Anchimeric Assistance by and Migration of the Vinyl Group in Reactions of Sterically Hindered Organosilicon Compounds of the Type $(Me_3Si)_2C(SiMe_2CH{=}CH_2)(SiR_2X)$

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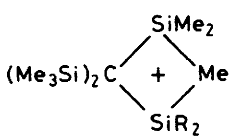
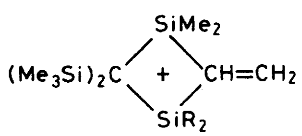
The compound $VsiSiMe_2I$ [Vsi = $(Me_3Si)_2C(SiMe_2CH{=}CH_2)$] (**1**) is very similar in reactivity to $(Me_3Si)_3CSiMe_2I$ (**2**) in reactions with methanol and with alkali-metal salts in MeOH or MeCN, but (**1**) is much the more reactive towards electrophiles which induce rate-determining ionization of the Si–I bond, *viz.* CF_3CH_2OH (the factor *f* is >500), CF_3CO_2H (*f* >1 800), $AgBF_4$ in CH_2Cl_2 (*f ca.* 150), or AgSCN in CH_2Cl_2 (*f* >500). The large differences are attributed to anchimeric assistance by the γ-vinyl group to the leaving I^- under the influence of the electrophile, leading to formation of a 1,3 vinyl-bridged cation. In accord with this, reactions of $VsiSiEt_2I$ with $AgBF_4$ or AgO_2CCF_3 in CH_2Cl_2 give *ca.* 1:2 mixtures of unrearranged and rearranged products, $VsiSiEt_2Y$ and $(Me_3Si)_2C(SiEt_2CH{=}CH_2)(SiMe_2Y)$ (Y = F or O_2CCF_3). Anchimeric assistance by the γ-vinyl group is much greater than that by a γ-Me group but much smaller than that by a γ-OMe group. The chloride $VsiSiEt_2Cl$ reacts with AgO_3SCF_3 in CH_2Cl_2 by loss of the vinyl group (with anchimeric assistance by the γ-Cl atom), apparently to give a chlorine-bridged cation, and hence a mixture of the unrearranged $(Me_3Si)_2C(SiEt_2Cl)(SiMe_2O_3SCF_3)$ and the rearranged $(Me_3Si)_2C(SiEt_2O_3SCF_3)(SiMe_2Cl)$.

Reactions of compounds of the type $TsiSiR_2I$ [Tsi = $(Me_3Si)_3C$] with various electrophiles, such as Ag^I or Hg^{II} salts, ICl, and CF_3CO_2H, are thought to involve rate-determining formation of bridged cations of type (**I**), which can be attacked by a nucleophile Y^- at either the α- or the γ-silicon centre, so that rearranged products of the type $(Me_3Si)_2C(SiR_2Me)(SiMe_2Y)$ can be formed exclusively (*e.g.* R = Ph) or along with the unrearranged $TsiSiR_2Y$ (*e.g.* R = Et).[1,2] In contrast, solvolyses of the compounds $TsiSiR_2I$ in MeOH or aqueous organic media do not result in rearrangement, and so do not go through the bridged cations.[3] When the much more powerful bridging group OMe is present on the γ-Si, as in the compounds $(Me_3Si)_2C(SiMe_2OMe)(SiR_2X)$, the reactivity towards electrophiles is greatly enhanced; *e.g.* alcoholyses of $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Cl)$ are much faster than those of $TsiSiMe_2Cl$ (the factor is $>10^6$ in methanolysis[4]) and involve rate-determining ionization, and in keeping with this the reaction of $(Me_3Si)_2C(SiMe_2OMe)(SiPh_2Cl)$ with EtOH gives exclusively the rearranged $(Me_3Si)_2C(SiMe_2OEt)(SiPh_2OMe)$.[5]


(I)


(II)

The bridging in the ions of type (**I**) bears some analogy to that in the dimers formed by triorganoaluminium compounds,[2] Si^+ being isoelectronic with Al, and since the vinyl group bridges more effectively than the Me group in such dimers[6] it seemed likely that the vinyl-bridged ions (**II**) would be more stable than the methyl-bridged ions (**I**), and thus that compounds of the type $VsiSiMe_2X$ would be more reactive than the corresponding $TsiSiMe_2X$ species, and that 1,3-migration of the vinyl group would occur. This proved to be the case, but the effects of the vinyl group were much larger than we had expected. (A preliminary publication has appeared.[7])

$VsiSiMe_2I$	$TsiSiMe_2I$
(1)	(2)
Vsi = $(Me_3Si)_2C(SiMe_2CH{=}CH_2)$	Tsi = $(Me_3Si)_3C$

Results and Discussion

Preparation of Compounds of the Type VsiSiRR′X.—The chloride VsiCl was first made by treatment of $(Me_3Si)_2C(Cl)Li$ with $Me_2Si(CH{=}CH_2)Cl$. Metallation of the VsiCl with BuLi in Et_2O–THF–pentane (THF = tetrahydrofuran) at −100 °C gave VsiLi, which reacted satisfactorily with a range of organosilicon chlorides to give products of the type VsiSiRR′X (X = H, Cl, or Me) as shown in Table 1.

It is noteworthy that although the VsiLi coupled normally with Ph_2SiHCl and PhMeSiHCl, no reaction was observed with the more sterically hindered Ph_2SiCl_2 and $PhMeSiCl_2$, and the product isolated after treatment of the VsiLi solution with these dichlorides was $VsiBu^n$, formed (during the warming to room temperature) by reaction of the VsiLi with the Bu^nCl produced in the metallation. The related reagent TsiLi {which actually[8] has the structure $[Li(THF)_4][Li(Tsi)_2]$} likewise coupled satisfactorily with all the silicon halide substrates listed in Table 1 (and also with Ph_2SiF_2), but gave only a very low yield with Ph_2SiCl_2.[9] In contrast the reagent $(PhMe_2Si)_3CLi$ (denoted by TpsiLi), which is a monomeric species in which there is a strong intramolecular interaction between one of the Ph groups and the lithium,[10] does not react with Me_3SiCl, Et_2SiCl_2, Ph_2SiHCl, PhMeSiHCl, or Ph_2SiF_2, though it does react normally with the less hindered Me_2SiHCl.[11] It is thus of interest to consider whether VsiLi resembles TsiLi or TpsiLi in structure.

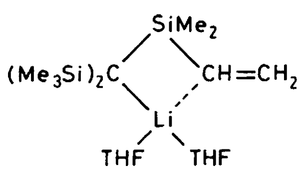
An attempt to determine the crystal structure of VsiLi was unsuccessful, apparently because of extensive disorder in the crystal. We observed, however, that, unlike TsiLi, VsiLi is readily soluble in hydrocarbon solvents, and moreover in $[^2H_8]$toluene gives only one ^7Li n.m.r. signal, at δ −0.086 p.p.m., whereas two would be expected for a structure like that of TsiLi. [The latter compound also, in fact, gave only one

Table 1. Reactions of VsiLi with organosilicon chlorides

Chloride	Product	Yield/%
Me_2SiHCl	$VsiSiMe_2H$	67
Me_2SiCl_2	$VsiSiMe_2Cl$	66
Me_3SiCl	$VsiSiMe_3$	88
Et_2SiCl_2	$VsiSiEt_2Cl$	54
Et_2SiHCl	$VsiSiEt_2H$	65
Ph_2SiHCl	$VsiSiPh_2H$	58
PhMeSiHCl	VsiSiPhMeH	69
Ph_2SiCl_2	$VsiBu^{n}$ [a]	60
$PhMeSiCl_2$	$VsiBu^{n}$ [a]	

[a] From Bu^nCl formed from $(Me_3Si)_2C(Cl)(SiMe_2CH{=}CH_2)$ and Bu^nLi.

detectable signal in [$^2H_8$]toluene, that from the cation (at δ +0.88 p.p.m.), but this was because of its low solubility in that solvent, and in THF there was a signal from the anion (at δ +3.1 p.p.m.[12]).] It thus seems likely that VsiLi is a non-ionic, probably monomeric species, and that there is probably some interaction between the lithium and the vinyl group analogous to that involving the Ph groups in TpsiLi, since otherwise there seems no reason why the type of structure found for TsiLi should not be adopted. The higher reactivity of VsiLi than of TpsiLi could then perhaps be attributed to smaller steric shielding of the Li centre in the vinyl compound. [It is attractive to attribute it primarily to steric shielding by all three Ph groups in TpsiLi, but VsiLi is also somewhat more reactive than the monophenyl analogue $(Me_3Si)_2C(SiMe_2Ph)Li$, which reacts with Et_2SiHCl but not with Et_2SiCl_2.] The integrated ^1H n.m.r. spectrum of a solution of VsiLi in [$^2H_8$]toluene indicated that there are two THF molecules per Vsi group, which matches the findings for TsiLi but contrasts with those for TpsiLi, which has only one THF per Tpsi group, but this can reasonably be associated with the smaller steric hindrance in VsiLi towards co-ordination of two THF molecules to the carbon-bound lithium to give the four-co-ordination state preferred by Li. The probable structure of VsiLi made in THF is thus that shown in (III).



(III)

The compound $VsiSiMe_2H$ was the starting point for a range of other derivatives. Thus it reacted with one molar equivalent of I_2 in CCl_4 at room temperature in the presence of an excess of $Me_3SiCH{=}CH_2$ to give the iodide $VsiSiMe_2I$ (**1**). [The $Me_3SiCH{=}CH_2$ is used to take-up the HI, which otherwise, with assistance from the γ-I, causes cleavage of the Si–vinyl bond of (**1**) to give some $(Me_3Si)_2C(SiMe_2I)_2$.] The diethyl compound $VsiSiEt_2H$ likewise gave $VsiSiEt_2I$. In contrast, treatment of $VsiSiPh_2H$ with I_2 in CCl_4 for 4 days at room temperature gave a product whose ^1H n.m.r. spectrum showed no signals from vinyl protons but did show a signal for the SiH proton; it appears that the I_2 preferentially cleaves the Si–vinyl bonds, and this is not altogether surprising since on the one hand the related hydride $TsiSiPh_2H$ does not react with 1 molar equivalent of I_2 in CCl_4 during several days under reflux, and on the other the related vinyl compound $TsiSiMe_2CH{=}CH_2$ reacts under such conditions to give $TsiSiMe_2I$.[13]

An attempt to make (**1**) by treatment with one molar equivalent of ICl in CCl_4 was unsuccessful; after 30 min at room temperature the ^1H n.m.r. spectrum indicated that (**1**), the dichloride $(Me_3Si)_2C(SiMe_2Cl)_2$, and unchanged $VsiSiMe_2H$ were present in a 2:1:2 ratio. We think it likely that the iodide (**1**) is initially produced, and then the γ-I assists (*cf.* ref. 4) the cleavage of the Si–vinyl bond to give $(Me_3Si)_2C(SiMe_2Cl)(SiMe_2I)$, which then reacts with the ICl with assistance by the γ-Cl to give the dichloride. (The reactions of $TsiSiR_2I$ with ICl, to give rearranged and/or unrearranged chloride, are known to involve formation of an intermediate methyl-bridged cation,[1,14] and thus assistance by γ-Cl would be expected.) However, it is possible to write other reasonable sequences involving anchimerically assisted processes after introduction of the first halide ligand.

Reaction of $VsiSiMe_2H$ at −20 °C with one molar equivalent of Br_2 in CCl_4 containing an excess of $Me_3SiCH{=}CH_2$ gave, after work-up, exclusively $VsiSiMe_2Br$. In contrast, $VsiSiPh_2H$ under similar conditions reacted by cleavage of the Si–vinyl bond, the Si–H bond remaining intact.

Reactions of $VsiSiMe_2X$ (X = Cl, Br, *or* I) *with Alkali-metal Salts.*—Treatment of the iodide (**1**) with an excess of CsF, NaN_3, KSCN, or KOCN in MeCN gave the corresponding $VsiSiMe_2Y$ compounds with Y = F, N_3, NCS, or NCO, respectively.

