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HALOMETHYL–METAL COMPOUNDS
L*. PREPARATION OF MONOHALOMETHYL DERIVATIVES OF GERMANIUM, TIN, LEAD AND MERCURY VIA HALOMETHYLZINC HALIDES**

DIETMAR SEYFERTH AND S. BRIAN ANDREWS
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.

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SUMMARY

The reaction of iodomethylzinc iodide or bromomethylzinc bromide in THF with the appropriate metal or organometallic halide was used in the preparation of Me_3SnCH_2I, Me_3SnCH_2Br, $Me_2Sn(CH_2I)_2$, $Me_2Sn(CH_2Br)_2$, $Me_2PhSnCH_2I$, Ph_3SnCH_2I, $Sn(CH_2I)_4$, Ph_3PbCH_2I, $Hg(CH_2I)_2$ and $Hg(CH_2Br)_2$. In most cases the product yields were very good. The reaction of iodomethylzinc iodide with trimethylchlorogermane gave in low yield both Me_3GeCH_2I and $Me_3GeCH_2GeMe_3$. These compounds were obtained in much better yield when ICH_2ZnI was allowed to react with germanium tetrachloride and the reaction product was methylated with MeMgBr. The reaction of iodomethyl–tin compounds with silver chloride and bromide in acetonitrile served well in the preparation of Me_3SnCH_2Cl. Me_3SnCH_2Br, $Me_2Sn(CH_2Cl)_2$, $Me_2Sn(CH_2Br)_2$ and $Me_2PhSnCH_2Cl$.

Experiments in which mixtures of Et_3SiD and n-Bu_3SiH were allowed to react with ICH_2ZnI in refluxing ether or with $Hg(CH_2I)_2/Ph_2Hg$ in refluxing benzene gave *only* Et_3SiCH_2D and n-Bu_3SiCH_3. This eliminates from consideration the possibility that these reactions proceed by a two-step alkylation-reduction or reduction-alkylation sequence.

INTRODUCTION

While methyl substituent halogenation serves well in the preparation of chloromethyl and bromomethyl derivatives of silicon[3] and germanium[4] and even of (chloromethyl)dimethylborane[5,6], this route cannot be applied to synthesis of monohalomethyl compounds of tin, lead and mercury because of the facility with which the halogens cleave heavy metal-to-carbon bonds. For the preparation of halomethyl derivatives of these metals other routes must be used. Iodomethylmercuric iodide can be prepared by the light-initiated reaction of diiodomethane with metallic

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* Part XLIX: Ref. 1.
** Preliminary communication: Ref. 2.

mercury[7,8] and other (halomethyl)mercuric halides have been prepared by reaction of mercuric halides with (halomethyl)chromium(III) reagents[9]. However, the general procedure usually used in the synthesis of monohalomethyl compounds of mercury, tin and lead involves methylenation of metallic or organometallic halides with diazomethane [eqn. (1)][10]. While such reactions often proceed in good yield, the potential hazards associated with diazomethane and its precursors restrict the scale of their application and make the methylenation reaction a "last resort" procedure.

$$\text{M-X} + \text{CH}_2\text{N}_2 \rightarrow \text{M-CH}_2\text{X} + \text{N}_2 \qquad (1)$$

We have used diazomethane methylenation of organotin and organogermanium halides to good advantage in earlier research[11,12] despite the limitations encountered in the scope of application*. In more recent studies devoted to the investigation of (halomethyl)mercury compounds as CH_2 transfer agents[13,14], we required these reagents in larger amounts and during the course of those studies became interested in the possible development of new procedures for the synthesis of monohalomethyl derivatives of mercury and other heavy metals.

The discovery in 1958 by Simmons and Smith[15] that the reaction product of diiodomethane with zinc-copper couple (believed to be ICH_2ZnI) transferred CH_2 to olefins to give cyclopropanes revived interest in this reagent which was first reported by Emschwiller in 1929[16]. Simmons and his coworkers showed that ICH_2ZnI behaved as an *electrophilic* reagent in its reactions with olefins[17,18]. However, it seemed to us that this organozinc reagent should also exhibit *nucleophilic* reactivity when presented with the appropriate substrate. It was clear from Emschwiller's studies that a zinc–carbon bond was present in this reagent: its hydrolysis gave iodomethane and iodinolysis afforded diiodomethane[16]. It was these results which led to the formulation of this reagent as ICH_2ZnI. If this species were to exhibit typical organozinc reactivity, it would be expected to alkylate halides of various metals, including those of mercury, tin and lead**.

Monohalomethyllithium compounds do not appear to be useful reagents[22], but procedures for the preparation of monohalomethyl Grignard reagents have been developed recently[23,24], and these have been shown to have typical organomagnesium reactivity. A drawback associated with their use is their very limited thermal stability which requires the application of low temperature techniques, and the C=O addition product yields generally were only 35–50%. In contrast, ICH_2ZnI in ether or tetrahydrofuran (THF) solutions appears to be stable for at least several hours between 0° and 25°.

These considerations led us to initiate a study of ICH_2ZnI and $BrCH_2ZnBr$ as potential reagents for the synthesis of (halomethyl)metal compounds. As will be apparent as our discussion develops, these compounds serve excellently in this application.

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* For example, R_2SnX_2 react to give $R_2Sn(CH_2X)X$ but not $R_2Sn(CH_2X)_2$, and R_3SnX and Ar_3SnX generally are unreactive toward diazomethane[12]. Thus the preparation of Me_3SnCH_2Cl was accomplished via methylenation of Me_2SnCl_2 to $Me_2Sn(CH_2Cl)Cl$ and subsequent methylation of the latter with methyl Grignard reagent.

** Note the use of diethylzinc in the preparation of diethylmercury[19], tetraethyltin[20], and tetraethyllead[21] in reactions with the appropriate metal halides by Frankland over 100 years ago.

RESULTS AND DISCUSSION

Initial experiments to test the feasibility of our new approach to the synthesis of monohalomethyl derivatives of heavy metals were carried out using trimethyltin chloride as substrate. It was found that the desired reaction did occur [eqn. (2)]. The solvent of choice is THF, and it was found that generally good yields of product were obtained when a filtered zinc reagent solution prepared from *two* molar equivalents each of diiodomethane and zinc (as Zn/Cu) was allowed to react with *one* molar

$$ICH_2ZnI + Me_3SnCl \xrightarrow[2-4\text{ h}]{\text{THF, }35-40°} Me_3SnCH_2I + ZnClI \qquad (2)$$

equivalent of trimethyltin chloride. Hydrolytic work-up (5% HCl) was required in order to remove zinc halides. In one such experiment carried out on a 0.2 mole scale, trimethyl(iodomethyl)tin was isolated in 82% yield. The results of reactions of ICH_2-ZnI with other metal halides are summarized in Table 1. With the exception of the reactions with tin tetrachloride and triphenyllead chloride, the product yields are quite good and thus the objective of this research has been realized. Of special interest is the preparation of $Hg(CD_2I)_2$, a reagent suitable for preparation of *gem*-dideuteriocyclopropanes.

