100 (JOEL). All boiling points and melting points are uncorrected.

Diphenylaminoethyl Chloride (1e).—A solution of diphenylaminoethanol (21.3 g, 0.1 mol) and triphenylphosphine (26.2 g, 0.1 mol) in 110 ml of carbon tetrachloride was stirred at room temperature for 7 hr, then heated under reflux for 3 hr. After the removal of the solvent, the residue was extracted with petroleum ether (bp 30–60°). The extract was concentrated and distilled, giving 18.2 g (78%) of a pale yellow oil, bp 105–108° (0.05 mm).

Anal. Calcd for $C_{14}H_{14}ClN$: C, 72.13; H, 6.09; N, 6.05. Found: C, 72.39; H, 6.05; N, 6.40.

***N*-(2-Hydroxyethyl)acetanilide.**—Sodium borohydride (0.6 g, 0.014 mol) was added in small portions with stirring to a cold solution of *N*-(2-acetoxyethyl)acetanilide (5 g, 0.023 mol) in 45 ml of methanol. The mixture was stirred below 10° for 2.5 hr, and then at room temperature for 4 hr. After the addition of 30 ml of a saturated sodium chloride solution, the methanol was removed. The residue was extracted with benzene. The extract was dried and concentrated. Recrystallization of the residue from petroleum ether–carbon tetrachloride gave 3.2 g (78%) of *N*-(2-hydroxyethyl)acetanilide, mp 61–62° (lit.[10] mp 62–63°).

***N*-(2-Chloroethyl)acetanilide (1g).**—A solution of thionyl chloride (10.0 g, 0.084 mol) in 20 ml of dry toluene was added to an ice-cold solution of *N*-(2-hydroxyethyl)acetanilide (10.0 g, 0.056 mol) in 30 ml of dry toluene. After the addition, the mixture was stirred at room temperature for 18 hr and distilled, giving 9.0 g (81.8%) of **1g**: bp 83–86° (0.07 mm); nmr ($CDCl_3$) δ 1.85 (s, 3, $NCOCH_3$), 3.70 (t, J = 6 Hz, 2, CH_2Cl), 4.10 (t, J = 6 Hz, 2, NCH_2).

Anal. Calcd for $C_{10}H_{12}ClNO$: C, 60.87; H, 6.13; N, 7.10. Found: C, 61.17; H, 6.32; N, 7.10.

***N*-(2-Triphenylstannylethyl)dimethylamine (3a).**—A solution of triphenyltinlithium (**2**, 0.03 mol) in THF[11] was added to an ice-cold solution of dimethylaminoethyl chloride (**1a**, 2.26 g, 0.021 mol) in 15 ml of THF. After the addition, the mixture was stirred at room temperature for 7 hr, and then it was hydrolyzed with a saturated ammonium chloride solution. The THF layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried and concentrated. Recrystallization of the residue from ethanol gave 7.75 g (85.3%) of **3a**: mp 81–83°; nmr (CCl_4) δ 1.63 (t, J = 7 Hz, 2, $SnCH_2$), 2.06 (s, 6, NCH_3), 2.60 (t, J = 7 Hz, 2, NCH_2), 7.0–8.0 (m, 15 aromatic protons). The ethanol-insoluble solid was recrystallized from petroleum ether to give 0.53 g (5%) of hexaphenylditin (**4**). Nmr data are given in Table IV.

(10) A. B. Boese, Jr., U. S. Patent 2,355,141 (1944).

(11) C. Tamborski, F. E. Ford, and E. J. Soloski, *J. Org. Chem.*, **28**, 181 (1963).

