Anchimeric Assistance by the Methoxy Group in Solvolysis of the Compounds (Me$_3$Si)$_2$C(SiMe$_2$OMe)(SiMe$_2$X)

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In a study of the solvolysis of the compounds (Me$_3$Si)$_2$C(SiMe$_2$OMe)(SiMe$_2$X) (1), it has been shown that the reaction of (1; X = Cl) with MeOH–dioxane is (*a*) little accelerated by NaOMe and (*b*) markedly slower than that with CF$_3$CH$_2$OH–dioxane; these results confirm that the much greater reactivity of (1; X = Cl) than of (Me$_3$Si)$_3$CSiMe$_2$Cl in such solvolyses arises from anchimeric assistance by the γ-OMe group to the rate-determining departure of Cl$^-$ and formation of a cationic intermediate. In reactions with MeOH or MeOH–dioxane the order of reactivity of compounds (1) appears to be (X =) Br > NO$_3$ > O$_3$SC$_6$H$_4$Me-*p* > Cl, SCN > O$_2$CCF$_3$ > NCS > O$_2$CPh, O$_2$CMe > F, N$_3$, H. Autocatalysis was observed for X = Br, O$_2$CMe, and O$_2$CPh, and in these cases and for X = O$_2$CCF$_3$ catalysis by HX was demonstrated. Marked catalysis by HBr was observed in several cases, and the reactivity sequence in the catalysed reactions is (X =) Br ≫ N$_3$, O$_2$CMe > O$_2$CPh > O$_2$CCF$_3$, the catalysis being especially marked for X = N$_3$. The chloride (1; X = Cl) was found to be *ca.* 13 times as reactive as (Me$_3$Si)$_3$CSiMe$_2$Cl towards KOCN or KSCN in refluxing MeCN (possibly because of smaller steric hindrance by OMe than Me in this direct bimolecular displacement) but the factor is very small compared with that (>10^6) in methanolysis.

It has previously been shown that compounds of the type TsiSiR$_2$I, where Tsi denotes the (Me$_3$Si)$_3$C group, for which direct nucleophilic displacement of iodine is markedly inhibited by steric hindrance, react with electrophiles (*e.g.* Ag^I or Hg^{II} salts,[1] ICl,[2] CF$_3$CO$_2$H[1]) to give, wholly or in part, rearranged products of the type (Me$_3$Si)$_2$C(SiR$_2$Me)(SiMe$_2$Y), apparently *via* bridged cations of the type (I; Z = Me), the γ-Me group providing anchimeric assistance to the departure of I$^-$ in the formation of such cations.[1–3] It was at first thought that methanolysis of the compounds TsiSiMe$_2$X with X = I or OClO$_3$, or of the compounds TsiSiRHX (R = Me, X = H; or R = Ph, X = I or OClO$_3$), also involved rate-determining formation of such cations, in an S_N1 process, since the reactions are not significantly accelerated by the presence of NaOMe.[4,5] (In contrast, methanolyses of the compounds TsiSiPhHX with X = Br or ONO$_2$ are accelerated by NaOMe, apparently in an S_N2 process, showing that there is a duality of mechanism in such solvolyses, the choice between the mechanisms being determined by the nature of the leaving group.[4]) However, doubt was cast on that view by the observation that solvolysis in the more electrophilic but weakly nucleophilic alcohol CF$_3$CH$_2$OH was much slower than that in MeOH,[1] whereas the opposite would be expected for rate-determining ionization, and it was later shown that no rearrangement took place on solvolysis of TsiSiEt$_2$I in MeOH or aqueous dioxane, ruling out the intermediacy of cations of type (I; Z = Me) in the reactions, which seemingly involve some nucleophilic participation by the solvent.[6]

Calculations (on simpler model ions)[7] indicated that bridging of the type shown in (I), and thus anchimeric assistance to the departure of X, should be much more effective for Z = OH (and hence for Z = OMe) than for Z = Me, and this would also be expected from consideration of bridging between aluminium centres, which bears some analogy to that in (I).[3] Compounds of the type (Me$_3$Si)$_2$C(SiMe$_2$OMe)-(SiMe$_2$X) (1) would thus be expected to be much more reactive than the corresponding TsiSiMe$_2$X species towards electrophiles, so that their alcoholysis might be of the S_N1 type. In keeping with these expectations the compounds (1; X = Cl or H) were found to be much more reactive than corresponding

