TABLE II

Compound	Retention time, min Method A	Retention time, min Method B
Phenylcyclohexane	16.0	8.5
3-Phenyl-1,4-cyclohexadiene (4)	16.0	11.4
1-Phenylcyclohexene	25.3	13.4
2-Phenyl-1,3-cyclohexadiene (3)	21.5	15.8
Biphenyl	21.0	20.1
1-Phenyl-1,3-cyclohexadiene (1)	25.3	18.1
1-Phenyl-1,4-cyclohexadiene (2)	28.4	20.1

was analyzed as 80 ± 2% 1-phenyl-1,3-cyclohexadiene (1) and 20 ± 2% 1-phenyl-1,4-cyclohexadiene (2). In some runs, only traces of biphenyl were formed; in others, as much as 20% was observed. The use of lower injection port and detector temperatures (230°) had no effect on this ratio. Compound 1 melted at 38–39°. Since 1 reacted rapidly with oxygen, routine elemental analyses of several samples gave consistently low C and H values. The high-resolution mass spectrum of a freshly isolated sample indicated a parent ion peak at m/e 156.0929 (duplicate measurements). $C_{12}H_{12}$ requires 156.0939. Diene 2 melted at 89–90°.

Anal. Calcd for $C_{12}H_{12}$: C, 92.3; H, 7.7. Found: C, 91.9; H, 8.0.

B. From the Chloro Compound (6a).—A mixture of 4-chloro-1-phenylcyclohexene (1.0 g) and potassium *t*-butoxide (1.0 g) in *t*-butyl alcohol (50 ml) was heated under reflux for 16 hr. The solution was then poured into cold water and the solid which was isolated by filtration and dried weighed 0.2 g and melted at 40–52°. Glpc analysis (method A) indicated a mixture of biphenyl (3%), 1-phenyl-1,3-cyclohexadiene (80%), and 1-phenyl-1,4-cyclohexadiene (17%).

Alkali Metal Reduction of Biphenyl. A. Sodium in Liquid Ammonia.—Biphenyl was reduced with sodium in liquid ammonia according to the method of Hückel and Bretschneider.[5] The crude product was chilled overnight to remove some unchanged biphenyl. The liquid portion of the chilled product was analyzed by glpc (method B). In addition to unreacted biphenyl, there was obtained phenylcyclohexane, 21%; 3-phenyl-1,4-cyclohexadiene, 4, 52%; 1-phenylcyclohexene, 20%; and 2-phenyl-1,3-cyclohexadiene, 3, 6%. In a second run, traces of a $C_{12}H_{16}$ isomer (mass spectrum m/e 160) were eluted after 8.1 min. Diene 3 was extremely sensitive to air, but a freshly isolated sample had a parent ion peak at m/e 156.0939 in its high-resolution mass spectrum. $C_{12}H_{12}$ requires m/e 156.0939. Diene 4 had $n^{25}D$ 1.5595.

Anal. Calcd for $C_{12}H_{12}$: C, 92.3; H, 7.7. Found: C, 92.6; H, 8.0.

B. Sodium in Liquid Ammonia.—Reduction of biphenyl according to the method of Hückel and Schwen[6] and treatment as just described yielded 3-phenyl-1,4-cyclohexadiene (4) in addition to recovered biphenyl. No other dienes or reduced products were observed.

C. Lithium in Ether.—Reduction of biphenyl with lithium in ether according to the method of Egorov, *et al.*,[3] and treatment as described yielded, in addition to unreacted biphenyl, phenylcyclohexane, 19%; 3-phenyl-1,4-cyclohexadiene, 4, 72%; and 1-phenylcyclohexene, 9%. No diene 3 was detected.

Phenylcyclohexadienes 3-d_2 and 4-d_2.—4,4′-Dideuteriobiphenyl, prepared by treatment of the corresponding dilithio derivative[15] with D_2O, was reduced as under A to yield the dideuterio compounds corresponding to the hydrogen analogs described earlier.

Registry No.—**1,** 15619-32-6; **2,** 13703-52-1; **3,** 15619-34-8; **4,** 4794-05-2; **6a,** 15619-36-0; **6b,** 15619-37-1; **6c,** 15619-38-2; **6d,** 15619-39-3; **7,** 10345-94-5; 4-phenyl-3-cyclohexen-1-ol, 15619-51-9.