TABLE IV

N-(2-TRIPHENYLSTANNYLETHYL)AMINES (3)

3	R¹	R²	Formula[a]	Nmr, δ, —NCH₂CH₂Sn—	
a	CH_3	CH_3	$C_{22}H_{25}NSn$	2.60	1.63
b	C_2H_5	C_2H_5	$C_{24}H_{29}NSn$	2.79	1.73
c	$(-CH_2CH_2)_2O$		$C_{24}H_{27}NOSn$	2.70	1.75
d	CH_3	C_6H_5	$C_{27}H_{27}NSn$	3.68	1.72
e	C_6H_5	C_6H_5	$C_{32}H_{29}NSn$	4.20	1.93
f	H	C_6H_5	$C_{26}H_{25}NSn$	3.50	1.75
g	CH_3CO	C_6H_5	$C_{28}H_{27}NOSn$	4.10	1.6–2.2

[a] Satisfactory analytical data (±0.3% for C, H, N) and vapor-pressure molecular weight data were reported for all new compounds listed in the table: Ed.

N-(2-Triphenylstannylethyl)diethylamine (3b).—In a similar manner as described for **3a**, the reaction of diethylaminoethyl chloride (**1b**, 4.418 g, 0.033 mol) with **2** (0.03 mol) gave 8.570 g (63.5%) of **3b** [mp 48.5–49.5° (recrystallized from ethanol); nmr (CCl_4) δ 0.80 (t, 6, CH_3CH_2N), 1.73 (t, J = 7.5 Hz, 2, $SnCH_2$), 2.43 (q, 4, CH_3CH_2N), 2.79 (t, J = 7.5 Hz, 2, NCH_2CH_2Sn), 6.8–8.0 (m, 15 aromatic protons)] and 0.52 g (5%) of **4**.

N-(2-Triphenylstannylethyl)morpholine (3c).—In a similar manner as described for **3a**, the reaction of β-4-morpholinoethyl chloride (**1c**, 4.170 g, 0.027 mol) with **2** (0.03 mol) gave 7.031 g (56.1%) of **3c** [mp 125–126° (recrystallized from ethanol); nmr ($CDCl_3$) δ 1.75 (t, J = 7.5 Hz, 2, $SnCH_2$), 2.2–2.6 (m, 4, CH_2NCH_2), 2.70 (t, J = 7.5 Hz, 2, $SnCH_2CH_2$), 7.0–8.0 (m, 15, aromatic protons)] and 0.74 g (7%) of **4**.

N-(2-Triphenylstannylethyl)-N-methylaniline (3d).—In a similar manner as described for **3a**, the reaction of N-(2-chloroethyl)-N-methylaniline (**1d**, 3.2 g, 0.019 mol) with **2** (0.023 mol) gave 5.92 g (62.0%) of **3d** [mp 59.5–60° (recrystallized from ethanol); nmr ($CDCl_3$) δ 1.72 (t, J = 7.5 Hz, 2, $SnCH_2$), 2.80 (s, 3, NCH_3), 3.68 (t, J = 7.5 Hz, 2, NCH_2), 6.5–8.2 (m, 20, aromatic protons)] and 0.40 g (5%) of **4**.

N-(2-Triphenylstannylethyl)diphenylamine (3e).—In a similar manner as described for **3a**, the reaction of **1e** (2.42 g, 0.01 mol) with **2** (0.015 mol) gave 4.50 g (78.5%) of **3e** [mp 98–100° (recrystallized from ethanol); nmr (CCl_4) δ 1.93 (m, 2, $SnCH_2$), 4.20 (m, 2, NCH_2), 6.4–7.7 (m, 25, aromatic protons)] and 0.26 g (5%) of **4**.

N-(2-Triphenylstannylethyl)acetanilide (3g) and N-(2-Triphenylstannylethyl)aniline (3f).—A solution of **2** (0.03 mol) was added to a cold solution of 1g (4.10 g, 0.021 mol) in 15 ml of THF. The mixture was stirred at room temperature for 18 hr and then refluxed for 2 hr. After the addition of a saturated ammonium chloride solution, the THF layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried. Removal of the solvent afforded a mixture which was separated on a silica gel column eluting with benzene. The first elution gave 0.411 g (4%) of **3f**: mp 91–92.5° (recrystallized from ethanol); nmr ($CDCl_3$) δ 1.75 (t, J = 7.5 Hz, 2, $SnCH_2$), 3.34 (s, 1, NH), 3.50 (t, J = 7.5 Hz, 2, NCH_2), 6.3–8.2 (m, 20, aromatic protons); ir (CCl_4) 3500 cm^{-1} (NH). The second elution gave 6.811 g (65%) of **3g**: mp 106–108° (recrystallized from ethanol); nmr (CCl_4) δ 1.76 (s, 3, $NCOCH_3$), 1.6–2.2 (m, 2, $SnCH_2$), 4.10 (m, 2, NCH_2), 6.9–8.2 (m, 20, aromatic protons); ir (CCl_4) 1660 cm^{-1} (C=O).

