SYNTHESIS AND REACTIVITY OF SOME t-BUTYL-DISILANES AND -DIGERMANES

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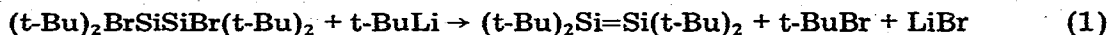
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Summary

Efficient methods of coupling R_2EHCl (R = Me, t-Bu; E = Si, Ge) to give R_2HEEHR_2 have been developed. These dihydrides are readily halogenated with Br_2 or I_2 to give the corresponding 1,2-dihalo-disilane or -digermane. High yields of $Me_2ClGeGeClMe_2$ are obtained by treating hexamethyldigermane with conc. sulfuric acid and ammonium chloride. Conc. sulfuric acid exclusively cleaves methyl groups from $[t-BuMe_2Ge—]_2$ to give $[t-BuMeClGe—]_2$ after treatment with ammonium chloride. The latter dichlorodigermane is formed as a mixture of *d,l*-enantiomers and the *meso* isomer as shown by NMR evidence. The bulky t-butyl groups render $(t-Bu)_4Si_2Br_2$ inert to nucleophilic substitution or metal—halogen exchange with organolithium reagents.
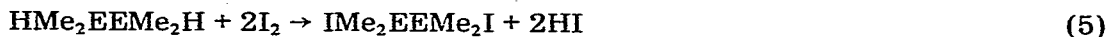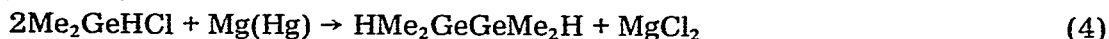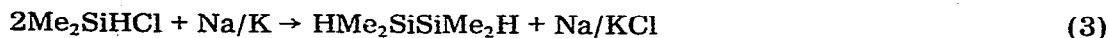
Introduction

It recently was proposed that Si=Si double bonds might be stabilized against self-condensation if the double bond were shielded by bulky groups, e.g. t-butyl, on silicon [1]. As a possible route to compounds containing the Si=Si double bond, we have considered the elimination reaction 1, analogous to reaction 2 which is known to occur readily with 1,2-dihalo organic compounds.

$(t-Bu)_2BrSiSiBr(t-Bu)_2 + t-BuLi \rightarrow (t-Bu)_2Si=Si(t-Bu)_2 + t-BuBr + LiBr$ (1)

$BrCH_2CH_2Br + t-BuLi \rightarrow CH_2=CH_2 + t-BuBr + LiBr$ (2)

We here report the details of the preparation of some new t-butyl-substituted disilanes and digermanes and note some features of their reactivity pertinent to the elimination reaction 1. In addition, we report our results with corresponding methyl derivatives which were used initially to test certain reaction schemes.

Results and discussion

The diiodo derivatives, IMe_2EEMe_2I (E = Si, Ge), were prepared according to reactions 3—5.

$$2Me_2SiHCl + Na/K \rightarrow HMe_2SiSiMe_2H + Na/KCl \qquad (3)$$

$$2Me_2GeHCl + Mg(Hg) \rightarrow HMe_2GeGeMe_2H + MgCl_2 \qquad (4)$$

$$HMe_2EEMe_2H + 2I_2 \rightarrow IMe_2EEMe_2I + 2HI \qquad (5)$$

Although $HMe_2SiSiMe_2H$ has been previously prepared by other methods [2,3], we desired a quick, direct method for preparing this dihydride from commercially available Me_2SiHCl. The yield of $HMe_2SiSiMe_2H$ from reaction 3 is typically near 40%. The yield was not appreciably increased by different solvents, increased reaction temperature, prolonged stirring, or changes in the disilane:metal ratio. Apparently side reactions, e.g. further coupling of the disilane, limit the yield by this method. However, the yield compares favorably with the overall yields of previous methods. Iodine reacts sluggishly with $HMe_2SiSiMe_2H$ to give the diiododisilane, $IMe_2SiSiMe_2I$, which is exceedingly moisture sensitive and produces voluminous clouds of HI upon contact with moist air. Due to the extreme sensitivity of this compound, satisfactory elemental analyses were not obtained, but the compound's spectroscopic properties leave little doubt of its formulation. No Si—H stretch is observed in the IR and a single, sharp methyl resonance is found in the NMR spectrum. In addition to the parent ion at m/e 270, fragment ions with m/e corresponding to $Me_2SiSiIMe_2^+$ and Me_2SiI^+ were observed in the mass spectrum. A mass spectrum of the viscous oil which results from the air hydrolysis of $IMe_2SiSiMe_2I$ suggests the presence of cyclosiloxanes with $(Me_4Si_2O)_3$ being the major component.

