The Effect of the γ-OMe Group on the Reactivity of the Germanium Chloride $(Me_3Si)_2C(SiMe_2OMe)(GeMe_2Cl)$

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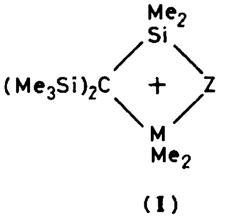
The germanium chloride $(Me_3Si)_2C(SiMe_2OMe)(GeMe_2Cl)$ (**2a**) has been found to be much more reactive than the related chloride $(Me_3Si)_3C(GeMe_2Cl)$ (**1**) towards silver salts. The compound $(Me_3Si)_2C(SiMe_2OMe)(GeMe_3)$ is correspondingly much more reactive than $(Me_3Si)_3C(GeMe_3)$ towards CF_3CO_2H. These findings are consistent with anchimeric assistance by the γ-OMe group to leaving of Cl^- or Me^-, but a firm conclusion that such an effect operates was prevented by the finding that (**2a**) is also much more reactive than (**1**) towards NaOMe–MeOH. The methanolysis of (**2a**) in NaOMe–MeOH differs mechanistically from that of the analogous silicon chloride $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Cl)$.

It is believed that reactions of compounds of the type $TsiSiMe_2X$ (*e.g.* X = H) [Tsi = $(Me_3Si)_3C$ throughout] with electrophiles, such as Ag^I or Hg^{II} salts, ICl, and CF_3CO_2H, proceed through Me-bridged cations of type (I; M = Si, Z = Me], the Me γ to the Si–X bond providing anchimeric assistance to the leaving of X^-.[1–3] In contrast, for the reactions of $TsiGeMe_2Cl$ (**1**) with silver salts an alternative mechanism appears to be favoured, and a cationic intermediate is not involved, and thus there is no anchimeric assistance by an Me group on a γ-Si atom.[4] [There does, however, appear to be such assistance by an Me group on the γ-Ge atom in reactions of $(Me_3Si)_2C(GeMe_3)(SiMe_2Br)$ with silver salts, which are thought to involve cations (I; M = Ge, Z = Me)[4]]. It is known that the γ-OMe group [*e.g.* in reactions of $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Cl)$] can provide much more powerful assistance than a γ-Me group in reactions with Ag^I salts;[5,6] it thus seemed of interest to explore the possibility that a γ-OMe group on Si would provide significant anchimeric assistance to reactions at a Ge centre, and so we prepared and studied the germanium chloride (**2a**). The latter was, in fact, found to be much more reactive than (**1**) towards Ag^I salts, but this could not be confidently attributed to the postulated anchimeric assistance because (**2a**) was also found to be much more reactive than (**1**) in reaction with MeONa–MeOH, which would not be expected to involve a cationic intermediate.



(I)

$TsiGeMe_2Cl$ [Tsi = $(Me_3Si)_3C$]

(**1**)

$(Me_3Si)_2C(SiMe_2OMe)(GeMe_2X)$

(**2**)

a; X = Cl

Results and Discussion

Compound (**2a**) was rapidly formed on treatment of (**2**; X = Me) with ICl in CCl_4; the bromide (**2**; X = Br) was made analogously by use of Br_2. Compound (**2**; X = Me) was itself obtained by treatment (with Me_3GeBr) of the organolithium reagent $(Me_3Si)_2C(Li)(SiMe_2OMe)$ made by metallation of $(Me_3Si)_2C(Cl)(SiMe_2OMe)$[7,8] at low temperature.

