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HALOMETHYL–METAL COMPOUNDS
XL. TRIMETHYLSILYL-SUBSTITUTED BROMOMETHYLLITHIUM AND -MAGNESIUM REAGENTS. TRIMETHYLTINDIBROMOMETHYLMAGNESIUM CHLORIDE*

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SUMMARY

The low temperature reactions of n-butyllithium with trimethyl(tribromomethyl)silane, trimethyl(dibromomethyl)silane and bis(trimethylsilyl)dibromomethane served well in the preparation of trimethylsilyldibromomethyllithium, trimethylsilylbromomethyllithium and bis(trimethylsilyl)bromomethyllithium, respectively. The low temperature reaction of isopropylmagnesium chloride in THF with trimethyl(tribromomethyl)silane and trimethyl(tribromomethyl)tin gave the trimethylsilyldibromomethylmagnesium chloride and trimethyltindibromomethylmagnesium chloride reagents. Reactions of these lithium reagents with trimethylchlorosilane, trimethyltin chloride, mercuric halide, dimethyl sulfate and water are described. The action of isopropylmagnesium chloride in THF on trimethyl(dibromomethyl)silane, trimethyl(diiodomethyl)silane and bis(trimethylsilyl)dibromomethane led principally to reduction to the respective monohalo compounds. The new Grignard reagents, diiodomethylmagnesium chloride and bromochloromethylmagnesium chloride, and their reactions with trimethylchlorosilane are reported. Trimethyl(bromodichloromethyl)silane was prepared in good yield by bromination of trimethyl(dichloromethyl)silane, while bromination of trimethyl(dibromomethyl)silane with *N*-bromosuccinimide gave trimethyl(tribromomethyl)silane in high yield.

INTRODUCTION

In past papers of this series we reported the preparation, via Me_3SiCCl_2Li, of bis(trimethylsilyldichloromethyl)mercury[2], and the use of the latter as a source of the carbene Me_3SiCCl and the radical Me_3SiCCl_2[3]. Also prepared, via $(Me_3Si)_2CCl$-Li, was $[(Me_3Si)_2CCl]_2Hg$[2], a compound which was a potential source of bis(trimethylsilyl)carbene. Since Hg–Br elimination from halomethylmercury compounds is a much more favorable process than Hg–Cl elimination[4,5], it was of interest to prepare

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trimethylsilyl-substituted halomethylmercury compounds containing the Hg–C–Br moiety. Of specific interest were $(Me_3SiCBr_2)_2Hg$ (a potential source of Me_3SiCBr), $[(Me_3Si)_2CBr]_2Hg$ (a potential source of $(Me_3Si)_2C$) and $(Me_3SiCHBr)_2Hg$ (a potential precursor for Me_3SiCH). The synthesis of such organomercury compounds required the development of the appropriate, as yet unknown active metal reagents, Me_3SiCBr_2M, $(Me_3Si)_2CBrM$ and $Me_3SiCHBrM$, where M most reasonably is Li, MgX or ZnX. In the present report we describe useful routes to these reagents, as well as examples of their application in synthesis, including preparation of the desired trimethylsilyl-substituted mercury compounds.

RESULTS AND DISCUSSION

Preparation of dihalomethyl- and trihalomethyl-silicon starting materials

The polyhalomethyl Grignard reagents, especially $CHBr_2MgCl$, of Normant and Villieras[6] served admirably as a starting point. As these authors had shown, $CHBr_2MgCl$ can be used to prepare Me_3SiCBr_2H in high yield[6b,c]. Among the other reagents they developed were CBr_3MgCl, CCl_3MgCl, $CH_2BrMgCl$ and CH_2IMgCl, and using their general procedures, we have added $CHBrClMgCl$ and CHI_2MgCl to this list (eqns. 1 and 2).

$$Me_2CHMgCl + HCBr_2Cl \xrightarrow{THF,\ -95^\circ} CHBrClMgCl + Me_2CHBr \tag{1}$$

$$Me_2CHMgCl + HCI_3 \xrightarrow{THF,\ -85^\circ} CHI_2MgCl + Me_2CHI \tag{2}$$

We have used these reagents to prepare a number of dihalomethyl and trihalomethyl compounds of silicon and tin (Table 1). In general, the product yields were moderate to good, and no attempts were made to optimize the yields.

TABLE 1

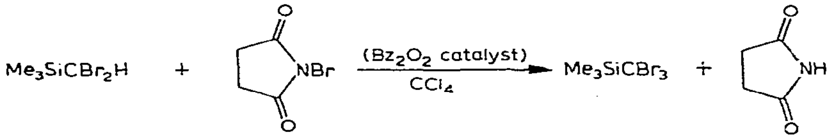
SYNTHESES WITH POLYHALOMETHYL GRIGNARD REAGENTS

Reagent	Reactant	Product	Yield (%)
$CHBr_2MgCl$	Me_3SiCl	Me_3SiCBr_2H	78
	$Me_2(CH_2{=}CH)SiCl$	$Me_2(CH_2{=}CH)SiCBr_2H$	62
	Me_2SiCl_2	$Me_2Si(CBr_2H)_2$	31
	Me_2HSiCl	$Me_2HSiCBr_2H$	55
	Me_3SnBr	Me_3SnCBr_2H	41
CBr_3MgCl	Me_3SiCl	Me_3SiCBr_3	16
$CHBrClMgCl$	Me_3SiCl	$Me_3SiCBrClH$	63
CHI_2MgCl	Me_3SiCl	Me_3SiCI_2H	77
	Me_2HSiCl	Me_2HSiCI_2H	74

The limited stability of CBr_3MgCl resulted in only poor yields of trimethyl(tribromomethyl)silane, a compound which was required in larger quantities. This led us to examine the bromination of trimethyl(dibromomethyl)silane as an alternate route. The direct bromination of methylsilanes has been reported previously[7–9], and of particular interest to the present investigation was the course of the bromination of tetramethylsilane as described by Brynolf (eqn. 3)[9]. It was demonstrated that the

$$Me_4Si \xrightarrow[UV]{Br_2\ (trace\ Cl_2)} \underset{\substack{(major\\product)}}{Me_3SiCH_2Br} + \underset{(trace)}{Me_3SiCBr_2H} + \underset{\substack{(major\\by\text{-}product)}}{Me_3SiCBr_3} \qquad (3)$$

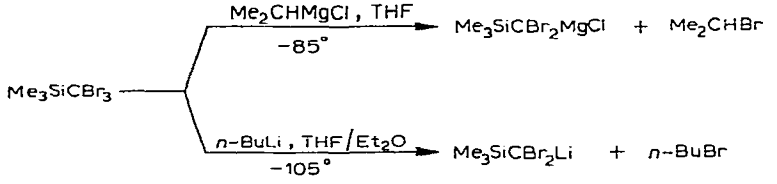
presence of bromine substituents on a methyl group attached to silicon served to increase the rate of bromination of C–H linkages present on that carbon atom. This effect appeared to be cumulative, and thus the bromination of Me_3SiCBr_2H occurred more rapidly than that of Me_3SiCH_2Br, leading to the product distribution shown in eqn. (3). We have used such bromination to prepare Me_3SiCBr_3 (from Me_3SiCBr_2H in 90% yield) and Me_3SiCCl_2Br from Me_3SiCCl_2H in 83% yield. The reaction of trimethyl(dibromomethyl)silane with *N*-bromosuccinimide was equally specific, giving trimethyl(tribromomethyl)silane in 96% yield (eqn. 4).