Acknowledgment.—The authors would like to thank Messrs. G. P. Happ and D. P. Maier for determining the mass spectra.

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[15] H. Gilman, W. Langham, and F. W. Moore, *J. Amer. Chem. Soc.*, **62**, 2327 (1940).

Preparation of Mixed Organotin Chlorides by the Redistribution Reaction[1a]

HENRY G. KUIVILA, RICHARD SOMMER,[1b] AND DENNIS C. GREEN

Department of Chemistry, State University of New York at Albany, Albany, New York 12203

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Under appropriate reaction conditions, organotin dichlorides with two different alkyl or aryl groups can be prepared in good yields by redistribution between organotin trichlorides and tetraalkyltins or trialkyltin chlorides. Some of these organotin dichlorides have been converted into trialkyltin chlorides with three different alkyl groups by alkylation with tetraalkyltins. The following organotin dichlorides have been prepared: butylmethyl, isobutylmethyl, methylphenyl, ethylphenyl, propylphenyl, butylethyl, and butylpropyl. In addition, butylethylmethyl, butylmethylvinyl, butylethylvinyl, and butyldimethyltin chlorides have been prepared.

Organotin halides with two or more different alkyl or aryl groups are usually prepared by alkylation of an organotin halide with Grignard reagent, followed by cleavage of one of the alkyl groups with a halide,[2] *e.g.*, eq 1 and 2.

In many cases special care has to be taken in the cleavage step in order to avoid a mixture of organotin halides (*e.g.*, in eq 2 RR'_2SnX and $R_2R'SnX$). This proved to be extremely difficult, especially when R and R′ are very similar, for example ethyl and butyl. The preparation of organotin dihalides of the type $RR'SnX_2$ or monohalides of the type $RR'R''SnX$ is even more difficult. In order to prepare the latter, a series of alkylations and cleavage reactions has to be carried out.[2] The stepwise addition of different groups by Grignard reagents in most cases is impossible.[2]

$$R_2SnCl_2 \xrightarrow{2R'MgX} R_2R'_2Sn \qquad (1)$$

$$R_2R'_2Sn \xrightarrow{X_2} RR'_2SnX \qquad (2)$$
$$(X = Cl, Br, I)$$

A more convenient synthesis of these halides seemed to be desirable and would be a prerequisite in the investigation of asymmetric organotin compounds.

The most frequently applied method for the preparation of organotin halides is the redistribution reaction, first investigated by Kocheshkov.[3,4]

Recently it was observed that these reactions (eq 3–5)

$$3R_4Sn + SnX_4 \longrightarrow 4R_3SnX \qquad (3)$$

$$R_4Sn + SnX_4 \longrightarrow 2R_2SnX_2 \qquad (4)$$

$$R_4Sn + 3SnX_4 \longrightarrow 4RSnX_3 \qquad (5)$$

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[1] (a) This research was supported by the National Science Foundation under Grant GP-5285; (b) R. S. thanks the Deutschen Forschungsgemeinschaft for a travel grant.

[2] For a review, see R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 459 (1960).

[3] K. A. Kocheshkov, *Ber.*, **62**, 996 (1929).

[4] K. A. Kocheshkov, *ibid.*, **66**, 1661 (1933).

occur stepwise and that it is possible to interrupt them before the final products were formed.[5-7] The first step in eq 4 is the exchange of an alkyl group and a halogen (eq 6), then at higher temperature the two products react to form the organotin dihalide (eq 7).[5]

$$R_4Sn + SnX_4 \longrightarrow R_3SnX + RSnX_3 \quad (6)$$

$$R_3SnX + RSnX_3 \longrightarrow 2R_2SnX_2 \quad (7)$$

Although it has been stated[2] that these redistribution reactions are "undesirable for the preparation of organotin halides in which all of the organic groups are not identical," they have not been investigated in detail.

We find that under appropriate conditions redistributions analogous to that of eq 7 can provide an easy route for the preparation of mixed organotin dihalides, $RR'SnX_2$. In some cases even organotin monohalides with three different alkyl or aryl groups can be prepared. All reactions were monitored by glpc, which proved to be especially valuable, because in some cases further reactions occurred during attempted isolation of the products.