The reaction of Me_2GeHCl with either sodium—potassium alloy or sodium amalgam in ether solvents gave only polymeric material. Magnesium amalgam does give the coupled product, $HMe_2GeGeMe_2H$, according to reaction 4. The parent ions of this digermane is not observed in its mass spectrum, but the peak corresponding to $Me_2GeGeMe_2H^+$ is very intense. Fragment ion peaks due to loss of methyl groups and methane were also observed. Iodine reacts much more rapidly with $HMe_2GeGeMe_2H$ than with the analogous disilane. The parent ion, $IMe_2GeGeMe_2I^+$, and the fragments, $IMe_2GeGeMe_2^+$ and Me_2GeI^+, were observed in the mass spectrum.

Since Me_2GeHCl is not readily available, a more convenient route to 1,2-dihalodigermanes is the adaption of Kumada's method [5] of demethylating disilanes with concentrated sulfuric acid and ammonium chloride. The demethylation of Me_6Ge_2 proceeds smoothly to give $ClMe_2GeGeMe_2Cl$ in 87% yield (eq. 6).

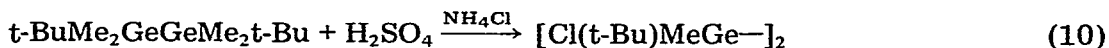$$Me_6Ge_2 + 2H_2SO_4 \xrightarrow{NH_4Cl} ClMe_2GeGeMe_2Cl + 2CH_4 + 2NH_4HSO_4 \qquad (6)$$
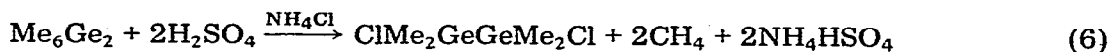
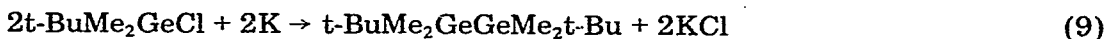Cleavage of phenyl groups from $PhMe_2GeGeMe_2Ph$ with HCl, and the redistribution of methyl groups on Me_6Ge_2 with $SnCl_4$ [6] have previously been used to prepare 1,2-dichlorotetramethyldigermane, but these procedures are not as convenient as the sulfuric acid cleavage reported here.

We have prepared Me_6Ge_2 in 60% yield by coupling Me_3GeCl with molten

potassium in refluxing cyclohexane. The use of magnesium amalgam in THF was also investigated as a coupling reagent. In addition to hexamethyldigermane (45%), we also obtained a 15% yield of $(Me_3Ge)_2Hg$ [7]. In situ transmetallation of the mercury compound with lithium ribbon, followed by the addition of more Me_3GeCl, gave an overall 62% yield of Me_6Ge_2 (eq. 7, 8).

$$(Me_3Ge)_2Hg + 2Li \rightarrow 2Me_3GeLi + Hg \tag{7}$$

$$Me_3GeLi + Me_3GeCl \rightarrow Me_6Ge_2 + LiCl \tag{8}$$

The synthesis of digermanes incorporating t-butyl groups was accomplished via reactions 9 and 10.

$$2t\text{-}BuMe_2GeCl + 2K \rightarrow t\text{-}BuMe_2GeGeMe_2t\text{-}Bu + 2KCl \tag{9}$$

$$t\text{-}BuMe_2GeGeMe_2t\text{-}Bu + H_2SO_4 \xrightarrow{NH_4Cl} [Cl(t\text{-}Bu)MeGe{-}]_2 \tag{10}$$

The 1,2-di(t-butyl)tetramethyldigermane was obtained in only 43% yield, compared to a 60% yield for Me_6Ge_2 under comparable conditions. The lower yield may be due to the steric bulk of the t-butyl groups. No steric effects were noted in the demethylation reaction 10 since the chlorinated digermane was obtained in high yield. No evidence was obtained for cleavage of the t-butyl groups by sulfuric acid, although Ge—Ge bond cleavage did occur to a slight degree.