TABLE 1

REACTIONS OF ICH_2ZnI WITH METAL HALIDES

Metal halide	Product	Yield (%)
Me_3SnCl	Me_3SnCH_2I	82
Me_2SnCl_2	$Me_2Sn(CH_2I)_2$	79
Me_2PhSnI	$Me_2PhSnCH_2I$	94
Ph_3SnCl	Ph_3SnCH_2I	66
$SnCl_4$	$Sn(CH_2I)_4$	17
Ph_3PbCl	Ph_3PbCH_2I	31
HgI_2	$Hg(CH_2I)_2$	86
HgI_2 (+ICD_2ZnI)	$Hg(CD_2I)_2$	76

Also examined as reactants were trimethylchlorosilane and trimethylchlorogermane. Reaction of the former with ICH_2ZnI in our hands did not give trimethyl(iodomethyl)silane, while reaction of the chlorogermane with this reagent gave *two* organogermanium products in low yield: the expected Me_3GeCH_2I (2%) and $Me_3GeCH_2GeMe_3$ (7%). Formation of the methylene-bridged digermane can be rationalized in terms of a halogen-metal exchange-alkylation sequence [eqn. (3) and (4)]. Better results were obtained (as expected) when germanium tetrachloride was used in place of trimethylchlorogermane, with reactant stoichiometry appropriate to formation of Cl_3GeCH_2I. The Ge–Cl bonds remaining in this reaction mixture were methylated with MeMgBr. Again, both products were obtained, Me_3GeCH_2I in 31%

$$Me_3GeCH_2I + ICH_2ZnI \rightarrow Me_3GeCH_2ZnI + CH_2I_2 \qquad (3)$$

$$Me_3GeCH_2ZnI + Me_3GeCl \rightarrow Me_3GeCH_2GeMe_3 + ZnClI \qquad (4)$$

yield, $Me_3GeCH_2GeMe_3$ in 25% yield. Curiously, a change in the reaction medium from pure THF to 9/1 THF/$(Me_2N)_3PO$ suppressed almost completely the formation of the methylene-bridged digermane in the $GeCl_4$/ICH_2ZnI reaction. Upon methylation as before trimethyl(iodomethyl)germane was obtained in 29% yield, but $Me_3GeCH_2–GeMe_3$ was present in only trace amount. The expected effect of adding $(Me_2N)_3PO$ was an increase in the reactivity of the zinc reagent[25].

It had been shown by Le Goff[26] that a zinc-copper couple prepared from metallic zinc and copper(II) acetate monohydrate in HOAc/Et_2O would react with dibromomethane to give a reagent, presumably $BrCH_2ZnBr$, which would transfer CH_2 to olefins. We have found that this reagent in THF solution also alkylates tin and mercury halides. Thus its reactions with trimethyltin chloride, dimethyltin dichloride and mercuric bromide gave Me_3SnCH_2Br (84%), $Me_2Sn(CH_2Br)_2$ (31%) and $Hg(CH_2Br)_2$ (59%). A reagent ratio of 4 CH_2Br_2/4 Zn/1 metal–halogen linkage was required to achieve these yields, and this introduced experimental difficulties due to the large volumes of solvent which had to be used. Thus CH_2Br transfer from zinc is much less attractive than CH_2I transfer.

The preparation of monochloromethyl derivatives of tin, lead and mercury by the organozinc route should in principle be possible. However, conditions for successful reaction of dichloromethane and zinc-copper couple have not yet been discovered. The only presently available route to a monochloromethylzinc species involves reaction of diazomethane with zinc chloride, which gives $Zn(CH_2Cl)_2$[27]. This procedure is of no synthetic advantage in our application since the reaction of diazomethane with the appropriate chlorides of tin, lead and mercury gives the monochloromethyl compounds of these metals more directly[10].

The mechanism of the reaction of ICH_2ZnI with metal halides such as trimethyltin chloride is of interest. Three possibilities exist: (a) direct (nucleophilic) alkylation of the metal halide by the organozinc reagent [as in eqn. (2)], or (b) CH_2 insertion into the metal–halogen linkage (a direct transfer, *not* a free methylene process), followed by halogen exchange [eqns. (5), (6)] and (c) halogen exchange followed by CH_2 insertion into the Sn–I bond [eqns. (7), (8)]. Possibility (b) can be

$$ICH_2ZnI + Me_3SnCl \rightarrow Me_3SnCH_2Cl + ZnI_2 \qquad (5)$$

$$Me_3SnCH_2Cl + ZnI_2 \rightarrow Me_3SnCH_2I + ZnClI \qquad (6)$$

$$Me_3SnCl + -ZnI \rightarrow Me_3SnI + -ZnCl \qquad (7)$$

$$ICH_2ZnI + Me_3SnI \rightarrow Me_3SnCH_2I + ZnI_2 \qquad (8)$$

eliminated since in an independent experiment it was shown that zinc iodide reacts only to a minor extent with Me_3SnCH_2Cl in THF (4 h at 40°): the chloromethyltin compound was recovered in 94% yield and Me_3SnCH_2I was formed in only 3% yield. Possibility (c) cannot be eliminated at this time since significant halogen exchange does occur between trimethyltin chloride and zinc iodide in THF at 40°: a roughly 2/1 mixture of Me_3SnI and Me_3SnCl was formed in an orientational experiment. The question of mechanism is thus still an open one and is receiving further attention. However, we favor strongly the view expressed early in this paper, namely that in these reactions between XCH_2ZnX species and metal halides it is a matter of nucleophilic attack by the organozinc reagent at the electrophilic heavy metal center.

Further research still in progress has demonstrated the Me_3SnCH_2Br and Me_3SnCH_2Cl serve better as starting halides for Grignard reagent preparation than does Me_3SnCH_2I. However, preparation of the latter is most convenient and proceeds in best yield. For this reason we sought other alternatives and have found a most useful one: Me_3SnCH_2I can be converted very easily to Me_3SnCH_2Cl and Me_3SnCH_2Br by reaction with the appropriate silver halide in acetonitrile solution at room temperature, *e.g.*, [eqn. (9)]. Table 2 lists results of experiments in which other iodomethyl–tin compounds were converted to chloro- or bromomethyl derivatives. The success of these reactions very likely is due to the relative solubilities of silver iodide *vs.* silver chloride and bromide which are similar to those for silver halides in aqueous solution.