(4)

Reactions of trimethylsilyl-substituted polybromomethanes with n-butyllithium and isopropylmagnesium bromide

(1). *Trimethyl(tribromomethyl)silane.* The bromine–metal exchange reactions of trimethyl(tribromomethyl)silane with isopropylmagnesium chloride and n-butyllithium gave the desired Grignard and lithium reagents:



(5)
(6)

The Grignard reagent thus prepared was treated with trimethylchlorosilane to give $(Me_3Si)_2CBr_2$ in 56% yield. The low reaction temperature definitely was required. A reaction carried out by adding Me_3SiCBr_3 slowly to a molar equivalent of tert-butylmagnesium chloride in ether at gentle reflux resulted in some (20%) reduction to Me_3SiCH_2Br, but the major product (44% yield) was bis(trimethylsilyl)acetylene. Had the Grignard reagent been present, the hydrolytic work-up used should have given trimethyl(dibromomethyl)silane. The formation of the acetylene possibly occurred via the transient formation of the Grignard reagent (eqn. 7). When treated with mercuric chloride in THF, Me_3SiCBr_2MgCl reacted to give $(Me_3SiCBr_2)_2Hg$ in 25% yield.

$$Me_3SiCBr_2MgCl \xrightarrow{Me_3SiCBr_3} Me_3SiCBr_2CBr_2SiMe_3 \xrightarrow{RMgCl} Me_3SiC{\equiv}CSiMe_3 \qquad (7)$$

Trimethylsilyldibromomethyllithium was investigated in similar fashion. Its reaction with trimethylchlorosilane at −105° gave $(Me_3Si)_2CBr_2$ in 89% yield.

However, this high yield is deceptive and it is not a measure of the lithium reagent present at the time of trimethylchlorosilane addition since it appears that another route (eqn. 8) also leads to this product. Thus, when such a Me_3SiCBr_2Li solution

$$Me_3SiCBr_2Li + Me_3SiCBr_3 \rightarrow Me_3SiCBr_2SiMe_3 + LiCBr_3 \tag{8}$$

was treated with trimethyltin chloride, not only the expected $Me_3SiCBr_2SnMe_3$ was obtained (53% yield), but also $(Me_3Si)_2CBr_2$ in 23% yield. A similar complication had already been observed in the preparation of Me_3SiCCl_2Li, *i.e.*, the coupling of Me_3SiCCl_2Li with the Me_3SiCCl_2H starting material to give $(Me_3Si)_2CCl_2$[2].

The preparation of $(Me_3SiCBr_2)_2Hg$ by the lithium route was even less successful, a yield of only 10% being obtained.

(2). *Trimethyl(dibromomethyl)silane.* No stable Grignard reagent could be prepared by reaction of isopropylmagnesium chloride with trimethyl(dibromomethyl) silane in THF at −95°. Addition of trimethylchlorosilane to such a reaction mixture gave no $(Me_3Si)_2CHBr$ or $(Me_3Si)_2CBr_2$, and the only silicon-containing product was Me_3SiCH_2Br (65%). Apparently a reduction process similar to that which occurs on reaction of *gem*-dibromocyclopropanes with MeMgBr in THF[10] or of $PhCCl_2CO_2Et$ with isopropylmagnesium chloride in diethyl ether[11] had taken place.

With trimethyl(dibromomethyl)silane, one might, in principle, expect n-butyllithium to react in two different ways: via Li–Br exchange (as in the case of Me_3SiCBr_3) to give $Me_3SiCHBrLi$, or via Li–H exchange (as in the case of Me_3SiCCl_2H[2]) to give Me_3SiCBr_2Li. It has been established[12] that lithium–bromine exchange in general occurs more rapidly than does lithium–hydrogen exchange, and thus it was not surprising that the action of n-butyllithium on Me_3SiCBr_2H at −105° gave $Me_3SiCHBrLi$.

The hydrolysis of such $Me_3SiCHBrLi$ solutions showed that the n-BuLi/Me_3SiCBr_2H reaction also was accompanied by complicating side reactions. Slow addition of trimethyl(dibromomethyl)silane to a molar equivalent of n-butyllithium at −105°, followed 45 min later by hydrolysis with 1 *N* HCl, gave the expected hydrolysis product, trimethyl(bromomethyl)silane, in only 21% yield. Also present in the reaction mixture were $(Me_3Si)_2CH_2$ (22%) and $(Me_3Si)_2CHBr$ (9%), and this suggests a coupling reaction had occurred (eqn. 9), followed by lithiation of the coupling product (eqn. 10). To minimize the side reactions, the n-butyllithium and trimethyl(dibromomethyl)silane were added *simultaneously* to solvent at −120°, so that at no time would there be a large excess of either reactant present in the reaction mixture. This variation in procedure, followed by hydrolysis of the reaction mixture, raised the trimethyl(bromomethyl)silane yield to 73% and decreased the yield of bis(trimethylsilyl)methane to 7%.

$$Me_3SiCHBrLi + Me_3SiCBr_2H \rightarrow (Me_3Si)_2CHBr + CHBr_2Li \tag{9}$$

$$(Me_3Si)_2CHBr + RLi \rightarrow (Me_3Si)_2CHLi + RBr \tag{10}$$

The addition of trimethylchlorosilane to the $Me_3SiCHBrLi$ reagent (prepared via the simultaneous addition procedure) gave $(Me_3Si)_2CHBr$ in 52% yield, as well as Me_3SiCH_2Br (12%) and $(Me_3Si)_3CH$ (15%)*.