The alkylation of butyltin trichloride with tetramethyltin was exothermic yielding trimethyltin chloride and butylmethyltin dichloride. However, some dimethyltin dichloride and butyldimethyltin chloride were formed (eq 8).

$$Me_4Sn + BuSnCl_3 \longrightarrow Me_3SnCl + BuMeSnCl_2 + Me_2SnCl_2 + BuMe_2SnCl \quad (8)$$

On the other hand, when the tetramethyltin was added slowly to the butyltin trichloride at 0°, the formation of dimethyltin dichloride and butyldimethyltin chloride could be suppressed. Upon distillation, however, large amounts of the two latter compounds were again obtained. It was shown in additional experiments that on heating trimethyltin chloride with butylmethyltin dichloride to 150°, a very rapid reaction occurred, leading to an equilibrium mixture in which about 40% of the trimethyltin chloride had transferred a second methyl group to the butylmethyltin chloride to form dimethyltin dichloride and butyldimethyltin chloride (eq 9). (The same equilibrium mixture was formed from dimethyltin dichloride and butyldimethyltin chloride.)

$$Me_3SnCl + BuMeSnCl_2 \rightleftharpoons Me_2SnCl_2 + BuMe_2SnCl \quad (9)$$

Butylmethyltin dichloride was obtained in good yield when we used trimethyltin chloride instead of tetramethyltin to alkylate butyltin trichloride (eq 10).

$$Me_3SnCl + BuSnCl_3 \longrightarrow Me_2SnCl_2 + BuMeSnCl_2 \quad (10)$$

Only negligible amounts of side products were formed.

Furthermore, combination of eq 8 and 10 proved to be possible; butylmethyltin dichloride was obtained in 99% yield by adding 1 mol of tetramethyltin to 2 mol of butyltin trichloride at 0° and heating subsequently to 180°.

With isobutyltin trichloride similar results were obtained; alkylation with tetramethyltin led only to a 32% yield of isobutylmethyltin dichloride because of the reaction between trimethyltin chloride and isobutylmethyltin dichloride during distillation. Alkylation of the isobutyltin trichloride with trimethyltin chloride provided isobutylmethyltin dichloride in 80% yield.

Tetramethyltin reacted exothermically with phenyltin trichloride upon addition of the tetramethyltin slowly at 0°. Only trimethyltin chloride and methylphenyltin dichloride were formed. The trimethyltin chloride had to be removed at low temperature in order to avoid further alkylation of the methylphenyltin dichloride which was isolated in 85% yield. Ethylphenyltin dichloride and phenyl-*n*-propyltin dichloride were prepared in a similar manner from phenyltin trichloride and the tetraethyl or tetra-*n*-propyltin. Distillation of the alkylphenyltin dichlorides was not attempted since other mixed alkylaryltin halides disproportionated on distillation.[8,9]

Tetraalkyltins and trialkyltin halides with higher alkyl groups are less reactive toward organotin trichlorides than tetramethyltin and trimethyltin chloride. For this reason it was possible to prepare butylethyltin dichloride in 86% yield from tetraethyltin and butyltin trichloride. No detectable amounts of diethyltin dichloride or butyldiethyltin chloride were formed.

In those cases where the reaction products, R_3SnCl and $RR'SnCl_2$, have boiling points too close together to separate by distillation, the products can be isolated after conversion into the oxides. This was shown with the mixture of tri-*n*-propyltin chloride and butylpropyltin dichloride which resulted from the alkylation of butyltin trichloride with tetra-*n*-propyltin.

Butylethyltin dichloride could be alkylated with tetramethyltin to butylethylmethyltin chloride in 76% yield. In the same way, a methyl group can be introduced into other dialkyltin dichlorides, such as in butylmethyltin dichloride.