TABLE 2

REACTIONS OF IODOMETHYL–TIN COMPOUNDS WITH SILVER HALIDES

ICH_2–Sn Compound	AgX	Product	Yield (%)
Me_3SnCH_2I	AgCl	Me_3SnCH_2Cl	73
$Me_2PhSnCH_2I$	AgCl	$Me_2PhSnCH_2Cl$	93
$Me_2Sn(CH_2I)_2$	AgCl	$Me_2Sn(CH_2Cl)_2$	68
Me_3SnCH_2I	AgBr	Me_3SnCH_2Br	67
$Me_2Sn(CH_2I)_2$	AgBr	$Me_2Sn(CH_2Br)_2$	75

$$Me_3SnCH_2I + AgX \xrightarrow[\text{7 days}]{CH_3CN,\ 25°} Me_3SnCH_2X + AgI \quad (9)$$

$(X = Cl, Br)$

This work thus has shown that iodomethylzinc iodide serves excellently in the preparation of monoiodomethyl derivatives of tin, lead and mercury. If monochloro- or monobromomethyl derivatives are desired, preparation of the iodomethyl compounds followed by halogen exchange with the appropriate silver halide is the procedure of choice. The alternative methylenation of tin, lead and mercury halides with diazomethane thus is rendered obsolete. It is obvious that the ICH_2ZnI procedure should be applicable to the synthesis of ICH_2 derivatives of elements other than those mentioned in this report, and this possibility is receiving our attention.

In a previous study we had shown that iodomethylzinc iodide reacts with organosilicon hydrides to give methylsilicon derivatives [eqn. (10)][28]. Although a direct transfer of CH_2 from the zinc reagent to the Si–H bond was the favored reaction course, reaction sequences involving alkylation and reduction steps were not eliminated [eqns. (11), (12) and (13), (14)]. In order to resolve this question, the following experiment was carried out. A mixture of Et_3SiD and $(n\text{-}C_4H_9)_3SiH$ was allowed to

$$R_3SiH + ICH_2ZnI \rightarrow R_3SiCH_3 + ZnI_2 \quad (10)$$

$$R_3SiH + ICH_2ZnI \rightarrow R_3SiI + CH_3ZnI \quad (11)$$

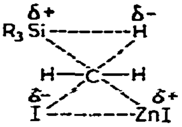
$$R_3SiI + CH_3ZnI \rightarrow R_3SiCH_3 + ZnI_2 \quad (12)$$

or, less likely,

$$R_3SiH + ICH_2ZnI \rightarrow R_3SiCH_2I + HZnI \quad (13)$$

$$R_3SiCH_2I + HZnI \rightarrow R_3SiCH_3 + ZnI_2 \quad (14)$$

react with an excess of ICH_2ZnI in diethyl ether. If either of the alkylation-reduction sequences were operative, then a mixture of Et_3SiCH_3, Et_3SiCH_2D, n-Bu_3SiCH_3 and n-Bu_3SiCH_2D would be expected. On the other hand, if a direct insertion of CH_2 into the Si–H bond were involved [transition state (I) was suggested[28]], then Et_3SiCH_2D and n-Bu_3SiCH_3 should be the only products formed. Examination of the methyltriethyl- and methyltri-n-butylsilane formed in this experiment by IR, NMR and mass spectroscopy showed that only Et_3SiCH_2D and n-Bu_3SiCH_3 were present. Thus it would appear that the direct insertion process is operative.



(I)

Halomethyl derivatives of mercury also insert CH_2 into the Si–H bond of organosilicon hydrides[14], *e.g.*, [eqn. (15)]. Here also mechanisms analogous to those

$$ICH_2HgI + Ph_2Hg + Et_3SiH \rightarrow Et_3SiCH_3 + 2\ PhHgI \qquad (15)$$

discussed for the R_3SiH/ICH_2ZnI reaction are in principle possible. However, a Hammett study[14] indicated that the product-forming step involved electrophilic attack at the Si–H bond and thus a direct CH_2 transfer process seemed indicated. A definite answer excluding an alkylation-reduction sequence [the mercury analogs of eqn. (11), (12) and (13), (14)] has now been obtained. Reaction of a mixture of Et_3SiD and n-Bu_3SiH with the bis(iodomethyl)mercury/diphenylmercury reagent pair gave only Et_3SiCH_2D and n-Bu_3SiCH_3*. We suggest that CH_2 transfer to the Si–H bond occurs by way of a transition state analogous to I, with IZn replaced by ICH_2Hg.

EXPERIMENTAL

General comments

All reactions were carried out in flame-dried glassware under an atmosphere of prepurified nitrogen using rigorously dried solvents. Organozinc reagent solutions were filtered using a Schlenk filter under nitrogen pressure.

Infrared spectra were recorded using a Perkin–Elmer Model 337, 237 B or 257 grating infrared spectrophotometer, NMR spectra using either a Varian Associates A60 or T60 spectrometer. Chemical shifts are expressed in δ units, using either tetramethylsilane (TMS δ 0.00 ppm), dichloromethane (δ 5.30), cyclohexane (δ 1.43) or, more usually, chloroform (δ 7.27) as internal standards. Mass spectra were recorded using a Hitachi–Perkin–Elmer RMU6D mass spectrometer.

Gas-liquid partition chromatography (GLC) was used routinely for yield determinations and for collection of analytical samples. Commercial stainless steel columns were employed with either an F and M Model 700, 720 or 5754 gas chroma-

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* The $Hg(CH_2I)_2/Ph_2Hg$ reagent, which was not examined previously (*i.e.*, ref. 14), was shown to react with Et_3SiH (in benzene at 80° for 72 h) to give Et_3SiMe in 72% yield (based on *both* CH_2I groups) and PhHgI in 79% yield.

tograph, glass columns with the MIT isothermal unit. Several different columns were used: (A) 4 ft. 10% UC-W98 silicone rubber (5754); (B) 6 ft. 10% Dow Corning DC-200 silicone oil (5754); (D) 6 ft. 20% UC-W98 (700); (E) 6 ft. 20% DC-200 (700 or 720); (G) 2 ft. 20% General Electric SE-30 silicone rubber gum (720); (J) 6 ft. 20% General Electric XE-60 (700 or 720); (L) 80 in. 15% UC-W98 (F and M 776); (M) 8 ft. 20% SE-30 (MIT isothermal); (N) 8 ft. 15% SE-30 (MIT). All columns were packed with acid-washed, dimethylchlorosilane-treated Chromosorb W; a helium carrier gas flow rate of 40–60 ml/min was commonly employed. Internal standards were used in all yield determinations. Empirical response factors were determined separately using standard solutions.