The 1,2-dichloro-1,2-di(t-butyl)dimethyldigermane so obtained is a mixture of *d,l*-enantiomers and the *meso* form as shown by the NMR spectrum in Fig. 1. The t-butyl resonances are separated by only 0.8 Hz and are resolved only in expanded sweep widths, but the methyl resonances of the enantiomers and the
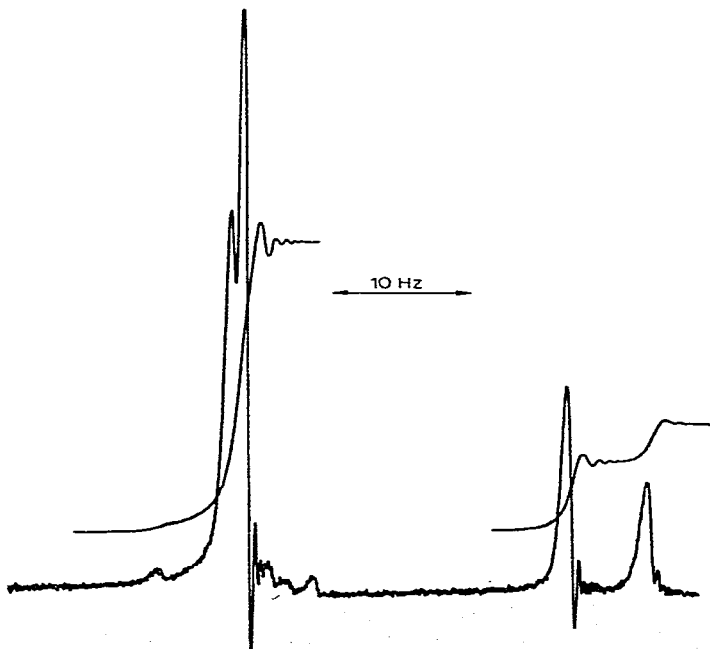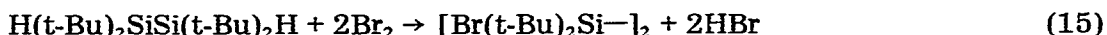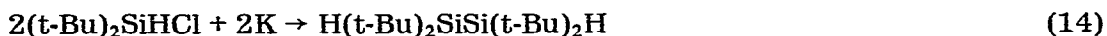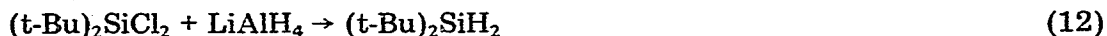

Fig. 1. Proton NMR spectrum of the mixture of *d,l*-enantiomers and *meso* isomer of [(t-Bu)MeClGe—]₂.

meso form differ by 5.8 Hz and are easily resolved. It is not possible at this time to assign the peaks to a specific stereoisomer. A completely random formation of [Cl(t-Bu)MeGe—]₂ would result in a 1:1 ratio of *d,l*-pair to *meso* isomer, so the spectrum shows a preferential formation of one isomer over the other. Féher and Plichta [8] have previously reported an NMR differentiation of stereoisomeric digermanes.

The preparation of Br(t-Bu)₂SiSi(t-Bu)₂Br was planned according to reactions 11—15.

$$SiCl_4 + 2t\text{-BuLi} \rightarrow (t\text{-Bu})_2SiCl_2 \tag{11}$$

$$(t\text{-Bu})_2SiCl_2 + LiAlH_4 \rightarrow (t\text{-Bu})_2SiH_2 \tag{12}$$

$$(t\text{-Bu})_2SiH_2 + HgCl_2 \rightarrow (t\text{-Bu})_2SiHCl \tag{13}$$

$$2(t\text{-Bu})_2SiHCl + 2K \rightarrow H(t\text{-Bu})_2SiSi(t\text{-Bu})_2H \tag{14}$$

$$H(t\text{-Bu})_2SiSi(t\text{-Bu})_2H + 2Br_2 \rightarrow [Br(t\text{-Bu})_2Si\text{—}]_2 + 2HBr \tag{15}$$

Di(t-butyl)dichlorosilane was readily reduced to di(t-butyl)silane with lithium aluminum hydride. The dihydride, however, was completely inert to HgCl₂ even in refluxing toluene. This is in sharp contrast to unhindered diorganosilanes. A molar equivalent of bromide readily gave bromodi(t-butyl)silane in quantitative yield according to reaction 16.