Tetravinyltin transfers one vinyl group to an organotin dichloride at 20°. Thus, upon reaction with butylmethyltin dichloride only butylmethylvinyltin chloride and trivinyltin chloride were obtained. On distillation of the reaction mixture, however, the starting materials were recovered nearly quantitatively. This is due to an equilibrium (eq 11) which is shifted upon distillation to the left.

$$Vin_4Sn + BuMeSnCl_2 \rightleftharpoons BuMeVinSnCl + Vin_3SnCl \quad (11)$$

Experimental Section

Boiling points are uncorrected. Carbon, hydrogen, and chlorine analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Tin analyses were carried out by oxidation to stannic oxide with 1:1 (volumes) mixture of concentrated sulphuric and nitric acid in quarz test tubes as described.[10] For analytical glpc separations, an F & M Model 720 temperature programmed gas chromatograph was used, with a flow rate of 60 cc of helium/min, using an 8 ft column of 10% silicone rubber SE 30 on Chromosorb W 60-80. Preparative glpc separations were carried out on an F & M Model 775 using a 13 ft by 0.25 in. i.d. column with the same packing material as above.

Materials.—Tetramethyltin, trimethyltin chloride, and butyltin trichloride were gifts from M & T Chemicals. The other tetraalkyltins were prepared from stannic chloride with trialkylaluminum;[10] vinylmagnesium chloride[11] with stannic chloride

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[5] W. P. Neumann and G. Burkhardt, *Ann.*, **663**, 11 (1963).

[6] Metal and Thermit Corp., British Patent 739,883.

[7] E. V. van den Berghe and G. P. van der Kelen, *J. Organometal. Chem.*, **6**, 522 (1966).

[8] S. D. Rosenberg and A. J. Gibbons, Jr., *J. Amer. Chem. Soc.*, **79**, 2138 (1957).

[9] D. Seyferth, *ibid.*, **79**, 2133 (1957).

[10] W. P. Neumann, *Ann.*, **653**, 157 (1962).

[11] S. D. Rosenberg, A. J. Gibbons, Jr., and H. E. Ramsden, *J. Amer. Chem. Soc.*, **79**, 2137 (1957).

TABLE I

PREPARATION OF MIXED ORGANOTIN CHLORIDES BY THE REDISTRIBUTION REACTION

Starting materials				Products (% yield)[a]			Conditions	
							Temp, °C	Time, hr
Me_3SnCl		$BuSnCl_3$		$BuMeSnCl_2$ (88)		Me_2SnCl_2 (96)	180–190	3.5
Me_3SnCl		i-$BuSnCl_3$		i-$BuMeSnCl_2$ (80)		Me_2SnCl_2 (97)	180–190	3.5
Me_4Sn		i-$BuSnCl_3$		i-$BuMeSnCl_2$ (32)		Me_3SnCl (54)	0	
				i-$BuMe_2SnCl$		Me_2SnCl_2		
Me_4Sn		$BuSnCl_3$		$BuMeSnCl_2$ (37)		Me_3SnCl (59)	0	
				$BuMe_2SnCl_2$		Me_2SnCl_2	0	
Me_4Sn		$2BuSnCl_3$		$2BuMeSnCl_2$ (99)		Me_2SnCl_2	Then 180	2
$2Me_4Sn$		$BuSnCl_3$		$BuMe_2SnCl$		$2Me_3SnCl$	75–85	3
Me_4Sn		$BuMeSnCl_2$		$BuMe_2SnCl$ (91)		Me_3SnCl (96)	75–85	3
Me_3SnCl	+	$BuMeSnCl_2$	⇄	$BuMe_2SnCl$	+	Me_2SnCl_2	150	5
Me_4Sn		$PhSnCl_3$		$MePhSnCl_2$ (85)		Me_3SnCl (99)	0	
Et_4Sn		$PhSnCl_3$		$EtPhSnCl_2$ (98)		Et_3SnCl	20	1
$Prop_4Sn$		$PhSnCl_3$		$PropPhSnCl_2$ (69)		$Prop_3SnCl$ (98)	60	4.5
							25	3
Et_4Sn		$BuSnCl_3$		$BuEtSnCl_2$ (86)		Et_3SnCl (83)	Then 100	3
$Prop_4Sn$		$BuSnCl_3$		$PropBuSnCl_2$ (62)		$Prop_3SnCl$	180–190	2
Me_4Sn		$BuEtSnCl_2$		$BuEtMeSnCl$ (76)		Me_3SnCl (91)	120–130	4
							20	4
Vin_4Sn	+	$BuMeSnCl_2$	⇄	$BuMeVinSnCl$	+	Vin_3SnCl	60	2
							20	4
Vin_4Sn	+	$BuEtSnCl_2$	⇄	$BuEtVinSnCl$	+	Vin_3SnCl	60	2