The monohalomethyl–metal compounds prepared, their physical properties, their analyses and their NMR spectra are listed in Table 3.

General procedure for the preparation and utilization of a homogeneous solution of iodomethylzinc iodide

The reactions to be described were carried out using a solution of iodomethylzinc iodide prepared by the following general procedure. Zinc-copper couple was prepared by the method of LeGoff[26]. The proportions of reagents used in the preparation of the couple were always in the ratio of 1.0 g of cupric acetate monohydrate : 1.0 g-atom of granular zinc : 100 ml per portion of glacial acetic acid : 200 ml per portion of diethyl ether.

In a three-necked, round-bottom flask, 1.0 part by weight (g) of cupric acetate monohydrate (Mallinckrodt) was dissolved in 100 parts by volume (ml) of hot glacial acetic acid using a steam bath. To this solution was added 1.0 molar part of granular zinc (Mallinckrodt 30-mesh), and the hot mixture was shaken for 1–2 min. The acetic acid was decanted from the metal, an additional 100 parts of fresh acetic acid was added, and the process repeated. The cooled couple then was washed three times by shaking with 200 parts (ml) per portion of diethyl ether. The reddish-brown couple was dried in a stream of nitrogen.

The remainder of the apparatus, consisting of an appropriate dropping funnel, reflux condenser, gas-inlet tube, and magnetic stirbar, was affixed to the flask and flame-dried under nitrogen. The dropping funnel was charged with a 5–10 *M* solution of 1.0 equivalent of diiodomethane (Eastman) in THF, and an equal volume of THF added to the couple. The reaction was initiated readily by the addition of a few drops of the diiodomethane solution, as evidenced by an exothermic reaction and the formation of a purple color. The reaction mixture was diluted with three volumes of THF, a quantity such that the final concentration of the mixture was ca. 2 *M* based on original diiodomethane. The contents of the dropping funnel then were added at a rate sufficient to maintain the reaction mixture at ca. 40°. This reaction was carried out for 150–180 min, with mild heating over the last hour, by which time the zinc had been mostly consumed.

The reaction mixture was cooled to ca. 0° and filtered under nitrogen using a Schlenk-type filter with a medium-to-coarse fritted disc into a dried apparatus similar to that described above. The solution thus obtained usually was a cloudy purple, but free from excess metal. This solution generally was employed in a reaction with an organometal halide in the manner to be described. Work-up of the resultant cloudy, gray reaction mixture was accomplished by the following technique. To the cooled

TABLE 3

HALOMETHYL DERIVATIVES OF GERMANIUM, TIN AND LEAD PREPARED

Halomethyl compound	B.p. (°C/mm) or m.p. (°C)	n_D^{25}	Analysis found (calcd.) (%) C	H	Hal.	NMR[a]
$(CH_3)_3SnCH_2I$	B.p. 54–55/5.5	1.5511				0.22 [s, 9H, $J(^{117}Sn–H)$ 52 Hz, $J(^{119}Sn–H)$ 55 Hz, Me_3Sn 1.90 [s, 2H, $J(Sn–H)$ 20 Hz, $–SnCH_2I$]
$(CH_3)_2Sn(CH_2I)_2$	B.p. 60–61/0.01	1.6448	11.18 (11.15)	2.29 (2.34)		0.42 [s, 6 H, $J(^{117}Sn–H)$ 54 Hz, $J(^{119}Sn–H)$ 56 Hz, Me_2Sn] 2.07 [s, 4 H, $J(Sn–H)$ 20 Hz, $Sn(CH_2I)_2$]
$(CH_3)_2(C_6H_5)SnCH_2I$	B.p. 78–81/0.05	1.6068	29.75 (29.47)	3.66 (3.57)	34.27 (34.60)	0.60 [s, 6 H, $J(^{117}Sn–H)$ 52 Hz, $J(^{119}Sn–H)$ 54 Hz, Me_2Sn] 2.20 [s, 2 H, $J(Sn–H)$ 20 Hz, $–SnCH_2I$] 7.3–7.7 (m, 5 H, Ph)
$(C_6H_5)_3SnCH_2I$	M.p. 86–87		46.69 (46.48)	3.54 (3.49)		2.33 [s, 2 H, $J(Sn–H)$ 22 Hz, $–SnCH_2I$] 7.1–7.6 (m, 15 H, Ph_3Sn)
$(CH_3)_3SnCH_2Br$	B.p. 46–48/12	1.5078				0.20 [s, 9 H, $J(^{117}Sn–H)$ 52 Hz, $J(^{119}Sn–H)$ 55 Hz, Me_3Sn] 2.55 [s, 2 H, $J(Sn–H)$ 17 Hz, $–SnCH_2Br$]
$(CH_3)_2Sn(CH_2Br)_2$	GLC isolation	1.5561	14.18 (14.27)	3.03 (2.99)	47.21 (47.48)	0.38 [s, 6 H, $J(^{117}Sn–H)$ 54 Hz, $J(^{119}Sn–H)$ 56 Hz, Me_2Sn] 2.70 [s, 4 H, $J(Sn–H)$ 18 Hz, $–Sn(CH_2Br)_2$]
$(CH_3)_3SnCH_2Cl$	B.p. 69–70/57	1.4863				[b]0.23 [s, 9 H, $J(^{117}Sn–H)$ 52 Hz, $J(^{119}Sn–H)$ 54 Hz, Me_3Sn] 3.02 [s, 2 H, $J(Sn–H)$ 19 Hz, $–SnCH_2Cl$]
$(CH_3)_2(C_6H_5)SnCH_2Cl$	B.p. 60–66/18	1.5592	39.15 (39.25)	4.77 (4.76)	13.14 (12.99)	0.60 [s, 6 H, $J(^{117}Sn–H)$ 53 Hz, $J(^{119}Sn–H)$ 55 Hz, Me_2Sn] 3.28 [s, 2 H, $J(Sn–H)$ 20 Hz, $–SnCH_2Cl$] 7.3–7.7 (m, 5 H, Ph)
$(CH_3)_2Sn(CH_2Cl)_2$	B.p. 68–70/4.8	1.5219	19.27 (19.39)	4.03 (4.07)	28.58 (28.51)	[b]0.32 [s, 6 H, $J(^{117}Sn–H)$ 55 Hz, $J(^{119}Sn–H)$ 57 Hz, Me_2Sn] 3.12 [s, 4 H, $J(Sn–H)$ 20 Hz, $–Sn(CH_2Cl)_2$]
$(C_6H_5)_3PbCH_2I$	M.p. 72–73.5°		39.41 (39.38)	3.14 (2.96)		3.02 [s, 2 H, $J(^{207}Pb–H)$ 9 Hz, $–PbCH_2I$] 7.2–7.8 (m, 15 H, Ph_3Pb)
$(CH_3)_3GeCH_2I$		1.5107				[b]0.27 (s, 9 H, Me_3Ge) 2.08 (s, 2 H, $–GeCH_2I$)

[a] In CCl_4; δ ppm downfield from TMS. [b] Neat.

reaction mixture was added an equal volume of benzene, and this was poured into a separatory funnel. This was followed by extraction *four* times with *double-volume* portions of 5% HCl. The aqueous layers were *not* back-extracted, since then the combined organic layers were prone to decomposition, and the yield of desired product obtained from the aqueous phases was minimal.

