

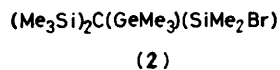
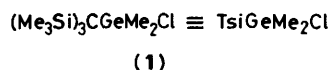
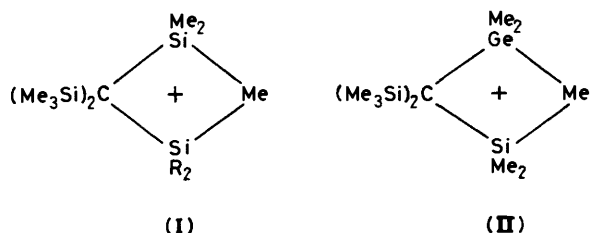
1,3-Migration of a Methyl Group from Germanium to Silicon in Reactions of $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)(\text{SiMe}_2\text{Br})$ with Silver Salts

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The compound $\text{TsiGeMe}_2\text{Cl}$ (**1**) [$\text{Tsi} = (\text{Me}_3\text{Si})_3\text{C}$] has been shown to react with AgO_2CCF_3 in $\text{CF}_3\text{CO}_2\text{H}$ and with AgBF_4 or AgO_3SCF_3 in CH_2Cl_2 to give $\text{TsiGeMe}_2\text{Y}$ ($\text{Y} = \text{O}_2\text{CCF}_3$, F , or O_3SCF_3). In contrast, reaction of $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)(\text{SiMe}_2\text{Br})$ (**2**), (i) with AgO_2CCF_3 in $\text{CF}_3\text{CO}_2\text{H}$ gives a 35:65 mixture of the unrearranged $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)(\text{SiMe}_2\text{O}_2\text{CCF}_3)$ and the rearranged $\text{TsiGeMe}_2\text{O}_2\text{CCF}_3$, (ii) with AgO_3SCF_3 in CH_2Cl_2 gives almost exclusively the rearranged $\text{TsiGeMe}_2\text{O}_3\text{SCF}_3$, and (iii) with AgBF_4 in CH_2Cl_2 gives a 70:30 mixture of unrearranged $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)(\text{SiMe}_2\text{F})$ and the rearranged $\text{TsiGeMe}_2\text{F}$. It is suggested that the reactions of (**2**) involve anchimeric assistance to leaving of Br^- by an Me group of the GeMe_3 ligand, with formation of a cationic intermediate having an Me bridge between Ge and Si . Since compound (**2**) is much more reactive towards silver salts than $\text{TsiSiMe}_2\text{Br}$ it appears that an Me group attached to Ge provides markedly more assistance than one attached to Si . The absence of rearrangement in reactions of (**1**) indicates that cationic intermediates are not formed in this case.

It was shown a few years ago that reactions of compounds of the type TsiSiR_2I [$\text{Tsi} = (\text{Me}_3\text{Si})_3\text{C}$] with electrophiles such as Ag^+ or Hg^{II} salts, ICl , or $\text{CF}_3\text{CO}_2\text{H}$ can involve rearrangement, to give wholly (e.g. $\text{R} = \text{Ph}$) or in part (e.g. $\text{R} = \text{Et}$) rearranged products of the type $(\text{Me}_3\text{Si})_2\text{C}(\text{SiR}_2\text{Me})(\text{SiMe}_2\text{Y})$.^{1,2} The reactions are thought to proceed through bridged cations of type (I), which are then attacked by a nucleophile Y^- at either



the α - or the γ -Si centre, the choice being determined largely by the relative degrees of steric hindrance at these centres.^{1,3} We considered it of interest to see whether a similar [1,3]-migration of an Me group could take place between germanium and silicon centres, and so we made the compounds $\text{TsiGeMe}_2\text{Cl}$ (**1**), and $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)(\text{SiMe}_2\text{Br})$ (**2**), and examined their reactions with silver salts. The results are presented here. (A preliminary account has appeared.⁴) Some other reactions of (**1**) are also described.

