Halomethyl-Metal Compounds. XXIII. The Preparation of Bis(triorganotin)dihalomethanes by Dihalocarbene Insertion into the Sn-Sn Bond of Hexaorganoditin Compounds[1]

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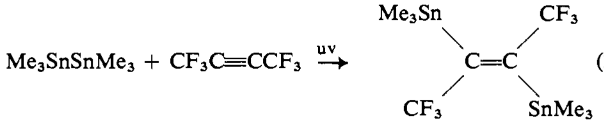
Abstract: Phenyl(trihalomethyl)mercury-derived dihalocarbenes have been found to insert into the Sn–Sn bond of hexaorganoditin compounds. The compounds $Me_3SnCCl_2SnMe_3$, $Me_3SnCClBrSnMe_3$, $Me_3SnCBr_2SnMe_3$, $Ph_3SnCCl_2SnPh_3$, and $Me_3SnCCl_2SnPh_3$ have been prepared in this manner.

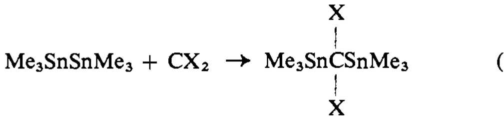
Hexamethylditin contains a very reactive Sn–Sn bond, and of special interest are those reactions in which a neutral molecule or atom is inserted into this bond. Hexamethylditin is oxidized readily by atmospheric oxygen at room temperature to give $Me_3SnOSnMe_3$ and reacts with elemental sulfur, forming $Me_3SnSSnMe_3$.[4] The action of sulfur dioxide on hexamethylditin gives polymeric Me_3SnSO_2,[5] while photo initiated reactions with perfluoroolefins[6-8] and perfluoroacetylenes[9] insert a two-carbon bridge between the trimethyltin groups of hexamethylditin (eq 1 and 2).

$$Me_3SnSnMe_3 + CF_2{=}CF_2 \xrightarrow{uv} Me_3SnCF_2CF_2SnMe_3 \qquad (1)$$



(2)

This well-documented, high reactivity of the Sn–Sn bond of hexamethylditin suggested to us that it might also be capable of reacting with dihalocarbenes (eq 3). In previous work we had observed the insertion of phenyl(trihalomethyl)mercury-derived dihalocarbenes into various single bonds: C–H;[10] Si–H and Ge–H;[11] O–H;[12,13] B–C;[14] Hg–X;[15] Sn–X;[16] Si–Hg and Ge–Hg.[17] In the case of the silicon–mercury and germanium–mercury bonds in the respective $(Me_3M)_2Hg$ compounds, stable insertion products could not be isolated, but products were obtained, $Me_3MCCl{=}CCl_2$, Me_3MCl, and metallic mercury, which provided strong, indirect evidence for the formation of $Me_3MCCl_2HgMMe_3$ as the primary product when $PhHgCCl_2Br$ was the carbene source. The fact that a stable dihalocarbene insertion product into a metal–metal bond had not yet been isolated gave this study both interest and significance. Furthermore, it was expected that the $Me_3SnCX_2SnMe_3$ compounds which would result would have interesting and useful chemistry in their own right.


$$Me_3SnSnMe_3 + CX_2 \rightarrow Me_3Sn\overset{X}{\underset{X}{C}}SnMe_3 \qquad (3)$$

Results and Discussion

The reaction of 100 mmol each of hexamethylditin and phenyl(bromodichloromethyl)mercury in benzene solution at reflux gave a mixture of products which contained the expected bis(trimethyltin)dichloromethane (55% yield) as well as phenylmercuric bromide (36%), diphenylmercury (24%), metallic mercury (19%), and trimethyltin bromide. Bis(trimethyltin)dichloromethane, a clear, distillable liquid, was shown to have this structure by its spectroscopic properties. The simplicity of its infrared spectrum and the presence of only one signal in its proton nmr spectrum spoke for a high order of symmetry in the product. In its mass spectrum, the molecular ion pattern was very similar to that calculated for a molecule with two tin and two chlorine atoms (both Cl isotopes and the three most abundant Sn isotopes were used in the calculation). The parent ion corresponded to a Me_3Sn^+ fragment. If CCl_2 had inserted anywhere other than in the Sn–Sn bond, the most facile cleavage of the Sn–Sn bond would be expected to produce also a fragment with a molecular weight equal to $[Me_3Sn + CCl_2]^+$. No such ion was observed. The only major fragments corresponded to Me_2SnCl^+ and $MeSn^+$.