The extracted organic phase, most often clear and only very slightly yellow, was dried over magnesium sulfate and filtered. Further work-up of this solution then could be accomplished by the usual techniques. The above procedure has been described for a reaction on a scale of approximately 0.05–0.10 mol. These experiments often have been carried out on a preparative scale (1.0 mol of zinc-copper couple), in which cases the following exceptions applied. The preparation of the organozinc reagent itself required a longer reaction time, *i.e.*, approximately 8–9 h. Filtration of the zinc reagent using a Schlenk-type filter was not feasible, since the volume involved was unwieldy, and the fritted disc is apt to plug. In this case, the reagent is best filtered in the air *quickly* through a Scott paper towel.

The importance of strict adherence to experimental detail for the success of these reactions cannot be stated too strongly. For this reason the following detailed description of the preparation of (iodomethyl)trimethyltin further illustrates the general procedure.

Reaction of iodomethylzinc iodide with trimethyltin chloride. In a 100-ml, three-necked, round-bottom flask was placed 0.04 g of cupric acetate monohydrate, and this was dissolved in 4 ml of glacial acetic acid by heating on a steam bath with shaking. To the hot solution was added 2.60 g (40.0 mg-atom) of *granular* zinc, and this was shaken for 1–2 min while heating was continued. The acetic acid was decanted from the settled couple; 4 ml of fresh acetic acid was added and shaken *hot* for 1–2 min, and again was decanted. The cooled couple then was similarly washed three times with 8 ml portions of diethyl ether. The couple was dried by a stream of nitrogen.

The flask was equipped with a dropping funnel, reflux condenser, gas-inlet tube, and magnetic stirbar, and the apparatus was flame-dried under an atmosphere of nitrogen. The couple was covered with 7 ml of THF, and the reaction was initiated with a few drops of diiodomethane. Upon the appearance of a purple color, an additional 13 ml of THF was added to the flask. In the dropping funnel was placed 10.75 g (40.2 mmoles) of diiodomethane in 7 ml of THF, and this was added dropwise at a rate which allowed the mixture to maintain a temperature of ca. 40°.

The reaction was carried out for 150 min, occasionally applying mild heating during the last h, and subsequently was cooled using an ice bath. The solution was filtered using a Schlenk-type apparatus into another dry, 100-ml, three-necked flask. This flask then was equipped as had been the former. The dropping funnel of the new apparatus was charged with 4.25 g (21.3 mmol) of trimethyltin chloride (M & T Chemicals) in 10 ml of THF, and this was added dropwise over 30 min to the organozinc reagent at ca. 40°. The reaction mixture was stirred for 3 h, after which time GLC (Column N, 170°) indicated that product formation had ceased.

The cloudy, gray reaction mixture was poured into a separatory funnel, and 25 ml of benzene was added. The mixture was extracted four times with 50 ml portions of 5% HCl, and the resultant light yellow organic phase dried (magnesium sulfate), filtered, and concentrated using a 7" Vigreux column. Trap-to-trap distillation, 100° (0.01 mm), of the concentrate afforded 17.8 g of distillate. GLC analysis (Column B, 120°) indicated the presence of 18.3 mmoles (86%) of a single product, which was isolated by preparative GLC (Column N, 170°) and characterized as (iodomethyl)trimethyltin, n_D^{25} 1.5511 (lit.[12] n_D^{25} 1.5510). The product subsequently was isolated by fractional distillation using a 7″ Vigreux column; 4.1 g (65%), b.p. 54–55°/5.5 mm (lit.[12] b.p. 53–54°/6.5 mm).

In a separate experiment carried out on a 0.2 mole scale, 24.87 g (82%) of (iodomethyl)trimethyltin was isolated by fractional distillation, b.p. 55–57°/6.0 mm.

Reaction of iodomethylzinc iodide with dimethyltin dichloride. A solution of iodomethylzinc iodide was prepared from 65.4 g (1.0 g-atom of granular zinc and 268 g (1.0 mol) of diiodomethane in 500 ml of THF (9 h reaction time). A solution of 44.6 g (0.20 mol) of dimethyltin dichloride (M & T Chemicals, recrystallized to m.p. 107.0–107.5°) in 200 ml of THF was added dropwise to the organozinc reagent over one h at ca. 40°, and the mixture was stirred for an additional 2 h. It then was combined with 700 ml of benzene in a separatory funnel, and extracted four times with 2000 ml portions of 5% HCl. The organic phase was dried, filtered, and concentrated at reduced pressure. Distillation of the concentrate using a short-path distillation apparatus (a copper wire coil in the receiver and pot minimized decomposition) into a *receiver at* −196° provided 67.8 g (79%) of bis(iodomethyl)dimethyltin, b.p. 68–70°/0.05 mm, >95% pure by GLC [Column (B), 170°].

Further fractionation of this distillate using a 4″ Vigreux column afforded a center cut of analytical purity, b.p. 60–61°/0.01 mm. This product has been found to have only marginal stability at ambient conditions, and must be stored in a brown bottle under nitrogen at < 5°. GLC analysis was in general not applicable to this compound. Prior conditioning of a nonpolar stationary phase (*e.g.*, DC-200) by the successive injection of at least five 10 μl samples was necessary before a reliable trace could be obtained. Isolation of this material by GLC was not accomplished.

Reaction of iodomethylzinc iodide with phenyldimethyltin iodide. A solution of the organozinc reagent was prepared from 9.20 g (0.141 g-atom) of zinc-copper couple and 37.6 g (0.137 mol) of diiodomethane in 100 ml of THF. The solution was treated with 25.10 g (0.071 mol) of phenyldimethyltin iodide* in 25 ml of THF at 40° for 210 min. Work-up as usual afforded 24.37 g (94%) of (iodomethyl)phenyldimethyltin, b.p. 78–81°/0.05 mm, ca. 98% pure by GLC [Column (A), 160°]. Further fractionation (4″ Vigreux column) using acid-washed glassware gave a center cut of analytical purity, b.p. 69°/0.01 mm.