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* An authentic sample of tris(trimethylsilyl)methane was prepared by the Barbier reaction of Me_3SiCBr_2H, Me_3SiCl and magnesium in THF.

Tris(trimethylsilyl)methane very likely was formed via Li–Br exchange between $(Me_3Si)_2CHBr$ and lithium reagent present in solution, followed by the reaction of the $(Me_3Si)_2CHLi$ thus formed with trimethylchlorosilane.

The $Me_3SiCHBrLi$ reagent (via the simultaneous addition procedure) reacted with mercuric bromide to give $(Me_3SiCHBr)_2Hg$ in 44% yield. If the preparation of the lithium reagent was carried out by adding the n-butyllithium solution to Me_3SiCBr_2—conditions which favor formation of $(Me_3Si)_2CHBr$ and hence of $(Me_3Si)_2CHLi$—the mercurial $[(Me_3Si)_2CH]_2Hg$ was isolated in 16% yield.

(3). *Bis(trimethylsilyl)dibromomethane.* As in the case of trimethyl(dibromomethyl)silane, the reaction of $(Me_3Si)_2CBr_2$ with isopropylmagnesium chloride in THF at −95° resulted principally in reduction. After the reaction mixture had been quenched with trimethylchlorosilane, only bis(trimethylsilyl)bromomethane (60%) was obtained. However, n-butyllithium reacted with $(Me_3Si)_2CBr_2$ at −105° to give $(Me_3Si)_2CBrLi$ in good yield. Reaction of this reagent with dimethyl sulfate gave $(Me_3Si)_2CBrCH_3$ (88%). With trimethylchlorosilane, tris(trimethylsilyl)bromomethane was produced in 78% yield, and hydrolysis gave $(Me_3Si)_2CHBr$ in 77% yield. However, attempts to prepare a pure $(Me_3Si)_2CBr$–Hg compound were unsuccessful.

When bis(trimethylsilyl)bromomethyllithium was allowed to warm slowly to room temperature in the presence of an excess of cyclohexene, no $(Me_3Si)_2C$ transfer to the olefin occurred. Instead, the lithium reagent reacted very cleanly with the n-butyl bromide in the system to give 1,1-bis(trimethylsilyl)-1-bromopentane in 89% yield.

$$\begin{aligned}(Me_3Si)_2CBr_2 + n\text{-}C_4H_9Li &\xrightarrow{-105^\circ} (Me_3Si)_2CBrLi + n\text{-}C_4H_9Br\\ &\qquad \xrightarrow[\text{to r.t.}]{\text{warm}} (Me_3Si)_2CBrC_4H_9\text{-}n + LiBr \qquad (11)\end{aligned}$$

(4). *Trimethyl(diiodomethyl)silane.* The major reaction which occurred when isopropylmagnesium chloride and trimethyl(diiodomethyl)silane were allowed to react in THF at −90° was reduction of the silane to Me_3SiCH_2I. However, a small-to-moderate amount of $Me_3SiCHIMgCl$ also was formed, since the addition of trimethylchlorosilane to such a reaction mixture gave $(Me_3Si)_2CHI$ (5%) as well as Me_3SiCH_2I (65%). The former appeared to be somewhat unstable and therefore its yield is not a measure of how much of the Grignard reagent actually was formed.

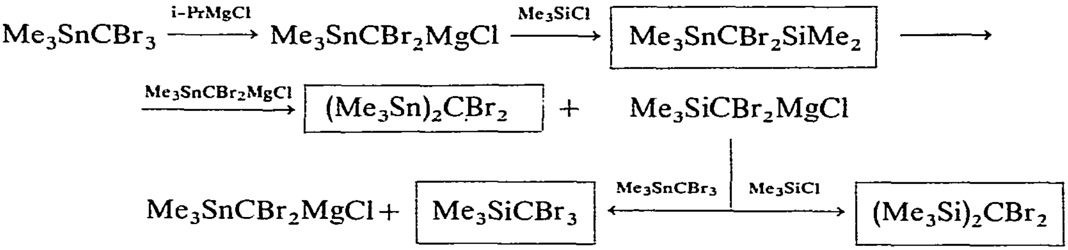
Trimethyltindibromomethylmagnesium chloride

In a previous study[13] we had prepared the trimethyltindihalomethyllithium reagents Me_3SnCCl_2Li, $Me_3SnCClBrLi$ and Me_3SnCBr_2Li. However, the route employed (eqn. 12) was based on hexamethylditin, a compound whose preparation is time-consuming. Furthermore, one of the trimethyltin groups was lost in the form of n-butyltrimethyltin. Therefore, a preparation of a Me_3SnCX_2M reagent based on the readily available Me_3SnCX_3 reagents[14] seemed worth investigating.

$$Me_3SnCX_2SnMe_3 + n\text{-}BuLi \xrightarrow{\text{low temp.}} Me_3SnCX_2Li + Me_3SnBu\text{-}n \qquad (12)$$

It was found that the low temperature reaction of trimethyl(tribromomethyl)-tin with isopropylmagnesium chloride in THF gave the hoped-for trimethyltindibromomethylmagnesium chloride, Me_3SnCBr_2MgCl. The deep yellow color of the THF solution of this reagent was discharged upon addition of trimethylchlorosilane, and subsequent gas chromatographic examination of the high-boiling products showed that $Me_3SiCBr_2SnMe_3$ had been formed in 41% yield. In addition, lesser amounts of $(Me_3Si)_2CBr_2$, $(Me_3Sn)_2CBr_2$ and Me_3SiCBr_3 also were present. The formation of these products can be rationalized as shown in Scheme 1. A very similar reaction course occurred when Me_3SnCCl_2Li reacted with trimethylchlorosilane[13a].

SCHEME 1



$$Me_3SnCBr_3 \xrightarrow{i\text{-PrMgCl}} Me_3SnCBr_2MgCl \xrightarrow{Me_3SiCl} \boxed{Me_3SnCBr_2SiMe_2} \longrightarrow$$

$$\xrightarrow{Me_3SnCBr_2MgCl} \boxed{(Me_3Sn)_2CBr_2} + Me_3SiCBr_2MgCl$$

$$Me_3SnCBr_2MgCl + \boxed{Me_3SiCBr_3} \xleftarrow{Me_3SnCBr_3} \quad \xrightarrow{Me_3SiCl} \boxed{(Me_3Si)_2CBr_2}$$

(Isolated products are enclosed in boxes.)