The reactivities of (**1**) and (**2a**) were first compared in reactions with AgOCN. No reaction occurred when a mixture of (**1**) (0.34 mmol), AgOCN (1.0 mmol), and CH_2Cl_2 (10 cm^3) was stirred at room temperature for 460 h then boiled under reflux for 92 h. In contrast, when (**2a**) was used the reaction was complete within 2 h at room temperature, and (**2**; X = NCO) was isolated in 90% yield. The ^1H and ^{29}Si n.m.r. spectra of the product indicated that no rearrangement had taken place; the smaller ^{29}Si signal at 15.7 p.p.m. was at the position expected for an $SiMe_2OMe$ group [*cf.* δ_{Si} 14.8 p.p.m. in (**2**; X = Me)] but not that expected for $SiMe_2NCO$ (*cf.* δ_{Si} 0.13 p.p.m. in $TsiSiMe_2NCO$[9]), and the ^1H signal for the MMe_2OMe protons (δ 0.28) was at a position expected for $SiMe_2OMe$ [*cf.* δ 0.26 in (**2a**)] but not consistent with $GeMe_2OMe$ (*cf.* δ 0.56 in $TsiGeMe_2OMe$). The n.m.r. and i.r. data pointed to the presence of a GeNCO rather than a GeOCN grouping. It is evident that (**2a**) is >1 000 times as reactive as (**1**), which is what would be expected if there were substantial assistance by the γ-OMe group.

A similar result was obtained in the reactions of (**1**) and (**2a**) with AgO_3SCF_3 in CH_2Cl_2. With (**1**) there was no detectable reaction in 20 h at room temperature (though conversion into $TsiGeMe_2O_3SCF_3$ was effectively complete after an additional 196 h refluxing[4]), whereas with (**2a**) *ca.* 40% of the starting material disappeared within 10 min at room temperature, and reaction was complete within 180 min, so that (**2a**) is >500 times as reactive as (**1**). The identification of the products from (**2a**) was not straightforward (but this does not invalidate the observations on relative reactivities). Thus, when the reaction was carried out in a closed (but not rigorously sealed) n.m.r. tube, the ^1H n.m.r. spectrum of the solution after complete disappearance of (**2a**) apparently consisted of two sets of peaks in *ca.* 3:2 height ratio, both sets seemingly from Me_3Si, Me_2SiX, Me_2GeY, and OMe groupings in 2:1:1:1 ratio (*i.e.* with protons in 6:2:2:1 ratio). The chemical shifts for either set were consistent with assignment to the expected product (**2**; X = O_3SCF_3) [but not with that for the rearranged isomer $(Me_3Si)_2C(SiMe_2O_3SCF_3)(GeMe_2OMe)$], and it seems likely that the other set came from the hydroxide $(Me_3Si)_2C(SiMe_2OH)(GeMe_2O_3SCF_3)$ arising from the reaction of traces of water on the initial product, with the OMe peak associated with this set actually coming from MeOH (or, *e.g.* MeO_3SCF_3) produced in equivalent amount by the hydrolysis. G.l.c. gave only one broad peak. The mass spectrum of the mixture was complex, but the presence of a little $(Me_3Si)_2C(SiMe_2O_3SCF_3)(GeMe_2O_3SCF_3)$ was suggested by the appearance of a small peak at *m/z* 603 (M^+ − Me), and there was a prominent peak at *m/z* 321 which could have come from $(Me_3Si)_2C(SiMe_2OH)(GeMe_2O_3SCF_3)$ (by loss of CF_3SO_3H

to give $(Me_3Si)_2\overline{CSiMe_2OGe}Me_2$, which then loses an Me group).

Following a reaction on a larger scale, filtration and evaporation of the solution followed by sublimation of the residue left a solid which appeared to be a single compound, showed only one peak in the ^{19}F n.m.r. spectrum, and gave a set of peaks in the ^1H n.m.r. spectrum effectively coincident with the larger of the sets of peaks noted in the n.m.r. scale experiment except for the absence of the OMe signal, and so it is believed to be $(Me_3Si)_2C(SiMe_2OH)(GeMe_2O_3SCF_3)$, presumably formed during work up from (**2**; X = O_3SCF_3). The seemingly great ease of replacement of the OMe group of (**2**; X = O_3SCF_3) by OH may well arise from substantial anchimeric assistance by the O_3SCF_3 group attached to Ge [compare the very high reactivity of $(Me_3Si)_2C(SiMe_2O_3SCF_3)_2$ in methanolysis],[10] coupled with acid catalysis by traces of CF_3SO_3H.

It is known that, apparently because of anchimeric assistance by the OMe group, $TsiSiMe_2OMe$ reacts rapidly with CF_3CO_2H at room temperature to give $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2O_2CF_3)$ [and hence $(Me_3Si)_2C(SiMeO_2CCF_3)_2$] whereas $TsiSiMe_3$ is inert even on prolonged reflux.[11] It was thus of interest to examine the behaviour of $(Me_3Si)_2C(SiMe_2OMe)(GeMe_3)$, *i.e.* (**2**; X = Me), and $TsiGeMe_3$ towards the acid.