Results and Discussion

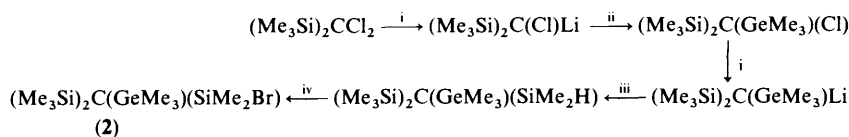
Preparation of Compounds (1) and (2).—The chloride (**1**) was prepared by reaction of TsiGeMe_3 ⁵ with ICl in CCl_4 . The bromide (**2**) was prepared by the route shown in the Scheme. It

is noteworthy that treatment of $(\text{Me}_3\text{Si})_2\text{CCl}_2$ with BuLi at low temperature followed by coupling with Me_3GeBr gave, along with the expected $(\text{Me}_3\text{Si})_2\text{C}(\text{Cl})(\text{GeMe}_3)$, a substantial amount of $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)_2$.

Reactions with Silver Salts.—The reaction of (**1**) with AgBF_4 in CH_2Cl_2 was found to give exclusively the unrearranged fluoride $\text{TsiGeMe}_2\text{F}$; the presence of only one signal in the ^{19}F n.m.r. spectrum was strong evidence that very little, if any, of the rearranged species $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)(\text{SiMe}_2\text{F})$ was formed. Likewise, the reactions of (**1**) with AgO_2CCF_3 in $\text{CF}_3\text{CO}_2\text{H}$ and with AgO_3SCF_3 in CH_2Cl_2 gave only the unrearranged $\text{TsiGeO}_2\text{CCF}_3$ and $\text{TsiGeO}_3\text{SCF}_3$, respectively. (In each case the product gave only one signal in the ^{19}F n.m.r. spectrum). No reaction took place when (**1**) was treated in CH_2Cl_2 with AgOCN (under reflux) or AgNO_3 (at room temperature).

In contrast, when the bromide (**2**) was treated with AgBF_4 in CH_2Cl_2 , the product was found to be an *ca.* 70:30 mixture of the unrearranged $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)(\text{SiMe}_2\text{F})$ and the rearranged $\text{TsiGeMe}_2\text{F}$ in the following ways: (a) linked g.l.c.-mass spectrometry gave two peaks, in 70:30 area ratio, both giving mass spectra consistent with the proposed formulae, with the minor component having a retention time identical with that of authentic $\text{TsiGeMe}_2\text{F}$; (b) the ^{19}F n.m.r. spectrum showed two septets in *ca.* 30:70 integration ratio, the first centred at $\delta_{\text{F}} - 144.4$ p.p.m., assignable to $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)(\text{SiMe}_2\text{F})$ [*cf.* the value of -138.0 p.p.m. for $(\text{Me}_3\text{Si})_2\text{C}(\text{SiPh}_2\text{Me})(\text{SiMe}_2\text{F})$], and the second at $\delta - 176.1$ p.p.m., identical with that for an authentic sample of $\text{TsiGeMe}_2\text{F}$; (c) the ^1H n.m.r. spectrum was as expected for a 70:30 mixture of the two fluorides, and the set of peaks of lower intensity coincided with that from an authentic sample of $\text{TsiGeMe}_2\text{F}$.

Reaction of (**2**) with AgO_2CCF_3 in $\text{CF}_3\text{CO}_2\text{H}$ likewise gave a mixture of unrearranged and rearranged products, $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)(\text{SiMe}_2\text{O}_2\text{CCF}_3)$ and $\text{TsiGeMe}_2\text{O}_2\text{CCF}_3$, but in a *ca.*



Scheme. Reagents and conditions: i, BuLi -THF- Et_2O -light petroleum, -110°C ; ii, Me_3GeBr ; iii, Me_2SiHCl ; iv, Br_2 - CCl_4

35:65 ratio, as shown by ^1H and ^{19}F n.m.r. spectroscopy and linked g.l.c.—mass spectrometry; authentic samples of both products were available. (We should note that the examination of the product mixture was made on material isolated by sublimation, and it is conceivable that the isomer ratio before sublimation would have been somewhat different, but we think this is unlikely).