Reaction of iodomethylzinc iodide with triphenyltin chloride. Following the general procedure, 6.50 g (0.09 g-atom) of zinc-copper couple and 28.3 g (0.106 mol) of diiodomethane were used to prepare a solution of ICH_2ZnI in 50 ml of THF. A solution of 18.1 g (0.047 mol) of triphenyltin chloride (M & T Chemicals) in THF was added dropwise, and the mixture allowed to react in the usual manner. Extraction as outlined in the general procedure afforded a dry organic phase, which was concentrated at reduced pressure. Recrystallization of the solid residue from hexane gave two crops of white, crystalline plates, m.p. 86–87°. The total weight of 15.09 g represented a yield of 66% of Ph_3SnCH_2I.

Reaction of four equivalents of iodomethylzinc iodide with tin tetrachloride. To a

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* Prepared by cleavage of Me_2Ph_2Sn with iodine in CCl_4 in 88% yield; b.p. 69–71°/1.0 mm, n_D^{25} 1.6244. (Found: C, 27.21; H, 3.18. $C_8H_{10}ISn$ calcd.: C, 27.23; H, 3.14%.)

filtered solution of ICH_2ZnI in 130 ml of THF, prepared from 13.1 g (0.20 g-atom) of zinc-copper couple and 54.0 g (0.20 mol) of diiodomethane, was added dropwise a solution of 5.1 g (0.0196 mol) of tin tetrachloride in 30 ml of benzene. The resulting mixture was stirred at 40° for 3 h. Hydrolysis and extraction of the final mixture was followed by concentration of the resultant benzene solution and by extraction and crystallization of the oily residue using ether and 1/2 benzene/ethanol, successively. Recrystallization from ethanol provided two crops of white needles, m.p. 74–76°, tetrakis(iodomethyl)tin (lit.[29] m.p. 76°), 2.30 g (17%). NMR spectrum (CCl_4): δ 2.28 ppm [s, J(Sn–H) 20 Hz, $Sn(CH_2I)_4$].

Reaction of iodomethylzinc iodide with mercuric iodide. A solution of ICH_2ZnI in 55 ml of THF prepared from 6.50 g (0.10 g-atom) of zinc-copper couple and 27.3 g (0.10 mol) of diiodomethane was allowed to react with 9.65 g (0.0199 mol) of red mercuric iodide (Mallinckrodt) in 15 ml of THF at 40° for 6 h. The reaction mixture was combined with 100 ml of benzene in a separatory funnel, and extracted four times with 100 ml portions of distilled water. The dry organic phase was concentrated to ca. 25 ml and placed in the freezer. This procedure gave 6.91 g of a white, crystalline precipitate, m.p. 77–80°. A further concentration of the mother liquor provided an additional 0.58 g, m.p. 78–81°. The total weight of 7.49 g represented a yield of 78% of bis(iodomethyl)mercury. Recrystallization from benzene afforded 6.48 g (68%) of shiny, white plates in two crops, m.p. 80–81.5° (lit.[27] m.p. 80–82°).

Bis(iodomethyl)mercury has been prepared routinely for use in other studies by this procedure and yields of up to 92% have been recorded.

Essentially the same procedure was used in the preparation of $Hg(CD_2I)_2$ using 0.075 mol of zinc-copper couple, 0.074 mol of CD_2I_2 (97.8% CD_2I_2, 2.2% $CHDI_2$ by mass spectrometry) and 0.019 mol of HgI_2*. The crude yield was 87%; the yield of recrystallized product (m.p. 78–79.5°) was 76%. A 1 mmol sample of this product was treated with 2 mmol of iodine in CCl_4. The diiodomethane isolated by distillation and GLC was shown by mass spectrometry to be 97.2% CD_2I_2, 2.8% $CHDI_2$.

Reaction of iodomethylzinc iodide with triphenyllead chloride. To a solution of ICH_2ZnI prepared from 1.64 g (25.0 mg-atom) of zinc-copper couple and 7.78 g (29.0 mmol) of diiodomethane in 20 ml of THF was added a solution of 4.74 g (10.0 mmol) of triphenyllead chloride in 20 ml of THF. The mixture was stirred and heated at 40° for 3 h. The usual work-up techniques provided a yellow, oily concentrate. Extraction and crystallization with ethanol gave 1.76 g (31%) of crude (iodomethyl)triphenyllead, m.p. 67–70°. An analytical sample, m.p. 72–73.5°, was obtained by successive recrystallizations from ethanol.

Reaction of iodomethylzinc iodide with germanium tetrachloride. A solution of the organozinc reagent prepared from 2.61 g (40.0 mg-atom) of zinc-copper couple and 11.54 g (43.0 mmol) of diiodomethane in 50 ml of THF was filtered into a standard apparatus in which, however, a mechanical stirrer was substituted for the magnetic stirbar. This solution was treated with 4.03 g (18.8 mmol) of germanium tetrachloride (Eagle–Pitcher Industries) in 10 ml of THF at 40° for 2 h. The reaction mixture subsequently was alkylated by the addition of 40 ml of 2.44 *N* methylmagnesium bromide in ether over 4 h at room temperature. The mixture was stirred at 40° for an additional

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* Experiment by Dr. G. L. Larson.

15 h, then was hydrolyzed and extracted in the manner of the general procedure, and trap-to-trap distilled at 25° (0.01 mm) to give 29.7 g of distillate. A portion of this distillate was saved for GLC yield determination, and the remainder was concentrated using a short-path distillation apparatus. Preparative GLC [Column (J), 110°] was used to collect pure samples of the two major products. The first of these was characterized as (iodomethyl)trimethylgermane, n_D^{25} 1.5107 (lit.[30] n_D^{20} 1.5112), by IR analysis, as well as by comparison of the NMR spectrum with that reported in the literature[31]. The second product was characterized as bis(trimethylgermyl)methane, n_D^{25} 1.4478 (lit.[32] n_D^{20} 1.4502), by comparison of the IR spectrum with that reported in the literature[32]. Additionally, the NMR spectrum agreed well with that reported[33].

A GLC yield determination [Column (A), 70°, as well as Column (J), 70°] indicated the presence of 5.79 mmol (31%) of the former product, and 2.36 mmol (25%, based on Me_3Ge- groups) of the latter. The molar ratio of the iodomethylgermane to the digermylmethane was 71/29, based on the above GLC analysis. Integration of the respective methylene resonances of an NMR spectrum of the trap-to-trap distillate similarly showed this ratio to be 71/29.