When a solution of $TsiGeMe_3$ in CF_3CO_2H was kept at room temperature for 24 h the ^1H n.m.r. spectrum showed no change. The solution was then boiled under reflux; the change in the ^1H n.m.r. spectrum indicated that two products (*A*) and (*B*) were formed; after 12 h *ca.* 15% of the starting material had reacted, with (*A*) the only detectable product, but after 24 h *ca.* 50% had reacted to give (*A*) and (*B*) in 70:30 ratio, and after 72 h >95% had reacted to give (*A*) and (*B*) in 45:55 ration. (Thus, puzzlingly, the reaction appeared to speed up as it progressed, and the ratio of (*A*) to (*B*) seemed to change substantially.) Work-up (including sublimation, which probably did not significantly affect the composition) gave a solid mixture, whose ^1H n.m.r. spectrum showed the same two sets of peaks in 45:55 ratio. The smaller set was assigned to the expected $TsiGeMe_2O_2CF_3$, and the larger set to its isomer $(Me_3Si)_2C(SiMe_2O_2CCF_3)(GeMe_3)$. The ^{19}F n.m.r. spectrum showed (along with several very small peaks) two large closely spaced peaks in 45:55 ratio, as expected for the two isomers. Linked g.l.c.–mass spectrometery also revealed the presence of two main components (and several very minor components, one of which was the starting material), which gave mass spectra containing the same ions but in somewhat different relative abundances, both consistent with either of the isomeric products.

We had expected that $TsiGeMe_3$ would be attacked by the acid much more readily than $TsiSiMe_3$ (we confirmed that the latter underwent no reaction in 72 h under reflux), since Ge–Me are normally much more reactive than Si–Me bonds towards electrophiles, but it was surprising that cleavage of the Si–Me bonds of the $TsiGeMe_3$ competed effectively with that of the Ge–Me bonds. The cleavage of an Si–Me bond of $TsiGeMe_3$ can reasonably be attributed to anchimeric assistance by an Me group attached to Ge.[4]

As expected, (**2**; X = Me) reacted much more readily with CF_3CO_2H, reaction being complete within 1 h at room temperature. The product after work-up showed many peaks at δ 0.0—1.0 (but none in the OMe region), but one dominant set of peaks was judged to be from the bis(trifluoroacetate) $(Me_3Si)_2C(SiMe_2O_2CF_3)(GeMe_2O_2CF_3)$, and the appearance of two greatly dominant closely spaced peaks in the ^{19}F n.m.r. spectrum was consistent with this. Linked g.l.c.–mass spectrometry confirmed the presence of one dominant component, representing >80% of the mixture, and its mass spectrum was consistent with the proposed formula. The observed product is doubtless formed *via* (**2**; X = O_2CCF_3), in which the O_2CCF_3 group on Ge would provide anchimeric assistance to loss of OMe from Si — *cf.* the formation of $(Me_3Si)_2C(SiMe_2O_2CCF_3)_2$ from $TsiSiMe_2OMe$ *via* $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2O_2CCF_3)$.[11]

The observations that (**2a**) is much more reactive than (**1**) towards silver salts and $(Me_3Si)_2C(SiMe_2OMe)(GeMe_3)$ much more reactive than $TsiGeMe_3$ towards CF_3CO_2H can be most simply explained in terms of anchimeric assistance by the OMe group. However, two features cast some doubt on this interpretation. First if a methoxy-bridged cation (**I**; M = Ge, Z = OMe) were involved in the reactions with silver salts AgY, the formation of some rearranged product $(Me_3Si)_2C(SiMe_2Y)(GeMe_2OMe)$ might reasonably be expected, as a result of attack of Y^- at the silicon end of the bridge, just as the intermediacy of the analogous methyl-bridged cation (**I**; M = Ge, Z = Me) leads to a mixture of unrearranged and rearranged products, $(Me_3Si)_2C(SiMe_2Y)(GeMe_3)$ and $TsiGeMe_2Y$, in reactions of $(Me_3Si)_2C(GeMe_3)(SiMe_2Br)$.[4] (It is conceivable, however, that the γ-OMe group on Si can stabilize a partly positively-charged Ge centre in the transition state by electrostatic interaction between that centre and the oxygen lone pairs without formation of an actual intermediate.) Secondly, (**2a**) has also been found, as described below, to be much more reactive than (**1**) in reaction with the nucleophilic system NaOMe–MeOH.