Reaction of (2) with AgO_3SCF_3 in CH_2Cl_2 gave very predominantly the rearranged $\text{TsiGeMe}_2\text{O}_3\text{SCF}_3$; the ^1H and ^{19}F n.m.r. spectra were identical with those of an authentic sample except for the presence of small additional peaks which can reasonably be attributed to the presence of a little (< 5%) of the unrearranged $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)(\text{SiMe}_2\text{O}_3\text{SCF}_3)$; again the analysis was carried out on sublimed product.

It is evident from the reactions of (2) that the migration of an Me group from Ge to Si can indeed occur, and this can be assumed to involve the bridged cation (II). It is noteworthy that $\text{TsiSiMe}_2\text{Br}$ is inert towards AgBF_4 and AgO_3SCF_3 under the conditions used for reactions of (2), and so it seems that anchimeric assistance by an Me group attached to a γ -Ge is greater than that by one attached to a γ -Si, which would be consistent with the fact that the Me-Ge is weaker than the Me-Si bond.

It appears that once the cation (II) is formed, attack of the nucleophile Y^- takes place predominantly at Ge for $\text{Y} = \text{O}_2\text{CCF}_3$ and O_3SCF_3 , but mainly at Si for $\text{Y} = \text{F}$. Presumably, the lower steric hindrance at the Ge centre normally favours attack there (the compounds $\text{TsiGeMe}_2\text{X}$ are known to be more reactive towards nucleophiles than the corresponding $\text{TsiSiMe}_2\text{X}$ species,⁶ even though nucleophilic attack at germanium is usually slower than at silicon in the absence of serious steric hindrance), but in the case of attack of F^- the very high energy of the Si-F bond favours its formation rather than that of the weaker Ge-F bond.

The absence of rearrangement in the reaction of (1) with silver salts, especially in the reaction with AgBF_4 , indicates that these reactions do not proceed through an intermediate cation (II). We assume that this is because such reactions do not require anchimeric assistance (it is noteworthy that $\text{TsiSiMe}_2\text{Cl}$ is inert towards the silver salts under the conditions used), and presumably do not involve a cationic intermediate, attack of Y^- possibly being synchronous with removal of X^- by Ag^+ ; the lower steric hindrance around the Ge centre could permit such a process, which is inhibited at an analogous silicon centre.

Reaction of Compound (1) with NaOMe.—The silicon chloride $\text{TsiSiMe}_2\text{Cl}$ reacts with 2.0M-NaOMe-MeOH upon prolonged reflux to give $(\text{Me}_3\text{Si})_2\text{CHSiMe}_2\text{OMe}$, apparently *via* the sila-alkene $(\text{Me}_3\text{Si})_2\text{C}=\text{SiMe}_2$,⁷ and it was of interest to see whether the germanium analogue, (1), would undergo a similar reaction [a corresponding elimination, to give initially $(\text{Me}_3\text{Si})_2\text{C}=\text{GePh}_2$, is thought to occur when $\text{TsiGePh}_2\text{Cl}$ is treated with CsF in diethyleneglycol dimethyl ether (diglyme)⁸].

No reaction was observed when a solution of (1) in MeOH was kept at 60 °C for 15 days. [When water-MeOH (2% v/v) was used as the solvent there was < 10% reaction in 70 days.] When 0.10M-NaOMe-MeOH was used as the solvent, reaction was *ca.* 40% complete after 24 h, 55% after 48 h, and 85% after 170 h, and the product was solely the methoxide $\text{TsiGeMe}_2\text{OMe}$; these results are consistent with those previously reported for reaction at the reflux temperature except that the latter gave small amounts of other products.⁵ When 2.0M-NaOMe-MeOH was used, this methoxide was again the sole product after 48 h at 50 °C.