TsiSiMe$_2$X species towards silver salts.[8,9] Furthermore, the chloride (1a) was found to react with MeOH at 35 °C > 10^6 times as readily as TsiSiMe$_2$Cl, and this was reasonably attributed to assistance by the OMe group to the departure of Cl$^-$ in a unimolecular rate-determining step,[10] and the observation that rearrangement occurred in the reaction of (Me$_3$Si)$_2$C(SiMe$_2$OMe)(SiPh$_2$Br) with EtOH [the sole product being (Me$_3$Si)$_2$C(SiPh$_2$OMe)(SiMe$_2$OEt)] confirmed that cationic intermediates were involved in alcoholysis of this type.[8] We now describe a study of the alcoholysis of the compounds of type (1), the results of which are consistent with the view that the reactions are of the S_N1 type and provide information on the relative leaving group abilities (nucleofugalities) of various X groups. Some of the results have been briefly outlined previously.[9]
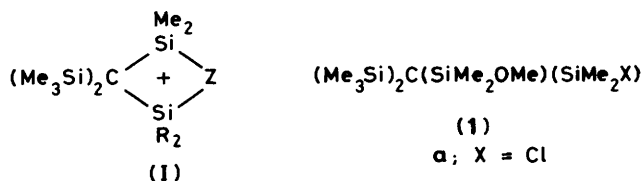
Results and Discussion

We should first note that the procedure used to determine the reaction rates does not give very precise data, and the use of $t_{\frac{1}{2}}$ values rather than rate constants is in part intended to reflect this. Reproducibility of plots of percentage reaction against time was fairly good (±5%), especially for slower reactions, but in the case of runs with half lives <2 min the uncertainty in the absolute value of $t_{\frac{1}{2}}$ could be as high as ±10%; relative values of $t_{\frac{1}{2}}$ for runs under similar conditions are somewhat more precise. The possible inaccuracies are of no significance in the following discussion.

The chloride (1a) was examined first. The reaction with MeOH to give (1; X = OMe) was monitored by observing the change in the ratio of the heights of appropriate peaks from reactant and product in the ^{1}H n.m.r. spectrum. The reaction

Table. Solvolysis of $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2X)$ compounds in ROH–dioxane[a]

X	Conc. (M)	R	% ROH[b]	Additive	θ/°C	$t_{\frac{1}{2}}$	Notes
Br	0.050	Me	10	None	35		c
			10	0.050M-NaOMe		17 min	
			10	0.10M-NaOMe		12 min	
			10	0.05M-HBr		55 s	
			5	0.05M-HBr		130 s	
NO₃	0.060		40	None		14 min	
			40	0.08M-NaOMe		6.1 min	
			40	0.16M-NaOMe		5.0 min	
			40	0.32M-NaOMe		4.0 min	d
			40	0.64M-NaOMe		4.2 min	d
O₃SC₆H₄Me-p	0.040		60	None		10 min	
			60	0.06M-NaOMe		9.5 min	
			60	0.12M-NaOMe		8.6 min	
			60	0.24M-NaOMe		7.8 min	
			60	0.48M-NaOMe		7.5 min	
SCN	0.050		80	None		7.9 min	
			80	0.08M-NaOMe		6.4 min	
			80	0.16M-NaOMe		6.0 min	
Cl	0.060		100	None	0	81 min	
			80	None	35	7.6 min	
			80	0.80M-NaOMe		5.0 min	
			80	0.16M-NaOMe		4.5 min	
			80	0.32M-NaOMe		6.0 min	
			80	0.64M-NaOMe		6.4 min	
	0.030	H	20	None		210 min	d
	0.030	CF₃CH₂	89e	None		<15 s	f
			80	None		<30 s	g
			60	None			h
			60	0.10M-Et₃N		7.3 min	i
			60	0.60M-CF₃CH₂ONa		3.8 min	i
			60	0.12M-CF₃CH₂ONa		2.7 min	i
O₂CCF₃	0.050	Me	100	None	50	280 min	
			100	0.050M-CF₃CO₂H		200 min	
			100	0.050M-HBr		14.5 min	
					35	45 min	
			100	0.20M-NaOMe	50	<1.5 min	j
O₂CMe	0.050	Me	100	None	50		k
			100	0.050M-MeCO₂H		290 min	
	0.060		100	0.060M-HBr	35	5.5 min	
			100	0.20M-NaOMe	50		l
O₂CPh	0.025		100	None	50		c
				0.025M-PhCO₂H		160 h	
	0.020		100	0.020M-HBr	35	32 min	
	0.025	CF₃CH₂	100	None	35	10 min	i
					50		m
NCS	0.030	Me	100	None	50	51 h	
				0.030M-NaOMe		17 min	n
N₃	0.030		100	None	50	>200 days	o
			100	0.030M-HBr		8 min	
				0.20M-NaOMe		170 h	p
F	0.030		100	None	50	>2 yr	q
			100	0.030M-HBr			r
			100	0.20M-NaOMe		135 h	s
		CF₃CH₂	100	None	50	>1 yr	r
H	0.030	Me	100	None	50	>1 yr	o
				0.20M-NaOMe		260 min	
OMe	0.030		100	0.20M-NaOMe	50		o
OH	0.030		100	0.20M-NaOMe	35	42 min	t