When solutions of (**1**) or (**2a**) in MeOH were kept at 60 °C, <10% reaction took place in 70 days. In 0.10M-NaOMe–MeOH (**1**) underwent no detectable reaction during 1 h at 60 °C, but conversion into $TsiGeMe_2OMe$ was *ca.* 40% complete after 24 h, 56% after 48 h, and 85% after 170 h. In contrast, with (**2a**) in 0.10M-NaOMe–MeOH at 60 °C, conversion into $(Me_3Si)_2C(SiMe_2OMe)(GeMe_2OH)$ was *ca.* 15% complete after 3 min and complete within 30 min; thus under these conditions (**2a**) is >300 times as reactive as (**1**)

The behaviour of the germanium chloride (**2a**) in the methanolysis contrasts with that of the analogous silicon chloride $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Cl)$ in two obvious respects: (*a*) the latter is extremely reactive towards MeOH alone, and (*b*) its methanolysis is not significantly accelerated by the presence of NaOMe.[5,6]

It is evident that the reaction of (**2a**) with NaOMe–MeOH (and probably that with MeOH alone) is not an S_N1 process, and the simplest assumption is that the rate-determining step involves attack of MeO^- on (**2a**). However, in S_N2 reactions with alkali metal salts, $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Cl)$ is only *ca.* 15 times as reactive as $TsiSiMe_2Cl$,[6] a relatively small difference (compare the factor of $>10^6$ in methanolysis) which can reasonably be attributed to reduction in steric hindrance in this highly crowded system on replacement of a γ-Me by a γ-OMe group, and it is not easy to see why, if nucleophilic attack on (**2a**) is the rate-determining step in the reaction of the latter with NaOMe–MeOH, there should be so much difference in steric hindrance between the reaction of (**2a**) and that of (**1**). It is conceivable that the solvolysis of (**2a**) involves anchimerically-assisted but reversible formation of an ion pair, which is attacked by OMe^- in the rate-determining step, but unless definite evidence can be found that anchimeric assistance to the leaving of Cl^- is involved in this reaction of (**2a**) there must remain some doubt about interpreting the high reactivity of (**2a**) towards electrophiles in terms of such assistance.

Experimental

All reactions were carried out under dry nitrogen in carefully dried solvents. N.m.r. spectra refer to solutions in $CDCl_3$ unless otherwise indicated; ^{19}F shifts are relative to external $CFCl_3$, ^{13}C shifts are relative to internal $SiMe_4$, and ^{29}Si shifts are relative to external $SiMe_4$.

Columns of OV101 on Chromasorb G were used for linked g.l.c.–mass spectrometry. All mass spectra reports were obtained by electron impact at 70 eV; *m/z* values given for germanium-containing ions are based on the ^{74}Ge isotope.

Preparation of $(Me_3Si)_2C(SiMe_2OMe)(GeMe_3)$.—A solution of $(Me_3Si)_2C(SiMe_2OMe)(Cl)$[7] (18.8 mmol) in a mixture of THF (tetrahydrofuran) (100 cm^3), diethyl ether (5 cm^3), and pentane (5 cm^3) was cooled to -120 °C, and a solution of BuLi (19 mmol) in hexane (20 cm^3) at -77 °C was added dropwise with stirring during 45 min. The mixture was subsequently stirred for 1 h at -110 °C then allowed to warm to -80 °C, and a solution of Me_3GeBr (18.9 mmol) in diethyl ether (10 cm^3) was added dropwise during 15 min. The mixture was allowed to warm to room temperature then set aside overnight. The solvent and any excess of Me_3GeBr were removed under reduced pressure. The residue was extracted with pentane, the extract was evaporated, and the remanent solid was sublimed (150 °C at 0.01 mmHg) then recrystallized from pentane to give *(methoxydimethylsilyl)(trimethylgermyl)bis(trimethylsilyl)methane* (6.15 g, 89%), m.p. 217 °C (Found: C, 43.0; H, 9.8. $C_{13}H_{36}GeOSi_3$ requires C, 42.7; H, 9.9%); δ_H 0.17 (18 H, s, $SiMe_3$), 0.22 (6 H, s, $SiMe_2$), 0.35 (9 H, s, $GeMe_3$), and 3.39 (3 H, s, OMe); δ_C 2.50 (quat. C), 2.62 ($SiMe_2$), 4.69 ($SiMe_3$), 5.30 ($GeMe_3$), and 49.00 (OMe); δ_{Si} 14.83 ($SiMe_2$) and -1.03 ($SiMe_3$) p.p.m.; *m/z* 351 [100%, $(M^+ - Me)$], 247 [5, $(M^+ - Me_3SiOMe)$], 232 [2, $(M^+ - Me_4Ge)$], 217 [15, $(M^+ - Me_4Ge - Me)$], and 73 [35, $(Me_3Si)^+$].