Thermolysis of Compound (1).—We examined the thermal decomposition of (1) because of the possibility that there might be loss of Me_3SiCl to give $(\text{Me}_3\text{Si})_2\text{C}=\text{GeMe}_2$ as an

intermediate (*cf.* the loss of Me_3SiF from $\text{TsiSiPh}_2\text{F}^9$), although the mass spectrum indicates that under electron impact Me_3GeCl is lost more readily than Me_3SiCl (see the Experimental section). When a sample of (1) was kept in a sealed tube at 350 °C for 12 h substantial change occurred. Analysis by linked g.l.c.—mass spectrometry revealed the presence of five components, A—E (with well separated peaks) in a *ca.* 20:10:20:20:30 ratio. The mass spectrum of A was consistent with its being TsiH , and that of B was consistent with the chloride $(\text{Me}_3\text{Si})_2\text{CH}(\text{GeMe}_2\text{Cl})$ or an isomer of it, and it is noteworthy that this chloride would probably be produced by interaction of HCl and $(\text{Me}_3\text{Si})_2\text{C}=\text{GeMe}_2$ if these species were formed. Components C, D, and E all had the peak of the highest m/z value at 355, corresponding to loss of Me from (2) or its isomers. The retention time of D was the same as that for an authentic sample of (1), and the peaks from that starting material were evident in the ^1H n.m.r. spectrum. It is likely that either C or E is the isomer $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)(\text{SiMe}_2\text{Cl})$ produced by interchange of Me and Cl ligands between Si and Ge, and the appearance of a peak in the ^1H n.m.r. spectrum at δ 0.62 is consistent with this (*cf.* δ 0.64 for $\text{TsiSiMe}_2\text{Cl}$) but the presence of a third isomer indicates that a more complex rearrangement also occurs.

Experimental

Mass spectra were obtained by electron impact at 70 eV. For linked g.l.c.—mass spectrometry columns of OV-101 were used; m/z values for bromine-containing ions refer to the ^{79}Br isotope; isotope patterns were as expected.

Solutions in CDCl_3 were used for recording ^1H and ^{19}F n.m.r. spectra; ^{19}F chemical shifts are relative to external CFCl_3 . Melting points were obtained with samples in sealed capillaries.

Preparation of TsiGeMe₂Cl. (1).—A solution of ICl (17.1 mmol) in CCl_4 (5 cm^3) was added to one of TsiGeMe_3 ⁵ (5.7 mmol) in the same solvent, and the mixture was stirred for 30 min at room temperature. The solvent and excess of halogen were removed under reduced pressure, and the residue was sublimed (100 °C at 0.01 mmHg) to give *dimethyl[tris(trimethylsilylmethyl)]germyl chloride* (91%), m.p. > 340 °C (Found: C, 39.2; H, 8.7. Calc. for $\text{C}_{12}\text{H}_{33}\text{ClGeSi}_3$: C, 39.0, H, 8.9%); m/z 355 [30%, ($M^+ - \text{Me}$)], 335 [5, ($M^+ - \text{Cl}$)], 247 [10, ($M^+ - \text{Me}_3\text{SiCl} - \text{Me}$)], 221 [15, ($M^+ - \text{Me}_4\text{Ge} - \text{Me}$)], 201 [95, ($M^+ - \text{Me}_3\text{GeCl} - \text{Me}$)], and 73 [100, (Me_3Si)⁺]; δ_{H} 0.28 (27 H, s, Me_3Si) and 0.90 (6 H, s, GeMe_2) (lit.,⁵ δ_{H} 0.38 and 0.95).

Reactions of (1) with Silver Salts.—(a) A solution of (1) (0.27 mmol) in CH_2Cl_2 (10 cm^3) was boiled under reflux with AgBF_4 (0.81 mmol) for 30 min. The solution was filtered and evaporated to dryness, and the residue was sublimed (100 °C at 0.05 mmHg) to give *dimethyl[tris(trimethylsilyl)methyl]germyl fluoride* (76%), m.p. 285 °C (Found: C, 40.7; H, 9.3. $\text{C}_{12}\text{H}_{33}\text{FGeSi}_3$ requires C, 40.7; H, 9.3%); δ_{H} 0.19 (27 H, s, SiMe_3) and 0.66 (6 H, d, J 7 Hz, GeMe_2); δ_{F} -176.1 p.p.m. (septet); m/z 339 [30%, ($M^+ - \text{Me}$)], 247 [20, ($M^+ - \text{Me}_3\text{SiF} - \text{Me}$)], 205 [100, ($M^+ - \text{Me}_4\text{Ge} - \text{Me}$)], and 73 (100).