CONCLUSIONS

This research has shown that reagents of type Me_3SiCBr_2M, $Me_3SiCHBrM$, $(Me_3Si)_2CBrM$ and Me_3SnCBr_2M can be prepared and that at low temperatures they are sufficiently stable to make possible their utilization in synthesis. Complicating side reactions involving attack of the initially formed active metal reagents at the metal atom of as yet unconverted starting material or of the product can lower seriously the product yields. However, in most cases the products (which would be difficultly accessible by other routes) are produced in yields of 50% or better, and thus these new reagents should be useful in the preparation of various brominated organosilanes and tin compounds. The preparation of trimethylsilyl-substituted bromomethylmercury compounds via these reagents did not proceed satisfactorily. However, our experiments with the small quantities of those mercurials which became available indicated that they did not serve especially well as divalent carbon transfer agents[15], and for this reason no attempts were made to improve the synthesis of such mercurials using these reagents.

Finally, it should be noted that in a paper which appeared after the conclusion of the present work Brook *et al.*[15a] reported the reduction of R_3SiCBr_2R' compounds to the monohalo derivatives, $R_3SiCHBrR'$, by treatment with n-butyllithium at low temperature and subsequent protolysis of the lithium reagent formed, $R_3SiCBrLiR'$, with anhydrous hydrogen bromide.

EXPERIMENTAL

General comments

All reactions were carried out under an atmosphere of dry nitrogen or argon in flame-dried glassware. Infrared spectra were recorded using a Perkin–Elmer Model 337 or 237B grating infrared spectrophotometer, NMR spectra using either a Varian Associates A60 or T60 NMR spectrometer. Unless otherwise stated, chloroform was used as internal standard and related to an external chloroform–TMS sample. Chemical shifts are expressed in δ units, ppm downfield from TMS. Mass spectra were obtained using a Hitachi–Perkin–Elmer RMU6D spectrometer. Gas-liquid partition chromatography (GLC) was used extensively for separation and purification of products and for yield determinations. The instruments used included the MIT isothermal unit and F&M Model 700, 720 and 5754 gas chromatographs. The internal standard method was employed in yield analysis.

All solvents used were dried prior to use, THF, pentane and diethyl ether by distillation from lithium aluminum hydride, methylal (dimethoxymethane) by distillation from $LiAlH_4$ or potassium. Dimethyl ether, a gas, was dried by passing it through a drying tower containing activated alumina (Woelm neutral), anhydrous calcium sulfate and P_4O_{10}.

The preparation of lithium reagents at low temperature was carried out in a three-necked Morton (creased) flask equipped with a high-speed stirrer ("Stir-O-Vac", Labline catalog no. 1280), a pentane thermometer and an addition funnel with pressure-equalizing side-arm topped with a gas inlet tube (henceforth "standard apparatus").

n-Butyllithium was purchased in hexane solution from the Foote Mineral Company. Trimethylchlorosilane, dimethylchlorosilane and dimethyldichlorosilane were obtained from the Union Carbide Corp., trimethyltin chloride from M&T Chemicals, Inc.

The compounds prepared during the course of this study, their physical constants, analyses and NMR spectra are given in Table 2.

Preparation of polyhalomethyl compounds of silicon and tin by the Grignard procedure

The preparation of trimethyl(dibromomethyl)silane is described in order to illustrate the general procedure[6b,c] used. A dry, one-liter three-necked flask equipped with a mechanical stirrer, a nitrogen inlet tube, a pentane thermometer and a pressure-equalizing addition funnel was charged with 62.0 g (0.245 mole) of bromoform and 300 ml of dry THF. The mixture was chilled to ca −90° and 0.25 mole of isopropylmagnesium chloride in 200 ml of THF was added during ca. 30 min. (The addition rate is not a critical factor, except that the addition must be sufficiently slow so as to maintain the temperature at −80° or below.) The resulting mixture was stirred at −90° for 15 min and then 0.25 mole of trimethylchlorosilane in 100 ml of THF was added at such a rate that the temperature did not exceed −80°. After the mixture had been stirred for 1 h, it was allowed to warm to room temperature and then was hydrolyzed with saturated ammonium chloride solution until large lumps of salt cake had been produced. The organic layer was poured off, dried over anhydrous sodium sulfate and distilled at atmospheric pressure to remove most of the THF. A trap-to-trap distillation of the residue at 0.1 mm was followed by distillation of the volatiles using an 11″ Vigreux column. Trimethyl(dibromomethyl)silane was isolated in 78% yield (47.9 g), b.p. 49.5–51.5° (12 mm).

Essentially the same procedure was used in the preparation of the other compounds listed in Table 1. The yields given are yields of distilled product.