The relative reactivities of the iodides (**1**) and (**2**) were assessed in some representative reactions with the alkali metal salts in MeCN or MeOH. Thus a solution of (**1**) (0.125 mmol) and KSCN (0.50 mmol) (*i.e.* 0.05M) in MeCN was kept at 60 °C and the reaction was monitored by the removal of samples at appropriate times and the determination of the relative heights of the ^1H n.m.r. signals from the Me_3Si protons of (**1**) and the product $VsiSiMe_2NCS$. A satisfactory pseudo-first-order plot was obtained up to 80% completion of the reaction, and the half-life was *ca.* 61 min. When 1.00 and 2.00 mmol of KSCN were present the half-lives were *ca.* 30 and 15.5 min, respectively, showing that the reaction is of first-order with respect to the salt, and so second order overall. In the reaction of (**2**) with KSCN (0.50 mmol) under similar conditions the half-life was *ca.* 66 min, *i.e.* (**1**) is *ca.* 1.1 times as reactive as (**2**) in this reaction.

In a similar procedure but with (**1**) or (**2**) (0.125 mmol) and KOCN (2.0 mmol) in MeCN at 60 °C the half-life was *ca.* 18 h for (**1**) and 21 h for (**2**), indicating that in this case (**1**) is *ca.* 1.2 times the more reactive. Under similar conditions but with NaN_3 (2.0 mmol) (little of which dissolved), the half-life was *ca.* 11 h for (**1**) and 13 h for (**2**), indicating that (**1**) is *ca.* 1.2 times the more reactive.

Comparisons of the reactivities in MeOH were made with a solution of (**1**) or (**2**) (0.023 mmol) (initially dissolved in *ca.* 0.01 cm^3 of CCl_4) in an 0.25M solution of the relevant salt (0.25 mmol) in MeOH (1 cm^3) contained in a capped n.m.r. tube which was kept at 60 °C. The reaction was monitored by ^1H n.m.r. spectroscopy as before. With NaN_3 the products seemed from the ^1H n.m.r. spectrum to be exclusively the corresponding azides $VsiSiMe_2N_3$ and $TsiSiMe_2N_3$, and the half-lives were *ca.* 5.5 h for (**1**) and *ca.* 6.5 h for (**2**); *i.e.* (**1**) is *ca.* 1.2 times the more reactive. In the reaction with CsF, (**1**) appeared from the ^1H spectrum to give $VsiSiMe_2F$ and $VsiSiMe_2OMe$ in *ca.* 10:1 ratio; the half-life for the disappearance of (**1**) was *ca.* 7 h, and that for conversion into $VsiSiMe_2F$ would be *ca.* 7.7 h. With (**2**), $TsiSiMe_2F$ and $TsiSiMe_2OMe$ appeared to be formed in *ca.* 18:1 ratio, with a half-life of *ca.* 9 h for the overall disappearance of (**2**) and thus one of *ca.* 10 h for conversion into $TsiSiMe_2F$, so that (**1**) again appears to be *ca.* 1.3 times as reactive as (**2**). [We should note that more detailed studies of reactions of (**2**) with CsF in MeOH, under conditions similar to those used here, have revealed that small amounts of the other products are also formed,[15] and this is presumably also the case for the reaction of (**1**), but this does not affect our conclusion that (**1**) and (**2**) have rather similar reactivities in the main reactions.]

Table 2. Rate constants for reaction of (1) and $VsiSiMe_2O_3SCF_3$ with MeOH or H_2O–MeOH

Substrate	Medium	T/°C	$10^7\ k$/s^{-1} [a]	$10^7\ k'$/s^{-1} [b]	Notes
(1)	MeOH	49	7.0	7.0	*c*
	0.05M-NaOMe–MeOH		7.8	7.8	*c*
	0.10M-NaOMe–MeOH		8.8	8.1	*d*
	0.20M-NaOMe–MeOH		9.7	8.8	*e*
	0.40M-NaOMe–MeOH		11.0	9.8	*f*
$VsiSiMe_2O_3SCF_3$	MeOH	35	24		*c*
	0.10M-NaOMe–MeOH		30		*c*
	0.20M-NaOMe–MeOH		32		*c*
	1% v/v H_2O–MeOH		123		*g*

[a] Rate constant for disappearance of substrate. [b] Rate constant for conversion of (1) into $VsiSiMe_2OMe$. [c] Product exclusively $VsiSiMe_2OMe$. [d] Value of ratio, R, of $VsiSiMe_2OMe$ to $(Me_3Si)_2CH(SiMe_2OMe)$ in products was 6. [e] R = 4. [f] R = 2. [g] Product exclusively $VsiSiMe_2OH$.

Table 3. Half-lives, $t_{\frac{1}{2}}$, for hydrolysis of (1) and $TsiSiMe_2I$ (2)[a]

Medium	T/°C	$t_{\frac{1}{2}}$ for (1)/min	$t_{\frac{1}{2}}$ for (2)/min
5% v/v H_2O–MeOH	60	885	1 225
0.10M-NaOH in 5% v/v H_2O–MeOH	60	870	—
2% v/v H_2O–Me_2SO	45	21	26
2% v/v H_2O–$HCONMe_2$	60	9	19
2% v/v H_2O–MeCN	60	2 200	3 350

[a] Products were $VsiSiMe_2OH$ and $TsiSiMe_2OH$, respectively.

In the reactions of the bromides $VsiSiMe_2Br$ and $TsiSiMe_2Br$ with CsF in MeOH under similar conditions the ratios of fluoride to methoxide products were *ca.* 12:1 and 17:1, respectively, and values of $t_{\frac{1}{2}}$ for the disappearance of the initial bromides were *ca.* 14 and 24 h, respectively, indicating that $VsiSiMe_2Br$ was *ca.* 1.7 times the more reactive. In the corresponding reactions of $VsiSiMe_2Cl$ and $TsiSiMe_2Cl$ the fluorides appeared to be the only products (but small amounts of other products would have escaped detection) and the values of $t_{\frac{1}{2}}$ were 29 and 35 h, respectively, indicating that $VsiSiMe_2Cl$ is *ca.* 1.2 times the more reactive, and that the chlorides are *ca.* 4 times less reactive than the corresponding iodides (1) and (2). The unusually small difference in reactivity between chlorides and iodides in this type of reaction has been commented on previously.[16]

Solvolysis of $VsiSiMe_2X$ (X = I *or* O_3SCF_3).—A solution of (1) in MeOH was kept at 49 °C, and the reaction was monitored by determining at intervals the relative heights of the signals from the Me_3Si groups of (1) and $VsiSiMe_2OMe$ in the ^1H spectrum. A good first-order plot was obtained up to >90% completion of the reaction, and a value of 7.0×10^{-7} s^{-1} was derived for the first-order rate constant (see Table 2), corresponding to a half-life of *ca.* 11.5 days. In a similar procedure with 0.05M-NaOMe present no other product could be detected from the ^1H n.m.r. spectrum, but with higher base concentrations significant amounts of the fragmentation product $(Me_3Si)_2CH(SiMe_2OMe)$ were also formed, and from the heights of the relevant Me_3Si peaks the ratio of $VsiSiMe_2OMe$ to the latter product were *ca.* 6:1, 4:1, and 2:1 with 0.10, 0.20, and 0.40M-NaOMe, respectively. First-order rate constants were derived for the overall disappearances of (1) and for its conversion into $VsiSiMe_2OMe$, as shown in Table 2, and it will be seen that the base has only a small effect on the latter rate constant, as was previously observed for the corresponding reaction of (2).[17] [Again more careful analysis has shown that (2) gives small amounts of other by-products under these conditions,[15] and no doubt (1) does also, but this would have no significant effect on the present discussion.]

The rate constant derived similarly for reaction of (2) with MeOH alone under identical conditions was *ca.* 5.6×10^{-7} s^{-1} (half-life *ca.* 14 days), and so once again (1) is *ca.* 1.25 times as reactive as (2).

The rate of reaction of the trifluoromethanesulphonate $VsiSiMe_2O_3SCF_3$ with MeOH was determined at 35 °C by *in situ* monitoring of the ^1H n.m.r. spectrum. The conversion into $VsiSiMe_2OMe$ gave a good first-order plot and the half-life was *ca.* 50 min. Under comparable conditions $TsiSiMe_2O_3SCF_3$ was shown previously to have the same approximate half-life,[18] and so once again the replacement of an Me by a vinyl group has little, if any, effect on the reactivity. The presence of base has a somewhat larger influence than in the methanolysis of the iodide (1) (see Table 2) [the same feature was noted previously in methanolysis of $TsiSiMe_2O_3SCF_3$[18] and (2)[17]], but the effect is still much too small to suggest that the reaction in the absence of base has an S_N2 type of mechanism. The presence of 1 vol % of water in MeOH resulted in a 5-fold increase in rate, and the product appeared to be exclusively the hydroxide $VsiSiMe_2OH$; a similar sensitivity to the presence of water was noted previously for the reactions of $TsiSiMe_2O_3SCF_3$[18] and $TsiSiMe_2OClO_3$[17] with MeOH.

Similar procedures were used to determine the half-lives for reactions of (1) and (2) with water in organic media (to give exclusively the corresponding hydroxides) (see Table 3). The features are: (*i*) (1) is *ca.* 1.2—2.0 times as reactive as (2) in the reactions; (*ii*) the presence of 0.1M-NaOH has little effect on the rate of reaction of (1) with 5% v/v H_2O–MeOH, indicating again that the hydrolysis is not an S_N2 process (*cf.* ref. 16), and (*iii*) water in Me_2SO is the most effective medium for the hydrolysis. (Note that the H_2O–Me_2SO solutions were used at 45 °C.)

When a solution of (1) (initially dissolved in a little CCl_4) in CF_3CH_2OH in an n.m.r. tube was kept at 50 °C, monitoring of the ^1H n.m.r. spectrum in the usual way indicated that (1) was undergoing conversion into the bis(trifluoroethoxide) $(Me_3Si)_2C(SiMe_2OCH_2CF_3)_2$ (which was subsequently isolated for confirmation of its identity), and no signals from the intermediate $VsiSiMe_2OCH_2CF_3$ were observed. The half-life for the conversion was *ca.* 2.5 h. When the procedure was repeated but with one molar equivalent of Et_3N present to neutralize the liberated HI, the product was exclusively Vsi-

$SiMe_2OCH_2CF_3$, and the half-life was *ca.* 2.4 h, *i.e.* not significantly different. In contrast no reaction was observed when a solution of (**2**) in CF_3CH_2OH was kept at 50 °C for 5 days, indicating that (**1**) is at least 500 times as reactive as (**2**) under these conditions. It appears that in CF_3CH_2OH, which provides markedly more electrophilic assistance than MeOH to the leaving of I^-, the anchimeric assistance by the vinyl group is sufficient to induce quite ready (rate-determining) ionization of (**1**).

As expected, (**1**) reacted still more rapidly with the even more electrophilic solvent CF_3CO_2H. Monitoring of the reaction at 50 °C showed that after 5 min *ca.* 35% of (**1**) had been converted into a 1:1.3 mixture of the monotrifluoroacetate $VsiSiMe_2O_2CCF_3$ and the bistrifluoroacetate $(Me_3Si)_2C(SiMe_2O_2CCF_3)_2$; after 15 min *ca.* 80% of (**1**) had been converted into these products in a *ca.* 1:2 ratio, and after 50 min only the bistrifluoroacetate was present; the time for disappearance of 50% of (**1**) was *ca.* 8 min. Since the monotrifluoroacetate $VsiSiMe_2O_2CCF_3$ was found to react only slowly with CF_3CO_2H under these conditions, it seemed likely that once again the cleavage of the Si–vinyl bond was being catalysed by the HI generated in the initial reaction. This was confirmed by repeating the reaction in the presence of 1 molar equivalent of Et_3N, when the half-life was again *ca.* 8 min, but the product was exclusively $VsiSiMe_2O_2CCF_3$. The reaction of (**2**) with CF_3CO_2H at 50 °C was found to have a half-life of *ca.* 235 h, and so it seems that (**1**) is *ca.* 1 800 times as reactive as (**2**) in this S_N1 solvolysis.