[a] The product was $(Me_3Si)_2C(SiMe_2OMe)_2$ unless otherwise stated. HBr was introduced as Ph_3SiBr. [b] $x\%$ ROH indicates $x:(100-x)$ v/v ROH:dioxane. [c] First-order plot was curved as expected for autocatalysis. [d] Initial product $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2OH)$, final product $(Me_3Si)_2(SiMe_2OH)_2$. [e] 8:1 v/v CF_3CH_2OH–dioxane. [f] All starting material had been converted within 45 s into a 7:3 mixture of $(Me_3Si)_2C$-$(SiMe_2OMe)(SiMe_2OCH_2CF_3)$ and $(Me_3Si)_2C(SiMe_2OCH_2CF_3)_2$. [g] After 1 min <10% of starting material remained. [h] First-order plot unsatisfactory. [i] Product $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2OCH_2CF_3)$. [j] Conversion into $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2OH)$ was complete in <5 min. [k] Variable induction period, then plot characteristic of autocatalysis. [l] Starting material disappeared within 4 h; for products see text. [m] Conversion into a mixture of $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2OCH_2CF_3)$ and $(Me_3Si)_2C(SiMe_2OCH_2CF_3)_2$ was complete within 30 min. [n] Product was 55:45 mixture of $(Me_3Si)_2C(SiMe_2OMe)_2$ and $(Me_3Si)_2CH(SiMe_2OMe)$. [o] No detectable reaction in 20 days. [p] Product was 1:4 mixture of $(Me_3Si)_2C(SiMe_2OMe)_2$ and $(Me_3Si)_2CH(SiMe_2OMe)$. [q] No detectable reaction in 60 days. [r] No detectable reaction in 30 days. [s] Product $(Me_3Si)_2CH(SiMe_2OMe)$. [t] Product $(Me_3Si)_2CH(SiMe_2OSiMe_2OMe)$.

was too fast for convenient study at 35 °C, but a good first-order plot was obtained at 0 °C, with $t_{\frac{1}{2}}$ 81 min, a value consistent with that of ca. 1.5 min at 35 °C previously reported.[10] For more detailed studies a 4:1 v/v MeOH–dioxane mixture was used at 35 °C, and under these conditions $t_{\frac{1}{2}}$ was 7.6 min (see Table). The presence of 0.08M-NaOMe led to an increase in the rate of ca. 34%, and on going to 0.16, 0.32, and 0.64M-base the rate increased somewhat and then fell again, so that with 0.64M-NaOMe the rate was only ca. 20% greater than in MeOH alone. The precise origins of these medium effects of NaOMe are not clear, but the effects are much too small to be consistent with an ordinary S_N2 mechanism for the methanolysis.

The reaction of (1a) with 4:1 v/v CF_3CH_2OH–dioxane was then examined, and also that with an 8:1 mixture, in which the molar concentration of CF_3CH_2OH is almost exactly the same as that of MeOH in 4:1 MeOH–dioxane. With 4:1 mixture at 35 °C, by the time of the first measurement (ca. 1 min) < 10% of (1a) remained, indicating that the reaction is >30 times as fast as that in 4:1 MeOH–dioxane. In the 8:1 mixture at 35 °C all (1a) had disappeared within 45 s, and the ^1H n.m.r. spectrum of the solution indicated that (1; $X = OCH_2CF_3$) and $(Me_3Si)_2C(SiMe_2OCH_2CF_3)_2$ were present in ca. 7:3 ratio. The reaction is thus >40 times as fast as that in the MeOH–dioxane mixture of similar alcohol concentration. These results, which contrast sharply with those for solvolysis of $TsiSiMe_2I$ and $TsiSiMe_2OClO_3$, which react very slowly, if at all, with CF_3CH_2OH,[4,5] are consistent with our view that the solvolysis of (1) involves rate-determining ionization.

With 2:3 v/v CF_3CH_2OH–dioxane, reaction occurred at a conveniently measurable rate at 35 °C. The reaction in this case was monitored by observing the fall in the ^1H singlet from $SiMe_2Cl$ relative to that of the singlet from internal $SiMe_4$, since some new unidentified peaks appeared as the solvolysis proceeded. The first-order plot was curved, the rate appearing to fall off more rapidly than expected, and it seems that the HCl generated in the solvolysis interferes with the initial reaction (a feature which may merit further study) as well as assisting the departure of the OMe group in the subsequent conversion of (1; $X = OCH_2CF_3$) into $(Me_3Si)_2C(SiMe_2OCH_2CF_3)_2$. In keeping with this, when the reaction was carried out in the presence of 0.1M-Et_3N good first-order kinetics were observed, with $t_{\frac{1}{2}}$ 7.3 min, and the product was (1; $X = OCH_2CF_3$). The same product was obtained from reaction in the presence of 0.06 or 0.12M-$NaOCH_2CF_3$, the values of $t_{\frac{1}{2}}$ being ca. 2 and 4 times, respectively, smaller than that in the presence of Et_3N. These effects of base are again too small to be consistent with an S_N2 process.

