

HALOMETHYL-METAL COMPOUNDS
XXXVII*. THE TRIMETHYLSILYL-SUBSTITUTED
CHLOROMETHYLLITHIUM REAGENTS: $\text{Me}_3\text{SiCCl}_2\text{Li}$ AND
 $(\text{Me}_3\text{Si})_2\text{CClLi}^{**}$

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SUMMARY

The low temperature reactions of *n*-butyllithium with trimethyl(dichloromethyl)silane and bis(trimethylsilyl)dichloromethane have served in the preparation of trimethylsilyldichloromethylithium and bis(trimethylsilyl)chloromethylithium, respectively, in high yield. Reactions of these reagents with trimethyltin chloride, trimethylchlorosilane, mercuric halides and methyl iodide are described.

INTRODUCTION

We have devoted considerable effort to studies of the generation of halocarbenes via α -elimination from halomethyl-metal compounds, especially those of mercury^{***}. More recently, we have extended the scope of our investigations to the preparation of functional carbenes (*e.g.*, ClCCO_2Me) by such organometallic routes³. Of special interest was the possibility of the generation of metal- and metalloid-substituted carbenes of type XCMR_n and $\text{C}(\text{MR}_n)_2$. We had prepared several such carbenes (or carbenoids) via appropriate diazoalkanes, *e.g.*, Me_3SiCH^4 and $(\text{MeO})_2\text{-P}(\text{O})\text{CR}^5$, and we felt that our organometallic route also should be applicable. In view of our excellent success in the use of organomercury compounds in the generation of halocarbenes, it seemed appropriate to prepare mercurial reagents of type $\text{PhHg-CX}_2\text{MR}_n$ and $\text{PhHgCX}(\text{MR}_n)_2$, or the symmetrical compounds, $\text{Hg}(\text{CX}_2\text{MR}_n)_2$ and $\text{Hg}[\text{CX}(\text{MR}_n)_2]_2$. The preparation of such mercury compounds required the appropriate active metal reagents, $\text{R}_n\text{MCX}_2\text{M}'$ and $(\text{R}_n\text{M})_2\text{CXM}'$ (where $\text{M}' = \text{Li, Na, MgX, ZnX, etc.}$), and at the time we began this study such reagents were not known. Thus the problem of the synthesis of such reagents had to be dealt with first, before the possibility of the proposed mercurial-derived carbene route could be explored.

* For Part XXXVI see ref. 1.

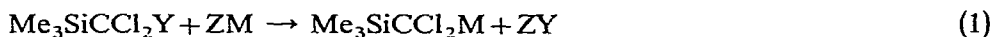
** Preliminary communication: ref. 2.

*** Cf. the previous papers of this Series.

RESULTS AND DISCUSSION

A. Trimethylsilyldichloromethylolithium

It was convenient to begin our studies with the system $R_nMCX_2Hg^- = Me_3SiCCl_2Hg^-$ since (polychloromethyl)silicon compounds are easily prepared⁶ and commercially available. The reaction desired was that shown in eqn. 1. If $Y = H$ and



$Y = H$ or halogen; $Z = R$ or RO ; $M = Li, Na, K$

$ZM = t\text{-BuOK}$, and if the reaction is carried out in the presence of phenylmercuric halide, then this would represent an extension of the one-step procedure used to prepare phenyl(trihalomethyl)mercury reagents in good yield^{7,8}. However, our attempts to carry out such a reaction were not successful: the addition of potassium tert-butoxide to a mixture of trimethyl(dichloromethyl)silane and phenylmercuric chloride in THF at -70° gave phenyl(dichloromethyl)mercury in 18% yield, but none of the desired $PhHgCCl_2SiMe_3$. Attack at silicon thus appeared to be the major if not the sole process occurring.

The previous literature^{6,9} suggests that the displacement of the dichloromethyl group from silicon by basic reagents is easily accomplished, and our lack of success in applying the standard (trihalomethyl)mercurial preparation procedure to $PhHgCCl_2SiMe_3$ was in line with this known chemistry. However, alkylolithium reagents such as *n*-butyllithium are both powerful bases and powerful nucleophiles and it was not clear to us which process should be more important when *n*-butyllithium attacked trimethyl(dichloromethyl)silane: proton abstraction at the CCl_2H group to give Me_3SiCCl_2Li or nucleophilic displacement of the dichloromethyl anion from silicon to give *n*-butyltrimethylsilane and dichloromethylolithium. The first possibility could not be discounted out of hand and available literature suggested that temperature factors could work in our favor. The work of Miller and Whalen, Hoeg and his co-workers and Köbrich *et al.* showed that polychloromethylolithium reagents such as CCl_3Li and CCl_2HLi must be prepared and handled at low temperatures (-60° to -120°)¹⁰. It therefore was to be assumed that trimethylsilyldichloromethylolithium also should be stable only at lower temperatures. However, work by Bey and Weyenberg¹¹ has shown that at low temperatures nucleophilic attack by alkylolithiums at silicon in trimethylchlorosilane is quite a slow process, slower, for instance, than lithium-bromine exchange between *n*-butyllithium and bromobenzene. Thus an examination of the reaction of *n*-butyllithium with trimethyl(dichloromethyl)silane was very worthwhile: attack at hydrogen might well be more rapid than attack at silicon. Accordingly, we devoted our attention to the possibility of preparing Me_3SiCCl_2Li , which in a second step could be treated with phenylmercuric or mercuric halide to give the desired mercury compound.