The other observed products (diphenylmercury, mercury, and trimethyltin bromide) could be rationalized in terms of a secondary reaction between the phenylmercuric bromide (note that its yield is far from quantitative) formed from $PhHgCCl_2Br$ and as yet unconverted hexamethylditin (eq 4 and 5).[18] This reaction sequence rep-

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[1] (a) Part XXII: D. Seyferth and F. M. Armbrecht, Jr., *J. Organometal. Chem.* (Amsterdam), **16**, 249 (1969); (b) preliminary communication: D. Seyferth and F. M. Armbrecht, Jr., *J. Am. Chem. Soc.*, **89**, 2790 (1967).

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[15] D. Seyferth, M. E. Gordon, and K. V. Darragh, *J. Organometal. Chem.* (Amsterdam), **14**, 43 (1968).

[16] D. Seyferth, F. M. Armbrecht, Jr., B. Prokai, and R. J. Cross, *ibid.*, 6, 573 (1966).

[17] D. Seyferth, R. J. Cross, and B. Prokai, *ibid.*, 7, P20 (1967).

resents an undesired diversion of hexamethylditin from

$$PhHgBr + Me_3SnSnMe_3 \rightarrow Me_3SnBr + [PhHgSnMe_3] \quad (4)$$

$$2[PhHgSnMe_3] \rightarrow Ph_2Hg + (Me_3Sn)_2Hg \rightarrow Hg + Me_3SnSnMe_3 \quad (5)$$

product formation and attempts were made to avoid or at least to minimize it. Maintaining the hexamethylditin/mercurial ratio at 1:1 but carrying out the reaction at room temperature during 6 days did not lead to a significant improvement; the bis(trimethyltin)dichloromethane yield was again only 52% and metallic mercury and trimethyltin bromide were formed. The yield of phenylmercuric bromide was around 50%. Thus the phenylmercuric bromide–hexamethylditin reaction proceeds at a significant rate even at room temperature. The attempt to accommodate both hexamethylditin-consuming reactions (eq 3 and 4) by using a 2:1 $Me_6Sn_2/PhHgCCl_2Br$ ratio (reaction at 80°) failed because of other complications. The increase in the yield of bis(trimethyltin)dichloromethane (to 60%) was minimal, and the work-up required became less straightforward. The reaction appeared to proceed normally, but the filtrate obtained upon removal of the reaction solids contained trimethyltin bromide as well as some unconverted hexamethylditin; when it was distilled, a red, apparently polymeric material began to coat the surfaces of the still, making distillation of product difficult. This red solid was found to be pyrophoric in air; it contained bromine but no mercury; it reacted with dilute hydrochloric acid to give methane and stannous chloride. A similarity to solids obtained by the aluminum chloride catalyzed decomposition of hexaethylditin and reported to be polymeric diethyltin[21a] was noted, and very pertinent also was the report by Italian workers[21b,c] that trimethyltin chloride induces the decomposition of hexamethylditin to tetramethyltin and dimethyltin polymer (eq 6). Confirmation that trimethyltin

$$Me_3Sn{-}SnMe_3 \xrightarrow{Me_3SnCl} Me_4Sn + \frac{1}{n}[Me_2Sn]_n \quad (6)$$

bromide decomposed hexamethylditin in similar fashion was provided by our observation that hexamethylditin could be converted to such a red solid upon being heated under nitrogen with a roughly equimolar quantity of trimethyltin bromide (100° for 2 hr, room temperature overnight).

The successful insertion of dichlorocarbene into the Sn–Sn bond of hexamethylditin prompted an investigation of the scope of this novel reaction, in terms of the carbene and the ditin compound used. Hexamethylditin was found to react well (1:1 ratio) with CClBr, CBr_2, and CClF mercurial precursors to give $Me_3SnCClBrSnMe_3$ (39%), $Me_3SnCBr_2SnMe_3$ (37%), and $Me_3SnCClFSnMe_3$[22] (36%). Here also the use of 2 mol of hexamethylditin/mol of mercurial resulted in only small increases in the yield of the desired product (compared with the respective 1:1 reactions) while giving much red solid during the work-up.