The hydrolysis of (1) was examined in 1:4 v/v H_2O–dioxane at 35 °C. The initially formed (1; $X = OH$) was subsequently converted into $(Me_3Si)_2C(SiMe_2OH)_2$, and the rate of disappearance of (1a) was determined by monitoring the ratio of heights of an appropriate ^1H n.m.r. peak of (1) to that of the combined heights of the corresponding peaks for the intermediate and final products. This gave a good first-order plot for the disappearance of (1a), with $t_{\frac{1}{2}}$ 210 min. The concentration of the intermediate (1; $X = OH$) reached a maximum after ca. 170 min, when (1a), the intermediate, and the final product were present in ca. 60:25:15 ratio. The loss of the OMe group from the intermediate is no doubt catalysed by HCl liberated in the initial step, the γ-OH group providing assistance.

Having established that the solvolysis of (1a) was of the S_N1 type, not involving nucleophilic assistance by the solvent, we turned to other compounds (1) containing a variety of leaving groups X. The results appear in the Table.

The bromide (1; $X = Br$) was found to be very reactive, and was examined in 1:9 v/v MeOH–dioxane. The first-order plot was curved in the direction associated with autocatalysis. In agreement with this, with an equivalent amount of HBr (i.e.

0.05M) (introduced here, as elsewhere in this work, as Ph_3SiBr) present the reaction was faster, and a good first-order plot was obtained with $t_{\frac{1}{2}}$ 55 s. (Under similar conditions but with about half the concentration of MeOH, i.e. with 0.5:9.5 v/v MeOH–dioxane, $t_{\frac{1}{2}}$ was a little more than doubled, at 130 s.) In the presence of 0.05M-NaOMe the solvolysis was, as expected, markedly slower, with $t_{\frac{1}{2}}$ 17 min, and again a good first-order plot was obtained. With 0.01M-NaOMe the rate was somewhat higher ($t_{\frac{1}{2}}$ 11.9 min), and it seems that the initial addition of NaOMe prevents the acid catalysis and further NaOMe causes an increase in rate by a medium effect such as that observed in reaction of (1a).

The nitrate (1; $X = ONO_2$) was somewhat less reactive than the bromide but more reactive than the chloride, and was examined in 0.06M solution in 2:3 v/v MeOH–dioxane. A good first-order plot (with $t_{\frac{1}{2}}$ 14 min) was obtained, suggesting that autocatalysis, if any, was slight. The presence of a small excess of NaOMe (0.08M) increased the rate rather more than usual (to give $t_{\frac{1}{2}}$ 6 min), but further increase in the base concentration had relatively little effect. (With 0.32 and 0.64M-NaOMe small amounts of side-products appeared, as discussed later.)

The tosylate (1; $X = O_3SC_6H_4Me$-p) was comparable in reactivity with the nitrate, and so was also studied (in 0.06M solution) in 3:2 v/v MeOH–dioxane. A good first-order plot (with $t_{\frac{1}{2}}$ 10 min) suggested that any autocatalysis was again minor; in keeping with this 0.08M-NaOMe had only a small effect ($t_{\frac{1}{2}}$ 9.5 min), and further increases in the base concentration caused only very small additional increases in rate.

The thiocyanate (1; $X = SCN$) was comparable with the chloride in reactivity, and so, like the latter, was studied in 4:1 v/v MeOH–dioxane. A good first-order plot, with $t_{\frac{1}{2}}$ 7.9 min, was obtained, suggesting that autocatalysis was unimportant, and base had a fairly small effect.

The trifluoroacetate (1; $X = O_2CCF_3$) was less reactive than the chloride and was studied (in 0.05M solution) in MeOH alone, initially at 50 °C. A good first-order plot ($t_{\frac{1}{2}}$ 283 min) was obtained, but there must have been a little undetected autocatalysis since the presence of an equivalent of CF_3CO_2H (i.e. also 0.05M) lowered $t_{\frac{1}{2}}$ to 200 min. The presence of 0.05M-HBr had a markedly larger accelerating effect, reducing $t_{\frac{1}{2}}$ to 14.5 min; under similar conditions but at 35 °C, $t_{\frac{1}{2}}$ was 45 min. A different reaction took place in the presence of NaOMe, as discussed later.