Hydrolysis of 3g.—A mixture of **3g** (0.63 g) and 30% potassium hydroxide–ethanol (35 ml) was refluxed for 7.5 hr. After the addition of water, the ethanol was removed under reduced pressure. The residue was extracted with chloroform, washed with water, and dried. Removal of the solvent afforded 0.27 g (47%) of **3f**.

Lithium Aluminum Hydride Reduction of 3g.—A solution of **3g** (1.00 g, 1.95 mmol) and lithium aluminum hydride (77 mg, 2.03 mmol) in 70 ml of ether was heated under reflux for 7 hr and then hydrolyzed with a saturated ammonium chloride solution. The reaction mixture was extracted with ether. The extract was washed with water, dried, and then concentrated. Recrystallization of the residue from ethanol gave 0.75 g (81.5%) of **3f**.

Acetylation of 3f with Acetic Anhydride.—A mixture of **3f** (100 mg), acetic anhydride (2 ml), and glacial acetic acid (30 ml) was stirred at room temperature for 3 hr, and then made alkaline by adding of a saturated sodium carbonate solution. The reaction mixture was extracted with ether. The extract was washed with water, dried, and concentrated to give 90 mg (82%) of **3g**.

Reaction of 3f with Methyl Halides. A.—A mixture of **3f** (47 mg, 0.1 mmol), methyl bromide (9.5 mg, 0.1 mmol) in absolute ethanol (2 ml), and dry ether (1 ml) was heated in a sealed tube at 40–50° for 2 hr, and then at 70–80° for 2 hr. After the addition of 20 ml of water, the organic solvent was removed under reduced pressure. The aqueous layer was made slightly alkaline (pH 8) by adding of a sodium bicarbonate solution and it was extracted with ether. The extract was dried and concentrated. Glc analysis of the residue on Lubrol-MO column and silicon SE-30 column showed the presence of N-methylaniline (18%), N,N-dimethylaniline (2%), aniline (3%), triphenyltin bromide (20%), and unreacted **3f** (60%).

B.—A mixture of **3f** (94 mg, 0.2 mmol), methyl iodide (30 mg, 0.2 mmol) in absolute ethanol (4 ml), and dry ether (2 ml) was heated in a sealed tube at 40–50° for 5 hr. The treatment of the products in the same manner as described above showed the presence of N-methylaniline (36%), N,N-dimethylaniline (6%), aniline (6%), triphenyltin iodide (43%), and unreacted **3f** (40%).

Reaction of 3d with Hydrogen Bromide.—A mixture of hydrogen bromide (0.5 mmol) in dry ether (2 ml) and **3d** (0.242 g, 0.5 mmol) in dry ether (15 ml) was allowed to stand at room temperature for 1.5 hr. The precipitated white crystals were filtered to give 35 mg (12%) of **3d** hydrobromide (**3d**-HBr), mp 78–80° dec. Glc analysis of the filtrate on Lubrol-MO and silicone SE-30 showed the presence of N-methylaniline (75%) and triphenyltin bromide (84%).

N-(2-Triphenylstannylethyl)aniline Hydrobromide (3f-HBr).—A mixture of hydrogen bromide (1.0 mmol) in dry ether (14 ml) and **3f** (0.470 g, 1.0 mmol) in dry ether (20 ml) was allowed to stand for 1.5 hr to give 0.550 g (100%) of **3f**-HBr, mp 124–125°.