In contrast to the reactive Sn–Sn bond to hexamethylditin, the Sn–Sn bond in hexaphenylditin is much less labile. For example, there appears to be no appreciable reaction between hexaphenylditin and atmospheric oxygen. Thus it was not surprising that a 1:1 reaction of phenyl(bromodichloromethyl)mercury with hexaphenylditin in benzene at reflux gave the expected bis(triphenyltin)dichloromethane in only 1.8% yield. A 68% recovery of unconverted hexaphenylditin was realized. Phenylmercuric bromide was isolated in 88% yield, indicating a high resistance of the Sn–Sn bond in hexaphenylditin to attack by PhHgBr. As might have been expected, the Sn–Sn bond in $Me_3SnSnPh_3$ was intermediate in reactivity toward phenyl(bromodichloromethyl)mercury, compared with the Sn–Sn bonds of hexamethyl- and hexaphenylditin. Here the usual 1:1 reaction in refluxing benzene solution gave $Me_3SnCCl_2SnPh_3$ in 16% yield. It should be stressed that there was no indication of the formation of $Me_3SnCCl_2SnMe_3$ or $Ph_3SnCCl_2SnPh_3$ in this reaction. In this reaction the phenylmercuric bromide yield was *ca.* 75%, so reaction of the latter with $Me_3SnSnPh_3$ was not an important complication.

Other hexamethyl compounds with group IVb metal–metal bonds were treated with phenyl(bromodichloromethyl)mercury in refluxing benzene in order to establish if the CX_2 insertion observed in the case of the Sn–Sn bond was capable of further extension within the group. However, the Sn–Sn bond appears to be unique; no CCl_2 insertion was observed with $Me_3SiSnMe_3$, $Me_3GeSnMe_3$, $Me_3GeGeMe_3$, and $Me_3SiSiMe_3$. In all cases the substrate recovery was nearly quantitative, although the presence of a small amount of trimethylmetal halides suggested the occurrence of some M–Sn (M = Si and Ge) bond cleavage by the phenylmercuric bromide formed in the thermolysis of $PhHgCCl_2Br$.

At present the exact nature of this CX_2 insertion into the Sn–Sn bond is not known. A radical-chain mechanism was considered as a possibility since evidence for a methyl radical–dichlorocarbene reaction has been presented[23] and since the light-catalyzed perfluoroolefin and perfluoroacetylene insertions into hexamethylditin are free-radical processes.[6-9] For instance, in the case of the hexamethylditin–tetrafluoroethylene reaction $Me_3SnCF_2CF_2SnMe_3$ was by no means the only product formed; the compound $Me_3SnCF_2CF_2H$ and higher telomers, $Me_3Sn(CF_2CF_2)_nH$ (n = 2 and 3) and $Me_3SnCF_2CF_2CF_2CF_2SnMe_3$, were produced as well,[8] and the following reaction course was proposed by the authors.

$$Me_3SnSnMe_3 \xrightarrow{uv} 2Me_3Sn\cdot$$

$$Me_3Sn\cdot + CF_2{=}CF_2 \rightarrow Me_3SnCF_2CF_2\cdot$$

$$Me_3SnCF_2CF_2\cdot + Me_3SnSnMe_3 \rightarrow Me_3SnCF_2CF_2SnMe_3 + Me_3Sn\cdot$$

$$Me_3SnCF_2CF_2\cdot + CF_2{=}CF_2 \rightarrow Me_3SnCF_2CF_2CF_2CF_2\cdot$$

$$Me_3Sn(CF_2CF_2)_n\cdot + Me_3SnSnMe_3 \rightarrow Me_3Sn(CF_2CF_2)_nSnMe_3 + Me_3Sn\cdot$$

$$Me_3Sn(CF_2CF_2)_n\cdot + \text{Me on Sn} \rightarrow Me_3Sn(CF_2CF_2)_nH + \cdot CH_2 \text{ on Sn}$$

Other photochemical or radical-initiated cleavages of

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(18) A compound of type $(R_3Sn)_2Hg$ (R = Ph) has been isolated only recently and its poor stability in solution was noted.[19] Bis(trialkyltin)mercurials apparently are even less stable.[20]

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(22) For preliminary details concerning the $Me_3SnSnMe_3$–$PhHgCCl_2F$ reaction see D. Seyferth and K. V. Darragh, *J. Organometal. Chem.* (Amsterdam), **11**, P9 (1968).