The acetate (1; $X = O_2CMe$) evidently reacts only very slowly with MeOH in the absence of acid. In several apparently identical runs with the compound at 0.05M concentration in MeOH at 50 °C, in some cases no change at all was observed for 2—3 weeks, then reaction began and gave a curved first-order plot typical of an autocatalysed process. Occasionally, however, reaction began at once, and it must be assumed that traces of acid or alkali initially present markedly affect the induction period. When 0.05M-$MeCO_2H$ was present reaction began at once, and a good first-order plot was obtained, with $t_{\frac{1}{2}}$ 290 min, a value close to that (ca. 200 min) observed for the reaction of the trifluoroacetate in the presence of the stronger acid CF_3CO_2H under otherwise similar conditions. The reaction of the acetate (0.060M) with MeOH containing HBr (0.060M) at 35 °C ($t_{\frac{1}{2}}$ 5.5 min) was several times as fast as that of the trifluoroacetate (0.05M) in the presence of HBr (0.05M), and it seems that whereas $CF_3CO_2^-$ is a markedly better leaving group than $MeCO_2^-$ in the absence of acid catalysis, the greater ease of protonation of the carbonyl group in the acetate results in the latter being more reactive than the trifluoroacetate in the acid-catalysed process. The behaviour of the acetate in the presence of NaOMe is considered later.

The benzoate (1; $X = O_2CPh$) underwent reaction with MeOH at 50 °C without any induction period, but first-order plots were again characteristic of autocatalysis and were not

reproducible. A satisfactory first-order plot, with $t_{\frac{1}{2}}$ 160 h, was obtained for a 0.025M solution of the benzoate in MeOH containing 0.025M-PhCO$_2$H at 50 °C. A 0.020M solution in MeOH containing 0.020M-HBr also gave a good first-order plot with $t_{\frac{1}{2}}$ 10 min, the benzoate thus being about half as reactive as the acetate under comparable conditions of HBr catalysis. Interestingly the benzoate reacted rapidly, in a first-order process with $t_{\frac{1}{2}}$ 10 min, with CF$_3$CH$_2$OH at 35 °C (almost 1 000 times as rapidly as with MeOH containing 0.025M-PhCO$_2$H), to give (1; X = OCH$_2$CF$_3$) (which would, no doubt, have reacted further if the solution had been kept for a longer time at 35 °C). Under similar conditions but at 50 °C, after 30 min only (1; X = OCH$_2$CF$_3$) and (Me$_3$Si)$_2$C(SiMe$_2$OCH$_2$CF$_3$)$_2$ were present.

The isothiocyanate (1; X = NCS) in a 0.03M solution in MeOH at 50 °C gave a good first-order plot, with $t_{\frac{1}{2}}$ 51 h, indicating that autocatalysis, if any, was slight. (The effect of added strong acid was not examined but catalysis is to be expected.) The reaction with NaOMe in MeOH is considered later.

There was no detectable reaction when an 0.030M solution of the azide (1; X = N$_3$) in MeOH was kept at 50 °C for 20 days, but a rapid first-order reaction, with $t_{\frac{1}{2}}$ 8 min, took place even at 35 °C with 0.030M-HBr present. Azide is thus a very poor leaving group in the absence of acid, but somewhat better than acetate in the presence of HBr. (In making the comparison, allowance must be made for the different concentrations of HBr used.) The reaction with NaOMe in MeOH is considered later.

There was no detectable reaction when a 0.030M solution of the fluoride (1; X = F) in MeOH was kept at 50 °C for 60 days. There was similarly no detectable reaction when a 0.030M solution of the hydride (1; X = H) in MeOH was kept at 50 °C for 50 days, but with 0.20M-NaOMe present conversion into (1; X = OMe) occurred, and gave a good (pseudo) first-order plot with $t_{\frac{1}{2}}$ 260 min. It is likely that this reaction involves direct bimolecular displacement of H$^-$ by OMe$^-$ (with electrophilic assistance by proton donation from the solvent to the separating H$^-$, to give H$_2$), which is presumably made possible by the small size of the hydride ligand.

There seems little doubt that in all cases in which solvolyses of the compounds (1) occurred under initially neutral or acidic conditions the rate-determining step was the ionization of the Si–X bond. [The mechanism is, by definition, S_N1, but since the departure of X$^-$ is assisted by the γ-OMe group, to give the cation (I; R = Me, Z = OMe), the rate-determining step can also be regarded as an internal nucleophilic substitution.] In the reactions without acid catalysis the sequence of leaving group abilities (nucleofugalities) appears to be Br > NO$_3$ > O$_3$SC$_6$H$_4$Me-p > Cl, SCN > O$_2$CCF$_3$ > NCS > O$_2$CMe > F, N$_3$, H. Under catalysis by HBr, the sequence in the cases studied appears to be Br ≫ N$_3$, O$_2$CMe > O$_2$CPh > O$_2$CCF$_3$ > F. Acid catalysis is especially effective for X = N$_3$.