$$(t\text{-Bu})_2SiH_2 + Br_2 \rightarrow (t\text{-Bu})_2SiHBr + HBr \tag{16}$$
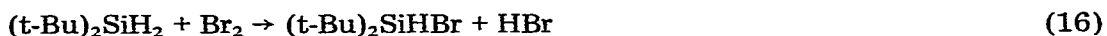
We then discovered that a slight modification of Sommer's preparation [9] of (t-Bu)₂SiCl₂ gave good yields of (t-Bu)₂SiHCl directly from t-BuLi and SiCl₄ (see Experimental). In addition to (t-Bu)₂SiHCl, smaller amounts of (t-Bu)₂SiH₂ and (t-Bu)₂SiCl₂ are also obtained. After submission of this manuscript, other workers [10] reported the formation of silyl hydrides in the reaction of t-BuLi with SiCl₄. Hydride formation has also been observed with other bulky organolithium reagents [11,12]. Under our conditions (prolonged reflux in cyclohexane), the hydrides could be formed by three possible mechanisms:
(a) β-hydrogen shift during the reaction of (t-Bu)₂SiCl₂ with a third mole equivalent of t-BuLi.
(b) metallation of solvent to give C₆H₁₁Li, followed by β-hydrogen shift as in eq. 9.
*(c)* decomposition of RLi to LiH and alkene, followed by the reduction of Si—Cl bonds by LiH to Si—H.

The coupling of (t-Bu)₂SiHCl with molten potassium in refluxing cyclohexane resulted mainly in the formation of the desired dihydride, H(t-Bu)₂SiSi(t-Bu)₂H. This coupling reaction was unique in all that we performed in that the reaction mixture turns red. A similar red color has been observed in the reaction between (i-Pr)₃GeCl and sodium—potassium alloy [13]. These red colors presumably are due to (t-Bu)₂SiHK and (i-Pr)₃GeK which are formed faster than they react with the sterically hindered halides.

The bromination of [H(t-Bu)₂Si—]₂ by bromine to form [Br(t-Bu)₂Si—]₂ (reaction 15) occurs in quantitative yield at —20°C, at which temperature no Si—Si bond cleavage was observed.

Reactivity of XR_2EER_2X

The behavior of the above dihalo-disilanes and -digermanes with various alkyllithium reagents has been investigated. In some experiments, 1,3-dienes were present as trapping agents. It was hoped that the R_2XEEXR_2 species would lose halogen according to eq. 1, and the resulting alkene analog would react with the dienes via eq. 17.

$$R_2EER_2 \quad + \quad \text{[diene]} \quad \longrightarrow \quad \text{[ring with } ER_2\text{-}ER_2 \text{]} \quad (17)$$
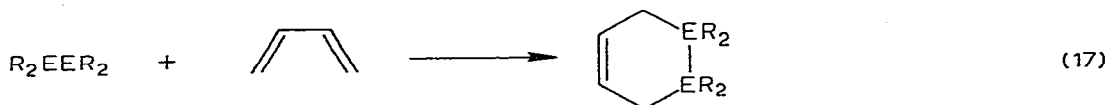
The bulky t-butyl groups render $(t\text{-}Bu)_2BrSiSiBr(t\text{-}Bu)_2$ exceedingly inert toward alkyllithium and other reagents. No reaction was observed with lithium, sodium, or magnesium amalgams at room temperature in THF medium. With molten potassium in refluxing cyclohexane, $[(t\text{-}Bu)_2BrSi\text{—}]_2$ formed a viscous polymer, which was not investigated in detail, and small amounts of $(t\text{-}Bu)_3\text{-}Si_2H_3$ and $(t\text{-}Bu)_3Si_2H_3O$ (2:0.75). t-Butyllithium failed to react with this disilane in refluxing petroleum ether (30—60°C). Similarly, n-butyllithium, its tetramethylethylenediamine complex, and methyllithium failed to react with $[(t\text{-}Bu)_2BrSi\text{—}]_2$. The dibromosilane was also recovered unchanged after stirring for 24 h with $Na_2Fe(CO)_4$ in THF.

The digermane, $Me_2ClGeGeClMe_2$, also failed to react with t-BuLi at —60 to —40°C in either petroleum ether (30—60°C) or ethyl ether. Upon gradually warming these mixtures to room temperature, lithium chloride precipitated. From the petroleum ether, large quantities of polymer, and small amounts of distillable liquid could be isolated. The distillable liquid consisted of $(t\text{-}Bu)Me_2\text{-}GeGeMe_2(t\text{-}Bu)$ and $HMe_2GeGeMe_2(t\text{-}Bu)$ (ca. 2:1) and trace quantities of $(t\text{-}Bu)Me_2GeGeMe_2Cl$ and $HMe_2GeGeMe_2H$. These results were essentially unchanged when 1,3-dienes, e.g. cyclohexa-1,3-diene, or *trans,trans*-2,4-hexadiene were initially present.