(23) J. S. Shapiro and F. P. Lossing, *J. Phys. Chem.*, **72**, 1552 (1968).

the Sn–Sn bond of hexamethylditin and other hexaalkylditins (*e.g.*, by iodotrifluoromethane[24]) are known. However, in the case of the CCl_2 insertion into the Sn–Sn bond two observations speak against a free-radical mechanism. (a) At no time during our study of $Me_3SnSnMe_3$–$PhHgCCl_2Br$ reactions were products derivable from the $Me_3SnCCl_2\cdot$ radical found, neither Me_3SnCCl_2H (a compound known to us[25]) nor $Me_3SnCCl_2CCl_2SnMe_3$ or derived products such as $Me_3SnCCl{=}CCl_2$. (b) If a free-radical step involving attack of $Me_3SnCCl_2\cdot$ on hexamethylditin were involved, then in the case of $Me_3SnSnPh_3$ one might well expect to find $Me_3SnCCl_2SnMe_3$ and $Ph_3SnCCl_2SnPh_3$. This, as mentioned above, was not the case. While we do have this indirect evidence against a radical mechanism for the R_6Sn_2–$PhHgCX_3$ reaction, we have no evidence *for* a carbene mechanism. We note, however, that the observed reaction rates at 80° and at room temperature parallel those found for $PhHgCX_3$–olefin reactions which do involve a carbene intermediate.[26]

All bis(triorganotin)dihalomethanes prepared apparently are stable toward attack by atmospheric moisture, a property not shared by other α-polyhaloalkyltin compounds such as Me_3SnCCl_3 and Me_3SnCCl_2Ph. Probably both steric and electronic factors serve to explain this hydrolytic stability. The three $Me_3SnCX_2SnMe_3$ compounds (X = Cl, Br) slowly deposit a white powder upon standing at room temperature. The apparent order of decreasing stability on the purely qualitative observation of the increasing rate of appearance of this solid is $Me_3SnCCl_2SnMe_3 > Me_3SnCClBrSnMe_3 > Me_3SnCBr_2SnMe_3$. This decomposition is reduced by refrigeration of the materials. The compound $Me_3SnCCl_2SnPh_3$ also appeared to have limited stability.

The products of the hexamethylditin–$PhHgCX_2Br$ reactions have an interesting chemistry of their own. Their pyrolysis and their reactions with nucleophiles such as organolithium reagents[25] and sodium iodide[1b] are of particular interest and will be described in detail in later papers of this series.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen or argon. Hexamethylditin was obtained from M & T Chemicals, Inc., Rahway, N. J., butyllithium from the Foote Mineral Co. The latter was standardized using the double titration method in which 1,2-dibromoethane is the halide used. 1,1,1-Trimethyl-2,2,2-triphenylditin was prepared in 61% yield by the method of Neumann, *et al.*[27] The phenyl(trihalomethyl)mercury reagents used were prepared as described by us previously, first by the procedure in benzene,[28] later by the procedure in which diethyl ether is used as solvent.[26] (Note, however our improved procedure for these mercurials.[29]) Elemental analyses were performed by Dr. S. M. Nagy (MIT) or by the Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were recorded using a Perkin-Elmer 337 grating spectrophotometer, nmr spectra with a Varian Associates A-60 nmr spectrometer. Chemical shifts are given in parts per million (ppm) downfield from internal TMS. Mass spectra were recorded using either a Consolidated Electrodynamics Co. 130 or Hitachi-Perkin-Elmer RMU6D mass spectrometer.