[a] Yield after isolation. The actual yields were higher in many cases.

gave tetravinyltin. Organotin halides were prepared from tetraalkyltin and stannic chloride by redistribution (see Table I).[5]

For distillations, either a 30-cm, vacuum-jacketed, silvered column (column 1) or 12-cm heated column (column 2), both packed with stainless steel helices, or a 55-cm, vacuum-jacketed, silvered column, packed with glass helices (column 3), all equipped with heads for liquid–liquid separations, were used unless otherwise indicated.

Butylmethyltin Dichloride from Trimethyltin Chloride and Butyltin Trichloride.—Trimethyltin chloride (59.8 g, 0.3 mol) and 84.7 g (0.3 mol) of butyltin trichloride were heated for 1.5 hr to 180 to 190° and maintained at this temperature for 2 hr. Glpc (100 to 270°, 10°/min) showed that the reaction mixture contained dimethyltin dichloride and butylmethyltin dichloride and a very small amount of butyldimethyltin chloride. The mixture was separated by distillation through column 1, yielding 63.1 g (96%) of dimethyltin dichloride, bp 103–105° (40 mm), solidifying in the condenser. Fraction 2, bp to 116° (16 mm) (9.2 g), contained the rest of the dimethyltin dichloride, the butyldimethyltin chloride, and some butylmethyltin dichloride. Fraction 3, bp 117–119° (16 mm), consisted of 99% pure butylmethyltin dichloride (by glpc, as described above) and 69.2 g (88%) was obtained. It crystallized on cooling, mp 42–43°.

Anal. Calcd for $C_5H_{12}SnCl_2$: C, 22.94; H, 4.62; Cl, 27.09; Sn, 45.35. Found: C, 22.96; H, 4.60; Cl, 27.24; Sn, 45.2.

Butylmethyltin Dichloride from Tetramethyltin and Butyltin Trichloride.—Tetramethyltin (71.4 g, 0.4 mol) was added over a period of 1 hr at 0° to 225.7 g (0.8 mol) of butyltin trichloride. The reaction mixture was stirred for 1 hr at 20° and heated for 2 hr to 180°. Glpc (as above) indicated that only dimethyltin dichloride and butylmethyltin dichloride were formed. Distillation as above yielded 207.5 g (99.4%) of pure butylmethyltin dichloride.

Isobutylmethyltin Dichloride from Trimethyltin Chloride and Isobutyltin Trichloride.—Trimethyltin chloride (39.9 g, 0.2 mol) and 56.4 g (0.2 mol) of isobutyltin trichloride were treated as described for butylmethyltin dichloride. Glpc (100 to 270°, 10°/min) indicated that only dimethyltin dichloride and isobutylmethyltin dichloride were formed. Distillation through column 1 yielded 42.5 g (97%) of dimethyltin dichloride, bp 108–109° (52 mm), which solidified in the condenser, 9.9 g of a fraction containing dimethyltin dichloride, isobutyldimethyltin chloride, and isobutylmethyltin dichloride, bp to 124° (27 mm), and 41.6 g (80%) of isobutylmethyltin dichloride, bp 124–125° (27 mm), of 99.5% purity (by glpc), mp 41°.

Anal. Calcd for $C_5H_{12}SnCl_2$: C, 22.94; H, 4.62; Cl, 27.09; Sn, 45.35. Found: C, 22.75; H, 4.56; Cl, 26.96; Sn, 45.4.