The production of large quantities of polygermanes in the above reactions may indicate the formation of $Me_2Ge=GeMe_2$ which immediately polymerizes even in the presence of a trapping agent; but other mechanisms can also account for the polymer. In view of the lack of reactivity of $[Me_2ClGe\text{—}]_2$ toward t-BuLi at low temperatures, the reactivity of $[Cl(t\text{-}Bu)MeGe\text{—}]_2$ was not investigated.

Sodium tetracarbonylferrate, $Na_2Fe(CO)_4$, does react with $ClMe_2GeGeMe_2Cl$ to give cyclic 5- and 6-membered rings, e.g.:
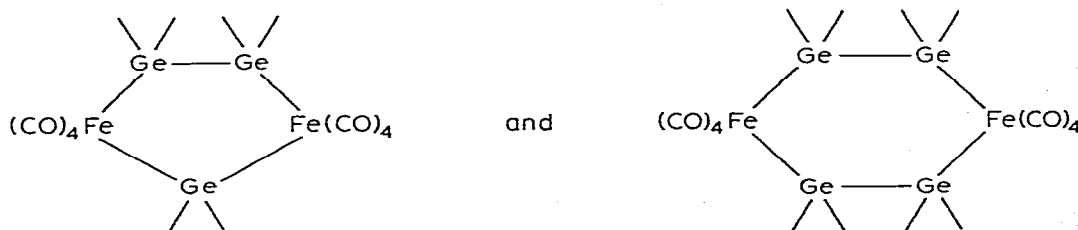
These results are reported elsewhere [14].

Experimental

Infrared spectra were obtained on a Perkin—Elmer 457 grating spectrometer. Proton NMR spectra were recorded on a Varian T-60 with benzene or chloroform as internal standards. Mass spectra were obtained on an AEI MS902 instrument using the direct inlet probe. GLC-mass spectra were obtained on an AEI MS30 double beam, double focusing spectrometer interfaced with a Digital PDP8/m computer and a PYE series 104 Chromatogram. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. and Spang Microanalytical Laboratory, Ann Arbor, Mi. Unless specified otherwise, all operations were conducted under a nitrogen atmosphere. The t-butyllithium reagent was 0.75 M in n-pentane and was purchased from Alpha Products, Beverly, Mass.

1,1,2,2-Tetramethyldisilane

In a dry, three-necked, 250-ml flask equipped with a reflux condenser, equal pressure dropping funnel, and a glass * covered magnetic stirring bar were placed 0.075 mol of sodium and 0.15 mol of potassium. These metals were stirred together until the liquid amalgam was formed. Then 100 ml of dry ethyl ether was added, followed by the dropwise addition of dimethylchlorosilane (0.127 mol). A white coating appeared immediately on the alloy, and after about 1 h of stirring, a gentle reflux commenced and the mixture darkened. After ca. 2 h the mixture was filtered, giving a dark, pyrophoric powder and a clear filtrate. Fractional distillation of the filtrate yielded 3 g (40%) of 1,1,2,2-tetramethyldisilane, b.p. 86—87°C (lit. [2] 86—87°C). IR (CCl$_4$): ν(Si—H) 2100 cm^{-1}. NMR (CCl$_4$): Me, doublet (J 5 Hz) at τ 9.83; H, multiplet at τ 6.30. Parent ion at m/e 118.

1,1,2,2-Tetramethyl-1,2-diiododisilane

Iodine (9.15 g, 0.036 mol), dissolved in 250 ml of dichloromethane, was slowly added with stirring to 2.1 g (0.018 mol) of tetramethyldisilane dissolved in ca. 50 ml of dichloromethane at 0°C. At this temperature, the reaction appeared to be very sluggish, so the mixture was refluxed for 48 h. The still dark mixture was then concentrated and filtered to remove the iodine which crystallized. The solution was then treated with antimony powder to remove unreacted iodine. The solvent was then replaced with petroleum ether (30—60°C), and subsequent cooling to —60°C gave a crop of yellow crystals. After sublimation, 4.1 g (61%) of white product, m.p. 68—70°C, was obtained. NMR (CCl$_4$): τ 9.07. Parent ion at m/e 370. (Found: C, 12.99; H, 3.24. C$_4$H$_{12}$I$_2$Si$_2$ calcd.: C, 14.70; H, 3.54%.)