Anal. Calcd for $C_{26}H_{26}BrNSn$: C, 56.67; H, 4.76; N, 2.54. Found: C, 56.39; H, 4.81; N, 2.62.

A solution of **3f**-HBr (55 mg, 0.1 mmol) in 10 ml of ethanol was refluxed for 2 hr. The ethanol was removed and the residue was extracted with ether. The ethereal extract was dried and concentrated. Column chromatography of the residue on silica gel gave aniline (7 mg, 75%) and triphenyltin bromide (36 mg, 83%).

Reaction of 3d with Methyl Iodide.—A solution of **3d** (0.315 g, 0.65 mmol) and methyl iodide (93 mg, 0.65 mmol) in 10 ml of absolute ethanol was heated in a sealed tube at 70–80° for 4 hr. After the removal of the ethanol, column chromatography of the residue on silica gel gave N,N-dimethylaniline (53 mg, 67%), triphenyltin bromide (198 mg, 71%), and unreacted **3d** (47 mg, 15%).

Reaction of 3a or 3b with Methyl Bromide.—Methyl bromide gas was conducted into a solution of **3a** or **3b** (1 mmol) in 30 ml of dry ether for 7 hr, and then the mixture was allowed to stand overnight. The precipitate was filtered and it was identified with an authentic sample of tetramethylammonium bromide (**6a**) or dimethyldiethylammonium bromide (**6b**), respectively, yield 90–100%. Each filtrate was concentrated to give triphenyltin bromide in 90–100% yield.

N-(2-Triphenylstannylethyl)dimethylamine Hydrobromide (3a-HBr).—The addition of hydrogen bromide (1 mmol) in 11 ml of dry ether to **3a** (0.422 g, 1 mmol) in 25 ml of dry ether gave 0.352 g (70%) of **3a**-HBr, mp 138–141°.

Anal. Calcd for $C_{22}H_{26}BrNSn$: C, 52.53; H, 5.21; N, 2.68. Found: C, 52.08; H, 4.92; N, 2.77.

The filtrate was concentrated to give 0.122 g (28.4%) of triphenyltin bromide.

N-(2-Triphenylstannylethyl)dimethylamine Hydrochloride (3a-HCl).—The addition of hydrogen chloride (1.05 mmol) in 2 ml of dry ether to **3a** (0.444 g, 1.05 mmol) in 30 ml of dry ether gave 0.572 g (100%) of **3a**-HCl, mp 106–107.5°.

Anal. Calcd for $C_{22}H_{26}ClNSn$: C, 57.61; H, 5.51; N, 3.05. Found: C, 57.35; H, 5.47; N, 3.07.

(2-Dimethylaminoethyl)diphenyltin Chloride Hydrochloride (7a).—A mixture of hydrogen chloride (2.04 mmol) in 8.7 ml of dry ether and **3a** (0.430 g, 1.02 mmol) in 30 ml of dry ether was allowed to stand at room temperature for 4 hr. The precipitate was separated by filtration, giving 0.430 g (100%) of **7a**: mp 156–157° (recrystallized from methanol); nmr (DMSO-d_6–$CDCl_3$) δ 1.8–2.1 (m, 2, $SnCH_2$), 2.60 (s, 6, NCH_3), 7.2–8.2 (m, 10, aromatic protons).

Anal. Calcd for $C_{16}H_{21}Cl_2NSn$: C, 46.10; H, 5.08; N, 3.36. Found: C, 46.04; H, 5.19; N, 3.33.

(2-Substituted aminoethyl)phenyltin Dichloride Hydrochloride (8a–c,f) and (2-Acetylphenylaminoethyl)phenyltin Dichloride (10).—A mixture of a solution of **3a–c,f** or **3g** in dry ether and a saturated solution of hydrogen chloride (excess) in dry ether was allowed to stand at room temperature for 4–20 hr. Removal of the solvent and the excess hydrogen chloride under reduced pressure afforded **8a–c,f** or **10** in quantitative yield, respectively. Their data are shown in Tables II and V.