(b) A solution of (1) (0.27 mmol) and AgO_2CCF_3 (0.52 mmol) in $\text{CF}_3\text{CO}_2\text{H}$ (10 cm^3) was stirred at room temperature for 1 h, then filtered. The solvent was removed under reduced pressure and the residue was sublimed (100 °C at 0.05 mmHg) to give *dimethyl[tris(trimethylsilyl)methyl]germyl trifluoroacetate* (85%), m.p. 208 °C (Found: C, 37.4; H, 7.4. $\text{C}_{14}\text{H}_{33}\text{F}_3\text{GeO}_2\text{Si}_3$ requires C, 37.5; H, 7.4%); δ_{H} 0.25 (27 H, s, Me_3Si) and 0.95 (6 H, s, GeMe_2); δ_{F} -76.1 p.p.m. (s); δ_{Si} -0.63 p.p.m.; m/z 433 [70%, ($M^+ - \text{Me}$)], 335 [15, ($M^+ - \text{O}_2\text{CCF}_3$)], 311 [20, ($M^+ - \text{O}_2\text{CCF}_3 - \text{Me}^+$)], 247 [20, ($M^+ - \text{Me}_3\text{SiO}_2\text{CCF}_3 - \text{Me}$)], 205 (80), and 73 (100).

(c) When a solution of (1) (0.27 mmol) in CH_2Cl_2 (10 cm^3) was stirred with AgO_3SCF_3 (0.54 mmol) at room temperature for 20 h, ^1H n.m.r. spectroscopy indicated that no reaction had occurred. The mixture was then boiled under reflux for 8 days, after which the solution was filtered and evaporated to dryness under reduced pressure. The residue was sublimed (100 °C at 0.01 mmHg) to give *dimethyl[tris(trimethylsilyl)methyl]germyl trifluoromethanesulphonate* (85%), m.p. 202 °C (Found: C, 32.5; H, 7.1. $\text{C}_{13}\text{H}_{33}\text{F}_3\text{GeO}_3\text{Si}_3$ requires C, 32.2; H, 6.8%; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.27 (27 H, s, Me_3Si) and 1.08 (6 H, s, Me_2Ge); δ_{F} -76.4 p.p.m. (s); m/z 469 [25%, ($M^+ - \text{Me}$)], 335 [15, ($M^+ - \text{O}_3\text{SCF}_3$)], 319, 247, 201 [15, ($M^+ - \text{Me}_3\text{GeO}_3 - \text{SCF}_3 - \text{Me}$)], and 73 (100).