1,1,2,2-Tetramethyldigermane

Dimethylchlorogermane (13.4 g, 0.097 mol) was added dropwise to magnesium amalgam, prepared by stirring 2.0 g of magnesium with 100 g of mercury, under 50 ml of THF in a three-necked, 250-ml flask equipped with dropping funnel, reflux condenser, and a mechanical stirrer. An exothermic reaction ensued and

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* We have found that liquid sodium—potassium alloy occasionally reacts violently with Teflon ®, presumably producing the metal fluorides and carbon.

a grey precipitate formed. The mixture was stirred and heated to reflux for 60 min. After removal of the excess amalgam, the mixture was hydrolyzed with water; petroleum ether (30—60°C) was added, and the organic layer separated and dried over sodium sulfate. Fractional distillation gave 3 g of HMe$_2$GeGeMe$_2$H, b.p. 65°C/130 Torr. IR (CCl$_4$): ν(Ge—H) 2000 cm^{-1}. NMR (C$_6$D$_6$): Me, doublet (J 4 Hz) at τ 9.70; H, multiplet at τ 6.11. The ion Me$_4$Ge$_2$H$^+$ was observed at m/e 207. (Found: C, 23.25; H, 6.85. C$_4$H$_{14}$Ge$_2$ calcd.: C, 23.17; H, 6.76%.)

1,1,2,2-Tetramethyl-1,2-diiododigermane

Iodine (1.4 g, 4.8 mmol) was added with stirring to a solution of Me$_4$Ge$_2$H$_2$ (0.6 g, 2.9 mmol) in petroleum ether (30—60°C). After the iodine color disappeared, the solvent was removed, leaving an oily, white solid which was recrystallized from petroleum ether (30—60°C) at −15°C. Sublimation of this solid gave 0.65 g (49%) of pure IMe$_2$GeGeMe$_2$I, m.p. 62°C. NMR (C$_6$D$_6$): τ 8.96. Parent ion at m/e 460. (Found: C, 10.33; H, 2.52. C$_4$H$_{12}$Ge$_2$I$_2$ calcd.: C, 10.45; H, 2.62%.)

Hexamethyldigermane

(a) From potassium and trimethylchlorogermane. Potassium (3.8 g, 0.098 mol) was melted in 150 ml of refluxing cyclohexane contained in a three-necked flask equipped with mechanical stirrer, reflux condenser, and dropping funnel. Trimethylchlorogermane (15 g, 0.098 mol) was then added dropwise with rapid stirring to give a blue reaction mixture which was stirred for 2 h at reflux. After filtering away the blue, pyrophoric solid, fractional distillation of the filtrate yielded 7.0 g (60%) of hexamethyldigermane, b.p. 136°C (lit. [15] 137°C/772 Torr).

(b) From magnesium amalgam and trimethylchlorogermane. Trimethylchlorogermane (10.0 g, 0.066 mol) was added to magnesium amalgam (1.0 g Mg/50.0 g Hg) in 50 ml of THF using the above described apparatus. The mixture turned green and was then heated to reflux for 2 h. After filtration from the yellow-green solid, the filtrate was trap-to-trap distilled to give hexamethyldigermane in 46% yield. The yellow-green powder, and the residue from the trap-to-trap distillations were extracted with petroleum ether (30—60°C). Concentration and cooling of this solution yielded 2.0 g of bis(trimethylgermyl)mercury, m.p. 120—122°C (lit. [7] 120—122°C). NMR (C$_6$D$_6$): τ 9.70 (lit. [7] τ 9.53).

In a similar experiment, lithium ribbon was added to the reaction mixture after the initial exothermic reaction was complete and the excess amalgam had been removed. Trimethylchlorogermane (2.5 g) was then added to the caramel colored solution. Work-up as before gave a 62% yield of hexamethyldigermane.

1,1,2,2-Tetramethyl-1,2-dichlorodigermane

The procedure is adapted from that of Kumada [5]. Hexamethyldigermane (11.0 g, 0.047 mol) was allowed to react at room temperature with conc. sulfuric acid (48 g). After stirring for 30 h, gas evolution had ceased and 7.7 g of ammonium chloride (previously dried in an Abderhalden pistol at 110°C under vacuum) was added in portions to the reaction mixture cooled in an ice bath. A white precipitate formed immediately. After 30 min, of stirring, the precipitate was dissolved in petroleum ether (30—60°C). Following separation and concentra-

tion of the organic phase, white crystals were obtained. Recrystallization from petroleum ether (30—60°C) at —15°C gave pure product, m.p. 45—47.5°C, in 87% yield. NMR (C_6H_6): τ 9.27. (Found: C, 17.37; H, 4.42. $C_4H_{12}Cl_2Ge_2$ calcd.: C, 17.38; H, 4.35%.)