Preparation of $(Me_3Si)_2C(SiMe_2OMe)(GeMe_2Cl)$ (**2a**).—A solution of $(Me_3Si)_2C(SiMe_2OMe)(GeMe_3)$ (0.27 mmol) and ICl (1 mmol) in CCl_4 (2 cm^3) was stirred at room temperature. After 8 min the solvent was quickly evaporated off under reduced pressure and the residue was extracted with pentane. The extract was evaporated, and the residue was recrystallized from CCl_4–pentane (7:3 v/v) then sublimed (150 °C at 0.01 mmHg) to give *(chlorodimethylgermyl)(methoxydimethylsilyl)bis(trimethylsilyl)methane* (0.090 g, 85%), m.p. 264 °C (Found: C, 37.1; H, 8.6. $C_{12}H_{33}ClGeOSi_3$ requires C, 37.35; H, 8.6%); δ_H 0.26 (18 H, s, $SiMe_3$), 0.31 (6 H, s, $SiMe_2$), 0.85 (6 H, s, $GeMe_2$), and 3.38 (3 H, s, OMe); *m/z* 371 [60%, $(M^+ - Me)$], 321 [10, $(M^+ - MeCl - Me)$], 267 [20, $(M^+ - Me_3Ge)$], 237 [50, $(M^+ - Me_4Ge - Me)$], 217 [90, $(M^+ - Me_3GeCl - Me)$], 187 (60), 89 [100, $(Me_2SiOMe)]^+$, and 73 (100).

Preparation of $(Me_3Si)_2C(SiMe_2OMe)(GeMe_2Br)$.—A solution of $(Me_3Si)_2C(SiMe_2OMe)(GeMe_3)$ (0.47 mmol) and Br_2 (2.5 mmol) was kept at room temperature for 3 h then evaporated under reduced pressure. The residue was sublimed (110 °C at 0.05 mmHg) to give *(bromodimethylgermyl)(methoxydimethylsilyl)bis(trimethylsilyl)methane* (0.14 g, 70%), m.p. 284 °C (Found: C, 33.6; H, 7.6. $C_{12}H_{33}BrGeOSi_3$ requires C, 33.5; H, 7.7%); δ_H 0.35 (18 H, s, $SiMe_3$), 0.42 (6 H, s, $SiMe_2$), 0.93 (6 H, s, $GeMe_2$), and 3.41 (3 H, s, OMe); *m/z* 415 [50%, $(M^+ - Me)$], 351 [10, $(M^+ - Br)$], 321 [25, $(M^+ - MeBr - Me)$], 247 [10, $(M^+ - Me_2BrSiOMe)$], 217 [85, $(M^+ - Me_2BrGe - Me)$], and 73 (100).