When a solution of *n*-butyllithium in hexane was added to a solution containing an equimolar amount of trimethyl(dichloromethyl)silane in a 3/1/1/1 THF/ Et_2O /pentane/ $(MeO)_2CH_2$ solvent mixture* at -130° , the reaction which occurred was lithium-hydrogen exchange (eqn. 2). The lithium reagent formed was treated with

* A mixture suitable for work with organolithium reagents at very low temperatures¹². At later stages of our research the more practical THF/dimethyl ether mixtures¹ were used instead.



trimethyltin chloride (which reacts rapidly with organolithiums at low temperatures); the products formed in this reaction sequence were $\text{Me}_3\text{SiCCl}_2\text{SnMe}_3$ (37%), $(\text{Me}_3\text{Si})_2\text{CCl}_2$ (8%), $\text{Me}_3\text{SnCCl}_2\text{H}$, $\text{Me}_3\text{SnC}_4\text{H}_9$, and some starting silane was recovered. The presence of the by-products suggested that the reaction shown in eqn. (2) had not gone to completion and furthermore, that a side reaction was consuming some of the trimethyl(dichloromethyl)silane (eqn. 3). The trimethyl(di-

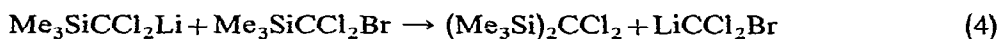


chloromethyl)tin then would result from reaction of trimethyltin chloride with dichloromethyl lithium. To minimize reaction (3), trimethylsilyldichloromethyl lithium was prepared by an inverse addition of trimethyl(dichloromethyl)silane to the *n*-butyllithium. The reaction temperature was raised to -105° and the reaction time also was increased to ensure complete reaction. This variation of procedure (in which THF/ Me_2O solvent was used), followed by treatment of the reaction mixture with trimethyltin chloride, gave $\text{Me}_3\text{SiCCl}_2\text{SnMe}_3$ in 82% yield. Only trace amounts of $(\text{Me}_3\text{Si})_2\text{CCl}_2$ and $\text{Me}_3\text{SnCCl}_2\text{H}$ were present.

The occurrence of the reaction shown in eqn. (3) was confirmed by experiment. Treatment of the reagent obtained by reaction of trimethyl(dichloromethyl)silane with *n*-butyllithium (slight excess) at -110° with an additional equimolar quantity of trimethyl(dichloromethyl)silane was followed by addition of trimethyltin chloride. The products obtained and their percentage yields based on initially charged trimethyl(dichloromethyl)silane were: $\text{Me}_3\text{SnCCl}_2\text{H}$, 34%; $(\text{Me}_3\text{Si})_2\text{CCl}_2$, 35%; $\text{Me}_3\text{SiCCl}_2\text{SnMe}_3$, 47%. Although less than half of the additional quantity of trimethyl(dichloromethyl)silane had reacted in the sense of eqn. (3), the formation of approximately equal amounts of $(\text{Me}_3\text{Si})_2\text{CCl}_2$ and $\text{Me}_3\text{SnCCl}_2\text{H}$ confirms our postulated side reaction.

Trimethylsilyldichloromethyl lithium is stable only at low temperatures. A solution prepared at -105° in the THF/ Et_2O /pentane/ $(\text{MeO})_2\text{CH}_2$ solvent mixture was allowed to warm up slowly: at -70° the solution turned light gray; at -60° it was light brown; at -35° it was dark brown and at -25° it was jet black and obviously completely decomposed. We have found it best to prepare and utilize this lithium reagent at ca. -100° .

Trimethylsilyldichloromethyl lithium shows reactivity typical of normal organolithium reagents. Its reaction with trimethylchlorosilane gave bis(trimethylsilyl)dichloromethane in 75% yield. Coupling with methyl iodide gave $\text{Me}_3\text{SiCCl}_2\text{-CH}_3$ in 77% yield. Conversion of $\text{Me}_3\text{SiCCl}_2\text{Li}$ to trimethyl(bromodichloromethyl)silane also was investigated. When bromine in cold ether was added to $\text{Me}_3\text{SiCCl}_2\text{Li}$ at -115° , the desired product was obtained in only 7% yield, together with bis(trimethylsilyl)dichloromethane in 45% yield. The complicating factor which resulted in the low product yield very likely was the good opportunity that the as yet unconverted lithium reagent had to react with the product (eqn. 4), a very reasonable possibility in view of our confirmation of reaction (3). This difficulty could be minim-



ized by adding the lithium reagent to a solution of an excess of bromine. When this

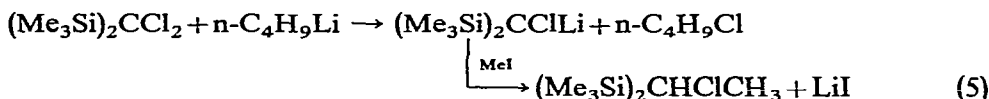
was done, under conditions which avoided as much as possible the decomposition of the lithium reagent during transfer, the trimethyl(bromodichloromethyl)silane yield was increased to 45% and the $(\text{Me}_3\text{Si})_2\text{CCl}_2$ yield was reduced to 5%.