Isobutylmethyltin Dichloride from Tetramethyltin and Isobutyltin Trichloride.—To 56.4 g (0.2 mol) of isobutyltin trichloride were added 35.8 g (0.2 mol) of tetramethyltin at 0° with magnetic stirring over a period of 2 hr. Glpc (100 to 270°, 10°/min) showed that *ca.* 16% of the isobutylmethyltin dichloride, formed in the first step, had reacted further to form isobutydimethyltin chloride. The mixture was distilled through column 1 yielding 21.5 g (54%) of pure trimethyltin chloride, bp 93° (91 mm). Then the boiling point rose slowly to 127° (32 mm). The fractions collected (total 47.5 g) consisted of mixtures containing trimethyltin chloride, dimethyltin dichloride, isobutyldimethyltin chloride, and isobutylmethyltin dichloride. Pure isobutylmethyltin dichloride distilled at 127° (32 mm) in 32% yield (16.5 g), mp 41°. Qualitatively the same results were obtained when *n*-butyltin trichloride was used instead of isobutyltin trichloride.

Methylphenyltin Dichloride from Tetramethyltin and Phenyltin Trichloride.—To 30.2 g (0.1 mol) of phenyltin trichloride 17.9 g (0.1 mol) of tetramethyltin were added under cooling to 0° and magnetic stirring over a period of 0.5 hr. Stirring was continued for an additional hour at 0°. The reaction mixture consisted of trimethyltin chloride and methylphenyltin dichloride, along with negligible amounts of other products. Trimethyltin chloride (22.3 g) was distilled off and collected in a trap cooled with liquid nitrogen at 0.1 mm by heating the flask slowly to 50°. It contained some higher boiling material and was redistilled, bp 154° (760 mm). The residue of the first distillation was nearly pure methylphenyltin dichloride (23.0 g, 85%); after recrystallization from hexane it had mp 43°.

Anal. Calcd for $C_7H_8SnCl_2$: C, 29.84; H, 2.86; Cl, 25.17; Sn, 42.13. Found: C, 29.73; H, 2.71; Cl, 24.90; Sn, 42.3.

When separation of the reaction mixture was attempted at higher pressure (30 mm), further reaction occurred between trimethyltin chloride and methylphenyltin dichloride.

Ethylphenyltin Dichloride from Tetraethyltin and Phenyltin Trichloride.—Tetraethyltin (23.5 g, 0.1 mol) and 30.2 g (0.1 mole) of phenyltin trichloride were treated under the same conditions as described for methylphenyltin dichloride. After stirring for 1 hr at 20°, the reaction mixture consisted of triethyltin chloride and ethylphenyltin dichloride. Triethyltin chloride 24.1 g (100%) was distilled at 0.002 mm up to a bath temperature of 50° and collected in a trap cooled with liquid nitrogen. The residue, 29.1 g (98%) of nearly pure ethylphenyltin dichloride, solidified on cooling and was recrystallized from hexane, mp 66°. (Ladenburg gives a melting point of 45°.[12])

Anal. Calcd for $C_8H_{10}SnCl_2$: C, 32.49; H, 3.41; Cl, 23.97; Sn, 40.13. Found: C, 32.34; H, 3.40; Cl, 24.13; Sn, 40.2.

Phenylpropyltin Dichloride from Tetrapropyltin and Phenyltin Trichloride.—Phenyltin trichloride (30.2 g 0.1 mol) and 29.1 g

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(12) A. Ladenburg, *Ann.*, **159**, 251 (1871).

(0.1 mol) of tetrapropyltin were stirred for 1 hr at 25°. Glpc (100 to 290°, 15°/min) showed considerable amounts of unreacted tetrapropyltin. Even after 1.5 hr at 60° the reaction was not yet complete. After additional heating for 3 hr to 60°, 34.3 g of tripropyltin chloride were distilled at 0.01 mm up to a bath temperature of 90°. It contained some higher boiling compounds and was redistilled at 12 mm. The residue, 25.0 g of 95% pure phenylpropyltin dichloride, solidified upon cooling and was recrystallized from heptane at −20 to −30° to yield 20.4 g (69%), mp 37–39°. After several additional recrystallizations from heptane the melting point rose to 40°.

Anal. Calcd for $C_9H_{12}SnCl_2$: C, 34.89; H, 3.90; Cl, 22.89; Sn, 38.31. Found: C, 34.77; H, 4.11; Cl, 23.01; Sn, 37.9.