TABLE V

(2-SUBSTITUTED AMINOETHYL)PHENYLTIN DICHLORIDE HYDROCHLORIDE (8a–c–f) AND (2-ACETYLPHENYLAMINOETHYL)PHENYLTIN DICHLORIDE (10)

Compd	R^1	R^2	Formula[a]	Nmr, δ
				DMSO-d_6–$CDCl_3$
8a	CH_3	CH_3	$C_{10}H_{16}Cl_3NSn$	1.5–2.0 (2, $SnCH_2$)
				3.1–3.6 (2, NCH_2)
				6.8–7.8
				(5, aromatic H)
				DMSO-d_6
8b	C_2H_5	C_2H_5	$C_{12}H_{20}Cl_3NSn$	1.6–2.2 (2, $SnCH_2$)
				7.0–8.0
				(5, aromatic H)
				DMSO-d_6
8c	$(-CH_2CH_2)_2O$		$C_{12}H_{18}Cl_3NOSn$	1.7–2.2 (2, $SnCH_2$)
				6.7–7.8
				(5, aromatic H)
8f	H	C_6H_5	$C_{14}H_{16}Cl_3NSn$	
				$CDCl_3$
10	CH_3CO	C_6H_5	$C_{16}H_{17}Cl_2NOSn$	1.9–2.3 (2, $SnCH_2$)
				4.0–4.4 (2, NCH_2)
				7.0–8.3
				(10, aromatic H)

[a] Satisfactory analytical data (±0.4% for C, H, N) were reported for all new compounds listed in the table, except for compound **8f**, which was too hygroscopic: Ed.

***N*-(2-Dimethylphenylstannylethyl)aniline (9). A.**—A solution of methylmagnesium iodide (25 mmol) in dry ether was added to a stirred suspension of **8f** (0.450 g, 1.60 mmol) in dry ether (15 ml). The mixture was stirred at room temperature for 2.5 hr and then heated under reflux for 2 hr. The reaction mixture was hydrolyzed with a saturated ammonium chloride solution and extracted with ether. The extract was dried and concentrated and the residue was then purified by column chromatography on silica gel to give 0.323 g (87.8%) of a pale yellow oil (**9**): nmr (CCl_4) δ 0.30 (s, 6, $SnCH_3$), 1.30 (t, J = 9 Hz, 2, $SnCH_2$), 3.32 (t, J = 9 Hz, 2, NCH_2), 3.20 (s, 1, NH), 6.2–7.5 (m, 10, aromatic protons); ir (CCl_4) 3400 cm^{-1} (NH).

Anal. Calcd for $C_{16}H_{21}NSn$: C, 55.54; H, 6.12; N, 4.05. Found: C, 55.46; H, 5.92; N, 3.86.

B.—A solution of **10** (800 mg, 1.86 mmol) in dry ether was added to a solution of methylmagnesium iodide (10.7 mmol) in ether. After the mixture was heated under reflux for 3 hr, the reaction temperature was raised to 80° by addition of dry benzene and evaporation of the ether. The reaction mixture was hydrolyzed with a saturated ammonium chloride solution and extracted with ether. The ethereal extract was dried and concentrated, and the residue was purified by preparative thin layer chromatography on silica gel to give 0.240 g (37.2%) of **9**.

***N*-(2-Dimethylphenylstannylethyl)acetanilide (11).**—A solution of **10** (1.340 g, 3.12 mmol) and methyl iodide (5 ml) in THF (30 ml) was added slowly to magnesium turnings (157 mg, 6.46 mg-atoms). After the addition, the mixture was stirred at room temperature for 5 hr and then heated under reflux for 3 hr. The reaction mixture was hydrolyzed with a saturated ammonium chloride solution. The THF layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried and concentrated, and the residue was purified by column chromatography on silica gel to give 0.848 g (70%) of a pale yellow oil (**11**): nmr (CCl_4) δ 1.22 (t, J = 8 Hz, 2, $SnCH_2$), 1.71 (s, 3, $NCOCH_3$), 0.32 (s, 6, $SnCH_3$), 3.92 (t, J = 8 Hz, 2, NCH_2), 6.9–7.6 (aromatic protons); ir (CCl_4) 1660 cm^{-1} (C=O).