The new trimethylsilyldichloromethyl lithium reagent was applied successfully to the preparation of the desired trimethylsilyldichloromethyl-mercury compound. Best results were obtained using mercuric bromide: reaction of the lithium reagent with mercuric bromide gave bis[trimethylsilyldichloromethyl]mercury in moderate yields. A 34% yield of this compound was obtained when two molar equivalents of the lithium reagent were treated with ca. one molar equivalent of mercuric bromide. This mercurial was produced in 44% yield (based on $\text{Me}_3\text{SiCCl}_2\text{Li}$), together with $\text{Me}_3\text{SiCCl}_2\text{HgBr}$ in 5% yield, when the lithium reagent and mercuric bromide were allowed to react in 1/1 molar ratio. Presumably, the $\text{Me}_3\text{SiCCl}_2\text{HgBr}$ formed first is more soluble in the solvent system at the low temperature used than is mercuric bromide and is alkylated at the expense of the latter. Reactions with mercuric chloride were less satisfactory: addition of mercuric chloride to an excess of $\text{Me}_3\text{SiCCl}_2\text{Li}$ gave $\text{Me}_3\text{SiCCl}_2\text{HgCl}$ (17%) and $(\text{Me}_3\text{SiCCl}_2)_2\text{Hg}$ (23%).

Trimethylsilyldichloromethyl lithium also has been generated by an *in situ* process, as reported by Bamford and Pant¹³, in which *n*-butyllithium was added to a mixture of trimethyl(dichloromethyl)silane and trimethylchlorosilane. Bis(trimethylsilyl)dichloromethane was produced in 50% yield. This procedure, however, is based on the slowness of the $\text{RLi}/\text{Me}_3\text{SiCl}$ reaction at low temperatures and would not be generalizable to many other reactions of $\text{Me}_3\text{SiCCl}_2\text{Li}$.

B. Bis(trimethylsilyl)chloromethyl lithium

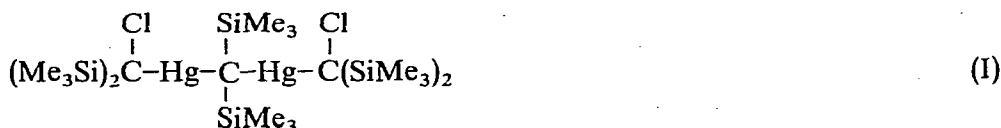
The ready metalation of trimethyl(dichloromethyl)silane by *n*-butyllithium suggested that bis(trimethylsilyl)chloromethyl lithium might be accessible via reaction of *n*-butyllithium with $(\text{Me}_3\text{Si})_2\text{CHCl}$. However, such behavior was not the case: when such a reaction was carried out at -110° and the reaction mixture was quenched with methyl iodide, a 93% recovery of the starting silane was obtained. An alternative to lithium-hydrogen exchange in organolithium preparation is lithium-halogen exchange and, as already noted, bis(trimethylsilyl)dichloromethane was readily available via $\text{Me}_3\text{SiCCl}_2\text{Li}$. Treatment of $(\text{Me}_3\text{Si})_2\text{CCl}_2$ with one molar equivalent of *n*-butyllithium at -75° to -90° for 4 h, followed by addition of methyl iodide, gave the expected methylation product in 95% yield (eqn. 5). Reaction of this new



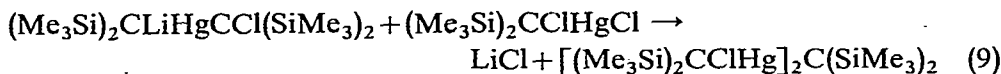
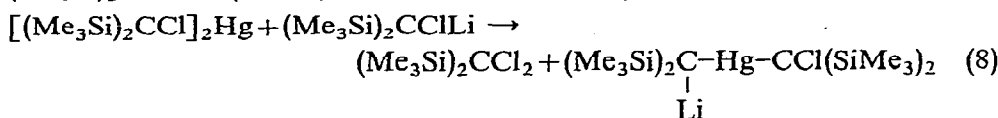
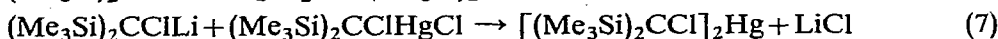
organolithium reagent with trimethylchlorosilane gave $(\text{Me}_3\text{Si})_3\text{CCl}$ in 74% yield, while its hydrolysis gave $(\text{Me}_3\text{Si})_2\text{CHCl}$ in 72% yield. We may note that the $\text{Me}_3\text{-SiCX}_2\text{R} \rightarrow \text{Me}_3\text{SiCXLiR} \xrightarrow{\text{HX}} \text{Me}_3\text{SiCHXR}$ sequence would appear to be an efficient reduction procedure for (α,α -dihaloalkyl)silanes to (α -monohaloalkyl)silanes and should be easily generalizable to other cases where $\text{R} = \text{alkyl}$ and aryl .