In order to confirm that the very large effect of the γ-OMe group in compounds (1) operates specifically in reactions which are believed to generate cations, we also looked briefly at reactions with alkali-metal salts in MeCN, reactions which in the case of TsiSiMe$_2$X appear to be S_N2 processes involving

direct nucleophilic displacement. (The question of whether the reaction involves a five-co-ordinate silicon intermediate is not considered here.) Reaction of the chloride (1a) (0.005M) with a 20-fold excess of KSCN in refluxing MeCN gave a good (pseudo) first-order plot, with $t_{\frac{1}{2}}$ ca. 21 min; the product was (1; X = NCS). Similar procedures with KOCN and CsF (which were not fully dissolved) in place of KSCN gave $t_{\frac{1}{2}}$ values of ca. 100 and 110 min, respectively. When reactions of (1a) or TsiSiMe$_2$Cl (0.006M) with a 17-fold excess of KOCN in refluxing MeCN were carried out alongside one another under conditions as closely similar as possible, after 4 h 85% of (1a) and 13% of TsiSiMe$_2$Cl had reacted, corresponding to a reactivity ratio of ca. 13.5 for (1a) relative to TsiSiMe$_2$Cl. With KSCN under similar conditions, 72% of (1a) had reacted after 30 min, and 55% of TsiSiMe$_2$Cl after 4 h, corresponding to a reactivity ratio of ca. 13. It is evident that although (1a) is distinctly more reactive than TsiSiMe$_2$Cl in these reactions the difference is very small compared with that in the solvolysis. The most likely explanation of the higher reactivity of (1a) is that steric hindrance is slightly but significantly smaller than for TsiSiMe$_2$Cl, the OMe group being able to rotate to place its Me group away from the reaction centre in order to minimize the increase in strain on going from the initial to the five-co-ordinate silicon transition state. In these very congested systems even a small decrease in crowding can be expected to result in a sizeable increase in rate. [It is noteworthy that in the crystal structure of the compound (Me$_3$Si)$_2$C(SiMe$_2$OMe)(SiPh$_2$Cl)[11] the OMe group lies closer to the silicon of the SiPh$_2$Cl than do the Me groups of the SiMe$_2$OMe entity (the C–Si–Me angles are ca. 115.3°, and the C–Si–OMe angle only 103.2°), with the Me of the OMe group directed away from the SiPh$_2$Cl, and with an O–SiPh$_2$–Cl angle of 168°. On attack of a nucleophile the OMe group could move away from the SiPh$_2$Cl centre for a significant distance before the crowding would be as great as that in the corresponding system involving TsiSiPh$_2$Cl.]

Reactions of Compounds (1) *with* NaOMe–MeOH.—The fluoride (1; X = F), which was effectively inert towards MeOH alone, reacted (at 0.03M concentration) with 0.20M-NaOMe in MeOH at 50 °C to give a good (pseudo) first-order plot with $t_{\frac{1}{2}}$ 135 h. However, the product was (Me$_3$Si)$_2$CHSiMe$_2$OMe, the same as that formed in the reaction of TsiSiMe$_2$F with 2M-NaOMe in MeOH under reflux.[12] By analogy with the findings for the latter reaction it can be assumed that the reaction of (1; X = F) involves attack of OMe$^-$ at the silicon atom of the SiMe$_2$OMe group, to bring about the elimination depicted in equation (1a), the sila-alkene thus formed then reacting rapidly with MeOH to give the observed product. The attack of OMe$^-$ on the SiMe$_2$OMe would, because of the inductive effect of the OMe group (cf. ref. 13), be expected to be easier than that on an SiMe$_3$ group in TsiSiMe$_2$F, giving rise to higher reactivity of (1; X = F).

The compound (Me$_3$Si)$_2$CH(SiMe$_2$OMe), presumably formed in the same way, was also the dominant product in the reaction of the azide (1; X = N$_3$) with 0.20M-NaOMe–MeOH at 50 °C. In this case, however, the normal substitution product (1; X = OMe) was also formed in ca. 20% yield in a time during which no detectable reaction took place in the absence of

$$\text{MeO}^- \quad \text{Me}_2(\text{MeO})\text{Si} \longrightarrow \text{C}(\text{SiMe}_3)_2 \longrightarrow \text{SiMe}_2 \longrightarrow \text{F}$$

$$(\text{MeO})_2\text{SiMe}_2 + (\text{Me}_3\text{Si})_2\text{C} = \text{SiMe}_2 + \text{F}^- \quad (1a)$$

$$(\text{Me}_3\text{Si})_2\text{C} = \text{SiMe}_2 + \text{MeOH} \longrightarrow (\text{Me}_3\text{Si})_2\text{CHSiMe}_2\text{OMe} \quad (1b)$$

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base. It is possible that there is direct displacement of azide by methoxide ion.