Anal. Calcd for $C_{18}H_{23}NOSn$: C, 55.71; H, 5.97; N, 3.61. Found: C, 55.51; H, 5.90; N, 3.58.

Reaction of 3d with Hydrogen Chloride. A.—A mixture of a solution of **3d** (0.534 g, 1.1 mmol) in dry ether (30 ml) and a solution of hydrogen chloride (1.1 mmol) in dry ether (2.7 ml) was stirred at room temperature for 1.5 hr. After removal of the ether, the residue was neutralized with a sodium bicarbonate solution and extracted with benzene. The benzene extract was dried and concentrated. Preparative thin layer chromatography of the residue on silica gel gave 49.9 mg (46.2%) of *N*-methylaniline, 0.229 g (53.8%) of triphenyltin chloride, and 0.109 g (20.4%) of **3d**.

B.—A mixture of a solution of **3d** (1.010 g, 2.09 mmol) in dry ether (30 ml) and a solution of hydrogen chloride (6.27 mmol) in dry ether (30 ml) was stirred at room temperature for 27 hr. After removal of the ether, the residue which was dissolved in 15 ml of THF was added to a solution of methylmagnesium bromide (25 mmol) in THF (20 ml). The mixture was heated under reflux for 5 hr, hydrolyzed with a saturated ammonium chloride solution, and extracted with ether. The ethereal extract was dried and concentrated. Glc analysis (silicone SE-30) of the residue showed the presence of *N*-methylaniline (78%), methyltriphenyltin (56%), dimethyldiphenyltin (31%), and trimethylphenyltin (4%).

Reaction of 3e with Hydrogen Chloride.—A mixture of a solution of **3e** (0.982 g, 1.79 mmol) in dry ether (25 ml) and a solution of hydrogen chloride (5.37 mmol) in dry ether (27 ml) was stirred at room temperature for 14 hr. Treatment of the reaction mixture in a similar manner as described above showed the presence of diphenylamine (84%), methyltriphenyltin (56%), dimethyldiphenyltin (34%), and trimethylphenyltin (1%).

Alkylphenyltin Dichlorides (13a–f).—A mixture of a solution of alkyltriphenyltin compounds (**12a–f**) (3 mmol) in dry ether (60 ml) and a saturated solution of hydrogen chloride in dry ether (12 ml) was allowed to stand at room temperature for 2–5 hr. The ether and the excess hydrogen chloride were removed under reduced pressure to yield alkylphenyltin dichlorides (**13a–f**) in quantitative yield, respectively. Their data are shown in Table III.

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Registry No.—**1a**, 107-99-3; **1b**, 100-35-6; **1c**, 3240-94-6; **1d**, 1669-85-8; **1e**, 42393-65-7; **1g**, 36842-84-9; **2**, 4167-90-2; **3a**, 42393-67-9; **3a**-HBr, 42393-68-0; **3a**-HCl, 42393-69-1; **3b**, 42393-70-4; **3c**, 42393-71-5; **3d**, 42393-72-6; **3d**-HBr, 42393-73-7; **3e**, 42393-74-8; **3f**, 42428-60-4; **3f**-HBr, 42393-75-9; **3g**, 42428-61-5; **7a**, 42393-76-0; **8a**, 42428-62-6; **8b**, 42393-77-1; **8c**, 42393-78-2; **8f**, 42393-79-3; **9**, 42393-80-6; **10**, 42428-63-7; **11**, 42393-81-7; **12a**, 1089-59-4; **12b**, 5424-25-9; **12c**, 42428-64-8; **12d**, 1446-45-3; **12e**, 2847-57-6; **12f**, 20451-88-1; **13a**, 15649-26-0; **13b**, 15649-27-1; **13c**, 15649-28-2; **13d**, 42393-84-0; **13e**, 26340-42-1; **13f**, 42393-85-1; diphenylaminoethanol, 6315-51-1; *N*-(2-hydroxyethyl)acetanilide, 28358-86-3.