TABLE 2

COMPOUNDS PREPARED: THEIR PHYSICAL CONSTANTS, ANALYSES AND NMR SPECTRA

Compound	B.p. [°C(mm)]	M.p. (°C)	n_D^{25}	Analysis, found (calcd.)			NMR[a]
				Carbon	Hydrogen	Halogen	
$(CH_3)_3SiCBr_2H$	49.5–51.5(12)		1.4950[h]				0.22 (Me_3Si) s; 5.12 ($CHBr_2$) s
$(CH_3)_2(CH_2{=}CH)SiCBr_2H$	87–89(27)		1.5149	23.55(23.27)	3.94(3.91)	61.68(61.94)	0.36 (Me_3Si) s; 6.2–5.9 (Vi) m; 5.06 ($CHBr_2$) s
$(CH_3)_3SnCBr_2H$	97–100(19)		1.5512	14.19(14.27)	2.91(3.00)	46.85(47.47)	0.32 (Me_3Sn) s [J(Sn–H) 55 Hz]; 5.25 ($CHBr_2$) s
$(CH_3)_2HSiCBr_2H$	67–68(40) 54–57(18)		1.5030	15.79(15.53)	3.49(3.48)	68.86(68.89)	0.33 (Me_2Si) d [J 3.0 Hz]; 4.30 (SiH) double septet [J 1.5, 3.0 Hz]; 5.18 ($CHBr_2$) d [J 1.5 Hz]
$(CH_3)_2Si(CH_2Br)(CBr_2H)$	GLC		1.5424	15.09(14.78)	2.82(2.79)	74.07(73.78)	0.45 (Me_2Si) s; 2.63 (CH_2Br) s; 5.01 ($CHBr_2$) s
$(CH_3)_2Si(CBr_2H)_2$	76–78(0.1)		1.5755	12.29(11.90)	2.09(2.00)	78.61(79.15)	0.52 (Me_2Si) s; 5.30 ($CHBr_2$) s
$(CH_3)_3SiCBr_3$	60(0.1)[c]	203–205[d,e]		14.58(14.79)	2.80(2.79)	74.23(73.80)	0.42 (Me_3Si) s
$(CH_3)_3SiCBrClH$	66–68(40)		1.4690	23.95(23.83)	4.92(5.00)		0.24 (Me_3Si) s; 5.20 (CHClBr) s
$(CH_3)_3SiCI_2H$	49–49.5(0.7)		1.5939	14.04(14.13)	3.01(2.96)	74.15(74.64)	0.14 (Me_3Si) s, 4.40 (CHI_2) s
$(CH_3)_2HSiCI_2H$	36–37(0.6)		1.6158	11.10(11.05)	2.43(2.47)	78.29(77.86)	0.27 (Me_2Si) d [J 3.0 Hz]; 4.4–4.0 (SiH and CHI_2) m
$(CH_3)_3SiCCl_2Br$	40°(0.1)[c]	152–153[d,f]					
$[(CH_3)_3Si]_2CBr_2$	77–79(3.6)	68–69[d]		26.34(26.41)	5.69(5.70)	50.39(50.23)	0.30 (Me_3Si) s
$(CH_3)_3SiCBr_2Sn(CH_3)_3$[b]	GLC		1.5370	20.76(20.56)	4.44(4.37)	39.44(39.10)	0.24 (Me_3Si) s; 0.36 (Me_3Sn) s [$J(^{117}Sn\text{–}H)$ 52 Hz, $J(^{119}Sn\text{–}H)$ 54.5 Hz]
$[(CH_3)_3SiCBr_2]_2Hg$		152–154[d]		14.27(13.91)	2.66(2.63)	45.70(46.28)	0.30 (Me_3Si) s
$[(CH_3)_3Si]_2CHBr$	GLC		1.4659	35.41(35.13)	8.09(8.00)	33.16(33.39)	0.15 (Me_3Si) s; 2.18 (CHBr) s (in $CHCl_3$)
$[(CH_3)_3Si]_3CH$	58–61(2.1)		1.4630[i]				0.09 (Me_3Si); −0.78 (CH) s
$[(CH_3)_3SiCHBr]_2Hg$		110–112		18.31(18.03)	3.88(3.78)	30.52(29.99)	0.20 (Me_3Si) s; 2.90 (CHBr) s (in $CHCl_3$)
$[(CH_3)_3Si]_2CHC_4H_9$-n	GLC		1.4425	61.44(61.07)	13.12(13.04)		−0.37 ($[Me_3Si]_2C\underline{H}Bu$) t [$J$ 5.0 Hz]; 0.02 (Me_3Si) s; 0.158–0.75 (C_4H_9) m (in $CHCl_3$)
$(CH_3)_3SiCHBrC_4H_9$-n	GLC		1.4568	43.33(43.06)	8.70(8.58)	35.59(35.82)	0.10 (Me_3Si) s; 1.9–0.7 (C_4H_9) m; 3.13 (CHBr) t [J 7.0 Hz]
$\{[(CH_3)_3Si]_2CH\}_2Hg$		34–35[d,g]		32.46(32.37)	7.39(7.37)		0.32 (Me_3Si) s; 0.05 (CH) s (in benzene)
$[(CH_3)_3Si]_3CBr$	25(0.001)[c]	194–195[d,j]		38.47(38.57)	8.72(8.74)	25.52(25.65)	0.20 (Me_3Si) s (in $CHCl_3$)
$[(CH_3)_3Si]_2CBrC_4H_9$-n	GLC		1.4833	44.95(44.72)	9.16(9.21)	26.80(27.05)	0.17 (Me_3Si) s; 0.66–2.17 (C_4H_9) m (in $CHCl_3$)
$[(CH_3)_3Si]_2CBrCH_3$		31–32		38.00(37.93)	8.40(8.35)	31.16(31.54)	0.234 (Me_3Si) s; 1.77 (CH_3CBr) s (in $CHCl_3$)
$[(CH_3)_3Si]_2CHI$	GLC		1.4990	29.35(29.36)	6.63(6.69)	44.11(44.32)	0.18 (Me_3Si) s; 1.75 (CHI) s

[a] In δ units, ppm downfield from TMS; CCl_4 solvent unless otherwise specified. [b] First characterized by F. M. Armbrecht, Jr., Ph.D. Thesis, Massachusetts Institute of Technology, 1968. [c] Sublimes. [d] *In a sealed capillary.* [e] Lit.[9] m.p. 201–203°. [f] Lit.[2] m.p. 152–153° (sealed capillary). [g] Lit.[17] m.p. 35°. [h] Lit.[6] n_D^{22} 1.4976. [i] Lit.[16] n_D^{25} 1.4604. [j] Lit.[26] m.p. 190.

In the reaction of $CHBr_2MgCl$ with dimethylchlorosilane, Me_2HSiCl, in ca. 1/1 molar ratio two other minor products were obtained: $Me_2Si(CH_2Br)CBr_2H$ (5%) and $Me_2Si(CBr_2H)_2$ (2%). It is possible that the former resulted from CHBr insertion the Si–H bond, $CHBr_2MgCl$ acting as a carbenoid reagent in a manner similar to the halomethylzinc halide reagents[18].

Trimethyl(diiodomethyl)silane is not very stable thermally and light sensitive. On distillation (short path) a light yellow liquid was obtained.

Preparation of trimethyl(bromodichloromethyl)silane by bromination

Into a 250 ml one-necked flask equipped with a reflux condenser topped with a drying tube was charged 21.4 g (136 mmole) of trimethyl(dichloromethyl)silane, 25 ml of carbon tetrachloride and some boiling chips. To this solution was added 24.5 g (153 mmole) of bromine in 50 cc of carbon tetrachloride and the resulting mixture was heated at reflux for 11 h. The reaction mixture was washed with 1 *M* sodium thiosulfate to destroy unconverted bromine. The dried organic layer was evaporated at reduced pressure and the solid residue was extracted with hexane. The hexane solution was evaporated and the solid remaining sublimed at 40° (0.1 mm) to give 26.5 g (83%) of Me_3SiCCl_2Br, m.p. 148–150° (sealed capillary). GLC analysis (F&M 5754, 6 ft Carbowax 20 M column at 140°) indicated a purity of at least 99%.

A similar procedure was used in the bromination of Me_3SiCBr_2H to Me_3SiCBr_3.