Preparation of Bis(trimethyltin)dichloromethane. Into a dried 500-ml, three-necked flask equipped with a reflux condenser, gas inlet tube, and a magnetic stirring unit was charged 44.44 g (0.1 mol) of phenyl(bromodichloromethyl)mercury and 250 ml of benzene (freshly distilled from calcium hydride) under an atmosphere of dry, oxygen-free argon. Hexamethylditin (32.63 g, 0.1 mol) was added quickly *via* syringe and the reaction mixture was heated to reflux. The mixture began to turn gray immediately and during the 7-hr reflux period a flocculent material precipitated. The reaction mixture was cooled and filtered to give a gray solid and an orange filtrate. Most of the solid dissolved in hot dimethylformamide (DMF) and filtration left 3.77 g (19%, based on $PhHgCCl_2Br$) of metallic mercury. Evaporation of the DMF extract at reduced pressure gave 12.76 g (36%) of phenylmercuric bromide, mp 276–280° subl. Concentration of the orange filtrate using a rotary evaporator at 15 mm caused crystallization of diphenylmercury. Further quantities of this material were obtained by adding pentane to the filtrate, and the total yield was 8.37 g (24%). Recrystallization from benzene–pentane gave pure material, mp 124–125°. The filtrate was concentrated further at reduced pressure and the high-boiling residue finally was distilled at 0.03 mm (mild heating with a heat lamp) into a trap at −78°. Gas–liquid partition chromatographic (glpc) analysis (MIT isothermal unit, 4-ft glass column containing 20% General Electric Co. SE-30 silicone rubber gum on Johns-Manville Chromosorb P, at 120°, *n*-butyrophenone internal standard) showed the presence of solvent, trimethyltin bromide, and bis(trimethyltin)dichloromethane (55.3 mmol; 55% yield). The crude distillate was distilled using a short-path distillation unit to give 18.90 g (46%) of pure product, bp 64–66° (0.06 mm), $n^{25}\text{D}$ 1.5326. *Anal.* Calcd for $C_7H_{18}Cl_2Sn_2$: C, 20.48; H, 4.42; Cl, 17.27; Sn, 57.83. Found: C, 20.22; H, 4.54; Cl, 17.38; Sn, 57.53. Nmr spectrum (in CS_2): singlet at 0.29 ppm ($J_{^{117}Sn-^1H} = 51.5$ cps; $J_{^{119}Sn-^1H} = 53.5$ cps). Ir spectrum (liquid film): 2980 (m), 2915 (m), 1390 (w), 1191 (m), 770 (s), 725 (m), 667 (m), 632 (s), and 527 (s) cm^{-1}.

A similar reaction between 10.0 mmol of the mercurial and 9.8 mmol of hexamethylditin in 30 ml of benzene at room temperature for 6 days gave phenylmercuric bromide (56% yield), trimethyltin bromide, and bis(trimethyltin)dichloromethane (52% yield, by glpc).

Reaction of Phenyl(Bromodichloromethyl)mercury with an Excess of Hexamethylditin. To a solution of 43.62 g (0.099 mole) of $PhHgCCl_2Br$ in 250 ml of benzene was added 63.64 g (0.194 mol) of hexamethylditin. The mixture was heated at reflux for 2.5 hr and turned gray during that period. Thin layer chromatography[26] at this point showed that almost all of the mercurial had been consumed. The green liquid layer was decanted from the gray powder which had settled on standing and two 5-ml benzene washings of the solid were added to it. The gray solid was washed with acetone and trichloroethylene to leave 8.08 g (81% yield) of metallic mercury. The green solution was concentrated at 40 mm and 150 ml of *n*-heptane was added to the residue. Diphenylmercury (12.30 g, 70% yield) crystallized on standing, mp 123–125°. Trap-to-trap distillation of the filtrate followed. The first fraction was taken at 0.03 mm without heating and shown by glpc to contain solvent, trimethyltin bromide, and unconverted hexamethylditin. When heating was begun, a red solid began to "distil" through the apparatus. Before it reached the receiver, the apparatus was washed out with acetone. Distillation then was continued at 0.03 mm and a second fraction of clear liquid was obtained. A green-black, tarry residue remained. The high-boiling fraction was redistilled through an 8-in. Vigreux column at 0.1 mm. The forerun was taken from 30 to 74° before more red solid began to "distil" to the top of the still head. None of this solid would distil over and, although the sides of the column were coated with this solid, clear liquid began to distil, yielding a fraction of pure bis(trimethyltin)dichloromethane at 65–68° (0.08 mm), 24.27 g (60%).