The preparation of the desired organomercury reagent, $[(\text{Me}_3\text{Si})_2\text{CCl}]_2\text{Hg}$, proved more difficult. A reaction of $(\text{Me}_3\text{Si})_2\text{CClLi}$ with mercuric chloride (2/1 molar ratio) gave this product, a distillable, crystalline solid in only 28% yield. A major

by-product (38% yield based on mercuric chloride) was identified by means of its combustion analysis (C, H, Hg), molecular weight and degradation with bromine as compound (I). An unusually high (23%) recovery of the starting silane also was



obtained. Formation of (I) can be rationalized in terms of the reaction sequence below. The step shown in eqn. (8) would serve to explain the high recovery of starting



silane. The occurrence of reaction (8) in competition with reactions (6) and (7) would be explicable in terms of the higher solubility of the fully alkylated mercurial, hence its greater accessibility with regard to the organolithium reagent. Another by-product (3% yield) was 1,1-bis(trimethylsilyl)-1-chloropentane, $(\text{Me}_3\text{Si})_2\text{CClC}_4\text{H}_9\text{-n}$, most likely formed by alkylation of $(\text{Me}_3\text{Si})_2\text{CClLi}$ by the *n*-butyl chloride formed in reaction (5).

A similar reaction was carried out with $(\text{Me}_3\text{Si})_2\text{CClLi}$ and mercuric chloride in 3/1 ratio. The yield of $[(\text{Me}_3\text{Si})_2\text{CCl}]_2\text{Hg}$ was 58% and that of (I) was 34%, while $(\text{Me}_3\text{Si})_2\text{CCl}_2$ was recovered in 12% yield. An attempt to prepare $\text{PhHgCCl}(\text{SiMe}_3)_2$ by the action of $(\text{Me}_3\text{Si})_2\text{CClLi}$ on phenylmercuric chloride gave diphenylmercury (40%) and $[(\text{Me}_3\text{Si})_2\text{CCl}]_2\text{Hg}$ (37%). Obviously, the desired unsymmetrical mercurial was not stable with respect to disproportionation to the symmetrical species. Such instability of a phenyl-halogenated alkyl-mercury compound had been encountered previously in the case of PhHgCH_2Cl ¹⁴, $\text{PhHgCBr}_2\text{H}$ ¹⁵, and others.

We have investigated the thermolysis of $(\text{Me}_3\text{SiCCl}_2)_2\text{Hg}$ and $[(\text{Me}_3\text{Si})_2\text{CCl}]_2\text{Hg}$ as an entry into Me_3SiCCl and $(\text{Me}_3\text{Si})_2\text{C}$ transfer chemistry. Our initial results obtained with the former reagent have been published¹⁶ and a full report concerning both is in preparation.

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 A 60 or T 60 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 RMU-6D 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 (LiAlH_4), 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 Co. Trimethyl(dichloromethyl)silane¹⁷ was prepared from commercial (Peninsular ChemResearch) dimethyl(dichloromethyl)chlorosilane by methylation with methylmagnesium bromide in diethyl ether. Yields of pure product averaged 70–75%.

Preparation of (trimethylsilyl)dichloromethyl lithium and its reaction with trimethyltin chloride

Into the standard apparatus was condensed 20 ml of dimethyl ether and then 60 ml of THF and 9.2 ml (14.9 mmole) of 1.63 *N* n-butyllithium in hexane was added. The resulting solution was cooled in a liquid nitrogen bath to -105° and 2.29 g (14.5 mmole) of trimethyl(dichloromethyl)silane in 6 ml of THF was added dropwise over 15 min with high-speed stirring. The colorless reaction mixture was stirred for 6 h at -100° to -105° and then 3.51 g (17.6 mmole) of trimethyltin chloride (M&T Chemicals, Inc.) in 6 ml of THF was added over 5 min. The reaction mixture was stirred for another $2\frac{1}{2}$ h at -100° to -105° before being allowed to warm slowly to room temperature. The pale yellow mixture was trap-to-trap distilled at 0.0001 mm into a receiver at -78° , leaving a white solid residue (LiCl). GLC analysis of the distillate (F&M 5754, 10% UC-W98, 60–190° program, 1-chloronaphthalene internal standard) showed the presence of the following: trimethyltin chloride; $\text{Me}_3\text{SiCCl}_2\text{SnMe}_3$ (11.8 mmole, 82%); $(\text{Me}_3\text{Si})_2\text{CCl}_2$ (trace); $\text{Me}_3\text{SnCCl}_2\text{H}$ (trace) and n-butyltrimethyltin (trace). Known compounds were identified by comparison of their infrared spectra with those of authentic samples. GLC examination of the distillate using a 10% Carbowax 20M column [on which trimethyltin chloride and trimethyl(dichloromethyl)silane are resolved] showed that the starting silane had been consumed completely. $\text{Me}_3\text{SiCCl}_2\text{SnMe}_3$ was characterized: b.p. 84° (10 mm), n_D^{25} 1.4992. (Found: C, 26.51; H, 5.34; Cl, 22.51. $\text{C}_7\text{H}_{18}\text{Cl}_2\text{SiSn}$ calcd.: C, 26.28; H, 5.67; Cl, 22.17%.) NMR (in CHCl_3): δ 0.18 (9 H, Me_3Si) s; 0.32 ppm (9 H, Me_3Sn) s, $J(^{117}\text{Sn}-^1\text{H})$ 52 Hz, $J(^{119}\text{Sn}-^1\text{H})$ 54 Hz. IR (liquid film): 2960 m, 2905 m, 2340 vw, 1700 w, 1430 sh, 1400 w, 1265 sh, 1255 vs, 1193 w, 870 vs, 840 vs, 770 s, 708 sh, 694 m, 670 m, 642 s, 616 m and 530 s cm^{-1} .