1,1,2,2-Tetramethyl-1,2-di-t-butyldigermane

This compound was prepared by coupling 6.8 g of t-BuMe$_2$GeCl [16] with a 10-fold excess of potassium in the manner described for hexamethyldigermane. The reflux time was 1 h, and the product, b.p. 48°C/0.2 Torr, was obtained in 43% yield. NMR (C_6H_6): Me, τ 9.83; t-Bu, τ 9.03. The parent ion was observed at m/e 320. (Found: C, 45.20; H, 9.36. $C_{12}H_{30}Ge_2$ calcd.: C, 45.12; H, 9.44%.)

1,2-Dichloro-1,2-di-t-butyl-1,2-dimethyldigermane

The product from the above reaction (2.8 g) was stirred with conc. sulfuric acid at room temperature for 24 h. Work-up following that described for Me$_4$Cl$_2$Ge$_2$ yielded a few drops of t-BuMe$_2$GeCl and 2.0 ml of Me$_2$(t-Bu)$_2$Cl$_2$Ge$_2$, b.p. 62.5—63.5°C/0.2 Torr. NMR (C_6H_6): Me, τ 9.22 and τ 9.15; t-Bu, two overlapping singlets at τ 8.95. Parent ion observed at m/e 360. (Found: C, 33.59; H, 6.74. $C_{10}H_{24}Cl_2Ge_2$ calcd.: C, 33.32; H, 6.66%.)

Di-t-butylchlorosilane

This procedure is essentially that due to Tyler et al. [9] for the preparation of (t-Bu)$_2$SiCl$_2$, except that after stirring overnight at room temperature, the mixture was quickly brought to a reflux temperature of 75°C by distilling off the pentane while adding cyclohexane. The reaction mixture was then refluxed at 75°C for 4 days. Thus, tetrachlorosilane (0.25 mol) and t-butyllithium (0.5 mol), gave upon work-up di-t-butylsilane (2.0 g), di-t-butylchlorosilane (21.0 g), and di-t-butyldichlorosilane (8.0 g). The products were characterized as follows: (t-Bu)$_2$SiH$_2$, b.p. 48°C/45 Torr; ν(Si—H) (neat) 2096 cm^{-1}; NMR (CDCl$_3$): t-Bu, τ 8.93; H, τ 6.58. (Found: C, 66.27; H, 13.71. C_8H_{20}Si calcd.: C, 66.55; H, 13.99.) (t-Bu)$_2$SiHCl, b.p. 38—40°C/10 Torr; ν(Si—H) (neat) 2129 cm^{-1}; NMR (CDCl$_3$): t-Bu, τ 8.92; H, τ 5.77. (Found: C, 53.77; H, 10.83. C_8H_{19}ClSi calcd.: C, 53.78; H, 10.64%.) (t-Bu)$_2$SiCl$_2$, b.p. 44—48°C/0.01 Torr (lit. [9] b.p. 190°C/729 Torr); NMR (CDCl$_3$): τ 8.83.

Di-t-butylbromosilane

The reduction of di-t-butyldichlorosilane (46.0 g, 0.22 mol) with lithium aluminium hydride (8.2 g, 0.22 mol) in ethyl ether gave 16.7 g (53%) of (t-Bu)$_2$-SiH$_2$ after 12 h at reflux temperature. This was dissolved in 50 ml of CCl$_4$ and cooled to —10°C. Dropwise addition of bromine (18.4 g, 0.115 mmol), dissolved in 60 ml of CCl$_4$, gave a pale orange solution. Fractional distillation yielded 19.7 g (78%) of (t-Bu)$_2$SiHBr, b.p. 52°C/4 Torr. NMR (CCl$_4$): t-Bu, τ 8.87; Si$\underline{H}$, τ 5.75. ν(Si—H) (neat) 2130 cm^{-1}; ν(Si—Br) 450 cm^{-1}. (Found: C, 43.08; H, 8.63. C_8H_{19}BrSi calcd.: C, 43.04; H, 8.60%.)

1,1,2,2-Tetra-t-butyldisilane

This compound was prepared from 15 g of (t-Bu)$_2$SiHCl and an equimolar quantity of potassium by the procedure outlined for hexamethyldigermane.