Reaction between Hexamethylditin and Trimethyltin Bromide. Into a 5-ml flask equipped with reflux condenser, gas inlet tube, and magnetic stirring unit under an atmosphere of prepurified nitrogen were added 1.75 g (5.35 mmol) of hexamethylditin and 1.53 g (6.27 mmol) of trimethyltin bromide. The mixture was heated at 100° for 2 hr. A small amount of white solid settled out from the pale yellow solution when heating was discontinued. The entire

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(29) D. Seyferth and R. L. Lambert, Jr., *ibid.*, **16**, 21 (1969).

solution stratified into a dark red mass with only a small amount of liquid remaining above the solid after it had been left to stand overnight.

Preparation of Bis(trimethyltin)bromochloromethane. The procedure described for the 1:1 reaction of $PhHgCCl_2Br$ with hexamethylditin was used in the preparation of bis(trimethyltin)bromochloromethane from 57.21 g (0.118 mol) of phenyl(dibromochloromethyl)mercury and 32.23 g (0.098 mol) of hexamethylditin in 270 ml of benzene at 80° for 3 hr. Metallic mercury and phenylmercuric bromide (56.5% yield) were obtained by filtration. Concentration of the filtrate gave a total of 4.70 g (11%) of diphenylmercury. Further distillation (trap-to-trap, at 0.03–0.001 mm) gave first 450 mg of white, air-sensitive solid, mp 91–96°. Its nmr spectrum showed a single resonance at 0.5 ppm with appropriate tin satellites; its hydrolysis on an 0.8-mmol scale gave dibromochloromethane (identification by glpc retention time and ir spectrum) and trimethyltin hydroxide, mp 114–116°. It will be noted that the mercurial was used in slight excess, and the $PhHgCClBr_2$–Me_3SnBr reaction no doubt is responsible for the formation of this small amount of trimethyl(dibromochloromethyl)tin.

After removal of this solid fraction the receiver was changed and a second fraction of liquid, 18.85 g, was collected. A second distillation using a short-path still gave 17.15 g (38.5%) of bis(trimethyltin)bromochloromethane, bp 61° (0.03 mm), $n^{25}D$ 1.5502. *Anal.* Calcd for $C_7H_{18}ClBrSn_2$: C, 18.48; H, 3.99; AgX, 16.24 mg. Found: C, 18.58; H, 3.95; AgX: a 22.445-mg sample gave 16.33 mg. Nmr spectrum (in CS_2): singlet at 0.3 ppm ($J_{^{117}Sn-^1H}$ = 50 cps; $J_{^{119}Sn-^1H}$ = 52 cps). Ir spectrum (liquid film): 2970 (m), 2900 (m), 2340 (w), 1705 (vw), 1695 (vw), 1390 (w), 1190 (m), 768 (vs), 720 (s), 674 (sh), 659 (m), 580 (s), and 526 (s) cm^{-1}.

A similar reaction was carried out using 0.014 mol of phenyl(dibromochloromethyl)mercury and 0.208 mol of hexamethylditin in 250 ml of benzene at reflux for 5 hr. No phenylmercuric bromide precipitated and metallic mercury was obtained in 94% yield. The isolated yield of diphenylmercury was 64%. Trimethyltin bromide again was formed. The distillation of the product again was complicated by formation of red solid, but bis(trimethyltin)bromochloromethane was obtained in 41% yield.