As mentioned in the discussion, addition of the n-butyllithium to the Me_3 -

SiCCl_2H results in lower product yields and in the formation of by-products in significant amounts.

Trimethyl(1,1-dichloroethyl)silane

The lithium reagent prepared in the standard apparatus at -115° from 5.02 g (31.9 mmole) of trimethyl(dichloromethyl)silane and 50 ml (30 mmole) of 0.76 N phenyllithium in diethyl ether in 90 ml of 3/1/1/1 THF/ Et_2O /pentane/ $(\text{MeO})_2\text{CH}_2$ (4 h) was quenched with 6.43 g (45.4 mmole) of methyl iodide in 6 ml of pentane. The reaction mixture was stirred for 1 h at -115° , warmed slowly to room temperature and treated with 50 ml of dry dioxane to precipitate the lithium halide as the insoluble dioxane complex. Filtration after 36 h was followed by trap-to-trap distillation of the filtrate at 0.01 mm. GLC analysis of the distillate showed the presence of some toluene, minor amounts of $\text{Me}_3\text{SiCCl}_2\text{H}$ and $(\text{Me}_3\text{Si})_2\text{CCl}_2$, and of $\text{Me}_3\text{SiCCl}_2\text{CH}_3$ (77% yield).

Trimethyl(1,1-dichloroethyl)silane, a very volatile white solid, melted at $117-119^\circ$ in a sealed capillary. (Found: C, 35.20; H, 7.09. $\text{C}_5\text{H}_{12}\text{Cl}_2\text{Si}$ calcd.: C, 35.09; H, 7.07%.) Mass spectrum (at 80 eV): parent peak at 170, 172, 174 (9/6/1), indicating the presence of two Cl atoms; other major fragments were: 73 (Me_3Si^+); 93, 95 (Me_2ClSi^+); 113, 115, 117 (MeCl_2Si^+); 155, 157, 159 ($\text{Me}_3\text{SiCCl}_2^+$). NMR (in CHCl_3): δ 0.22 (9 H, Me_3Si) s; 2.07 ppm (3 H, CH_3CCl_2) s.

Bis(trimethylsilyl)dichloromethane

The lithium reagent prepared in the standard apparatus at -110° from 0.36 mole of $\text{Me}_3\text{SiCCl}_2\text{H}$ and 0.36 mole of n-butyllithium in hexane in 390 ml of THF/ Et_2O /pentane/ $(\text{MeO})_2\text{CH}_2$ ($3\frac{1}{2}$ h) was quenched with 0.37 mole of trimethylchlorosilane (Union Carbide Corp). The reaction mixture was stirred at -115° for 2 h and then worked up as in the case of the reaction described above. GLC established the presence of the following products in the distillate: $\text{Me}_3\text{SiCCl}_2\text{H}$ (4%); $(\text{Me}_3\text{Si})_2\text{CHCl}$ (6%); $(\text{Me}_3\text{Si})_2\text{CCl}_2$ (75%); $(\text{Me}_3\text{Si})_3\text{CCl}$ (5%). A 10% DC-200 silicone oil column in the F&M 5754 gas chromatograph, 1-chloronaphthalene internal standard, served in this analysis.

Bis(trimethylsilyl)dichloromethane is a liquid, b.p. 50° (28 mm), n_D^{25} 1.4667. (Found: C, 36.60; H, 7.98; Cl, 30.83. $\text{C}_7\text{H}_{18}\text{Cl}_2\text{Si}_2$ calcd.: C, 36.67; H, 7.91; Cl, 30.92%.) NMR (in CHCl_3): δ 0.25 ppm (Me_3Si) s.

Bis(trimethylsilyl)chloromethane also was characterized: n_D^{25} 1.4461 (lit.¹⁸ n_D^{20} 1.4489). (Found: C, 43.47; H, 9.62; Cl, 17.95. $\text{C}_7\text{H}_{19}\text{Cl}_2\text{Si}_2$ calcd.: C, 43.15; H, 9.83; Cl, 18.19%.) NMR (in CHCl_3): δ 0.15 (18 H, Me_3Si) s and 2.44 ppm (1 H, CHCl) s.

Trimethyl(bromodichloromethyl)silane

The lithium reagent was prepared from 19.6 mmole of trimethyl(dichloromethyl)silane and 23.8 mmole of n-butyllithium in 60 ml of the THF/ Et_2O /pentane/ $(\text{MeO})_2\text{CH}_2$ solvent mixture at -115° (3 h). This reagent solution was added slowly with nitrogen pressure, while cooling the transfer tube with liquid nitrogen, to a flask containing 100 mmole of bromine in 60 ml of the solvent mixture at -110° . The bromine solution was stirred under nitrogen during the 90 min addition period and the resulting reaction mixture was stirred at -110° for another $1\frac{1}{2}$ h before being

warmed slowly to room temperature. The mixture consisted of two layers: a slightly red upper layer and a dark red lower layer. The upper organic layer was decanted and lower layer was washed with ether. The combined organic fractions were distilled at atmospheric pressure to remove most of the solvents. The residue was filtered and the filtrate trap-to-trap distilled at 0.0002 mm. GLC analysis of the filtrate showed the presence of many products, many of which no doubt resulted from undesired reactions of the excess bromine. The major product, however, was $\text{Me}_3\text{SiCCl}_2\text{Br}$ (45%).