Reaction with Silver Salts.—Treatment of (**1**) with the silver salts AgY in CH_2Cl_2 gave the compounds $VsiSiMe_2Y$ with Y = O_2CMe, O_2CPh, O_2CCF_3, $O_3SC_6H_4Me$-*p*, NCS, or OCN (see later). Comparisons of the reactivities of (**1**) and (**2**) in some such reactions were made as follows. (*a*) A mixture of (**1**) (0.25 mmol), (**2**) (0.25 mmol), and $AgO_3SC_6H_4Me$-*p* (0.25 mmol) in CH_2Cl_2 (20 cm^3) was stirred at room temperature and samples were removed at intervals for determination of the ^1H n.m.r. spectrum. This showed that *ca.* 40, 60, and 85% of (**1**) had reacted after 3, 13, and 27 min, respectively, and after 45 min only $VsiSiMe_2O_3SC_6H_4Me$-*p* and unchanged (**2**) were present in solution; the half-life for conversion of (**1**) into the toluene-*p*-sulphonate was thus *ca.* 7 min. When the procedure was repeated but without (**1**) present, $t_{\frac{1}{2}}$ for conversion of (**2**) into $TsiSiMe_2O_3SC_6H_4Me$-*p* was *ca.* 15 h, and so (**1**) is *ca.* 130 times as reactive as (**2**) under these conditions.

(*b*) When a mixture of (**1**) (0.25 mmol) and AgSCN (0.25 mmol) in CH_2Cl_2 (20 cm^3) was stirred at room temperature, monitoring as in (*a*) showed that formation of $VsiSiMe_2NCS$ was complete within 1.5 h. (The probability that $VsiSiMe_2SCN$ was formed as an intermediate is discussed later.) In contrast, all attempts to bring (**2**) into reaction with AgSCN have been unsuccessful.[19] Consistently, when a mixture of (**1**) (0.25 mmol), (**2**) (0.25 mmol), and AgSCN (0.50 mmol) was stirred at room temperature, *ca.* 25, 50, and 85% of (**1**) had reacted after 8, 20, and 55 min, respectively. After 48 h only $VsiSiMe_2NCS$ and unchanged (**2**) were present in solution, suggesting that (**1**) is probably at least 500 times as reactive as (**2**) under these conditions.

(*c*) The reaction of (**1**) (0.25 mmol) with AgO_2CMe (0.25 mmol) in CH_2Cl_2 (20 cm^3) was half complete in *ca.* 14 min. The corresponding half-life for (**2**) under similar conditions was *ca.* 33 h, indicating that (**1**) is *ca.* 140 times the more reactive.

Because of the assistance by the vinyl group, the bromide $VsiSiMe_2Br$ (0.25 mmol) reacted fairly readily with $AgO_3SC_6H_4Me$-*p* (0.25 mmol) in CH_2Cl_2 (20 cm^3) at room temperature, formation of $VsiSiMe_2O_3SC_6H_4Me$-*p* being complete within 4 h. No detectable reaction occurred in 48 h when $TsiSiMe_2Br$ was used under the same conditions, indicating that this bromide is >300 times less reactive than $VsiSiMe_2Br$. The chloride $VsiSiMe_2Cl$ underwent no detectable reaction with $AgO_3SC_6H_4Me$-*p* in CH_2Cl_2 in 96 h at room temperature, whereas the reaction of the methoxy compound $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Cl)$ is complete within 4 h under these conditions.[20]

The migration of the vinyl group was demonstrated by using $VsiSiEt_2I$ in reaction with $AgBF_4$ and with AgO_2CCF_3, these salts being chosen because ^{19}F n.m.r. spectroscopy assists in the identification of the products and determination of the composition of mixtures of them. When $VsiSiEt_2I$ was treated with $AgBF_4$ in Et_2O or CH_2Cl_2 for 30 min at room temperature, linked g.l.c.–mass spectrometry indicated that three products had been formed in a 3:6:1 ratio, the first two having mass spectra consistent with the expected monofluorides, and the third a mass spectrum revealing it to be a difluoride, such as $(Me_3Si)_2C(SiEt_2F)(SiMe_2F)$. The ^1H and ^{19}F n.m.r. spectra were likewise consistent with the presence of three products in a 3:6:1 ratio, and from the spectra these were identified as the unrearranged $VsiSiEt_2F$, the rearranged $(Me_3Si)_2C(SiEt_2CH{=}CH_2)(SiMe_2F)$, and the difluoride $(Me_3Si)_2C(SiEt_2F)(SiMe_2F)$, respectively. The ^{29}Si n.m.r. spectrum was also consistent with the presence of these three products. The possibility that the rearranged product might have been $(Me_3Si)C(SiMe_2CH{=}CH_2)(SiEt_2Me)(SiMe_2F)$, formed by migration of a γ-Me rather than a γ-vinyl group, was ruled out because the 360 Mz ^1H and ^{29}Si n.m.r. spectra gave no indicaton of either a unique Me group or of the two sets of $SiMe_2CH{=}CH_2$ signals which would be expected if that isomer were present along with the unrearranged $(Me_3Si)_2C(SiMe_2CH{=}CH_2)(SiEt_2F)$. Furthermore the integrated signals from the $Si\mathit{Me}_2CH{=}CH_2$ and $SiMe_2F$ protons in the ^1H n.m.r. spectrum were in a 1:2 ratio, showing that they could not come from $(Me_3Si)C(SiMe_2CH{=}CH_2)(SiEt_2Me)(SiMe_2F)$, but consistent with the presence of $VsiSiEt_2F$ and $(Me_3Si)_2C(SiEt_2CH{=}CH_2)(SiMe_2F)$ in a 1:2 ratio. The formation of the difluoride $(Me_3Si)_2C(SiMe_2F)(SiEt_2F)$ can be attributed to anchimeric assistance by the γ-F in either or both of the monofluorides to cleavage of the Si–vinyl bond by the electrophile.

When $VsiSiEt_2I$ was treated with AgO_2CCF_3 in Et_2O, the product mixture appeared from the ^1H n.m.r. spectrum to contain only the unrearranged $VsiSiEt_2O_2CCF_3$ and the rearranged $(Me_3Si)_2C(SiEt_2CH{=}CH_2)(SiMe_2O_2CCF_3)$, in a 1:2 ratio, but ^{19}F n.m.r. spectroscopy, while confirming that these products were indeed present in that ratio, revealed that some (<10%) of the bis(trifluoroacetate) $(Me_3Si)_2C(SiMe_2O_2CCF_3)_2$ was also present; its formation can be accounted for in the same way as that of the corresponding difluoride in the reaction involving $AgBF_4$. [The integrated signals from the $Si\mathit{Me}_2CH{=}CH_2$ and $SiMe_2O_2CCF_3$ protons were again in a 1:2 ratio, confirming that the rearranged isomer was not $(Me_3Si)C(SiMe_2CH{=}CH_2)(SiEt_2Me)(SiMe_2O_2CCF_3)$.] Linked g.l.c.-mass spectrometry gave only one main peak, with a mass spectrum consistent with $VsiSiEt_2O_2CCF_3$ or its isomers.

No reaction occurred when a solution of $VsiSiMe_2Cl$ in CH_2Cl_2 was stirred with AgO_3SCF_3 at room temperature for 96 h, but a reaction, of an unexpected type, did take place when $VsiSiEt_2Cl$ was treated with AgO_3SCF_3 in the same solvent under reflux. After 4 h the ^1H n.m.r. spectrum showed that some starting material remained, and linked g.l.c.–mass spectrometry gave two peaks in a *ca.* 35:65 ratio, one corresponding to that material and the other giving a mass spectrum consistent with a species in which a vinyl had been replaced by an O_3SCF_3 group. The ^{19}F n.m.r. spectrum showed that there were, in fact, two such species present, in a 40:60 ratio, and these can reasonably be assumed to be the unrearranged $(Me_3Si)_2C(SiEt_2Cl)(SiMe_2O_3SCF_3)$ and the rearranged $(Me_3Si)_2C(SiMe_2Cl)(SiEt_2OSCF_3)$, respectively. Apparently the anchimeric assistance by the γ-vinyl group to the leaving of Cl^- is not as effective as that by the γ-Cl to the leaving of $CH_2{=}CH^-$, and formation of a chlorine-bridged species leads to rearranged and unrearranged products in the same ratio as that from the corresponding vinyl-bridged cation. Anchimeric assistance by and migration of chlorine have been observed in related compounds containing more familiar leaving groups.[4,21]. Similar loss of vinyl group occured when $VsiSiEt_2Cl$ was treated with $AgBF_4$ in CH_2Cl_2; the ^1H n.m.r. spectrum of the solid product showed no signals from vinyl protons, and the mass spectrum was consistent with the solid being $(Me_3Si)_2C(SiMe_2F)(SiEt_2Cl)$ and/or $(Me_3Si)_2C(SiMe_2Cl)(SiEt_2F)$.

The product of the reaction of (**1**) with AgOCN in CH_2Cl_2 was the normal cyanate $VsiSiMe_2OCN$, whereas that from its reaction with KOCN in MeCN was the isocyanate $VsiSiMe_2NCO$; analogous results were obtained previously with (**2**). The main differences in spectroscopic properties between the two isomers matched those between $TsiSiMe_2OCN$ and $TsiSiMe_2NCO$;[22] thus the cyanate gave a ν(SiOCN) band in the i.r. at 2 220 and the isocyanate a ν(SiNCO) band at 2 245 cm^{-1}, and δ_H for the $SiMe_2OCN$ protons was 0.67 and that for the $SiMe_2NCO$ 0.48. The values of δ_C and δ_{Si} for the SiOCN group are identical with those for $TsiSiMe_2OCN$, *viz.* 109 and 38.1 p.p.m., respectively.[23] Some reactions of $VsiSiMe_2OCN$ are discussed later.

We noted above that treatment of (**1**) with AgSCN in CH_2Cl_2 for 1.5 h gave exclusively the isothiocyanate $VsiSiMe_2NCS$. However, after 0.5 h the ^1H n.m.r. spectrum of the solution showed three signals in the $SiMe_3$ region, at δ 0.36, 0.30, and 0.26, in *ca.* 2:2:3 ratio. The first of these signals is attributable to (**1**) and the second to $VsiSiMe_2NCS$, which was the only compound present in the solution after 1.5 h. [The isolated product was identical to that obtained from (**1**) and KSCN in MeCN.] It is very likely that the signal at δ 0.26 was due to the normal thiocyanate, $VsiSiMe_2SCN$, which is formed initially and then isomerizes. The only normal silicon thiocyanate so far isolated is $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2SCN)$, obtained by reaction of $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Cl)$ with AgSCN;[19] in that case the greater anchimeric assistance induces very rapid formation of the normal thiocyanate, which can thus be isolated before it isomerizes.

Treatment of (**1**) with $AgO_3SC_6H_4Me$-*p* in H_2O–MeCN gave the expected hydroxide, $VsiSiMe_2OH$.

Anchimeric Assistance by the Vinyl Group.—It is evident from above results that the vinyl group provides strong anchimeric assistance to the departure of the halide ion in reactions of (**1**) with the electrophiles CF_3CH_2OH, CF_3CO_2H, and silver salts, and of $VsiSiMe_2Br$ with the last of these, all reactions which involve formation of a bridged cation in the rate-determining step.[1,2] In contrast, in reactions which do not involve formation of a (nucleophile-free) cation, *viz.* those with MeOH, water in organic media, and alkali metal salts in MeCN or MeOH, the reactivities of (**1**), and, in the cases examined, those of $VsiSiMe_2Br$ and $VsiSiMe_2O_3SC_6H_4Me$-*p* are very similar to those of the corresponding $TsiSiMe_2X$ compounds, as would be expected since the electronic and steric influences of a remote vinyl should not be appreciably different from those of an Me group. [It is noteworthy in this context that the reactivities of $TsiSi(CH{=}CH_2)_2X$ compounds are very similar to those of the corresponding $TsiSiMe_2X$ compounds over the whole spectrum of reactions involving the leaving of X.[24]] The assistance by the vinyl group apppears to be smaller in reactions of (**1**) with silver salts than in those with CF_3CO_2H, and smaller for reactions with $AgBF_4$ than with the less reactive AgSCN, and this is in line with the likelihood that the need for assistance will be smaller the more powerful the electrophile. (The effect should be larger for reactions with CF_3CH_2OH than with CF_3CO_2H, but the available results do not give information on this point.) The anchimeric assistance by a γ-vinyl, while large, is markedly smaller than that by a γ-OMe group.