Reaction of trimethyl(dibromomethyl)silane with N-bromosuccinimide

A 2-liter, one-necked flask equipped with a reflux condenser topped with a nitrogen inlet tube was charged with 123 g (0.5 mole) of trimethyl(dibromomethyl)-silane, 96.0 g (0.54 mole) of *N*-bromosuccinimide, 0.6 g of benzoyl peroxide and 750 ml of reagent grade carbon tetrachloride. The reaction mixture was heated under nitrogen on the steam bath for 3 h, then was filtered to remove precipitated succinimide and the filtrate was evaporated at reduced pressure. The solid residue was sublimed at 60° (0.1 mm) to give 156 g (96%) of Me_3SiCBr_3, m.p. 199–201° (sealed capillary). A resublimed sample had the m.p. shown in Table 2.

Reaction of trimethyl(tribromomethyl)silane with isopropylmagnesium chloride

(*a*). *At low temperature.* The procedure described above for the $CHBr_3$/i-PrMgCl reaction was followed in the reaction of 65.0 g (0.20 mole) of Me_3SiCBr_3 and 0.23 mole of i-PrMgCl in 580 ml of THF at $-80°$ to $-90°$. The Me_3SiCBr_2MgCl thus formed (clear green THF solution) was quenched with 0.23 mole of trimethylchlorosilane at $-80°$. The reaction mixture was allowed to warm slowly to room temperature and was hydrolyzed with saturated NH_4Cl solution. The THF was distilled from the organic layer at 0.1 mm and the residue was distilled to give 35.7 g (56%) of bis(trimethylsilyl)dibromomethane, b.p. 77–79° (3.6 mm). The product is a solid (m.p. 68–69°) and the distillation temperature must exceed the m.p. to avoid formation of solid throughout the distillation apparatus.

(*b*). *At* 35°. To 70 ml of 1.5 *M* ethereal tert-butylmagnesium chloride[19] was added, under nitrogen with stirring, 16.25 g (0.05 mole) of Me_3SiCBr_3 in 45 ml of diethyl ether at such a rate (ca. 1 h) that a gentle reflux was maintained. The reaction mixture was stirred for 3 h, hydrolyzed with saturated NH_4Cl solution, and the organic layer was trap-to-trap distilled at reduced pressure. GLC analysis (F&M 700, 20% DC-200, 90°) of the distillate showed the presence of trimethyl(bromomethyl)silane (20%) and bis(trimethylsilyl)acetylene (44%). Both compounds were identified on the basis of their GLC retention times, IR and NMR spectra. Authentic samples were available for comparison. For $Me_3SiC{\equiv}CSiMe_3$, n_D^{25} was 1.4255 (lit.[20] n_D^{25} 1.4259).

Preparation of trimethylsilyldibromomethyllithium

(*a*). *Quench with trimethylchlorosilane.* Into the standard apparatus was charged 4.82 g (14.8 mmole) of trimethyl(tribromomethyl)silane and 60 ml of 2/1 by volume THF/diethyl ether. The resulting solution was cooled to −105° and 9.6 ml of 1.67 *M* n-butyllithium in hexane (16 mmole) was added dropwise over 15 min. After the bright yellow reagent solution had been stirred at −100° to −110° for 3 h, 3.1 g (28.6 mmole) of trimethylchlorosilane in 5 ml of THF was added over 5 min. The resulting mixture was stirred for 2.5 h at ca. −105°, allowed to warm to room temperature and then was treated with 20 ml of dry 1,4-dioxane to precipitate lithium bromide as the insoluble dioxanate. Filtration was followed by trap-to-trap distillation of the filtrate at 5×10^{-4} mm into a receiver at −78°. GLC analysis of the filtrate (F&M 720, DC-200, 45–185° at 5°/min, 1-chloronaphthalene internal standard) showed the presence of $(Me_3Si)_2CBr_2$ in 89% yield, as well as two minor by-products, Me_3SiCBr_2H (3%) and $(Me_3Si)_2CHBr$ (4%), and Me_3SiCBr_3 (3%).

In preparative scale (0.124 mole) reactions, the product was isolated by crystallization from methanol and purified by sublimation at 25° (0.25 mm).

(*b*). *Quench with trimethyltin chloride.* The standard apparatus was used, but the pentane thermometer was replaced with a Y-adapter holding the thermometer and another pressure-equalizing addition funnel. A 3/2/1.5 by volume mixture of THF, pentane and diethyl ether was used as solvent.

Forty-five ml of mixed solvent was cooled to −110° and 14.8 mmole of n-butyllithium in 9 ml of hexane and 13.8 mmole of Me_3SiCBr_3 in 15 ml of solvent mixture were added simultaneously from the two addition funnels with stirring to the solvent in the reaction flask. The bright yellow reaction mixture, after 4.5 h at ca. −110°, was treated with 3.35 g (16.5 mmole) of trimethyltin chloride in 5 ml of solvent mixture over 5 min. After 2.5 h at −110° the reaction mixture was allowed to warm to room temperature and worked up as described in (*a*) above. GLC analysis of the final distillate (10% DC-200, F&M 5754, 60–190° at 6°/min, n-decane internal standard) showed the presence of the expected product, $Me_3SiCBr_2SnMe_3$ (53%), as well as of ten others, including: n-butyltrimethyltin (4%), Me_3SiCBr_3 (2%), $(Me_3Si)_2CHBr$ (11%), $(Me_3Si)_2CBr_2$ (23%) and n-butyl bromide in large amount. The products were identified by comparison of their GLC retention times and IR spectra with those of authentic samples.

Preparation of bis(trimethylsilyldibromomethyl)mercury

Trimethylsilyldibromomethylmagnesium chloride was prepared on a 0.163 mole scale as described above. To the reagent solution at ca. −110° was added 16.3 g (60 mmole) of mercuric chloride in 150 ml of THF over 15 min. The resulting dark grey-green reaction mixture was stirred at low temperature for 7 h and then was allowed to warm to room temperature. Filtration followed by concentration of the filtrate left a brown oil. The latter was extracted with hot hexane and benzene. Evaporation of the extracts and recrystallization of the residue from hexane gave 8.48 g of the mercurial, m.p. 152–155°. Another 2.01 g of mercurial was recovered from the mother liquors, giving a total product yield of 25%. This procedure should be capable of improvement.