The mixture was refluxed for 3 h and became caramel-colored. Filtration gave a red solution which was fractionally distilled to give (t-Bu)$_4$Si$_2$H$_2$, b.p. 75°C/ 0.2 Torr, m.p. 32—33°C, in 45% yield. ν(Si—H) (CH$_2$Cl$_2$) 2062 cm^{-1}. NMR (CDCl$_3$): t-Bu, τ 8.85; H, τ 6.35. Parent ion at m/e 286. (Found: C, 67.00; H, 13.29. C$_{16}$H$_{38}$Si$_2$ calcd.: C, 67.13; H, 13.28%.)

1,1,2,2-Tetra-t-butyl-1,2-dibromodisilane

Bromine (6.45 g, 0.040 mol) in ca. 50 ml of CCl$_4$ was added dropwise to H(t-Bu)$_2$SiSi(t-Bu)$_2$H (5.8 g, 0.020 mol) dissolved in 50 ml of CCl$_4$ at —20°C. The mixture was allowed to warm to 25°C and then stirred overnight, after which time the solution was yellow. The solvent was removed under vacuum and the residue was recrystallized from petroleum ether (30—60°C) to give 9.0 g (100%) of Br(t-Bu)$_2$SiSi(t-Bu)$_2$Br, m.p. 195—197°C. NMR (CDCl$_3$), τ 8.7. Parent ion at m/e 444. (Found: C, 43.48; H, 8.23. C$_{16}$H$_{36}$Br$_2$Si$_2$ calcd.: C, 43.27; H, 8.11%.)

Several attempts were made to dehalogenate Br(t-Bu)$_2$SiSi(t-Bu)$_2$Br in the presence of conjugated dienes as trapping agents. The following experiment is illustrative.

In a Schlenk tube, 2.0 g (4.5 mmol) of Br(t-Bu)$_2$SiSi(t-Bu)$_2$Br was dissolved in 30 ml of petroleum ether (30—60°C) and cooled to —65°C. t-Butyllithium (5.15 mmol, 0.75 M in pentane) was added dropwise over a 10 min period, but no reaction was apparent. *trans,trans*-2,4-Hexadiene (2 ml) was then added, and the mixture was allowed to warm to ambient temperature. Still no reaction was evident, so the mixture was refluxed overnight to give a slight cloudiness. However, concentrating the solution and cooling to —15°C allowed the total recovery of starting dibromide.

Similar experiments with methyllithium, n-butyllithium, and the tetramethyl-ethylenediamine complex of n-butyllithium gave identical results. Likewise, no reaction was observed between Br(t-Bu)$_2$SiSi(t-Bu)$_2$Br and lithium, sodium, or magnesium amalgams in THF, or between the dibromide and Na$_2$Fe(CO)$_4$ in THF.

Stirring (t-Bu)$_4$Si$_2$Br$_2$ (0.6 g) with excess, molten potassium in refluxing cyclohexane for 52 h gave a green mixture. Filtration of this mixture gave a blue solid and a yellow filtrate, from which a viscous polymeric material was obtained upon removing the solvent. A short-path distillation of the polymer at 93°C/0.01 Torr gave a few drops of liquid, identified as a mixture of (t-Bu)$_3$-Si$_2$H$_3$ and (t-Bu)$_3$Si$_2$H$_3$O by the GLC-mass spectral technique.

Attempted dehalogenation of ClMe$_2$GeGeMe$_2$Cl

The following experiment is illustrative of several that were performed in an attempt to dehalogenate Me$_4$Cl$_2$Ge$_2$.

Following the above procedure, 1.0 g (3.6 mmol) of Me$_4$Ge$_2$Cl$_2$, 2 ml of *trans,trans*-2,4-hexadiene, and 4.5 mmol of t-BuLi were mixed in petroleum ether at —60°C. No reaction was evident, so the mixture was allowed to warm slowly, and a precipitate formed as the temperature increased. Upon reaching room temperature, the lithium chloride was filtered off and the solvent removed from the filtrate to give a viscous oil. Short-path distillation at 85°C/0.01 Torr gave a mixture which was analyzed by GLC-mass spectrometry. The main com-

ponent was $Me_4(t\text{-}Bu)_2Ge_2$ with ca. one half as much $Me_4(t\text{-}Bu)HGe_2$. Minor amounts of $Me_4(t\text{-}Bu)ClGe_2$ and $Me_4H_2Ge_2$ were noted. The results of the GLC-mass spectral analysis were corroborated by IR and NMR analysis of the mixture.

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