When the methanolysis of a compound (1) is much faster, interference from this side reaction is much less effective; *e.g.* no formation of $(Me_3Si)_2CH(SiMe_2OMe)$ was observed in the reaction of the chloride (1a) with 4:1 MeOH–dioxane even in the presence of 0.64M-NaOMe (though <5% of the by-product would have escaped detection). However, the reaction of the nitrate (1; $X = ONO_2$) in 2:3 MeOH–dioxane containing 0.32 or 0.64M-NaOMe did give rise to additional small ^1H n.m.r. peaks which probably arose from the presence of small amounts (<10%) of $(Me_3Si)_2CH(SiMe_2OMe)$; a similar result was observed in the reaction of the thiocyanate (1; $X = SCN$) with 0.64M-NaOMe in 4:1 MeOH–dioxane. It should be emphasized that the side-products do not come from subsequent reactions of initially formed (1; $X = OMe$), since no reaction was observed when a solution of the latter in 0.20M-MeONa in MeOH was kept at 50 °C for 21 days.

In contrast, the hydroxide (1; $X = OH$) reacted readily with 0.20M-NaOMe in MeOH at 35 °C to give the isomeric $(Me_3Si)_2CHSiMe_2OSiMe_2OMe$; a good first-order plot was obtained for the rearrangement, with $t_{\frac{1}{2}}$ *ca.* 42 min. The rearrangement apparently involves migration of the Me_2-(OMe)Si group from carbon to the negatively charged oxygen centre produced by deprotonation of (1; $X = OH$); the carbanion $(Me_3Si)_2[Me_2(MeO)SiOSiMe_2]C^-$ produced then rapidly acquires a proton (*cf.* ref. 14). The process is evidently much faster than it is for $TsiSiMe_2OH$, presumably because the internal attack of the O^- at the γ-Si atom is facilitated by the electron withdrawal by the OMe group.

Such rearrangement also occurred in a secondary step in reactions of the carboxylates (1; O_2CCF_3, O_2CMe, and O_2CPh) with NaOMe in MeOH. Thus when a solution of (1; $X = O_2CCF_3$) in 0.20M-NaOMe in MeOH was kept at 50 °C, conversion into the hydroxide (1; $X = OH$) was rapid (complete in <5 min), in a process involving attack of OMe^- at the carbonyl carbon atom with loss of the $(Me_3Si)_2C$-$(SiMe_2OMe)(SiMe_2O^-)$ ion;[15] further reactions subsequently took place, and after 90 min analysis by linked g.l.c.–mass spectrometry suggested the presence of $(Me_3Si)_2CH(SiMe_2OMe)$, $(Me_3Si)_2CH(SiMe_2OSiMe_2OMe)$, and $(Me_3Si)_2C$-$(SiMe_2OMe)_2$ in 15:75:10 ratio. (Since the only data available are from the mass spectra, in principle one or more of the components could have been isomers of the compounds shown, but suitable formulae cannot realistically be written for such isomers.)

It seems that the initially formed (1; $X = OH$) rearranges to $(Me_3Si)_2CH(SiMe_2OSiMe_2OMe)$, and that the latter undergoes base-catalysed solvolysis to give $(Me_3Si)_2CH$-$CHSiMe_2OMe$. We cannot account with any confidence for the formation of $(MeSi)_2C(SiMe_2OMe)_2$; it is unlikely to come from direct solvolysis of (1; $X = O_2CCF_3$), since this process is much too slow in the absence of NaOMe (see above) and base catalysis would not be expected.

The reaction of the acetate (1; $X = O_2CMe$) with 0.20M-NaOMe in MeOH at 50 °C was slower, and the intermediate formation of the hydroxide (1; $X = OH$) could not be demonstrated with certainty because of overlapping of ^1H n.m.r. peaks from several products. All the starting material had disappeared after 4 h, and linked g.l.c.–mass spectrometry revealed that the three products formed in the corresponding reaction of (1; $X = O_2CCF_3$) were again present, but in *ca.* 40:55:5 ratio.

The reaction of 0.20M-NaOMe in MeOH with the iso-thiocyanate (1; $X = NCS$) (which reacted with MeOH alone with $t_{\frac{1}{2}}$ 51 h) was surprisingly fast, with $t_{\frac{1}{2}}$ 17 min. The products appeared from the ^1H n.m.r. spectrum to be $(Me_3Si)_2C$-$(SiMe_2OMe)_2$ and $(Me_3Si)_2CH(SiMe_2OMe)$ in *ca.* 55:45 ratio.

The high rate of reaction and the nature of the products are puzzling, and further investigation is needed.

Experimental

Starting Materials.—The preparations and ^1H n.m.r. spectra of compounds (1) have been described previously.[8,16] Methanol was dried with $Mg(OMe)_2$; CF_3CH_2OH and MeCN were dried over and distilled from CaH_2 then stored over 4A Molecular Sieve; dioxane was stored over Na and distilled from it when required.