Trimethyl(bromodichloromethyl)silane is a volatile, white solid, m.p. 152–153° (sealed capillary). (Found: C, 20.25; H, 4.10. $\text{C}_4\text{H}_9\text{BrCl}_2\text{Si}$ calcd.: C, 20.32; H, 3.85%.) Mass spectrum (80 eV): parent peak at 234, 236, 238, 240 (9/15/7/1) indicating the presence of one Br and two Cl atoms; other major fragments: 73 (Me_3Si^+); 93, 95 (Me_2ClSi^+); 113, 115, 117 (MeCl_2Si^+); 157, 159, 161 (MeSiBrCl^+); 219, 221, 223, 225 ($\text{Me}_2\text{SiCBrCl}_2^+$). NMR (in CHCl_3): δ 0.37 ppm, singlet.

Bis[(trimethylsilyl)dichloromethyl]mercury

The lithium reagent was prepared in the standard apparatus from 0.18 mole of $\text{Me}_3\text{SiCCl}_2\text{H}$ and 0.2 mole of *n*-butyllithium in 300 ml of THF/ Et_2O /pentane/ $(\text{MeO})_2\text{CH}_2$ solvent mixture at -118° (2 h). To this reagent was added slowly with high-speed stirring 30.6 g (0.085 mole) of mercuric bromide in 50 ml of THF. The reaction mixture was stirred for an additional 4 h at -120° and then was allowed to warm to room temperature. To the resulting black mixture was added 75 ml of dioxane. After 12 h the mixture was filtered and concentrated at reduced pressure. A subsequent trap-to-trap distillation at 10^{-5} mm removed volatiles, leaving 46 g of brown solid. The latter was extracted with hot hexane. From the extracts there was obtained 4.3 g of yellow kernels and 14.52 g of white prismatic crystals, m.p. 143–146° (dec.), essentially pure $(\text{Me}_3\text{SiCCl}_2)_2\text{Hg}$, a yield of 34%*. (Found: C, 18.52; H, 3.30; Cl, 27.40; Hg, 39.05. $\text{C}_{10}\text{H}_{18}\text{Cl}_4\text{HgSi}_2$ calcd.: C, 18.74; H, 3.54; Cl, 27.65; Hg, 39.12%.) NMR (in CHCl_3): singlet at 0.33 ppm.

In a similar experiment, a solution of $\text{Me}_3\text{SiCCl}_2\text{Li}$ prepared by the reaction of 69.5 mmole of $\text{Me}_3\text{SiCCl}_2\text{H}$ and 66 mmole of *n*-butyllithium in 2.5/1 THF/dimethyl ether at -115° ($4\frac{1}{2}$ h) was treated with 70 mmole of mercuric bromide (8 h) with the aim of preparing $\text{Me}_3\text{SiCCl}_2\text{HgBr}$. Treatment with dioxane, filtration and trap-to-trap distillation of the filtrate left a solid residue which was extracted with hot hexane, chloroform and benzene. Evaporation of the extracts gave solid which then was recrystallized from hexane. The first crops obtained were mercuric bromide; the later crops contained a slightly soluble mercurial as well as large amounts of $(\text{Me}_3\text{SiCCl}_2)_2\text{Hg}$. Column chromatography (activated silica gel) served in their separation. Elution with hexane gave $(\text{Me}_3\text{SiCCl}_2)_2\text{Hg}$, 7.4 g (44% based on Me_3Si groups), while subsequent elution with 1/1 hexane/chloroform gave slightly impure $\text{Me}_3\text{SiCCl}_2\text{HgBr}$. Recrystallization from chloroform/hexane gave pure material, m.p. 132–135°. (Found: C, 11.31; H, 2.17; Hg, 45.62. $\text{C}_4\text{H}_9\text{BrCl}_2\text{HgSi}$ calcd.: C, 11.00; H, 2.08; Hg, 45.94%.) NMR (in CHCl_3): singlet at 0.33 ppm.

A reaction of 0.2 mole of $\text{Me}_3\text{SiCCl}_2\text{Li}$ in 3/1 THF/dimethyl ether at -110°

* The m.p. of this compound originally¹⁶ was reported as 151–153°, but subsequent m.p. determinations have shown the 143–146° dec. value to be the correct one (three recrystallizations from hexane). The sample decomposes to give a white solid and a liquid.

with 80 mmole of mercuric chloride was carried out in similar manner. Similar work-up gave $(\text{Me}_3\text{SiCCl}_2)_2\text{Hg}$ (23% based on HgCl_2) and $\text{Me}_3\text{SiCCl}_2\text{HgCl}$ (17%), m.p. 133–135° (sealed capillary). (Found: C, 12.38; H, 2.26; Cl, 26.16. $\text{C}_4\text{H}_9\text{Cl}_3\text{HgSi}$ calcd.: C, 12.25; H, 2.31; Cl, 27.12%.)