Reaction of iodomethylzinc iodide with trimethylchlorogermane. A solution of ICH_2ZnI prepared from 2.60 g (39.8 mg-atom) of zinc-copper couple and 12.18 g (45.4 mmol) of diiodomethane in 40 ml of THF was treated with 2.81 g (18.3 mmol) of trimethylchlorogermane in 10 ml of THF at 40° for 6 h. The standard work-up techniques provided 2.44 g of a concentrated trap-to-trap distillate.

GLC analysis (Column A, 80°) of this distillate indicated the presence of a major component, which subsequently was shown to consist of two products. These were characterized by comparison of GLC retention times to those of the authentic samples previously prepared as (iodomethyl)trimethylgermane and bis(trimethylgermyl) methane. In addition, at least 11 other minor products were present; the retention time of some of these obviated the determination of yields at GLC conditions which would separate the major components, *e.g.*, Column (J). Therefore, GLC analysis [Column (A), 80°] showed the presence of 5% of the combined products. NMR analysis of the distillate then indicated that the iodomethylgermane/digermylmethane ratio was 1/2, by integration of the appropriate methylene resonances. These data indicate that these products were present in yields of ca. 2% and 7% (based on Me_3Ge- groups), respectively.

General procedure for the preparation and utilization of a homogeneous solution of bromomethylzinc bromide

The reactions to be described were carried out using a solution of bromomethylzinc bromide prepared by a procedure that is closely related to the general procedure for iodomethylzinc iodide previously discussed. The following general description is focused on the significant differences between the two procedures. Zinc-copper couple was prepared by the method of LeGoff[26] and this method, as well as the appropriate apparatus, has been previously described. The dropping funnel was charged with an equimolar amount of a 5–10 *M* solution of dibromomethane in THF, and an equal volume of THF was added to the couple. A few drops of dibromomethane were placed in the flask, and this was warmed to ca. 40°. The appearance of a purple color, generally after ca. 15 min, indicated the successful initiation of the reaction. To the couple was added three volumes of THF, an amount such that the final concentration of the mixture was ca. 2 *M*, based on original dibromomethane. The contents of the dropping funnel were added at a moderate rate, *e.g.*, ca. 2 h, and heating was continued for 8–9 h, or until the metal had been consumed to the extent of 60–70%. Filtration and utilization of the resultant solution were as previously described. Similarly, at the conclusion of a reaction, work-up was effected by the addition of an equal volume of benzene to the reaction mixture in a separatory funnel, and the subsequent extraction of this mixture at least four times with double-volume portions of 5% hydrochloric acid. Further treatment of the resultant organic phase generally was accomplished using standard techniques.

The procedure described here is applicable to a reaction on a scale of ca. 0.1 mol (based on Zn/Cu). Larger reactions required proportionally longer times to consume the couple to the extent of 60–70%. Thus a 1.0 mol preparation required ca. 16 h. In the later stages of this research, an improved zinc-copper couple, developed by Friedrich[34], was employed. This couple was basically similar to that of LeGoff, but the washing steps with the appropriate volumes of the glacial acetic acid and ether were carried out five times and nine times, respectively. This couple exhibited greatly enhanced reactivity toward dibromomethane. Thus, a reaction of 0.1 mole of the improved couple with 0.1 mole of dibromomethane proceeded to the extent of ca. 60% in 4 h.

Reaction of bromomethylzinc bromide with trimethyltin chloride. A zinc-copper couple was prepared in a 200-ml, three necked flask from 13.00 g (0.20 mol) of 30-mesh granular zinc. The flask was equipped with a dropping funnel, magnetic stirrer, and reflux condenser topped with a gas-inlet tube, and the apparatus was flame-dried. The couple was covered with 25 ml of THF and a few drops of dibromomethane, and stirred at ca. 40° for 15 min, at which time a cloudy purple color developed in the flask. The dropping funnel was charged with 37.62 g (0.216 mol) of dibromomethane, and this solution was added dropwise over 2 h. The reaction mixture was maintained at 40° for 9 h. The cooled mixture then was filtered using a Schlenk-type apparatus into a dry, 300-ml flask, which subsequently was equipped as previously described.

The resulting purple, homogeneous solution of bromomethylzinc bromide was treated with 8.00 g (0.040 mol) or trimethyltin chloride in 25 ml of THF in the usual manner for 2 h. The reaction mixture thus obtained was combined with 50 ml of benzene in a separatory funnel, and extracted four times with 150 ml portions of distilled water. The organic phase was dried, concentrated, and trap-to-trap distilled at 40° (0.01 mm) to provide 22.00 g of distillate. An aliquot was retained for GLC yield determination, and fractionation of the remainder of the distillate using a 7" Vigreux column afforded 6.66 g (65%) of the expected product, (bromomethyl)trimethyltin, b.p. 46–48°/12 mm (lit.[12] b.p. 46–50°/11 mm), ca. 97% pure by GLC.

GLC analysis [Column (B), 120°] indicated the presence of 33.4 mmoles (84%) of this product in the original distillate. Preparative GLC [Column (E), 115°] provided a pure sample, n_D^{25} 1.5078 (lit.[12] n_D^{25} 1.5070).

Reaction of bromomethylzinc bromide with dimethyltin dichloride. A solution of bromomethylzinc bromide prepared from 26.0 g (0.40 mol) of zinc-copper couple and 74.4 g (0.43 mol) of dibromomethane in 260 ml of THF was treated with 8.8 g (0.04 mol) of dimethyltin dichloride in 25 ml of THF at 40° for 2 h. Work-up was carried out as described in the general procedure. The concentrated solution obtained was trap-to-trap distilled into two fractions: 19.75 g, 25°/0.2 mm; and 11.99 g, 40°/0.05

mm. Preparative GLC [Column (D), 120°] of the latter fraction provided a pure sample of the only component, which was identified as bis(bromomethyl)dimethyltin, n_D^{25} 1.5561, by comparison of its infrared and NMR spectra with those of an authentic sample (*cf.* Table 2). GLC analysis [Column (A), 14 min post inj. interval, 120–200° at 8°/min) of both distillates showed the presence of 0.20 g and 4.03 g of product, respectively. The total weight of 4.23 g represented at 31% yield.