Preparation of Bis(trimethyltin)dibromomethane. The same general procedure was used in the reaction of 13.29 g (25.2 mmol) of phenyl(tribromomethyl)mercury and 9.50 g (29.0 mmol) of hexamethylditin in 150 ml of benzene at reflux during 7.5 hr. The solution turned red and a gray powder precipitated. At this time, tlc showed that less than 5% of the starting mercurial remained. The solution was decanted from the powder and the latter was washed with benzene and separated by centrifugation. Metallic mercury, 2.44 g (49%), was thus obtained. The red solution was concentrated at reduced pressure; addition of heptane to the residue precipitated crude phenylmercuric bromide, mp 276–278°, with residue, 2.61 g (29%). Short-path distillation of the filtrate gave 4.67 g (37%) of bis(trimethyltin)dibromomethane, bp 75–78° (0.05 mm). An analytical sample, $n^{25}D$ 1.5646, was obtained by glpc (20% SE-30 on Chromosorb P, F & M 700 instrument, temperature programmed 90–197°). *Anal.* Calcd for $C_7H_{18}Br_2Sn_2$: C, 16.83; H, 3.63; Br, 32.00. Found: C, 16.94; H, 3.71; Br, 32.30. Nmr spectrum (in CCl_4): singlet at 0.3 ppm ($J_{^{117}Sn-^1H}$ = 52 cps; $J_{^{119}Sn-^1H}$ = 54 cps). Ir spectrum (liquid film): 2980 (m), 2915 (m), 2340 (w), 1715 (w), 1690 (w), 1460 (sh), 1380 (w), 1246 (w), 1190 (m), 856 (sh), 836 (sh), 767 (vs), 717 (s), 660 (m), 556 (vs), and 528 (vs) cm^{-1}.

Reaction of Phenyl(bromodichloromethyl)mercury with Hexaphenylditin. A mixture of 4.1 g of the mercurial (9.3 mmol) and 6.5 g (9.3 mmol) of hexaphenylditin in 25 ml of benzene was heated at reflux under nitrogen for 5 hr. After 15 min of heating phenylmercuric bromide began to precipitate; after 2.5 hr, the solution began to turn yellow. Upon completion of the heating period, 20 ml of benzene was added and the reaction mixture was filtered to remove phenylmercuric bromide and some hexaphenylditin (decolorization of an iodine solution). Concentration of the filtrate to one-half its volume resulted in precipitation of 3.00 g of colorless crystals, mp 222–226° (crude hexaphenylditin). Further concentration and cooling of the residual solution to 0° for 24 hr gave another 0.95 g of crude hexaphenylditin. The remaining solution was evaporated to dryness at 100° (20 mm) and the residue was recrystallized from benzene to give 0.1234 g (1.8% yield) of colorless needles, mp 230°. A second recrystallization from tetrahydrofuran–ethanol gave pure bis(triphenyltin)dichloromethane, mp 243–245°. *Anal.* Calcd for $C_{37}H_{30}Cl_2Sn_2$: C, 56.74; H, 3.86; Cl, 9.06. Found: C, 56.79; H, 4.10; Cl, 9.34. Glpc analysis of the original filtrate showed the presence of only benzene and tetrachloroethylene.

Reaction of Phenyl(bromodichloromethyl)mercury with 1,1,1-Trimethyl-2,2,2-triphenylditin. A mixture of 12.04 g (28.25 mmol) of the mercury compound and 14.5 g (28.25 mmol) of the ditin compound in 50 ml of benzene was heated and stirred at reflux under nitrogen for 3 hr. Filtration separated 7.05 g of crude phenylmercuric bromide (70%). The yellow-brown filtrate was shown by glpc to contain no volatiles other than benzene and a trace of tetrachloroethylene. Removal of solvent left 17.4 g of honey-colored oil containing a small amount of crystalline solid. This residue was treated with iodine in benzene until the iodine color no longer was discharged. Phenylmercuric iodide (0.97 g) was filtered off and the filtrate was treated with 120 ml of 10% potassium fluoride in 50% aqueous ethanol to precipitate 6.61 g of organotin fluorides. (Note that bis(trimethyltin)dichloromethane does not react with alcoholic–aqueous KF solution.) These were filtered, and the filtrate was evaporated at reduced pressure to leave 7.07 g of white, partially crystalline powder. Recrystallization from ethanol gave 2.70 g (16% yield) of trimethyltin(triphenyltin)dichloromethane, mp 100–102°. Further recrystallization from ethanol and 5:1 methanol–ethanol gave an analytical sample, mp 105.5–106.5°. *Anal.* Calcd for $C_{22}H_{24}Cl_2Sn_2$: C, 44.30; H, 4.04; Cl, 11.88. Found: C, 44.40; H, 4.15; Cl, 11.98. This compound did not decolorize iodine in benzene at room temperature.

Mass Spectra. The mass spectra of the three $Me_3SnCX_2SnMe_3$ compounds were in agreement with this structure and are tabulated in the Ph.D. thesis (MIT, 1968) of F. M. A.

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