We assume that the bridging by the vinyl group involves only one carbon atom as in (**II**), *i.e.* is analogous to that in vinyl bridges between Al centres. Such bridging, but 1,2 (to form a three-membered ring) rather than 1,3, is believed to provide anchimeric assistance to formation of some carbocations (of the simple homoallylic type in which there is stabilization by overlap of the *p* orbitals of the electron-deficient carbon with those of the *p* orbitals of the carbon atoms of the double bond), but more commonly there is direct interaction between the π-orbitals of the double bond and the electron-deficient centre, with both carbon atoms of the double bond becoming partially bonded to that centre to give a homocyclopropenyl cation;[25] such interaction is postulated, for example, in the cation formed during solvolysis of $CH_2{=}CH(CH_2)_2O_3SC_6H_4Me$-*p* and related species.[26]

The occurrence of the rearrangements we have observed is consistent with bridging as in (**II**), with the nucleophile Y^- preferentially attaching to the less hindered silicon centre, *viz.* that bearing two Me rather than that bearing two Et groups. The relative steric hindrance towards attack at the two centres should not be significantly different for (**I**) than for (**II**), and thus it could at first sight seem anomalous that in reactions involving the ion (**I**) roughly equal amounts of rearranged and unrearranged products were reported, whereas for reactions involving (**II**; R = Et) such products are in a 2:1 ratio, but in the case of reactions involving (**I**; R = Et) the ratios were subject to considerable uncertainty and, in addition, the more stable cation (**II**; R = Et) could be expected to be attacked more selectively than the less stable (**I**; R = Et).

Overall the results are consistent with a division of substitution reactions of highly sterically hindered compounds of the type under consideration into three types, *viz.*[16] (*a*) direct bimolecular substitutions (possibly involving five-co-ordinate intermediates), such as those in reactions of (**1**) and (**2**) with alkali metal salts and in the methanolysis of compounds of the type TsiSiPhHX with X = Br or ONO_2, which are markedly accelerated by NaOMe; (*b*) reactions with electrophiles such as silver salts or CF_3CO_2H, and, if there is sufficient anchimeric assistance, with CF_3CH_2OH or sometimes [*e.g.* in the case of $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Cl)$] even with MeOH, which involve rate-determining ionization to give bridged cations; and (*c*) reactions of species such as (**1**), (**2**), $TsiSiMe_2OClO_3$, and TsiSiRHI (R = Ph or Me) with MeOH, which are not significantly accelerated by the presence of NaOMe but which are much faster than the reactions with the more electrophilic but less nucleophilic CF_3CH_2OH, and so are assumed to have an intermediate type of mechanism. Especially significant in the present work is the observation that in contrast with (**2**), but like $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Cl)$, (**1**) reacts much more readily with CF_3CH_2OH than with MeOH.

Miscellaneous Reactions of $VsiSiMe_2X$ *Compounds.—Reactions of* $VsiSiMe_2X$ (X = OMe, OH, O_2CMe, O_2CCF_3, *or* H) *with* CF_3CO_2H. When a solution of $VsiSiMe_2OMe$ was made up in CF_3CO_2H at room temperature and the ^1H n.m.r. spectrum recorded as quickly as possible (within *ca.* 1 min) the spectrum showed that complete conversion into $(Me_3Si)_2C(SiMe_2O_2CCF_3)_2$ had occurred. When the procedure was repeated with 4:1 v/v CCl_4–CF_3CO_2H as solvent, the n.m.r. spectrum after 2 min at 35 °C indicated that only $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2O_2CCF_3)$ was present, but after 45 min complete conversion into $(Me_3Si)_2C(SiMe_2O_2CCF_3)_2$ had occurred. It appears that the strong anchimeric assistance by the γ-OMe group results in rapid cleavage of the Si–vinyl bond by CF_3CO_2H (which is not surprising since cleavage even of an Si–Me bond occurs when $TsiSiMe_2OMe$ is treated with CF_3CO_2H at room temperature[27]). The subsequent loss of the OMe group, assisted by the γ-O_2CCF_3 group, is distinctly slower.

The hydroxide $VsiSiMe_2OH$ reacted somewhat more slowly with CF_3CO_2H, but when a solution was made up at 35 °C the spectrum recorded within 1 min showed that some $(Me_3Si)_2C(SiMe_2OH)(SiMe_2O_2CCF_3)$ was present along with the $VsiSiMe_2OH$, and after 10 min these were present in a 3:7 ratio. After 1 h only $(Me_3Si)_2C(SiMe_2O_2CCF_3)_2$ was present. The anchimeric assistance by a γ-OH seems generally to be somewhat less powerful than that by a γ-OMe group.[28]

When a solution of $VsiSiMe_2O_2CMe$ in CF_3CO_2H was kept at 35 °C, the ^1H n.m.r. spectrum after 18 h indicated that the starting material and $(Me_3Si)_2C(SiMe_2O_2CMe)(SiMe_2O_2CCF_3)$ were present in a 3:2 ratio, and after 6 days only $(Me_3Si)_2C(SiMe_2O_2CF_3)_2$ was present. Similarly with a solution of $VsiSiMe_2O_2CPh$ in CF_3CO_2H at 35 °C, after 70 h about half of the starting material had been converted into $(Me_3Si)_2C(SiMe_2O_2CPh)(SiMe_2O_2CCF_3)$, and after 12 days only $(Me_3Si)_2C(SiMe_2O_2CCF_3)_2$ was present. It seems that under these conditions assistance by the O_2CR groups is markedly weaker than that by OMe or OH, and is weaker for R = Ph than for R = Me.

When a solution of $VsiSiMe_2H$ was kept at 60 °C, complete conversion into $VsiSiMe_2O_2CCF_3$ took place within 1 h, *i.e.* there was no cleavage of the Si–vinyl bond.

Reactions of $VsiSiMe_2OH$ *and* $VsiSiMe_2OMe$ *with* NaOMe–MeOH. When a solution of $VsiSiMe_2OH$ in 0.4M-NaOMe–MeOH was boiled under reflux for 2 h, 95% of the hydroxide underwent isomerization to $(Me_3Si)_2CH(SiMe_2OSiMe_2CH{=}CH_2)$. This is an example of a known type of rearrangement,[29] but it is of interest that the $CH_2{=}CHMe_2Si$ group migrates rather than one of the Me_3Si groups (though a small amount of product resulting from the latter type of migration would have escaped detection.)

When a solution of $VsiSiMe_2OMe$ in 0.40M-NaOMe–MeOH was boiled under reflux for 72 h no detectable reaction took place. However, when a solution of (**1**) in 1.0M-NaOMe–MeOH was boiled under reflux for 24 h, linked g.l.c.–mass spectrometry revealed the presence of five components, two of which, from their mass spectra, were probably $(Me_3Si)_2CH(SiMe_2OMe)$ and $(Me_3Si)CH(SiMe_2CH{=}CH_2)(SiMe_2OMe)$, and another (*ca.* 20% of the total) the starting material $VsiSiMe_2OMe$. The $(Me_3Si)_2CH(SiMe_2OMe)$ can be assumed to be formed in a fragmentation process of a known general type, involving the sila-alkene intermediate $(Me_3Si)_2C{=}SiMe_2$, though no detectable reaction took place when a solution of $TsiSiMe_2OMe$ in 2M-NaOMe–MeOH was boiled under reflux for 24 h.[30]

Treatment of $VsiSiMe_2X$ (X = $O_3SC_6H_4Me$-*p*, F, Cl, Br, NCO, or NCS) *with* MeOH. All these compounds were recovered unchanged after prolonged boiling (5—12 days) with MeOH.

Reactions of $VsiSiMe_2OCN$. When a solution of $VsiSiMe_2OCN$ in MeOH (carefully 'dried' but evidently still containing traces of water) was kept at 35 °C, after 0.5, 1, and 5 h *ca.* 25, 55, and 100%, respectively, of the starting material had disappeared, to give $VsiSiMe_2OH$ and $VsiSiMe_2OMe$ in a *ca.* 1:1 ratio. When a solution of the cyanate in 5% vol. H_2O–MeOH was stirred at room temperature for 30 min complete conversion into $VsiSiMe_2OH$ took place. In contrast, no reaction took place when a similar solution of the isocyanate was kept at 60 °C for 7 days.

A solution of $VsiSiMe_2OCN$ (0.044 mmol) in Ph_2O (0.5 cm^3) was kept at 195 °C in an n.m.r. tube and the progress of the reaction was monitored by ^1H n.m.r. spectroscopy and revealed after 2, 5, and 11 h, respectively, *ca.* 55, 75, and 90% isomerization into the $VsiSiMe_2NCO$; a plot of the reciprocal of the molar concentration of $VsiSiMe_2OCN$ against time gives a satisfactory straight line with a slope indicating a value of 7.7 $dm^3\ mol^{-1}\ h^{-1}$ for the second-order rate constant (and a half-life of *ca.* 1.5 h). When the initial concentration of the cyanate was slightly more than halved (7.0 mg in 0.5 cm^3), *ca.* 39 and 75% isomerization took place in 2.5 and 9 h, respectively, indicating a value of *ca.* 7.8 $dm^3\ mol^{-1}\ h^{-1}$ for the rate constant (and a half-life of *ca.* 3.1 h). These results, while only approximate, indicate clearly that the isomerization is a second-order process, as noted previously for $TsiSiMe_2OCN$.[22b] The second-order rate constants for the two cyanates have remarkably similar values, that for $TsiSiMe_2OCN$ being *ca.* 6.8 $dm^3\ mol^{-1}\ h^{-1}$ (*not* $dm^3\ mol^{-1}\ s^{-1}$ as previously erroneously reported).[22b]

Experimental

Starting Materials and Solvents.—The compounds $TsiSiMe_2X$ (X = Cl, Br, or I),[8] $(Me_3Si)_2CCl_2$,[31] Ph_2SiHCl,[32] and $(CH_2{=}CH)Me_2SiCl$[13] were made by published procedures.

Acetonitrile was dried over and distilled from P_2O_5 then stored over Molecular Sieve 4A. 2,2,2-Trifluoroethanol was dried over and distilled from CaH_2 then stored over Molecular Sieve 4A. Other solvents were purified as previously described.[33]

Spectra.—^1H N.m.r. spectra (at 60, 80, or 90 MHz unless otherwise indicated) were recorded with solutions in CCl_4 containing CH_2Cl_2 or Me_2CO as lock and reference. ^{19}F N.m.r. spectra were recorded with a Bruker WP80 Fourier transform spectrometer operating at 75.4 MHz; solutions were in CCl_4, and chemical shifts are in p.p.m. relative to internal $CFCl_3$. ^{13}C and ^{29}Si n.m.r. spectra were recorded with a Bruker WM360 Fourier transform spectrometer operating at 90.5 and 71.5 MHz, respectively; solutions were in $CDCl_3$, and shifts are in p.p.m. relative to internal Me_4Si.

I.r. spectra (for solutions in CCl_4 unless otherwise indicated) were recorded with a Perkin-Elmer 157G spectrophotometer. Mass spectra were determined by electron impact at 70 eV; isotope patterns for halogen-containing ions were as expected.