Reaction of bromomethylzinc bromide with mercuric bromide. A solution of bromomethylzinc bromide in 50 ml of THF prepared from 0.1 mol each of zinc-copper couple and dibromomethane was allowed to react for 3 h with 3.60 g (0.01 mol) of mercuric bromide (Mallinckrodt) in 20 ml of THF. The use of the general extraction procedure provided a dry organic layer, which was concentrated at reduced pressure to a few ml of a yellow oil. This was dissolved in 15 ml of chloroform and filtered. The addition of 45 ml of hexane to the filtrate, followed by cooling to ca. –20°, induced the precipitation of fine, white needles. These were collected in two crops, m.p. 42.5–44°, and characterized as bis(bromomethyl)mercury (lit.[35] m.p. 42–43°). The total weight of 1.66 g represented an overall yield of 43%. No melting point depression was observed upon mixing of this material with authentic bis(bromomethyl)mercury.

Bis(bromomethyl)mercury was prepared routinely for use in other studies by this procedure and yields of up to 59% have been obtained.

Reaction of (iodomethyl)trimethyltin with silver chloride

A dry, 250-ml, three-necked Morton (creased) flask equipped with a reflux condenser, gas-inlet tube, and magnetic stirbar was charged with 5.97 g (19.6 mmol) of (iodomethyl)trimethyltin, 5.71 g (40.0 mmol) of AgCl (Mallinckrodt), and 40 ml of acetonitrile (Eastman, spectrograde). The apparatus was placed in a darkened hood, and surrounded by a piece of aluminum foil in a manner designed to serve as a light shield. The heterogeneous mixture was stirred vigorously for 9 days at 25°, at which time GLC (Column M, 175°) indicated a >90% conversion of starting material.

Filtration provided 6.80 g of silver salts (85% by weight gain). The filtrate was diluted with 40 ml of methylene chloride, and extracted four times with 100 ml portions of 5% HCl. The dried organic phase was fractionated using a 7″ Vigreux column to give 2.26 g (54%) of (chloromethyl)trimethyltin, b.p. 69–70° (57 mm), n_D^{25} 1.4863 (lit.[12] b.p. 44–48°/15 mm, n_D^{25} 1.4860), >99% pure by GLC.

GLC analysis [Column (B), 110°] showed the presence of 3.56 mmoles (19%) of the product in the distillation forecut, giving an overall yield of 73%.

This simple procedure was used in the preparation of the other chloro- and bromomethyltin compounds indicated in Table 2. Reaction times of 6 to 9 days at room temperature were used.

Reaction of iodomethylzinc iodide with a mixture of Et_3SiD and n-Bu_3SiH

Zinc-copper couple (41.4 mmol) in 40 ml of diethyl ether was treated first with a few drops of diiodomethane and then a mixture of 1.37 g (11.7 mmol) of Et_3SiD (n_D^{25} 1.4092; prepared by reduction of Et_3SiCl with $LiAlD_4$ (Alfa Inorganics); purity >99% by mass spectrometry), 2.11 g (10.5 mmol) of n-Bu_3SiH and 8.69 g (32.4 mmol) of diiodomethane in 20 ml of ether was added dropwise with stirring under nitrogen. The reaction mixture was stirred and heated at reflux for 24 h. The mixture then was filtered. The filtrate was washed with 0.1 *N* HCl and with water, then with 0.2 *N* aqueous alcoholic $AgNO_3$ and again with cold 0.1 *N* HCl. The dried ether layer was concentrated (Vigreux column) and the residue was trap-to-trap distilled at 25°/0.01 mm. GLC of the distillate gave deuteriomethyltriethylsilane (34% yield). NMR (CCl_4); δ–0.02 (unsym. t, *J* 2 Hz, $-SiCH_2D$) and 0.3–1.2 ppm (m, 15, Et_3Si). In the IR spectrum (liquid film), ν(C–D) was observed at 2165 cm^{-1}. Mass spectrum [80 eV; *m/e* (relative intensity)]: 131 (9) M^+, 115 (3), 104 (4), 103 (11), 102 (91) ($Et_2SiCH_2D^+$), 87 (7), 76 (4), 75 (8), 74 (100) [$Et(H)SiCH_2D^+$], 73 (8), 72 (4), 59 (5), 57 (3), 55 (3), 46 (29) ($H_2SiCH_2D^+$), 45 (9), 44 (9), 43 (6). No Et_3SiCH_3 [M^+ *m/e* 130; most intense fragment $Et(H)SiCH_3^+$ at *m/e* 73] was present.

The residue from the trap-to-trap distillation was distilled (short path) at 80–84°/2 mm to give 1.30 g (61%) of $n\text{-}Bu_3SiCH_3$, n_D^{25} 1.4357, with spectroscopic properties identical with those of an authentic sample[28]. The mass spectrum, in particular, showed no trace of deuterium containing fragments; M^+ was seen at *m/e* 214 and the most intense fragment peaks occurred at *m/e* 157, $(C_4H_9)_2SiCH_3^+$ and 101, $C_4H_9(H)SiCH_3^+$.

Reaction of bis(iodomethyl)mercury/diphenylmercury with a mixture of Et_3SiD and $n\text{-}Bu_3SiH$

A mixture of 2.90 g (6.0 mmol) of $Hg(CH_2I)_2$, 2.14 g (6.0 mmol) of diphenylmercury, 0.71 g (6.1 mmol) of triethyldeuteriosilane and 0.95 g (4.7 mmol) of tri-n-butylsilane in 15 ml of dry benzene was stirred and heated at reflux under nitrogen for 73 h. Filtration gave 3.75 g (93%) of phenylmercuric iodide, m.p. 270–272°, and the filtrate was trap-to-trap distilled (26°/0.01 mm). The two products were isolated from the filtrate by GLC and were identified as Et_3SiCH_2D and $n\text{-}Bu_3SiCH_3$ by means of their IR, NMR and mass spectra as in the experiment above. The yields of Et_3SiCH_2D and $n\text{-}Bu_3SiCH_3$ (based on the silanes) were 62% and 82%, respectively.

Very similar results were obtained when the reaction of $Hg(CH_2I)_2$ with Et_3SiD and $n\text{-}Bu_3SiH$ was carried out in the absence of diphenylmercury. Et_3SiCH_2D (56%) and $n\text{-}Bu_3SiCH_3$ (73%) were obtained, and the organomercury product was ICH_2HgI, m.p. 109–112° (dec.) (68%). In this reaction, however, some minor by-products were formed: iodomethane, diiodomethane and hexaethyldisiloxane.

Another experiment, in which 10 mmol each of $Hg(CH_2I)_2$ and diphenylmercury were allowed to react with 19.1 mmol of Et_3SiH in 15 ml of benzene at reflux for 72 h, gave Et_3SiCH_3 (72%) and phenylmercuric iodide (79%).

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