Reaction of trimethyl(dibromomethyl)silane with isopropylmagnesium chloride

To ca. 0.1 mole of isopropylmagnesium chloride in 250 ml of THF at −90° to −95° under nitrogen was added slowly with stirring 25.72 g (0.109 mole) of Me_3SiCBr_2H in 20 ml of THF. After the mixture had been stirred at ca. −90° for 90 min, ca. 0.11 mole of trimethylchlorosilane was added. The reaction mixture was maintained at −90° for 3 h, then was allowed to warm to room temperature and hydrolyzed with saturated ammonium chloride solution. The dried organic layer was distilled at atmospheric pressure to remove solvent and then was trap-to-trap distilled at 50° (0.1 mm). GLC examination of the distillate (F&M 720, 6 ft Apiezon L column at 100°) showed the presence of Me_3SiCH_2Br (65% yield) as the major product n_D^{25} 1.4428 (lit.[21] n_D^{25} 1.4424). Its GLC retention time and infrared spectrum were identical to those of an authentic sample.

Preparation of trimethylsilylbromomethyllithium

(*a*). *Quench with trimethylchlorosilane.* To 50 ml of 3/1/1/1 THF/diethyl ether/pentane/dimethoxymethane at −105° in the standard simultaneous addition apparatus was added simultaneously 14.85 mmole of n-butyllithium in hexane and 3.38 g (13.75 mmole) of Me_3SiCBr_2H in 10 ml of the same solvent mixture during 15 min. The reaction mixture was stirred at ca. −110° for 4.5 h and then 17.3 mmole of trimethylchlorosilane in 10 ml of pentane was added to the pale yellow reagent solution. After the mixture had been stirred at ca. −110° for 2.5 h it was allowed to warm to room temperature and 15 ml of dry dioxane was added to remove lithium halide. Filtration was followed by trap-to-trap distillation of the filtrate at 10^{-4} mm. GLC analysis of the distillate (F&M 5754, 10% DC-200, 60–190° at 6°/min, 1-chloronaphthalene internal standard) showed the presence of n-butyl bromide (94%), Me_3SiCH_2Br (12%), $(Me_3Si)_2CHBr$ (52%) and $(Me_3Si)_3CH$ (15%). In other similar experiments another minor product (1–6%), $(Me_3Si)_2CH_2$, n_D^{25} 1.4152 (lit.[22] n_D^{25} 1.4155), was identified. The products were identified by comparison of their GLC retention times and IR (and in some cases NMR) spectra with those of authentic samples.

(*b*). *Hydrolysis.* The same procedure was used in the reaction of 12 mmole of n-butyllithium with 10 mmole of Me_3SiCBr_2H. To the reagent solution was added 14 ml of 1 *N* HCl in 10 ml of solvent mixture. After 2 h at ca. −110°, the reaction mixture was allowed to warm to room temperature. The dried organic layer was trap-to-trap distilled at 2×10^{-4} mm. GLC analysis of the distillate [same conditions as in (*a*)] showed the presence of n-butyl bromide (quantitative), trimethyl(bromomethyl)silane (73%), bis(trimethylsilyl)methane (7%) and other minor products.

(*c*). *Reaction with mercuric bromide.* The reagent prepared as described above from 0.178 mole of n-butyllithium and 0.179 mole of Me_3SiCBr_2H in 3/1 THF/dimethyl ether in the standard simultaneous addition apparatus at −110° was treated with 29 g (80.3 mmole) of solid mercuric bromide. The reaction mixture was stirred at $-110°$ for 5 h, warmed to room temperature and treated with 100 ml of dry dioxane. Filtration was followed by trap-to-trap distillation at 70° (5×10^{-4} mm). The residue was extracted with hot hexane. Concentration of the extracts at reduced pressure left a residue of white solid and liquid. Column chromatography using activated silica gel desiccant with hexane as eluent allowed isolation of white solid. Recrystallization of the latter from hexane gave $(Me_3SiCHBr)_2Hg$, m.p. 110–112°, in 44% yield.

Another experiment was carried out differently: 0.253 mole of n-butyllithium was added to 0.263 mole of trimethyl(dibromomethyl)silane in 3/1 THF/Me_2O at $-90°$. After the reaction mixture had been stirred at this temperature for 3.5 h, 120 mmole of mercuric bromide was added. Similar work-up after a 6 h reaction period gave 10.77 g (16%) of $[(Me_3Si)_2CH]_2Hg$, m.p. 34–35° (recrystallization from hexane). Bromination of 2.0 g of the latter in CCl_4/benzene with an excess of bromine gave 3.41 mmole of mercuric bromide, m.p. 234–236° dec., and as volatile products 6.25 mmole of $(Me_3Si)_2CHBr$ and 0.46 mmole of $(Me_3Si)_2CBr_2$ (by GLC).

Preparation of authentic tris(trimethylsilyl)methane

A one-liter, three-necked flask equipped with reflux condenser, mechanical stirrer, pressure-equalizing addition funnel and nitrogen inlet tube was charged with 22 g (0.9 g-atom) of magnesium turnings, 110 ml of trimethylchlorosilane and 200 ml of THF. To this mixture was added over an 8 h period a solution of 0.40 mole of Me_3SiCBr_2H in 400 ml of THF. The reaction mixture was stirred for 24 h, hydrolyzed with NH_4Cl solution and the organic layer was decanted. The salts were dissolved in dilute HCl and extracted with 500 ml of ether. Solvents were removed from the combined organic layers at atmospheric pressure and the residue was distilled at reduced pressure to give 45.5 g (49%) of $(Me_3Si)_3CH$, b.p. 58–61° (2.1 mm), n_D^{25} 1.4630; NMR (in CCl_4): δ 0.09 (Me_3Si) s and -0.78 ppm (Si_3CH) s.

A forecut was redistilled at atmospheric pressure to give 4.82 g (8%) of $(Me_3Si)_2CH_2$, b.p. 131.5–133°, n_D^{25} 1.4155.

Generation of trimethylsilylbromomethyllithium at room temperature in the presence of cyclohexene

Into a dry one liter, three-necked flask was distilled (from lithium aluminum hydride) 300 ml of cyclohexene under nitrogen. The flask was fitted with a mechanical stirrer, a reflux condenser and a constant rate addition funnel, and 74.0 g (0.30 mole) of Me_3SiCBr_2H was added. To this solution was added with stirring over a 20 h period at room temperature 200 ml of 1.6 *M* n-butyllithium in hexane. The reaction mixture was stirred for 2 h, then was hydrolyzed with 0.1 *N* HCl. The cyclohexene was removed in large part from the dried organic layer by distillation at atmospheric pressure. The residue was trap-to-trap distilled at reduced pressure to give 51.9 g of clear liquid. GLC analysis showed the presence of several components: *trans*-$Me_3SiCH{=}CHSiMe_3$ (14%), *cis*-$Me_3SiCH{=}CHSiMe_3$ (12%) and $Me_3SiCHBr$-C_4H_9-n (62%) (F&M 5754, DC-200, 180°, iodobenzene internal standard). Neither 7-trimethylsilylnorcarane isomer was present. Two explanations are possible for the formation of the major product: either it was formed by a direct coupling reaction between n-butyllithium and Me_3SiCBr_2H or the lithium–bromine exchange observed at low temperatures occurred first and was followed by coupling of the $Me_3SiCBrLi$

formed with n-butyl bromide.