Reactions of (**2a**) *with Silver Salts*.—(*a*) A solution of (**2a**) (0.26 mmol) in CH_2Cl_2 (10 cm^3) was stirred with AgOCN (0.78 mmol) at room temperature for 2 h. The solution was then filtered and evaporated, and the residue was sublimed (100 °C at 0.01 mmHg) to give *(isocyanotodimethylgermyl)(methoxydimethylsilyl)bis(trimethylsilyl)methane* (90%), m.p. 272 °C (Found: C, 39.9; H, 8.4; N, 3.1. $C_{13}H_{33}GeNO_2Si_3$ requires C, 39.7; H, 8.4; N, 3.6%); δ_H 0.23 (18 H, s, $SiMe_3$), 0.28 (6 H, s, $SiMe_2$), 0.69 (6 H, s, $GeMe_2$), and 3.35 (3 H, s, OMe); δ_{Si} -0.87 ($SiMe_3$) and 15.73 p.p.m. ($SiMe_2$); $\nu_{max.}$ 2 240 cm^{-1} (γSiNCO); *m/z* 378 [70%, $(M^+ - Me)$], 274 [5, $(M^+ - GeMe_3)$], 244 (15), 217 [100, $(M^+ - Me_3GeNCO - Me)$], and 73 (100). G.l.c. gave only one peak.

(*b*) A solution of (**2a**) (0.26 mmol) in CH_2Cl_2 (15 cm^3) was stirred with AgSCN (0.52 mmol) at room temperature. Monitoring by ^{1}H n.m.r. spectroscopy indicated that *ca.* half of the starting material had reacted after about 170 and *ca.* 65% after 340 h. The mixture was then boiled under reflux for 28 h, after which *ca.* 75% of the (**2a**) had disappeared. The solution was filtered and evaporated, and the residue was extracted with pentane. The extract was evaporated and the residue sublimed (100 °C at 0.05 mmHg). The ^{1}H n.m.r. spectrum showed two sets of signals in a 75:25 ratio, one consistent with $(Me_3Si)_2C(SiMe_2OMe)(GeMe_2NCS)$ [δ_H 0.25 (18 H, s, $SiMe_3$), 0.30 (6 H, s, $SiMe_2$), 0.76 (6 H, s, $GeMe_2$), and 3.34 (3 H, s, OMe)] and the other with unchanged (**2a**). However, linked g.l.c.–mass spectrometry gave three peaks (*i*)—(*iii*) in a *ca.* 15:30:55 ratio; the mass spectrum for (*ii*) was effectively identical with that noted above for (**2a**), that of (*iii*) was consistent with $(Me_3Si)_2C(SiMe_2OMe)(GeMe_2NCS)$ {*m/z* 394 [50%, $(M^+ - Me_3GeNCS - Me)$], 187 (10), 89 (80), and 73 (40)} and that of (*i*) could have come from $(Me_3Si)_2C(SiMe_2OH)(GeMe_2NCS)$ {*m/z* 321 [100%, $(M^+ - HNCS - Me)$], 187 (67), 171 (15), and 73 (25)}

(*c*) A solution of (**2a**) (0.26 mmol) and AgO_2CCF_3 (0.52 mmol) in CF_3CO_2H (10 cm^3) was stirred for 15 min at room temperature, after which the ^{1}H n.m.r. spectrum indicated that no (**2a**) remained. The solution was filtered then evaporated under reduced pressure, and the residue was sublimed (100 °C at 0.05 mmHg). The ^{1}H n.m.r. spectrum of the product showed two sets of peaks in a *ca.* 80:20 ratio, the first consistent with $(Me_3Si)_2C(SiMe_2O_2CCF_3)(GeMe_2O_2CCF_3)$ [δ_H 0.29 (18 H, s, $SiMe_3$), 0.65 (6 H, s, $SiMe_2$), and 0.99 (6 H, s, $GeMe_2$)] and the other with $(Me_3Si)_2C(SiMe_2OH)(GeMe_2O_2CCF_3)$ [δ_H 0.25 (18 H, s, $SiMe_3$), 0.35 (6 H, s, $SiMe_2$), and 0.97 (6 H, s, $GeMe_2$). The ^{19}F n.m.r. spectrum showed two peaks at δ -74.3 and -74.5 in a *ca.* 40:60 integration ratio, which is consistent with the product mixture suggested above if the peaks for the two types of $GeMe_2OCCF_3$ groups are assumed to coincide. Linked g.l.c.–mass spectrometry gave two peaks in a *ca.* 80:20 area ratio, but the separation was not complete. The first portion of the main peak gave a mass spectrum consistent with $(Me_3Si)_2C(SiMe_2O_2CCF_3)(GeMe_2O_2CCF_3)$; *m/z* 531 [65%, $(M^+ - Me)$], 433 [10, $(M^+ - CF_3CO_2)$], 299 [20, $(M^+ - Me_3GeO_2CCF_3 - Me)$], 205 (30), 395 (20), 261 (15), 151 (25), 77 [40, $(Me_2SiF)^+$], and 73 (100). Probably because of the presence of some of the main component, the second peak also gave ions at *m/z* 531 and 299, but an ion at *m/z* 321 could be from $(Me_3Si)_2C(SiMe_2OH)(GeMe_2O_2CCF_3)$ [*i.e.* $(M^+ - CF_3CO_2H - Me)$].