Preparation of $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)\text{Cl}$.—A solution of $(\text{Me}_3\text{Si})_2\text{CCl}_2$ (16 g, 0.070 mol) in a mixture of THF (10 cm^3), Et_2O (35 cm^3), and light petroleum (b.p. 30–40 °C) (10 cm^3) was cooled to -110 °C (internal temperature) under nitrogen and a solution of BuLi (0.069 mol) in hexane (46 cm^3) cooled to -80 °C, was added dropwise with stirring during 1 h. The temperature of the mixture was then allowed to rise to -80 °C and Me_3GeBr (13 g, 0.065 mol) was added dropwise with stirring. The stirred mixture was then allowed to warm to room temperature and set aside overnight. Careful treatment with ice-cold saturated aqueous NH_4Cl was followed by separation, washing, drying (MgSO_4), and evaporation of the organic layer. Methanol was added to the residue, and the mixture was shaken and then kept at -20 °C overnight. The solid was filtered off, and seemed from its ^1H n.m.r. spectrum to be an 85:15 mixture of two components. A solid was sublimed out (45 °C at 0.001 mmHg) and identified as *chloro(trimethylgermyl)bis(trimethylsilyl)methane* (10.1 g, 60%), m.p. 135 °C (Found: C, 38.6; H, 8.8. $\text{C}_{10}\text{H}_{27}\text{ClGeSi}_2$ requires C, 38.5; H, 8.65%; δ_{H} 0.15 (18 H, s, Me_3Si) and 0.31 (9 H, s, Me_3Ge); m/z 312 (1%, M^+), 297 [5, ($M^+ - \text{Me}$)], 178 [6, ($M^+ - \text{Me}_4\text{Ge}$)], 143 [20, ($M^+ - \text{Me}_3\text{GeCl} - \text{Me}$)], 119 [75, (Me_3Ge) $^+$], and 73 (100). The residue left after sublimation was recrystallized from MeOH, then tentatively identified by linked g.l.c.-mass spectrometry as $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)_2$ [m/z 379 [40%, ($M^+ - \text{Me}$)], 247 [20, ($M^+ - \text{Me}_4\text{Ge} - \text{Me}$)], 119 (30), and 73 (100)].

When the experiment was repeated on a smaller scale [$(\text{Me}_3\text{Si})_2\text{CCl}_2$ (1.6 g) and Me_3GeBr (1.3 g)], the initial product mixture was examined by linked g.l.c.-mass spectrometry and shown to be composed of (probably) $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)\text{Cl}$ (60%), $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)_2$ (30%), and $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)\text{H}$ (10%); the last component had m/z 263 [100%, ($M^+ - \text{Me}$)], 129 [80, ($M^+ - \text{Me}_4\text{Ge} - \text{Me}$)], 119 (40), and 73 (Me_3Si).

Preparation of $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)(\text{SiMe}_2\text{H})$.—A mixture of $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)\text{Cl}$ (5 g, 0.016 mol), THF (100 cm^3), Et_2O (35 cm^3), and pentane (10 cm^3) was cooled to -110 °C (internal temperature) under nitrogen and BuLi (0.016 mol) in hexane (10.7 cm^3) cooled to -80 °C was added dropwise during 30 min. The mixture was subsequently stirred at -110 °C for 30 min then allowed to warm to -80 °C. A solution of Me_2SiHCl (1.5 g, 0.016 mol) in THF (5 cm^3) was added dropwise, with stirring and the stirred mixture was allowed to warm to room temperature overnight then treated with an excess of saturated ice-cold aqueous NH_4Cl . The organic layer was separated, washed, and dried (MgSO_4), and the solvent was removed under reduced pressure. The ^1H n.m.r. spectrum of the residue suggested that it was a mixture of two components in 60:40 ratio, and this was confirmed by g.l.c. Sublimation (45 °C at 0.005 mmHg) gave unchanged $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)\text{Cl}$ and left a residue which was recrystallized from pentane to give *(trimethylgermyl)(dimethylsilyl)bis(trimethylsilyl)methane* (2.50 g, 46%), m.p. 201 °C (Found: C, 42.8; H, 9.7. $\text{C}_{12}\text{H}_{34}\text{GeSi}_3$ requires C, 42.85; H, 10.1%; δ_{H} 0.18 (18 H, s, SiMe_3), 0.26 (6 H,

d, J 4 Hz, SiMe_2H), 0.36 (9 H, s, GeMe_3), and 4.08 (1 H, m, SiMe_2H); m/z 335 [5%, $M^+ - \text{H}$], 321 [40, ($M^+ - \text{Me}$)], 247 [10, ($M^+ - \text{Me}_2\text{SiH} - \text{Me}$)], 217 [10, ($M^+ - \text{Me}_3\text{Ge}$)], 201 [60, ($M^+ - \text{Me}_3\text{GeH} - \text{Me}$)], 187 [45, ($M^+ - \text{Me}_4\text{Ge} - \text{Me}$)], and 73 (100).