Preparation of $(Me_3Si)_2C(Cl)(SiMe_2CH{=}CH_2)$ (VsiCl).—A solution of $(Me_3Si)_2CCl_2$ (11.0 g, 0.048 mol) in a mixture of THF (60 cm^3), Et_2O (8 cm^3), and pentane (3 cm^3) was cooled in a bath at −110 °C and a 1.6M solution of Bu^nLi in hexane (32 cm^3; 0.051 mol of Bu^nLi) precooled to −80 °C was added dropwise with stirring during 1 h. The mixture was stirred for a further 1 h at −110 °C, then $Me_2(CH_2{=}CH)SiCl$ (6.30 g, 0.052 mol) cooled to −80 °C was added and the mixture was allowed to warm to room temperature. Volatile materials were removed under reduced pressure and the residual solid was extracted with pentane. The extract was filtered and evaporated to leave a paste, which upon trituration with cold MeOH gave a solid, and this was sublimed (70 °C at 0.2 Torr) to give *chloro[dimethyl(vinyl)silyl]bis(trimethylsilyl)methane* (7.80 g, 58%), m.p. 120 °C; δ_H 0.19 (18 H, s, $SiMe_3$), 0.26 (6 H, s, $SiMe_2$), and 5.7—6.4 (3 H, m, $CH{=}CH_2$); ν(C=C) 1 590 cm^{-1}; *m/z* 263 (20%, $[M - Me]^+$), 251 (5, $[M - CH{=}CH_2]^+$), 217 (30), 213 (20, $[M - MeCl - Me]^+$), 155 (50, $[M - Me_3SiCl - Me]^+$), 85 (65, $[Me_2SiCH{=}CH_2]^+$), 73 (100, $[Me_3Si]^+$), and 59 (45, $[Me_2SiH]^+$) (Found: C, 46.9; H, 9.5. $C_{11}H_{27}ClSi_3$ requires C, 47.7; H, 9.7%).

Treatment of $(Me_3Si)_2C(SiMe_2CH{=}CH_2)(Li)$ (VsiLi) *with Various Organosilicon Halides.*—(*a*) A 1.5M solution of Bu^nLi in hexane (2.7 cm^3; 40.5 mmol of Bu^nLi) was added dropwise to a stirred solution of VsiCl (11.0 g, 39.5 mmol) in a mixture of THF (60 cm^3), Et_2O (8 cm^3), and pentane (3 cm^3) cooled in a bath at −100 °C. The mixture was subsequently stirred for 1 h at

-100 °C then allowed to warm to -75 °C, and Me_2SiHCl (4.25 g, 45 mmol), cooled to -80 °C, was added dropwise with stirring. The mixture was allowed to warm to room temperature and volatile materials were evaporated under reduced pressure to leave a solid, which was recrystallized from MeOH to give *(dimethylsilyl)[dimethyl(vinyl)silyl]bis(trimethylsilyl)methane* (7.60 g, 67%), m.p. 235 °C (Found: C 52.0; H, 11.3. $C_{13}H_{34}Si_4$ requires C, 51.7; H, 11.3%); δ_H 0.24 (18 H, s, $SiMe_3$), 0.29 (6 H, s, $SiMe_2CH{=}CH_2$), 0.32 (6 H, d, $SiMe_2H$), 4.17 (1 H, m, SiH), and 5.5–6.7 (3 H, m, $CH{=}CH_2$); ν(SiH) (KBr) 2 100 cm^{-1}; *m/z* 287 (90%, $[M - Me]^+$), 275 (10, $[M - CH{=}CH_2]^+$), 213 (20, $[M - Me_3SiH - Me]^+$), 201 (15, $[M - Me_2HSiCH{=}CH_2]^+$), 199 (30), 187 (10), 129 (5), 85 (10), 73 (100), and 59 (30).

(*b*) A similar procedure but with Me_2SiCl_2 in place of Me_2SiHCl and culminating in sublimation (100 °C at 0.5 Torr) instead of recrystallization gave *(chlorodimethylsilyl)[dimethyl(vinyl)silyl]bis(trimethylsilyl)methane* (66%), m.p. 302 °C (Found: C, 46.9; H, 9.8. $C_{13}H_{33}ClSi_4$ requires C, 49.4; H, 9.8%); δ_H 0.30 (18 H, s, $SiMe_3$), 0.34 (6 H, s, $SiMe_2CH{=}CH_2$), 0.60 (6 H, s, $SiMe_2Cl$), and 5.4—6.7 (3 H, m, $CH{=}CH_2$); *m/z* 321 (100%, $[M - Me]^+$), 221 (35, $[M - Me_3SiCH{=}CH_2 - Me]^+$), 213 (75, $[M - Me_3SiCl - Me]^+$), 201 (25, $[M - Me - CH_2{=}CHMe_2SiCl]^+$), 185 (20), 155 (20), 129 (15), 73 (90), and 59 (10).

(*c*) The procedure described under (*b*), but starting from Me_3SiCl, gave $VsiSiMe_3$ (88%), m.p. 324 °C (lit.,[13] > 325 °C); δ_H, as previously reported; ν(C=C) 1 585 cm^{-1} (lit.,[13] 1 649 cm^{-1}; band probably wrongly identified); *m/z* 301 (55%, $[M - Me]^+$), 213 (35, $(M - Me_4Si - Me]^+$), 201 (15, $[M - Me_3SiCH{=}CH_2 - Me]^+$), 129 (10), 73 (100), and 59 (20).

(*d*) The procedure described under (*a*), but on one quarter the scale and starting from Ph_2SiHCl, gave *[dimethyl(vinyl)silyl](diphenylsilyl)bis(trimethylsilyl)methane* (58%), m.p. 90 °C (Found: C, 65.0; H, 8.95. $C_{23}H_{38}Si_4$ requires C, 64.8; H, 8.9%); δ_H 0.24 (18 H, s, $SiMe_3$), 0.30 (6 H, s, $SiMe_2$), 5.18 (1 H, s, SiH), 5.4—6.7 (3 H, m, $CH{=}CH_2$), and 7.1—7.9 (10 H, m, Ph); ν(SiH) (KBr) 2 105 cm^{-1}; *m/z* 411 (20%, $[M - Me]^+$), 381 (20), 333 (100, $[M - PhH - Me]^+$), 321 (30, $[M - PhH - CH{=}CH_2]^+$), 233 (20), 197 (15), 175 (40), 135 (90, $[Me_2SiPh]^+$), 73 (70), and 59 (20).

(*e*) The procedure described under (*d*), but starting from PhMeSiHCl and culminating in sublimation (80 °C at 0.1 Torr) instead of recrystallization, gave *[dimethyl(vinyl)silyl][methyl(phenyl)silyl]bis(trimethylsilyl)methane* (69%), m.p. 75 °C (Found: C, 58.9; H, 10.0. $C_{18}H_{36}Si_4$ requires C, 59.3; H, 9.9%); δ_H 0.16 (18 H, s, $SiMe_3$), 0.24 (6 H, s, $SiMe_2$), 0.40 (3 H, d, SiMe), 4.62 (1 H, m, H), 5.5—6.6 (3 H, m, $CH{=}CH_2$), and 7.2—7.8 (5 H, m, Ph); ν(SiH) 2 100 cm^{-1}; *m/z* 349 (100%, $[M - Me]^+$), 324 (25), 313 (45), 287 (10, $[M - Ph]^+$), 247 (15), 213 (10), 199 (15), 175 (20), 135 (30), 85 (10), and 73 (90).

(*f*) The procedure described under (*e*), but starting from Et_2SiCl_2, and with sublimation at (120 °C at 0.1 Torr), gave *(chlorodiethylsilyl)[dimethyl(vinyl)silyl]bis(trimethylsilyl)methane* (55%), m.p. 250 °C (Found: C, 49.7; H, 9.9. $C_{15}H_{37}ClSi_4$ requires C, 49.4; H, 9.4%); δ_H 0.27 (18 H, s, $SiMe_3$), 0.33 (6 H, s, $SiMe_2$), 0.9—1.3 (10 H, m, Et), and 5.4—6.5 (3 H, m, $CH{=}CH_2$); *m/z* 349 (100%, $[M - Me]^+$), 335 (90), $[M - Et]^+$), 227 (35), 213 (35), 201 (15), 199 (25), 155 (10), 141 (20), 129 (20), 113 (20), 99 (10), 85 (13), 73 (75), and 59 (32).

(*g*) The procedure described under (*d*), but starting from Et_2SiHCl and culminating in recrystallization from MeOH, gave *(diethylsilyl)[dimethyl(vinyl)silyl]bis(trimethylsilyl)methane* (65%), m.p. 190 °C (Found: C, 54.4; H, 11.0. $C_{15}H_{38}Si_4$ requires C, 54.5; H, 11.5%); δ_H 0.20 (18 H, s, $SiMe_3$), 0.26 (6 H, s, $SiMe_2$), 0.90—1.08 (10 H, m, $SiEt_2$), 3.79—3.82 (1 H, m, SiH), and 5.6—6.4 (3 H, m, $CH{=}CH_2$); ν(SiH) 2 080 cm^{-1}; *m/z* 315 (30%, $[M - Me]^+$), 301 (100, $[M - Et]^+$), 286 (15), 273 (25), 213 (25), 201 (15), 199 (35), 187 (10), 129 (15), 115 (10), 99 (10), 87 (15), 85 (15), 73 (100), and 59 (57).

(*h*) The procedure described under (*d*), but starting from Ph_2SiCl_2 and culminating in recrystallization from MeOH, gave a solid: δ_H 0.27 (18 H, s), 0.32 (6 H, s), 1.05 (9 H, m), and 5.5—6.5 (3 H, m); *m/z* 285 (70%, $[M - Me]^+$) and 73 (100%), which was judged to be $VsiBu^n$ (60%).

(*i*) The procedure described under (*h*), but starting from $PhMeSiCl_2$, likewise gave $VsiBu^n$ as the only isolated product.

Reactions of $VsiSiMe_2H$ *with Halogens*.—(*a*) A 1M solution of Br_2 in CCl_4 (0.80 cm^3; 0.80 mmol of Br_2) was added dropwise with stirring to a solution of $VsiSiMe_2H$ (0.22 g, 0.73 mmol) in CCl_4 (5 cm^3) containing $CH_2{=}CHSiMe_3$ (0.1 g, 1.0 mmol) cooled in a bath at -20 °C. The mixture was stirred for 5 min, allowed to warm up, and then evaporated under reduced pressure. The residual solid was sublimed (100 °C at 0.2 Torr) to give *(bromodimethylsilyl)[dimethyl(vinyl)silyl]bis(trimethylsilyl)methane* (0.18 g, 65%), m.p. 310 °C; (Found: C 40.8; H, 8.2. $C_{13}H_{33}BrSi_4$ requires C, 40.9; H, 8.7%) δ_H 0.30 (18 H, s, $SiMe_3$), 0.37 (6 H, s, $SiMe_2CH{=}CH_2$), 0.77 (6 H, s, $SiMe_2Br$), and 5.1—6.8 (3 H, m, $CH{=}CH_2$); *m/z* 365 (80% $[M - Me]^+$), 353 (25, $[M - CH{=}CH_2]^+$), 301 (10, $[M - Br]^+$), 263 (40), 213 (90, $[M - Me_3SiBr - Me]^+$), 201 (70, $[M - CH_2{=}CHMe_2SiBr - Me]^+$), 187 (20), 185 (30), 155 (35), 129 (40), 113 (20), 85 (40), 73 (100), and 59 (40).

(*b*) A solution of I_2 (4.3 g, 17.0 mmol), $Me_3SiCH{=}CH_2$ (2.0 g, 20 mmol), and $VsiSiMe_2H$ (5.0 g, 16.5 mmol) in CCl_4 (100 cm^3) was stirred for 14 h at room temperature, then shaken with aqueous $NaHSO_3$ to remove residual I_2. The organic layer was washed, dried ($MgSO_4$), and evaporated to leave a solid, which was recrystallized twice from pentane to give *(iododimethylsilyl)[dimethyl(vinyl)silyl]bis(trimethylsilyl)methane* (5.2 g. 74%), m.p. 300 °C (Found: C, 36.4; H, 7.6. $C_{13}H_{33}ISi_4$ requires C, 36.45; H, 7.7%); δ_H 0.36 (18 H, s, $SiMe_3$), 0.45 (6 H, s, $SiMe_2CH{=}CH_2$), 1.08 (6 H, s, $SiMe_2I$), and 5.5—6.7 (3 H, m, $CH{=}CH_2$); *m/z* 413 (45%, $[M - Me]^+$), 401 (60, $[M - CH{=}CH_2]^+$), 301 (100, $[M - I]^+$), 213 (85, $[M - Me_3SiI - Me]^+$), 201 (72, $[M - Me_2(CH_2{=}CH)SiI]^+$), 187 (40), 155 (10), 149 (50), 129 (50), 85 (30), 73 (100), and 59 (65).