Rates of Solvolysis.—The required amount of the compound (1) was dissolved in 1.00 cm^3 of the appropriate medium (prewarmed to the reaction temperature in the case of fast runs) in an n.m.r. tube, which was then sealed and either (for runs with $t_{\frac{1}{2}}$ <2 h) kept in the spectrometer at the required temperature or placed in a bath at that temperature and transferred briefly at intervals to the spectrometer for recording of the spectrum. The disappearance of the starting material was monitored by determining the ratio of the height of a suitable peak from it (the SiMe$_3$ peak for X = Br, $O_3SC_6H_4Me$-p, ONO_2, SCN, O_2CPh, F, H, and sometimes Cl; the SiMe$_2$X peak for X = NCS, N$_3$, O_2CMe, O_2CCF_3, and sometimes Cl) relative to that of the corresponding peak from the product (or to the combined height of the peaks from more than one product where necessary). Unless otherwise indicated, first-order plots were satisfactorily linear up to >85% completion of the reaction. In the case of reaction of (1a) with 3:2 CF_3CH_2OH–dioxane the ratio of the height of the Me$_3$Si peak of (1a) to the of the peak from internal $C(SiMe_3)_4$ was used.

Where there was any doubt from the spectrum that the product was (1; X = OMe, OH, or OCH_2CF_3), $(Me_3Si)_2C$-$(SiMe_2OCH_2CF_3)_2$, or $(Me_3Si)_2CH(SiMe_2OMe)$ the identity was confirmed by enhancement of the relevant peaks upon addition of authentic samples.

An $x:y$ solvent mixture denotes a mixture of x vol of one component with y vol of the other. Hydrogen bromide was introduced by dissolving the appropriate amount of Ph_3SiBr in the medium.

Reactions of (1; X = O_2CR) *with* NaOMe–MeOH.—(i) When an 0.040M solution of (1; X = O_2CCF_3) in 0.20M-NaOMe–MeOH was kept at 50 °C the ^1H n.m.r. spectrum indicated that all the starting material had been converted into (1; X = OH) within 5 min. After 90 min analysis by linked g.l.c.–mass spectrometry (OV101 on Chromasorb G) revealed the presence of the components, A—C, in *ca.* 15:75:10 ratio: A, m/z (e.i.) 233 (40%, $[M − Me]^+$), 219 (100, $[M − MeH − Me]^+$), 203 (35, $[M − MeOH − Me]^+$), 129 (25), and 73 (30); B, m/z 307 (100, $[M − Me]^+$), 219 (5), 203 (15), 129 (10), 89 (10), 73 (30), and 59 (10); C, m/z 321 (95, $[M − Me]^+$), 305 (10, $[M − OMe]^+$), 217 (70, $[M − Me_3SiOMe − Me]^+$), 201 (100), 189 (20), 129 (10), 89 (5), and 73 (20). [The peak assignments are based on the assumption of the formulae $(Me_3Si)_2CH(SiMe_2OMe)$, $(Me_3Si)_2CH(SiMe_2OSiMe_2OMe)$, and $(Me_3Si)_2C(SiMe_2OMe)_2$ for A—C, respectively.]

(ii) When an 0.040M solution (1; X = O_2CMe) in 0.20M-NaOMe–MeOH was kept at 50 °C, the ^1H n.m.r. spectrum showed that all the starting material had disappeared after 4 h. Analysis by linked g.l.c.–mass spectrometry (OV101 on Chromasorb G) showed that the products A—C were present in *ca.* 40:55:5 ratio.

Reactions of (1a) *with Alkali-metal Salts in* MeCN.—(i) A 0.005M solution of (1a) in MeCN (30 cm^3) containing CsF sufficient if it had completely dissolved to give an 0.10M solution, was kept under gentle reflux with exclusion of moisture,

and samples were removed at intervals for determination of the ^1H n.m.r. spectra. A good first-order plot was obtained for the conversion into (1; X = F), with $t_{\frac{1}{2}}$ 107 min.

(ii) A similar procedure but with KOCN in place of CsF gave (1; X = NCO), and a good first-order plot was obtained with $t_{\frac{1}{2}}$ 102 min.

(iii) A similar procedure with KSCN (which was fully dissolved) gave (1; X = NCS), and a good first-order plot was obtained with $t_{\frac{1}{2}}$ 21 min.

(iv) A 0.006M solution in MeCN (5.0 cm³) containing sufficient KOCN for a 0.10M solution if it had fully dissolved was kept under gentle reflux for 4 h. The solution was then cooled and evaporated rapidly under reduced pressure. The residue was extracted with CCl_4, and the ^1H n.m.r. spectrum of the extract showed that it contained (1a) and (1; X = NCO) in ca. 15:85 ratio.

When $TsiSiMe_2Cl$ was used in place of (1a), the $TsiSiMe_2Cl:TsiSiMe_2NCO$ ratio was ca. 87:13.

(v) In the procedure described in (iv), but with KSCN in place of KOCN, when (1a) was used (1a) and (1; X = NCS) were present in ca. 28:72 ratio after 30 min, and $TsiSiMe_2Cl$ and $TsiSiMe_2NCO$ were present in ca. 45:55 ratio after 3.5 h.

Acknowledgements

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