Preparation of $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)(\text{SiMe}_2\text{Br})$ (2).—A solution of Br_2 (2.00 mmol) in CCl_4 (2 cm^3) was added with stirring to one of $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)(\text{SiMe}_2\text{H})$ (0.21 g, 0.63 mmol) in CCl_4 (2 cm^3). The mixture was stirred for 5 min, the solvent was removed under reduced pressure, and the residue was recrystallized from pentane to give the *title compound* (2) (0.23 g, 88%), m.p. 234 °C (Found: C, 35.1; H, 8.3. $\text{C}_{12}\text{H}_{33}\text{BrGeSi}_3$ requires C, 34.8; H, 8.0%; δ_{H} 0.30 (18 H, s, SiMe_3), 0.48 (9 H, s, GeMe_3), and 0.76 (6 H, s, SiMe_2Br); m/z 399 [50, ($M^+ - \text{Me}$)], 335 [5, ($M^+ - \text{Br}$)], 265 [20, ($M^+ - \text{Me}_4\text{Ge} - \text{Me}$)], 201 [95, ($M^+ - \text{Me}_3\text{GeBr} - \text{Me}$)], 129 (10), and 73 (100).

Reactions of Compound (2) with Silver Salts.—(a) A solution of (2) (0.24 mmol) in CH_2Cl_2 (25 cm^3) was stirred with AgBF_4 (0.97 mmol) at room temperature for 12 h. The solution was then filtered and evaporated, and the residue was sublimed (100 °C at 0.01 mmHg). The ^{19}F spectrum of the product showed two septets, centred at δ -144.4 and -176.1 p.p.m., in ca. 70:30 height ratio; the latter septet was assigned to $\text{TsiGeMe}_2\text{F}$ by comparison with that from an authentic sample (see above), and the former to $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)(\text{SiMe}_2\text{F})$ by comparison with that at δ -138.0 p.p.m. for $(\text{Me}_3\text{Si})_2\text{C}(\text{SiPh}_2\text{Me})(\text{SiMe}_2\text{F})$. The ^1H n.m.r. spectrum was also consistent with a 70:30 mixture of $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)(\text{SiMe}_2\text{F})$ [δ_{H} 0.21 (18 H, s, SiMe_3), 0.335 (6 H, d, SiMe_2F), and 0.41 (9 H, s, GeMe_3)] and $\text{TsiGeMe}_2\text{F}$ (for δ_{H} see above).

(b) Silver oxide (0.17 mmol) was dissolved in $\text{CF}_3\text{CO}_2\text{H}$ (10 cm^3) and compound (2) (0.096 mmol) was added. The mixture was stirred for 24 h at room temperature (reaction may have been complete in a much shorter time) then filtered. The filtrate was evaporated and the residue sublimed (100 °C at 0.01 mmHg). The product was judged from its n.m.r. spectra to be a ca. 65:35 mixture of $\text{TsiGeMe}_2\text{O}_2\text{CCF}_3$ [δ_{H} 0.255 (27 H, s, SiMe_3) and 0.95 (6 H, s, GeMe_2); δ_{F} -76.0 p.p.m.] and $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)(\text{SiMe}_2\text{O}_2\text{CCF}_3)$ [δ_{H} 0.23 (18 H, s, SiMe_3), 0.41 (9 H, s, GeMe_3), and 0.58 (6 H, s, SiMe_2); δ_{F} -76.2]. Analysis by linked g.l.c.-mass spectrometry confirmed the presence of two isomeric components in ca. 65:35 ratio; both gave the expected $M^+ - \text{Me}$ peak at m/z 433. The elemental analysis of the product was consistent with a mixture of the isomers (Found: C, 37.2; H, 7.7. Calc. for $\text{C}_{14}\text{H}_{33}\text{F}_3\text{GeO}_2\text{Si}_3$: H, 37.5; H, 7.4%).