When the same procedure was used but without the $Me_3SiCH{=}CH_2$, the [1]H n.m.r. spectrum and analysis by linked g.l.c.–mass spectrometry indicated that the product was a mixture of $VsiSiMe_2I$ and $(Me_3Si)_2C(SiMe_2I)_2$.

(*c*) A 1.0M solution of ICl in CCl_4 (0.73 cm^3; 0.73 mmol of ICl) was added dropwise to a stirred solution of $VsiSiMe_2H$ (0.22 g, 0.73 mmol) in CCl_4 (25 cm^3) at room temperature. The mixture was stirred for 30 min then shaken with aqueous $NaHSO_3$. The organic layer was washed, dried ($MgSO_4$), and evaporated to leave a solid, which was judged from its [1]H n.m.r. spectrum to be a 2:1:2 mixture of $VsiSiMe_2I$, $(Me_3Si)_2C(SiMe_2Cl)_2$, and $VsiSiMe_2H$; a solution of authentic samples of these compounds in 2:1:2 ratio gave a virtually identical spectrum.

Reaction of $VsiSiPh_2H$ *with* I_2 *and* Br_2.—(*a*) A solution of I_2 (0.44 g, 1.73 mmol) in CCl_4 (5 cm^3) was added to a solution of $VsiSiPh_2H$ (0.70 g, 1.63 mmol) in CCl_4 (10 cm^3) and the mixture was stirred at room temperature for 96 h. Work-up as in the preceding experiment left a solid, which was sublimed (90 °C at 0.2 Torr). The [1]H n.m.r. spectrum of the product showed no signal from $CH{=}CH_2$ protons but the signal from the SiH proton was still present.

(*b*) A 1.0M solution of Br_2 in CCl_4 (1.1 cm^3; 1.1 mmol of Br_2) was added to a stirred solution of $VsiSiPh_2H$ (0.43 g, 1.0 mmol) in CCl_4 (10 cm^3) cooled in a bath at -20 °C. Stirring at -20 °C was continued for 20 min then the mixture was allowed to warm up and then evaporated under reduced pressure. The residue was sublimed (70 °C at 0.5 Torr) to give a solid whose [1]H n.m.r. spectrum showed no signal from $CH{=}CH_2$ protons but did show one from SiH.

Preparations of $VsiSiMe_2X$ (X = O_2CMe, O_2CPh, $O_3SC_6H_4Me$-*p*, O_3SCF_3, F, OCN, *or* O_2CCF_3) *by Reactions of* (**1**) *with Silver Salts*.—(*a*) A mixture of (**1**) (0.21 g, 0.50 mmol) and AgO_2CMe (0.10 g, 0.60 mmol) in CH_2Cl_2 (10 cm^3) was stirred at room temperature for 1.5 h. The solution was then filtered and evaporated to leave a solid, which was sublimed (120 °C at 0.2 Torr) to give (*acetoxydimethylsilyl*)[*dimethyl*(*vinyl*)*silyl*]*bis*(*trimethylsilyl*)*methane* (0.14 g, 80%), m.p. 225 °C (Found: C, 50.4; H, 10.2. $C_{15}H_{36}O_2Si_4$ requires C, 50.0; H, 10.0%); δ_H 0.33 (18 H, s, $SiMe_3$), 0.40 (6 H, s, $SiMe_2CH=CH_2$), 0.60 (6 H, s, $SiMe_2O$), 2.06 (3 H, s, COMe), and 5.5—6.7 (3 H, m, $CH=CH_2$); ν(C=O) 1 725 cm^{-1}; *m/z* 345 (100%, $[M - Me]^+$), 335 (5, $[M - CH=CH_2]^+$), 303 (10), 287 (20), 275 (75), 213 (15), 201 (30), 187 (22), 155 (10), 129 (20), 85 (5), 73 (90), and 59 (15).

(*b*) The procedure described under (*a*), but with AgO_2CPh and culminating in recrystallization from pentane, gave (*benzoyloxydimethylsilyl*)[*dimethyl*(*vinyl*)*silyl*]*bis*(*trimethylsilyl*)*methane* (86%), m.p. 90 °C (Found: C, 56.7; H, 9.3. $C_{20}H_{38}O_2Si_4$ requires C, 56.9; H, 9.0%); δ_H 0.28 (18 H, s, $SiMe_3$), 0.35 (6 H, s, $SiMe_2CH=CH_2$), 0.62 (6 H, s, $SiMe_2O$), 5.6—6.8 (3 H, m, $CH=CH_2$), and 7.3—8.2 (5 H, m, Ph); ν(C=O) 1 725 cm^{-1}; *m/z* 407 (60%, $[M - Me]^+$, 395 (10, $[M - CH=CH_2]^+$), 287 (50), 275 (70), 213 (20), 201 (15), 137 (50), 179 (30), 155 (10), 129 (20), 122 (60), 105 (100, $[COPh]^+$), 85 (80), 77 (80), 73 (98), and 59 (63).

(*c*) A mixture of (**1**) (0.10 g, 0.23 mmol), $AgO_3SC_6H_4Me$-*p* (0.12 g, 0.25 mmol), and anhydrous Et_2O (15 cm^3) was stirred at room temperature for 1.5 h then filtered, and the filtrate was evaporated to leave a solid, which was recrystallized from pentane to give [*dimethyl*-(p-*tolylsulphonyloxy*)*silyl*][*dimethyl*(*vinyl*)*silyl*]*bis*(*trimethylsilyl*)*methane* (0.09 g, 81%), m.p. 85 °C (Found: C, 50.5; H 8.6. $C_{20}H_{40}O_3SSi_4$ requires C, 50.7; H, 8.5%); δ_H 0.21 (18 H, s, $SiMe_3$), 0.28 (6 H, s, $SiMe_2CH=CH_2$), 0.66 (6 H, s, $SiMe_2O$), 2.47 (3 H, s, Me), 5.5—6.6 (3 H, m, $CH=CH_2$), and 7.2—7.9 (5 H, m, Ph); *m/z* 457 (90%, $[M - Me]^+$), 445 (5, $[M - CH=CH_2]^+$), 357 (10), 349 (30), 301 (40, $[M - O_3SC_6H_4Me]^+$), 275 (70), 216 (60), 205 (80), 201 (50, $M - O_3SC_6H_4Me - Me]^+$), 187 (50), 155 (55), 129 (40), 91 (35), 85 (30), and 73 (100).

(*d*) A mixture of (**1**) (0.20 g, 0.47 mmol), AgO_3SCF_3 (0.12 g, 0.24 mmol), and Et_2O (20 cm^3) was stirred under dry N_2 for 30 min at room temperature. The solution was then filtered and evaporated, and the residue was sublimed (100 °C at 0.1 Torr) to give [*dimethyl*(*trifluoromethanesulphonyloxy*)*silyl*][*dimethyl*(*vinyl*)*sylyl*]*bis*(*trimethylsilyl*)*methane* (0.17 g, 81%) (Found: C, 36.8; H, 7.3. $C_{14}H_{33}F_3O_3SSi_4$ requires C, 37.3; H, 7.3%); δ_H 0.26 (18 H, s, $SiMe_3$), 0.32 (6 H, s, $SiMe_2CH=CH_2$), 0.67 (6 H, s, $SiMe_2O$), and 5.5—6.5 (3 H, m, $CH=CH_2$); δ_F −72.7 (s); *m/z* 435 (60%, $[M - Me]^+$), 423 (20, $[M - CH=CH_2]^+$), 349 (15), 301 (10, $[M - O_3SCF_3]^+$), 275 (50), 213 (60, $[M - Me_3SiO_3SC_6H_4Me - Me]^+$), 201 (40), 187 (40), 155 (25), 141 (15), 129 (30), 85 (50), 73 (10), and 59 (70).

(*e*) A mixture of (**1**) (0.12 g, 0.28 mmol), $AgBF_4$ (0.057 g, 0.29 mmol), and Et_2O (20 cm^3) was stirred at room temperature for 1 h, then the solution was filtered and evaporated. The residual solid was sublimed (90 °C at 0.1 Torr) to give [*dimethyl*(*vinyl*)*silyl*](*fluorodimethylsilyl*)*bis*(*trimethylsilyl*)*methane* (0.06 g, 67%), m.p. 190 °C (Found: C, 48.5: H, 10.5. $C_{13}H_{33}FSi_4$ requires C, 48.75; H, 10.3%); δ_H 0.23 (18 H, s, $SiMe_3$), 0.30 (6 H, s, $SiMe_2CH=CH_2$), 0.34 (6 H, d, $SiMe_2F$), and 5.4—6.6 (3 H, m, $CH=CH_2$); δ_F −143.8 (m); *m/z* 305 (85%, $[M - Me]^+$), 293 (15, $[M - CH=CH_2]^+$), 213 (100, $[M - Me_3SiF - Me]^+$), 205 (75), 201 (40), 187 (10), 155 (10), 129 (10), 85 (10), and 73 (70).

(*f*) A mixture of (**1**) (0.02 g, 0.47 mmol), freshly prepared AgOCN (0.025 g, 0.50 mmol), and CH_2Cl_2 (25 cm^3) was stirred under dry N_2 for 30 min. The solution was filtered under dry N_2 and then evaporated to leave a solid, which was recrystallized from pentane to give (*cyanatodimethylsilyl*)[*dimethyl*(*vinyl*)*silyl*]*bis*(*trimethylsilyl*)*methane* (0.12 g, 75%) (Found: C, 49.1; H, 9.4; N, 3.7. $C_{14}H_{33}ONSi_4$ requires C, 49.0; H, 9.6; N, 4.1%); δ_H 0.34 (18 H, s, $SiMe_3$), 0.40 (6 H, s, $SiMe_2CH=CH_2$), 0.67 (6 H, s, $SiMe_2OCN$), and 5.4—6.4 (3 H, m, $CH=CH_2$); δ_C 4.37 (s, $SiMe_3$), 4.56 (s) and 4.72 (s), (one of these from $SiMe_2OCN$ and the other from $SiMe_2CH=CH_2$), 109.9 (s, OCN), 132.4 (s) and 140.9 (s) (the last two from $CH=CH_2$); δ_{Si} − 9.22 (s, $SiMe_2CH=CH_2$), −1.4 (s, $SiMe_3$), and 38.1 (s, $SiMe_2OCN$); ν(SiOCN) (CH_2Cl_2) 2 220 cm^{-1}; *m/z* 328 (30%, $[M - Me]^+$), 316 (5, $[M - CH=CH_2)^+$], 303 (10), 285 (10), 275 (20), 213 (15, $[M - Me_3SiOCN - Me]^+$), 201 (10), 187 (10), 129 (10), 100 (10, $[Me_2SiOCN]^+$), 85 (10), 73 (100), and 59 (30).

(*g*) A mixture of (**1**) (0.21 g, 0.50 mmol), AgO_2CCF_3 (0.12 g, 0.60 mmol), and CH_2Cl_2 (10 cm^3) was stirred at room temperature for 15 min. The solution was filtered then evaporated, and the residual solid sublimed (100 °C at 0.5 Torr) to give [*dimethyl*(*vinyl*)*silyl*](*trifluoroacetoxydimethylsilyl*)*bis*(*trimethylsilyl*)*methane*, m.p. 185 °C (Found: C, 45.0; H, 8.2. $C_{15}H_{33}F_3O_2Si_4$ requires C, 44.8; H, 8.4%); δ_H 0.31 (18 H, s, $SiMe_3$), 0.37 (6 H, s, $SiMe_2CH=CH_2$), 0.64 (6 H, s, $SiMe_2O$), and 5.8—6.5 (3 H, m, $CH=CH_2$); δ_F −71.4 (s); ν(C=O) 1 765 cm^{-1}; *m/z* 399 (40%, $[M - Me]^+$), 387 (15, $[M - CH=CH_2]^+$), 297 (15), 275 (20), 213 (20, $[M - Me_3SiO_2CCF_3 - Me]^+$), 205 (75), 201 (20), 187 (10), 155 (10), 129 (10), 85 (15), 77 (20, $[Me_2FSi]^+$), and 73 (100).