Preparation of bis(trimethylsilyl)chloromethyl lithium and its reaction with methyl iodide

The standard apparatus was charged under nitrogen with 60 ml of 3/1 THF/dimethyl ether mixture and 2.38 g (10.4 mmole) of $(\text{Me}_3\text{Si})_2\text{CCl}_2$. To this solution, cooled to -95° , was added with high speed stirring 7.6 ml (12.52 mmole) of 1.65 *N* *n*-butyllithium in hexane over 5 min. The resulting mixture was stirred at -75° to -90° for 4 h and then 2.34 g (16.5 mmole) of methyl iodide in 5 ml of THF was added. After 3 h stirring at ca. -85° , the reaction mixture was allowed to warm to room temperature and treated with 30 ml of dry dioxane. Filtration was followed by trap-to-trap distillation at 0.01 mm. GLC analysis of the filtrate showed the presence of $(\text{Me}_3\text{Si})_2\text{CClCH}_3$ (99%), as well as of a minor amount of $(\text{Me}_3\text{Si})_2\text{CHCl}$. 1,1-Bis(trimethylsilyl)-1-chloroethane is a liquid, n_D^{25} 1.4563. (Found: C, 46.25; H, 10.27; Cl, 16.91. $\text{C}_8\text{H}_{21}\text{ClSi}_2$ calcd.: C, 46.00; H, 10.13; Cl, 16.97%.) NMR (in CHCl_3): δ 0.12 (18 H, Me_3Si) s; 1.52 ppm (3 H, CH_3CCl) s.

Tris(trimethylsilyl)chloromethane

The lithium reagent prepared from 12 mmole of $(\text{Me}_3\text{Si})_2\text{CCl}_2$ and 14.5 mmol of *n*-butyllithium in 60 ml of 2/1 THF/diethyl ether at -90° (4 h) and subsequently 16.2 mmole of trimethylchlorosilane in 3 ml of THF was added. The reaction mixture was stirred under nitrogen at -85° for 4 h, was allowed to warm to room temperature and then treated with 30 ml of dioxane. After 12 h the mixture was filtered and the filtrate was trap-to-trap distilled at 3×10^{-5} mm. GLC analysis of the distillate (F&M 5754, 10% DC-200 on Chromosorb W, 60–200°, 6° per min program, 1-chloronaphthalene internal standard) showed the presence of: $(\text{Me}_3\text{Si})_2\text{CHCl}$ (3%), $(\text{Me}_3\text{Si})_2\text{CCl}_2$ (3%) and $(\text{Me}_3\text{Si})_3\text{CCl}$ (74%). Tris(trimethylsilyl)chloromethane was recrystallized from hexane (in which it, however, is quite soluble) to give pure material, m.p. 156–158°. (Found: C, 45.26; H, 10.02; Cl, 13.32. $\text{C}_{10}\text{H}_{27}\text{ClSi}_3$ calcd.: C, 44.98; H, 10.19; Cl, 13.28%.) NMR (in CHCl_3): singlet at 0.22 ppm.

Hydrolysis of bis(trimethylsilyl)chloromethyl lithium

The lithium reagent prepared from 10.9 mmole of $(\text{Me}_3\text{Si})_2\text{CCl}_2$ and 11.75 mmol of *n*-butyllithium in 60 ml of 3/1 THF/diethyl ether at -90° (5 h) was treated at -90° with 12 ml (11.96 mmole) of 0.997 *N* HCl in 10 ml of THF/diethyl ether mixture. The reaction mixture was warmed to room temperature; the organic layer was dried and trap-to-trap distilled at 0.0001 mm. GLC analysis of the distillate showed the presence of bis(trimethylsilyl)chloromethane (72%) and bis(trimethylsilyl)-dichloromethane (7%).

Bis[bis(trimethylsilyl)]chloromethylmercury

To the lithium reagent prepared from 0.157 mole of $(\text{Me}_3\text{Si})_2\text{CCl}_2$ and 0.150 mole of *n*-butyllithium in 300 ml of THF at -90° ($4\frac{1}{2}$ h) was added at this temperature 0.060 mol of mercuric chloride in THF slurry over a 20 min period. The resulting

yellow solution was stirred at -80° for 7 h, then was warmed to room temperature and treated with 100 ml of dry dioxane. After 12 h the mixture was filtered and the filtrate was concentrated at reduced pressure. The residue was distilled at 3×10^{-4} mm using a Hickman still. The following fractions were collected (the temperatures given are those of the oil bath): (1) 60° , some $(\text{Me}_3\text{Si})_2\text{CCl}_2$ and $(\text{Me}_3\text{Si})_2\text{CHCl}$ (GLC analysis) and a small amount of the desired mercury compound; (2) $70-100^{\circ}$, 5.16 g, m.p. $42-44^{\circ}$ on solidification, bis[bis(trimethylsilyl)chloromethyl]mercury; (3) 125° , 2.71 g, white solid plus some liquid; (4) 180° , 10.8 g, m.p. $69-72^{\circ}$ after solidification*, product (I); (5) residue, 4.64 g of brown solid, m.p. $91-100^{\circ}$ with residue. The total yield of bis[bis(trimethylsilyl)chloromethyl]mercury was 16.62 mmole (28% based on mercuric chloride, the limiting reagent). The yield of product (I) was 11.4 mmoles, 38% based on mercuric chloride.