(*d*) A mixture of (**2a**) (0.051 mmol), AgO_3SCF_3 (0.11 mmol), and CD_2Cl_2 (0.5 cm^3) in a closed n.m.r. tube was agitated at room temperature for 3 h, after which the ^{1}H spectrum showed no peaks from (**2a**) but apparently two new sets of peaks in a *ca.* 60:40 ratio; the first set was consistent with $(Me_3Si)_2C(SiMe_2OMe)(GeMe_2O_3SCF_3)$ [δ_H 0.27 (18 H, s, $SiMe_3$), 0.38 (6 H, s, $SiMe_2$), 1.06 (6 H, s, $GeMe_2$), and 3.35 (3 H, s, OMe)] and the second with $(Me_3Si)_2C(SiMe_2OH)(GeMe_2O_3SCF_3)$ [δ_H 0.29 (18 H, s, $SiMe_3$), 0.41 (6 H, s, $SiMe_2$), and 1.10 (6 H, s, Me_2Ge)] except for the presence of an OMe peak (3 H) at δ 3.42, possibly due to MeOH. Linked g.l.c.–mass spectrometry gave two imperfectly separated peaks in a *ca.* 40:60 ratio, but because of the incomplete separation the mass spectra were not very helpful. However, the presence of a little $(Me_3Si)_2C(SiMe_2O_3SCF_3)(GeMe_2O_3SCF_3)$ was suggested by the appearance of an ion at *m/z* 603 [$(M^+ - Me)$] in the spectrum of the larger fraction, and both fractions had strong peaks at *m/z* 321 which would be consistent with loss of HO_3SCF_3 and Me from $(Me_3Si)_2C(SiMe_2OH)(GeMe_2O_3SCF_3)$.

The reaction was repeated on a larger scale by stirring a mixture of (**2a**) (0.51 mmol), AgO_3SCF_3 (1.1 mmol), and CH_2Cl_2 (10 cm^3) at room temperature. The change in the ^1H n.m.r. spectrum of the solution suggested that *ca.* 55% of the (**2a**) remained after 10 min, 40% after 90 min, and none after 180 min. The solution was filtered and evaporated, and the residue sublimed (100 °C at 0.05 mmHg). The sublimate gave only one set of signals in the ^1H n.m.r. spectrum, at δ 0.27 (18 H, s), 0.39 (6 H, s), and 1.05 (6 H, s), which matched fairly well that of the main component observed in the smaller scale experiment, except for the absence of any OMe peaks, and which can be tentatively attributed to $(Me_3Si)_2C(SiMe_2O_3SCF_3)(GeMe_2O_3SCF_3)$. The ^{19}F n.m.r. spectrum showed a single peak, at -76.5 p.p.m.