Butylethyltin Dichloride from Tetraethyltin and Butyltin Trichloride.—Upon mixing 47.0 g (0.2 mol) of tetraethyltin and 56.4 g (0.2 mol) of butyltin trichloride, a slightly exothermic reaction occurred. After stirring for 3 hr at 25° and 3 hr at 90–100°, the mixture consisted only of triethyltin chloride and butylethyltin dichloride as shown by glpc (100 to 270°, 10°/min). Distillation over column 1 yielded 40.2 g (83%) of triethyltin chloride, bp 126–127° (56 mm). Then the boiling point rose slowly from 98 to 126° (14 mm). Several fractions (totaling 14.2 g) taken showed, in addition to triethyltin chloride, increasing amounts of butylethyltin dichloride. This compound (45.5 g) was then distilled without a column, bp 126–127° (14 mm). It solidified on cooling. An additional 2.1 g was obtained from fraction 2 upon cooling to 0° to yield 47.5 g (86%), mp 39° (from hexane).

Anal. Calcd for $C_6H_{14}SnCl_2$: C, 26.13; H, 5.12; Cl, 25.71; Sn, 43.04. Found: C, 26.30; H, 5.35; Cl, 25.90; Sn, 43.3.

Butylpropyltin Dichloride from Butyltin Trichloride and Tetrapropyltin.—Butyltin trichloride (42.3 g, 0.15 mol) and 43.7 g (0.15 mol) tetrapropyltin were mixed and heated slowly for 2 hr to 180–190° and maintained at this temperature for 1 hr. After cooling, the reaction products were taken up in ether and converted into the oxides with 10% sodium hydroxide solution. The solid butylpropyltin dioxide was separated by filtration, washed with ether, and shaken with an ethereal solution of concentrated hydrochloric acid to form the dichloride. This was purified by converting it into the oxide a second time. The resulting dichloride was free from tripropyltin chloride but was contaminated by about 10% of dipropyltin dichloride. This was removed by distillation through column 3 (mp 80°) leaving 99% pure butylpropyltin dichloride (by glpc, 75 to 290°, 10°/min) which was distilled without a column to yield 26.8 g (63%), bp 140–142° (15 mm) and mp 44–45°. A sample was recrystallized from petroleum ether (bp 30–70°), mp 46–47° (lit.[13] mp 67–68°).

Anal. Calcd for $C_7H_{16}SnCl_2$: C, 29.01; H, 5.57; Cl, 24.47; Sn, 40.95. Found: C, 29.06; H, 5.58; Cl, 24.65; Sn, 40.7.

The bis(tripropyltin)oxide was converted into tripropyltin chloride by hydrochloric acid and isolated by distillation.

Butyldimethyltin Chloride from Butylmethyltin Dichloride and Tetramethyltin.—Tetramethyltin (17.9 g, 0.1 mol) and 26.2 g (0.1 mol) butylmethyltin dichloride were heated for 3 hr to 75–85°. Glpc (120 to 280°, 10°/min) indicated that only trimethyltin chloride and butyldimethyltin chloride were present along with negligible amounts of dimethyltin dichloride. Distillation through column 2 yielded 19.1 g (96%) of trimethyltin chloride (bp 83–84° (75 mm)), 0.6 g of a mixture of trimethyltin chloride and butyldimethyltin chloride (bp up to 105° (30 mm)), and 21.9 g (91%)) of butyldimethyltin chloride (99.5% purity, bp 108° (30 mm), $n^{20}D$ 1.4971. The residue (1.4 g) consisted of *ca.* 60% of butyldimethyltin chloride and 40% higher boiling materials.

Anal. Calcd for $C_6H_{15}SnCl$: C, 29.86; H, 6.27; Cl, 14.69; Sn, 49.18. Found: C, 29.72; H, 6.25; Cl, 14.49; Sn, 48.8.

Butyldimethyltin Chloride from Tetramethyltin and Butyltin Trichloride.—Tetramethyltin (35.8 g, 0.2 mol) and 28.2 g (0.1 mol) of butyltin trichloride gave, by the same procedure as described above, analogous results, *i.e.*, 0.2 mol of trimethyltin chloride and 0.1 mol of butyldimethyltin chloride.