(c) A solution of compound (2) (0.042 mmol) in CH_2Cl_2 (10 cm^3) was stirred with AgO_3SCF_3 (0.40 mmol) for 48 h at room temperature. The solution was filtered then evaporated, and the residue was sublimed (100 °C at 0.01 mmHg). The product was judged from its ^1H and ^{19}F n.m.r. spectra to be predominantly (>90%) $\text{TsiGeMe}_2\text{O}_3\text{SCF}_3$ (data for an authentic sample are given above). There were very small additional signals in the ^1H n.m.r. spectrum consistent with the presence of a little unchanged (2) (δ 0.26 and 0.68) and possibly $(\text{Me}_3\text{Si})_2\text{C}(\text{GeMe}_3)(\text{SiMe}_2\text{O}_3\text{SCF}_3)$ (δ 0.34 and 0.45), and the ^{19}F n.m.r. spectrum showed a small signal (4% of the main signal) at δ -75.8 p.p.m. which could have arisen from the latter compound. The mass spectrum of the product was effectively identical with that of authentic $\text{TsiGeMe}_2\text{O}_3\text{SCF}_3$ (see above) except for the appearance of two peaks of equal height, at m/z 399 and 401 ($M^+ - \text{Me}$), which could be attributed to the presence of a little unchanged (2).

Reaction of Compound (2) with MeOH and NaOMe-MeOH.—(a) A solution of (2) (0.04 mmol) in a drop of CCl_4 (ca.

0.02 cm³) was diluted with MeOH (0.5 cm³) in an n.m.r. tube, which was sealed and placed in a bath at 60 °C. No change in the ¹H n.m.r. spectrum was observed during 15 days.

(b) The procedure described in (a) was repeated but with 0.01M-NaOMe-MeOH. Monitoring of the ¹H n.m.r. spectrum showed that no detectable reaction had occurred after 1 h, but after 24, 48, and 168 h the conversion into TsiGeMe₂OMe (the sole product) was respectively 40, 56, and 85% complete.

(c) A solution of (2) (0.27 mmol) in 2.0M-NaOMe-MeOH (15 cm³) was kept at 50 °C for 48 h. An excess of water was added, and the organic material was extracted with CH₂Cl₂. The extract was separated, washed, dried (MgSO₄), and evaporated, and the residual solid identified as TsiGeMe₂OMe, from its ¹H n.m.r. spectrum [δ_{H} 0.23 (27 H, s), 0.56 (6 H, s), and 3.40 (3 H, s); the values are not significantly different from those previously reported⁵]. A sample after sublimation (100 °C at 0.01 mmHg) had m.p. 250 °C (lit.,⁵ 250–251 °C).

Thermolysis of Compound (1).—A sample of (1) (0.14 mmol) was sealed in a small glass tube, which was kept in a sand-bath at 350 °C for 12 h. The contents of the tube were then taken up in CHCl₃. Analysis of the CHCl₃ solution by linked g.l.c.-mass spectrometry revealed the presence of five components A–E (in order of retention time) in a ca. 20:10:20:20:30 ratio. The mass spectrum of A was identical with that of TsiH [m/z 217 ($M^+ - \text{Me}$)] and that of B was consistent with its being from (Me₃Si)₂CH(GeMe₂Cl) or an isomer [m/z 283 [50%, ($M^+ - \text{Me}$)], 129 [100, ($M^+ - \text{Me}_3\text{GeCl} - \text{Me}$)]]. Components C, D, and E gave very similar spectra, each consistent with (Me₃Si)₂C(GeMe₃)(SiMe₂Cl) or TsiGeMe₂Cl or their isomers [m/z 355 ($M^+ - \text{Me}$)], but that of D was essentially identical with that from an authentic sample of (1). The ¹H

n.m.r. spectrum of the solution showed many signals in the range δ 0.0–1.0, but the presence of peaks from (2) could be clearly distinguished. A peak at δ 0.62 could reasonably be attributed to an SiMe₂Cl group (cf. δ 0.64 for SiMe₂Cl in TsiSiMe₂Cl).

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