Reaction of $TsiGeMe_3$ *with* CF_3CO_2H.—When a solution of $TsiGeMe_3$ (0.14 mmol) (initially dissolved in 0.3 cm^3 of CH_2Cl_2) in CF_3CO_2H (5.0 cm^3) was kept at room temperature for 24 h the ^1H n.m.r. spectrum was unchanged. When the mixture was subsequently boiled under reflux two products (*A*) and (*B*) appeared; after 12 h *ca.* 15% of the starting material had disappeared to give, apparently, only product (*A*); after 24, 36, and 72 h, the extents of reaction with (in parentheses) the (*A*):(*B*) ratio were, respectively, 50 (75:25), 75 (70:30), and 100 (45:55). The solvent was subsequently evaporated off and the residue was extracted with pentane. Removal of the pentane from the extract was followed by sublimation (100 °C at 0.05 mmHg) of the residue. Analysis of the sublimate by linked g.l.c.–mass spectrometry revealed two components in a *ca.* 45–55 ratio, both of which gave mass spectra consistent with the formulation $TsiGeMe_2O_2CCF_3$ or $(Me_3Si)_2C(SiMe_2O_2CCF_3)(GeMe_3)$, {*e.g.* for (*A*), *m/z* 433 [60%, ($M^+ - Me$)], 335 [5, ($M^+ - O_2CCF_3$)], 205 [40, ($M^+ - Me_3GeO_2CCF_3 - Me$)], and 73 (100%)}. The two sets of n.m.r. signals were assigned as follows: (*A*) $TsiGeMe_2O_2CCF_3$: δ_H 0.26 (27 H, s, $SiMe_3$) and 0.95 (6 H, s, $GeMe_2$); δ_F -76.0 p.p.m.; (*B*) $(Me_3Si)_2C(SiMe_2O_3SCF_3)(GeMe_3)$: δ_H 0.24 (18 H, s, $SiMe_3$), 0.59 (6 H, s, $SiMe_2$), and 0.42 (9 H, s, $GeMe_3$); δ_F -76.1 p.p.m.

Reaction of (**2**; X = Me) *with* CF_3CO_2H.—A solution of (**2**; X = Me) (0.33 mmol) in CH_2Cl_2 (0.5 cm^3) was diluted with CF_3CO_2H (5 cm^3), and the mixture was stirred for 60 min at room temperature. The solvent was removed under reduced pressure, to leave a residue which gave many peaks in the δ 0—1 region of the ^1H n.m.r. spectrum, and two strong signals of equal height, at δ -76.1 and -76.2 p.p.m., along with three small additional peaks in the ^{19}F n.m.r. spectrum. Linked g.l.c.–mass spectrometry revealed the presence of a major component (> 80%) and four minor components. The mass spectrum of the major component was consistent with its being $(Me_3Si)_2C(SiMe_2O_2CCF_3)(GeMe_2O_2CCF_3)$; *m/z* 531 [100%, ($M^+ - Me$)], 299 [30, ($M^+ - Me_3GeO_2CCF_3 - Me$)], 205 (20), and 73 (70).

Methanolysis and Hydrolysis of (**1**) *and* (**2**).—(*a*) (*i*) A sample of (**1**) (0.4 mmol) was dissolved in a drop of CCl_4 (*ca.* 0.2 µl) then MeOH (0.5 cm^3) was added. The tube was sealed then kept at 60 °C. No change in the ^1H n.m.r. spectrum was observed during 15 days; (*ii*) an identical result was obtained when (**2a**) was used in place of (**1**).

(*b*). (*i*) The procedure described under (*a*) (*i*) was repeated but with H_2O–MeOH (2% v/v) as the medium. After 70 days *ca.* 10% of (**1**) had been converted into a single product, which was not studied further; (*ii*) when the procedure was repeated but with (**2a**) in place of (**1**), *ca.* 10% of (**2a**) had been converted after 70 days into a single product, which from its mass spectrum (obtained by linked g.l.c.–mass spectrometry) could have been (**2**; X = OMe); *m/z* 367 [45%, ($M^+ - Me$)], 351 [10, ($M^+ - OMe$)], 247 [40, ($M^+ - Me_2Si(OMe)_2 - Me$)], 217 [100, ($M^+ - GeMe_2OMe - Me$)], 89 (15), and 73 (25).

(*c*). (*i*) The procedure described under (*a*) (*i*) was repeated but with 0.10M-NaOMe–MeOH as the medium. The change in the ^1H n.m.r. spectrum indicated that no observable reaction had taken place after 1 h, but after 24, 48, and 168 h, *ca.* 40, 56, and 85% respectively of (**1**) had been converted into $TsiGeMe_2OMe$; (*ii*) The procedure was repeated but with (**2a**) in place of (**1**). After 3 min *ca.* 15% of (**2a**) had disappeared, and after 30 min all of it had been converted into $(Me_3Si)_2C(SiMe_2OMe)(GeMe_2OMe)$ (the identity of which was confirmed by the addition of an authentic sample).

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