Butylethylmethyltin Chloride from Butylethyltin Dichloride and Tetramethyltin.—Tetramethyltin (17.9 g, 0.1 mol) and 27.6 g (0.1 mol) of butylethyltin dichloride were heated for 4 hr to 120–130°. Glpc (100 to 270°, 10°/min) indicated a few per cent of unreacted tetramethyltin, trimethyltin chloride, butylethylmethyltin chloride, and negligible amounts of one other product. No butylethyltin dichloride was left over. Distillation through column 1 yielded 18.0 g (91%) of trimethyltin chloride, bp 72–74° (47 mm); then the boiling point rose slowly to 127° (35 mm). Fractions collected, totaling 5.2 g, contained mixtures of trimethyltin chloride, small amounts of an unknown compound, and butylethylmethyltin chloride. The latter compound (19.4 g, 76%) was distilled at 127–128° (35 mm) (99.5% purity). The residue contained butylethylmethyltin chloride and higher boiling compounds.

Anal. Calcd for $C_7H_{17}SnCl$: C, 32.93; H, 6.71; Cl, 13.89; Sn, 46.48. Found: C, 33.13; H, 6.75; Cl, 13.68; Sn, 46.3.

Reaction between Tetravinyltin and Butylmethyltin Dichloride.—Tetravinyltin (34.0 g, 0.15 mol) and 39.2 g (0.15 mol) of butylmethyltin dichloride were stirred for 4 hr at 20° and for an additional 2 hr at 60–70°. Glpc (100 to 270°, 10°/min) showed that only trivinyltin chloride and butylmethylvinyltin chloride were formed. A trace of starting materials was left over. Upon distillation through column 3, 31.6 g (93%) of tetravinyltin were recovered, bp 54–56° (20 mm). A higher boiling fraction (5.7 g) contained tetravinyltin, trivinyltin chloride, butylmethylvinyltin chloride, and butylmethyltin dichloride. The main part of the latter was in the residue and was distilled without column to yield 32.5 g (83%), bp 117–119° (16 mm). It contained no detectable amounts of vinyl groups (ir spectroscopy). The butylmethylvinyltin chloride can be isolated by preparative glpc (100 to 170°, 2°/min), bp 96° (16 mm).

Anal. Calcd for $C_7H_{15}SnCl$: C, 33.19; H, 5.97; Cl, 13.99; Sn, 46.85. Found: C, 33.39; H, 6.09; Cl, 14.02; Sn, 46.4.

Reaction between Tetravinyltin and Butylethyltin Dichloride.—Stoichiometric amounts of tetravinyltin and butylethyltin dichloride were treated as above. Glpc (100 to 270°, 10°/min) showed that most of the starting materials had reacted to form only trivinyltin chloride and butylethylvinyltin chloride. Upon attempted distillation redistribution back to the starting materials occurred. The butylethylvinyltin chloride was isolated by preparative glpc (180° isothermal). Under these conditions, the redistribution back occurred only to a small extent.

Anal. Calcd for $C_8H_{17}SnCl$: C, 35.94; H, 6.41; Cl, 13.26. Found: C, 35.86; H, 6.42; Cl, 13.42.

Reaction between Trimethyltin Chloride and Butylmethyltin Dichloride.—Trimethyltin chloride (1.99 g, 0.01 mol) and 2.61 g (0.01 mol) of butylmethyltin dichloride were heated for 5 hr to 150°. Glpc (100 to 250°, 10°/min) showed that 40–45% of the starting materials had reacted to form dimethyltin chloride and butyldimethyltin dichloride. On prolonged heating, this amount did not increase. Equimolar amounts of dimethyltin dichloride and butyldimethyltin chloride formed, on heating for 4 hr to 150°, the same equilibrium mixture with 55–60% trimethyltin chloride.

Registry No.—$BuMeSnCl_2$, 15649-24-8; *i*-$BuMeSnCl_2$, 15649-25-9; $MePhSnCl_2$, 15649-26-0; $EtPhSnCl_2$, 15649-27-1; $PropPhSnCl_2$, 15649-28-2; $BuEtSnCl_2$, 15649-29-3; $PropBuSnCl_2$, 15649-30-6; $BuMe_2SnCl$, 15649-31-7; BuEtMeSnCl, 15649-32-8; BuMeVinSnCl, 15649-33-9; BuEtVinSnCl, 15649-34-0.

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