(*h*) A solution of (**1**) (0.10 g, 0.23 mmol) in CH_2Cl_2 (10 cm^3) was stirred at room temperature in the presence of freshly prepared AgSCN (0.04 g, 0.24 mmol). After 30 min a sample was withdrawn and filtered, and its ^1H n.m.r. spectrum showed (in addition to peaks from $SiMe_2$ protons) three singlets in the $SiMe_3$ region, at δ 0.36, 0.30, and 0.26 ppm., in a *ca.* 2:2:3 ratio. [The signals at δ 0.36 and 0.30 p.p.m. are attributable to (**1**) and $VsiSiMe_2NCS$, respectively.] After a further 1 h the remaining solution was filtered then evaporated under reduced pressure to give $VsiSiMe_2NCS$, with properties identical to those described under (*a*) immediately below.

Preparation of $VsiSiMe_2X$ (X = NCS, N_3, NCO, *or* Cl) *by Reactions of* (**1**) *with Alkali Metal Salts*.—(*a*) A mixture of (**1**) (0.50 g, 1.17 mmol), KSCN (2.0 g, 20 mmol), and MeCN (25 cm^3) was boiled under reflux for 1 h then cooled to room temperature. Hexane was added, followed by an excess of water, and the organic layer was separated, washed, dried ($MgSO_4$), and evaporated to leave [*dimethyl*(*vinyl*)*silyl*](*isothiocyanatodimethylsilyl*)*bis*(*trimethylsilyl*)*methane* (0.35 g, 85%), m.p. 230 °C (Found: C, 46.5; H, 8.9; N, 3.8. $C_{14}H_{33}NSSi_4$ requires C, 46.8; H, 9.2; N, 3.9%); δ_H 0.30 (18 H, s, $SiMe_3$), 0.38 (6 H, s, $SiMe_2CH=CH_2$), 0.52 (6 H, s, $SiMe_2NCS$), and 5.5—6.6 (3 H, m, $CH=CH_2$); ν(SiNCS) 2 080 cm^{-1}; *m/z* 344 (50%, $[M - Me]^+$), 332 (10, $[M - CH=CH_2]^+$), 213 (20, $[M - Me_3SiNCS - Me]^+$), 201 (15), 155 (10), 129 (10), 85 (15), 73 (100), and 59 (33).

(*b*) A mixture of (**1**) (0.10 g, 0.23 mmol), NaN_3 (0.25 g, 3.85 mmol); and MeCN (20 cm^3) was boiled under reflux for 10 h then cooled and added to water. Extraction with hexane, followed by washing, drying ($MgSO_4$), and evaporation of the extract left a solid, which was sublimed (80 °C at 0.5 Torr) to give (*azidodimethylsilyl*)[*dimethyl*(*vinyl*)*silyl*]*bis*(*trimethylsilyl*)*methane* (0.060 g, 74%), m.p. 220 °C; δ_H 0.28 (18 H, s, $SiMe_3$), 0.34 (6 H, s, $SiMe_2CH=CH_2$), 0.50 (6 H, s, $SiMe_2N_3$), and 5.6—6.6 (3 H, m, $CH=CH_2$); ν(SiN_3) 2 140 cm^{-1}; *m/z* 328 (90%, $[M - Me]^+$), 316 (20, $[M - CH=CH_2]^+$), 301 (95, $(M - N_3]^+$), 284 (40), 274 (30), 258 (30), 242 (30), 228 (30), 212 (30), 202 (30), 188 (30), 100 (15, $[Me_2SiN_3]^+$), 85 (15), 73 (100), and 59 (30).

(*c*) The procedure described under (*a*) above but starting from (**1**) (0.16 g, 0.37 mmol), KOCN (0.50 g, 6.2 mmol), and MeCN (15 cm^3), and with reflux for 8 h, gave a solid, which was recrystallized from pentane to give [*dimethyl*(*vinyl*)*silyl*]-

(isocyanatodimethylsilyl)bis(trimethylsilyl)methane (0.090 g, 70%), m.p. 225 °C (Found: C, 48.7; H, 9.7. $C_{14}H_{33}NOSi_4$ requires C, 49.0; H, 9.6%); δ_H 0.28 (18 H, s, $SiMe_3$), 0.35 (6 H, s, Si*Me*$_2$CH=CH$_2$), 0.48 (6 H, s, $SiMe_2NCO$), and 5.5—6.7 (3 H, m, CH=CH$_2$); ν(SiNCO) (CH_2Cl_2) 2 245 cm^{-1}; *m/z* 343 (30%, [*M*]$^+$), 328 (100, [*M* − Me]$^+$), 316 (30, [*M* − CH=CH$_2$]$^+$), 301 (5, [*M* − NCO]$^+$), 285 (80), 228 (70), 213 (80), [*M* − Me$_3$SiNCO − Me]$^+$), 201 (45), 187 (15), 155 (30), 129 (30), 100 (40), [Me$_2$SiNCO]$^+$), 85 (40), and 73 (100).

(*d*) A mixture of (**1**) (0.50 g, 0.12 mmol), KCl (0.27 g, 3.6 mmol) and MeCN (20 cm^3) was boiled under reflux for 20 h. The solvent was then evaporated under reduced pressure, and the residual solid extracted with hexane. The extract was washed, dried, and evaporated to give VsiSiMe$_2$Cl (0.32 g, 80%), with properties identical to those reported above.

Preparation of VsiSiMe$_2$OMe.—(*a*) A solution of (**1**) (0.10 g, 0.30 mmol) in MeOH (20 cm^3) was boiled under reflux for 15 days. Evaporation of the solvent under reduced pressure left a solid, which was sublimed (100 °C at 0.5 Torr) to give *[dimethyl(vinyl)silyl](methoxydimethylsilyl)bis(trimethylsilyl)-methane* (0.060 g, 77%), m.p. 224 °C (Found: C, 50.8; H, 10.9. $C_{14}H_{36}OSi_4$ requires C, 50.6; H, 10.8%); δ_H 0.21 (18 H, s, SiMe$_3$), 0.27 (12 H, s, Si*Me*$_2$CH=CH$_2$ + Si*Me*$_2$OMe), 3.37 (3 H, s, OMe), and 5.45—6.65 (3 H, m, CH=CH$_2$); *m/z* 317 (100%, [*M* − Me]$^+$), 305 (35, [*M* − CH=CH$_2$]$^+$), 301 (15, [*M* − OMe]$^+$), 275 (20), 217 (30), 213 (35, [*M* − Me$_3$SiOMe − Me]$^+$), 201 (60), 187 (30), 155 (35), 129 (30), 89 (30, [Me$_2$SiOMe]$^+$), 85 (20), 73 (100), and 59 (50).

(*b*) A solution of (**1**) (0.050 g, 0.15 mmol) and AgO$_3$SCF$_3$ (0.040 g, 0.16 mmol) in MeOH (20 cm^3) was stirred under dry N$_2$ for 15 min at room temperature then filtered and evaporated, and the residual solid recrystallized from pentane to give Vsi-SiMe$_2$OMe (70%) with properties identical to those described under (*a*).

Preparation of VsiSiMe$_2$OH.—(*a*) A mixture of VsiSiMe$_2$H (0.10 g, 0.33 mmol), KMnO$_4$ (0.060 g, 0.38 mmol), and C$_5$H$_5$N (2 cm^3) in MeOH (25 cm^3) was boiled under reflux for 28 h. The solution was filtered and the solvent evaporated under reduced pressure, to leave a solid, which was extracted with hexane. The extract was filtered and evaporated, and the residue sublimed (80 °C at 0.2 Torr) to give *[dimethyl(vinyl)silyl](hydroxy-dimethylsilyl)bis(trimethylsilyl)methane* (0.071 g, 68%), m.p. 197 °C (Found: C, 49.0; H, 10.8. $C_{13}H_{34}OSi_4$ requires C, 49.05: H, 11.0%); δ_H 0.22 (18 H, s, SiMe$_3$), 0.30 (12 H, s, Si*Me*$_2$CH=CH$_2$ + Si*Me*$_2$OH), 1.4 (1 H, br s, OH), and 5.2—6.5 (3 H, m, CH=CH$_2$); ν(SiOH) 3 690 and 3 600—3 300 cm^{-1}; *m/z* 303 (55, [*M* − Me]$^+$), 291 (15, [*M* − CH=CH$_2$]$^+$), 287 (30), 275 (90), 213 (20, [*M* − Me$_3$SiOH − Me]$^+$), 201 (20), 187 (50), 155 (15), 129 (30), 85 (30), 73 (100), and 59 (45).

(*b*) A solution of (**1**) (0.12 g, 0.28 mmol) (initially dissolved in *ca.* 0.1 cm^3 of CCl$_4$) in 5% v/v H$_2$O–Me$_2$SO (20 cm^3) was kept at 60 °C for 2 h (after which the ^{1}H n.m.r. spectrum showed that reaction was complete). The solution was shaken with a mixture of CCl$_4$–H$_2$O, and the CCl$_4$ layer separated, washed, dried (MgSO$_4$), and evaporated to leave VsiSiMe$_2$OH, with properties identical to those described above.

(*c*) A mixture of (**1**) (0.15 g, 0.35 mmol) and AgO$_3$SCF$_3$ (0.090 g. 0.38 mmol) in a mixture of H$_2$O (0.5 cm^3) in MeCN (19.5 cm^3) was stirred at room temperature for 15 min. The solution was filtered and evaporated and the residue extracted with hexane. The extract was filtered and dried to give VsiSiMe$_2$OH (0.076 g, 68%), with properties identical to those described above.

Reactions of VsiSiMe$_2$X (X = OMe, OH, O$_2$CMe, O$_2$CCF$_3$, *or* H) *with* CF$_3$CO$_2$H.—(*a*) Trifluoroacetic acid (0.5 cm^3) at room temperature was added to a solution of VsiSiMe$_2$OMe (10 mg) in a drop (*ca.* 0.01 cm^3) of CCl$_4$ contained in a n.m.r. tube. The ^{1}H n.m.r. spectrum was recorded as soon as possible (*ca.* 1 min after mixing), and showed only singlets at δ 0.42 and 0.78 p.p.m. in a 3:2 integration ratio, attributable to (Me$_3$Si)$_2$C(SiMe$_2$OCCF$_3$)$_2$. Addition of an authentic sample enhanced the signals.

(*b*) The procedure described under (*a*) was repeated but with a 4:1 v/v mixture of CCl$_4$ and CF$_3$CO$_2$H. After 2 min at 35 °C the ^{1}H n.m.r. spectrum showed singlets at δ 0.33, 0.51, and 0.70 p.p.m. in a 3:1:1 ratio, thought to be due to (Me$_3$Si)$_2$C-(SiMe$_2$OMe)(SiMe$_2$O$_2$CCF$_3$). After 45 min only (Me$_3$Si)$_2$C-(SiMe$_2$O$_2$CCF$_3$)$_2$ was present. No further reaction occurred during 30 h at 60 °C.

(*c*) A little VsiSiMe$_2$OH (10 mg) was dissolved in a drop of CCl$_4$ (*ca.* 0.01 cm^3) in an n.m.r. tube and CF$_3$CO$_2$H (1 cm^3) at 35 °C was added. The ^{1}H n.m.r. spectrum recorded about 1 min after mixing showed singlets at δ 0.03 and 0.05 p.p.m. due to VsiSiMe$_2$OH, and other singlets at δ 0.08, 0.23, and 0.44 p.p.m. in a 3:1:1 ratio, attributable to (Me$_3$Si)$_2$C(SiMe$_2$OH)-(SiMe$_2$O$_2$CCF$_3$). After 10 min these two compounds were present in a *ca.* 3:7 ratio, and after 1 h only (Me$_3$Si)$_2$C-(SiMe$_2$O$_2$CF$_3$)$_2$ was present. No further reaction took place during 48 h at 60 °C.