A 50 mmole sample of $Me_3SiCHBrC_4H_9$-n was added to excess trimethylchlorosilane and magnesium in THF using the procedure outlined in the experiment above. A similar work-up gave two products: (*a*) the silylation product, $(Me_3Si)_2CHC_4H_9$-n, in 46% yield, and (*b*) the reduction product, n-amyltrimethylsilane, n_D^{25} 1.4065. (Speier *et al.*[25] report n_D^{25} 1.4069.)

Preparation of bis(trimethylsilyl)bromomethyllithium

(*a*). *Reaction with dimethyl sulfate.* To 50 ml of 3/1/1/1 THF/diethyl ether/pentane/dimethoxymethane at −105° in the standard simultaneous addition apparatus was added simultaneously 13.6 mmole of n-butyllithium in hexane and 11.35 mmole of bis(trimethylsilyl)dibromomethane in 10 ml of solvent mixture during 5 min. The bright yellow reagent solution was stirred at −110° for 4 h and then 14.2 mmole of dimethyl sulfate in 5 ml of ether was added. After 2.5 h at −110° the reaction mixture was allowed to warm to room temperature, treated with 25 ml of dioxane and filtered after 8 h. The filtrate was trap-to-trap distilled at 10^{-4} mm. GLC analysis of the distillate (F&M 5754, DC-200, 60–190° at 6°/min, 1-chloronaphthalene internal standard) showed the following to be present: n-butyl bromide, $(Me_3Si)_2CHBr$ and $(Me_3Si)_2CBrCH_3$ (88%).

(*b*). *Reaction with trimethylchlorosilane.* The lithium reagent prepared in the manner described in (*a*) from 10.3 mmole of bis(trimethylsilyl)dibromomethane was treated with 14.1 mmole of trimethylchlorosilane. A 3-h reaction period at −110° was followed by the usual work-up. GLC analysis of the final distillate indicated the presence of $(Me_3Si)_3CBr$ (78%), m.p. 194–195°, $(Me_3Si)_2CHBr$ (5%) and four other minor products. Tris(trimethylsilyl)bromomethane could be purified by sublimation at room temperature and 0.001 mm.

(*c*). *Hydrolysis.* The lithium reagent prepared from 8.96 mmole of $(Me_3Si)_2CBr_2$ was treated with 1 *N* HCl in THF at −110°. The dried organic layer was analyzed by GLC (F&M 5754, DC-200); the following were present: n-butyl bromide, $(Me_3Si)_2CHBr$ (77%) and $(Me_3Si)_2CBrC_4H_9$-n (6%).

Attempted decomposition of bis(trimethylsilyl)bromomethyllithium in the presence of cyclohexene

The reagent was prepared by the simultaneous addition procedure in 2/1/1 THF/diethyl ether/pentane at −105° from 11.15 mmole of $(Me_3Si)_2CBr_2$. To the resulting bright yellow solution was added 57 mmole of dry cyclohexene diluted with 15 ml of diethyl ether and the mixture was allowed to warm slowly over a 30-min period to −75°. It was kept at ca. −65° and then at ca. −55° for 15 min periods. Since no discharge of reagent color took place, the reaction mixture was allowed to warm to room temperature. Treatment with 20 ml of dioxane followed, then filtration and trap-to-trap distillation of the filtrate. GLC analysis of the distillate (F&M 5754, DC-200, 60–190° at 6°/min, n-decane internal standard) showed the presence of only a trace of n-butyl bromide, $(Me_3Si)_2CHBr$ (2%) and 1,1-bis(trimethylsilyl)-1-bromopentane (89%). GLC peak enhancement studies showed 7,7-bis(trimethylsilyl)norcarane to be absent.

Reaction of trimethyl(diiodomethyl)silane with isopropylmagnesium chloride

To a solution of ca. 58 mmole of i-PrMgCl in 150 ml of THF at −90° under nitrogen was added slowly with stirring 17.00 g (50 mmole) of trimethyl(diiodomethyl)-silane in 20 ml of THF over a 5-min period. The deep yellow-orange solution was kept at −90° for 10 min and then treated with 55 mmole of trimethylchlorosilane. The reaction mixture was stirred at −90° for 15 min and then kept at −65° to −70° until after 2 h the color changed to light green. The reaction mixture was allowed to warm to room temperature, hydrolyzed with saturated ammonium chloride, and the dried organic layer was analyzed by GLC (F&M 5754, 4 ft 10% UC-W98, 130°, internal standard, cyclohexyl chloride). The products were trimethyl(iodomethyl)silane (65%) and $(Me_3Si)_2CHI$ (5%). The former was identified by its refractive index, n_D^{25} 1.4874 (lit.[23] n_D^{25} 1.4917) and its NMR spectrum (in CCl_4): δ 0.15 (Me_3Si) s and 1.96 ppm (CH_2I) s.

Preparation of trimethyltindibromomethylmagnesium chloride

To a solution of 38 mmole of trimethyl(tribromomethyl)tion[14] in 150 ml of dry THF at −90° was added slowly ca. 45 mmole of i-PrMgCl in 25 ml of THF, with stirring under nitrogen. The resulting yellow reagent solution was stirred at −90° for 15 min; subsequently 47 mmole of trimethylchlorosilane was added. After it had been stirred at ca. −90° for 30 min, the reaction mixture was allowed to warm to room temperature and hydrolyzed with saturated ammonium chloride solution. The organic layer was distilled at atmospheric pressure to remove solvent and the residue was trap-to-trap distilled at 0.03 mm (pot temperature to 83°). GLC analysis of the distillate [F&M 5754, 10% UC-W98, 190°, tetrakis(trimethylsilyl)methane internal standard] showed the presence of the following: $(Me_3Si)_2CBr_2$ (12%), $Me_3SiCBr_2SnMe_3$ (41%), $(Me_3Sn)_2CBr_2$ (18%), as well as Me_3SiCBr_3 (6%). All products were identified by comparison of their GLC retention times, IR and/or NMR spectra with those of authentic samples. The compounds $Me_3SnCBr_2SnMe_3$[24] and $Me_3SiCBr_2SnMe_3$[13b] were available from previous investigations in these Laboratories.

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