A pure sample of bis[bis(trimethylsilyl)chloromethyl]mercury had m.p. $46-48^{\circ}$. (Found: C, 28.88; H, 6.19. $\text{C}_{14}\text{H}_{36}\text{Cl}_2\text{HgSi}_4$ calcd.: C, 28.58; H, 6.17%.) NMR (CCl_4 contg. CHCl_3): singlet at 0.234 ppm.

Product (I) was identified as $[(\text{Me}_3\text{Si})_2\text{CClHg}]_2\text{C}(\text{SiMe}_3)_2$. (Found: C, 26.90, 26.76; H, 5.72, 5.73; Cl, 7.19; Hg, 40.06; mol. wt. VPO, 976. $\text{C}_{21}\text{H}_{54}\text{Cl}_2\text{Hg}_2\text{Si}_6$ calcd.: C, 26.63; H, 5.75; Cl, 7.49; Hg, 42.35%; mol. wt., 947.4.) NMR (in CHCl_3): singlet at 0.19 ppm; in benzene: singlet at 0.46 ppm. When the sweep width was decreased to 50 Hz, the singlet split into two singlets separated by 1 Hz. The area ratio of the higher-field singlet to the lower-field singlet was ca. 2/1. IR (CCl_4/CS_2 composite): 2940 s, 2890 m, 1518 m, 1400 m (broad), 1295 w, 1260 s, 1250 s, 1090 w (broad), 1020 w, 985 w, 895 s, 860 sh, 845 s, 830 m, 818 w, 710 sh, 700 m and 680 m cm^{-1} .

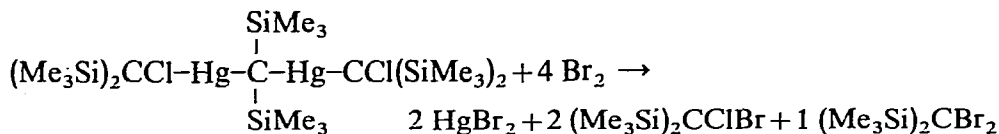
GLC analysis of all volatiles (F&M 5754, 10% DC-200 on Chromosorb W, $60-190^{\circ}$, 6° per min program, 1-chloronaphthalene internal standard) showed the presence of $(\text{Me}_3\text{Si})_2\text{CCl}_2$ (23% recovery), $(\text{Me}_3\text{Si})_2\text{CHCl}$ (3%) and $(\text{Me}_3\text{Si})_2\text{CCl}-\text{C}_4\text{H}_9-n$ (3%).

1,1-Bis(trimethylsilyl)-1-chloropentane, n_D^{25} 1.4678, is a new compound. (Found: C, 52.91; H, 10.81; Cl, 14.00. $\text{C}_{11}\text{H}_{27}\text{ClSi}_2$ calcd.: C, 52.64; H, 10.84; Cl, 14.13%.) NMR (in CHCl_3): δ 0.116 (18 H, Me_3Si) s; 0.53–2.17 ppm (9H, C_4H_9) m.

In another experiment carried out with ca. 41 mmol of the lithium reagent and 15 mmol of mercuric chloride in 2/1/1 THF/diethyl ether/pentane at -85° very similar results were obtained. Bis[bis(trimethylsilyl)chloromethyl]mercury was obtained in 58% yield and product (I) in 34% yield.

Further confirmation of the identity of product (I) was obtained from its brominolysis. Product (I), 2.08 g (2.2 mmol) in 20 ml of carbon tetrachloride was treated slowly with stirring under nitrogen with 14 ml of 1 M bromine in carbon tetrachloride. The reaction mixture was stirred at room temperature for 1 h. Filtration gave 1.53 g of off-white solid which was sublimed (100° at 1 mm) to give 1.525 g (4.02 mmol) of mercuric bromide, m.p. $232-238^{\circ}$. The filtrate was treated with 15 ml of 5% sodium thiosulfate solution. The resulting organic layer was trap-to-trap distilled at 5×10^{-4} mm. GLC analysis of the distillate showed the presence of 3.74 mmole of $(\text{Me}_3\text{Si})_2\text{CClBr}$ and 2.06 mmol of $(\text{Me}_3\text{Si})_2\text{CBr}_2$. Thus the brominolysis reaction shown below is indicated.

* Recrystallization did not improve the melting range.



Bis(trimethylsilyl)chlorobromomethane was characterized: m.p. 30–31° (sealed capillary). (Found: C, 30.76; H, 6.80; Br, 28.97; Cl, 13.11. $\text{C}_7\text{H}_{18}\text{BrClSi}_2$ calcd.: C, 30.71; H, 6.63; Br, 29.19; Cl, 12.95%.) NMR (in CHCl_3): singlet at 0.27 ppm.

Bis(trimethylsilyl)dibromomethane was known to us from other studies¹⁹. It should be noted that bis(trimethylsilyl)chlorobromomethane is not converted to bis(trimethylsilyl)dibromomethane by the action of bromine in the presence of mercuric bromide.

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