(*d*) A solution of VsiSiMe$_2$O$_2$CMe (20 mg) in CF$_3$CO$_2$H (1 cm^3) in an n.m.r. tube was kept at 35 °C. After 18 h the ^{1}H n.m.r. spectrum showed, in addition to the singlets from the starting material at δ 0.36, 0.42, and 0.66 p.p.m., singlets at δ 0.42, 0.44, and 0.78 p.p.m., assumed to be due to (Me$_3$Si)$_2$-C(SiMe$_2$O$_2$CCF$_3$)(SiMe$_2$O$_2$CMe), these two components being present in a 3:2 ratio. After 6 days only singlets at δ 0.42 and 0.78 p.p.m., attributable to (Me$_3$Si)$_2$C(SiMe$_2$O$_2$CCF$_3$)$_2$, were observed. Evaporation gave the latter compound with properties identical to those of an authentic sample.

(*e*) The procedure described under (*d*) was repeated, but starting with VsiSiMe$_2$O$_2$CCF$_3$. After 70 h the ^{1}H n.m.r. spectrum indicated that *ca.* 50% of the latter had been converted into (Me$_3$Si)$_2$C(SiMe$_2$O$_2$CF$_3$)$_2$ (δ_H 0.42 and 0.78 p.p.m.), and this conversion was complete after 12 days. Evaporation gave (Me$_3$Si)$_2$C(SiMe$_2$O$_2$CCF$_3$)$_2$ with properties identical to those of an authentic sample.

(*f*) Trifluoroacetic acid (10 cm^3) was added to a solution of VsiSiMe$_2$H (0.15 g) in a drop of CCl$_4$, and the mixture was kept at 60 °C. After 1 h the ^{1}H n.m.r. spectrum showed that no VsiSiMe$_2$H remained, so the mixture was diluted with water, and extracted with pentane, and the extract was washed, dried, and evaporated to give exclusively VsiSiMe$_2$O$_2$CCF$_3$, with properties identical to those of the sample made by reaction of (**1**) with AgO$_2$CCF$_3$, described above.

Treatment of Various VsiSiMe$_2$X *Compounds* (X = OH, O$_3$SC$_6$H$_4$Me-*p*, F, Cl, Br, NCO, *or* NCS) *with* MeOH *or* H$_2$O–MeOH.—The starting materials were recovered unchanged when solutions of the following VsiSiMe$_2$X compounds in MeOH were boiled under reflux for the time indicated: (X =) OH, 4 h; O$_3$SC$_6$H$_4$Me-*p*, 5 days; F, Cl, Br, or NCO, 2 days; and NCS, 12 days. (In the last case a sample made by use of KSCN and another made by use of AgSCN gave the same result.)

(*b*) When a solution of VsiSiMe$_2$NCO in 5% v/v H$_2$O–MeOH was kept at 60 °C for 7 days the starting material was recovered unchanged.

(*c*) A solution of VsiSiMe$_2$N$_3$ (10 mg) (initially dissolved in *ca.* 0.01 cm^3 of CCl$_4$) in 5% v/v H$_2$O–MeOH (1 cm^3) in a n.m.r. tube, was kept at 50 °C. In 10 days there was no change in the ^{1}H n.m.r. spectrum.

Reactions of VsiSiMe$_2$OCN.—(*a*) A little VsiSiMe$_2$OCN (10 mg) was dissolved in a drop of CCl$_4$ (*ca.* 0.01 cm^3) in an n.m.r. tube and MeOH (0.5 cm^3) was added. The tube was sealed, briefly shaken, and transferred to the probe of the spectrometer at 35 °C. The ^{1}H n.m.r. spectra indicated that after 0.5, 1, and 6 h, respectively, *ca.* 25, 55, and 100% of the cyanate had reacted, to give $VsiSiMe_2OMe$ and $VsiSiMe_2OH$ in a *ca.* 1:1 ratio.

(*b*) *A solution of* $VsiSiMe_2OCN$ (0.50 g) in 5% v/v H_2O–MeOH (20 cm^3) was stirred at room temperature for 30 min. The solvent was then evaporated off under reduced pressure to leave exclusively $VsiSiMe_2OH$ (0.033 g, 74%), with properties identical to those of an authentic sample.

(*c*) A little $VsiSiMe_2OCN$ (15 mg) was dissolved in Ph_2O (0.5 cm^3) in an n.m.r. tube, which was sealed, placed in a bath at 195 ± 3 °C, and removed at intervals for recording of the ^{1}H n.m.r. spectrum. From the relative heights of the $SiMe_2NCO$ and $SiMe_2OCN$ signals it was judged that after 2, 5, and 11 h, the isomerization into the isocyanate was, respectively, *ca.* 55, 75, and 90%, complete.

In a similar procedure but starting with a smaller amount (7 mg) of the cyanate, *ca.* 40 and 75% isomerization had occurred after 2.5 and 9 h, respectively.

Reaction of $VsiSiMe_2OH$ *with* NaOMe–MeOH.—A solution of $VsiSiMe_2OH$ (0.06 g) in 0.20M-NaOMe–MeOH (20 cm^3) was boiled under reflux for 2 h then cooled. Hexane was added, followed by an excess of water, and the organic layer was separated, washed, dried ($MgSO_4$), and evaporated, to leave a thick liquid. Linked g.l.c.–mass spectrometry (3% OV 101 on Chromasorb G at 180 °C) revealed only one new component (95%) along with unchanged starting material (5%). The product was isomeric with the starting material; *m/z* 303 (100%, $[M - Me]^+$), 215 (10), 203 (10), 129 (5), 85 (5), 73 (20), and 59 (5). The ^{1}H n.m.r. spectrum indicated that it was $(Me_3Si)_2CH(SiMe_2OSiMe_2CH{=}CH_2)$; δ_H −0.06 (1 H, s, CH), 0.16 (18 H, s, $SiMe_3$), 0.22 (12 H, s, $SiMe_2O$ + $SiMe_2CH{=}CH_2$), and 5.5—6.6 (3 H, m, $CH{=}CH_2$).

Treatment of $VsiSiMe_2OMe$ *with* 0.4M-NaOMe–MeOH.—A solution of $VsiSiMe_2OMe$ (0.10 g) in 0.40M-NaOMe–MeOH (20 cm^3) was boiled under reflux for 72 h. Work-up as in the preceding experiment gave exclusively unchanging starting material (0.090 g, 90%).

Reaction of (**1**)-*with* 1M-NaOMe–MeOH.—A solution of (**1**) (0.080 g) in 1M-NaOMe–MeOH (10 cm^3) was boiled under reflux for 24 h then cooled. Hexane was added, followed by an excess of water, and the organic layer was washed, dried ($MgSO_4$), and evaporated to leave a residue that was subjected to g.l.c.–mass spectrometry (5% OV 101 on Chromasorb G at 200 °C), to reveal the presence of five components (**A**)—(**E**), in the ratio (**A**):(**B**):(**C**):(**D**):(**E**) of *ca.* 2:3:1:1:2. The mass spectra of components (**A**), (**B**), and (**E**) were consistent with the formulations $(Me_3Si)_2CHSiMe_2OMe$, $(Me_3Si)CH(SiMe_2CH{=}CH_2)(SiMe_2OMe)$, and $(Me_3Si)_2C(SiMe_2CH{=}CH_2)(SiMe_2OMe)$: (**A**), *m/z* 233 (100%, $[M - Me]^+$), 219 (15), 203 (15), 187 (5), 129 (35), 89 (5, $[Me_2SiOMe]^+$), and 73 (25); (**B**), *m/z* 245 (100%, $[M - Me]^+$), 233 (35, $[M - CH{=}CH_2]^+$), 203 (10), 141 (25), 129 (25), 89 (10), 85 (5), 73 (35), and 59 (26); (**C**), *m/z* 275 (60%), 245 (10), 233 (10), 187 (7), 129 (30), 89 (10), 73 (10), and 59 (10); (**D**), *m/z* 319 (30%), 315 (25), 287 (40), 245 (100), 233 (10), 203 (10), 115 (12), 89 (15), 73 (35), and 59 (30); (**E**) 317 (100%, $[M - Me]^+$), 305 (20, $[M - CH{=}CH_2]^+$), 213 (10, $[M - Me_3SiOMe - Me]^+$), 201 (10, $[M - Me_2MeOSiCH{=}CH_2 - Me]^+$), 129 (10), 89 (10), 85 (5), and 73 (40).

Reaction of $VsiSiEt_2Cl$ *with* $AgBF_4$.—(*a*) A mixture of $VsiSiEt_2Cl$ (0.080 g, 0.22 mmol), $AgBF_4$ (0.045 g, 0.23 mmol), and CH_2Cl_2 (10 cm^3) was stirred at room temperature for 12 h, during which evolution of gas was noticed. The solution was filtered then evaporated to leave a solid, the ^{1}H n.m.r. spectrum of which showed no signals from vinyl protons. Its mass spectrum was consistent with it being $(Me_3Si)_2C(SiMe_2F)(SiEt_2Cl)$ and/or its isomer; *m/z* 341 (80, $[M - Me]^+$), 327 (65, $[M - Et]^+$), 321 (35, $[M - Cl]^+$), 235 (50, $[M - Me_3SiF - Me]^+$), 205 (65), 129 (30), 113 (20), 77 (30, $[Me_2SiF]^+$), and 73 (100).

(*b*) In a similar procedure but with Et_2O as solvent, there was no detectable reaction in 48 h.

Reaction of $VsiSiEt_2Cl$ *with* AgO_3SCF_3.—A mixture of $VsiSiEt_2Cl$ (0.081 g, 0.22 mmol), AgO_3SCF_3 (0.063 g, 0.24 mmol), and CH_2Cl_2 (10 cm^3) was boiled under reflux for 4 h. The solution was then filtered and evaporated to give a solid, the ^{1}H n.m.r. spectrum of which was complex, but included some signals in the vinyl proton region. The ^{19}F spectrum showed two singlets, at −72.5 and −74.1 p.p.m., in a 2:3 ratio. Linked g.l.c.–mass spectrometry gave two peaks in a 35:65 ratio, the second having a mass spectrum identical with that of the starting material and the first a mass spectrum consistent with the formulation $(Me_3Si)_2C(SiMe_2O_3SCF_3)(SiEt_2Cl)$ or its isomers; *m/z* 471 (65%, $[M - Me]^+$), 457 (30, $[M - Et]^+$), 337 (10, $[M - O_3SCF_3]^+$), 205 (12), 129 (10), and 73 (100).

Reaction of $VsiSiEt_2I$ *with* $AgBF_4$.—A mixture of (**1**) (0.10 g, 0.22 mmol), $AgBF_4$ (0.047 g, 0.24 mmol), and Et_2O (20 cm^3) was stirred at room temperature for 30 min. The solution was filtered and evaporated, to leave a solid. The ^{1}H n.m.r. spectrum (360 MHz) of this product showed it to be a mixture, and the components were judged to be: (*i*) $(Me_3Si)_2C(SiMe_2F)(SiEt_2F)$; δ_H 0.24 (18 H, s, $SiMe_3$), 0.39 (6 H, d, *J* 7.5 Hz, $SiMe_2$), and 0.94—1.26 (10 H, m, $SiEt_2$); (*ii*) $(Me_3Si)_2C(SiMe_2CH{=}CH_2)(SiEt_2F)$; δ 0.25 (18 H, s, $SiMe_3$), 0.30 (6 H, s, $SiMe_2CH{=}CH_2$), 0.94—1.26 (10 H, m, $SiEt_2$), and 5.4—6.4 (3 H, m, $CH{=}CH_2$); and (*iii*) $(Me_3Si)_2C(SiMe_2F)(SiEt_2CH{=}CH_2)$; δ_H 0.25 (18 H, s, $SiMe_3$), 0.37 (6 H, d, *J* 7.5 Hz, $SiMe_2$), 0.94—1.26 (10 H, m, $SiEt_2$), and 5.4—6.4 (3 H, m, $CH{=}CH_2$); these appeared to be present in a 1:3:6 ratio as judged from the heights of the signals from the $SiMe_2$ protons. The ^{19}F n.m.r. spectrum showed multiplets, with the splitting pattern expected for $SiEt_2F$ signals, at −154.5 and −155.4, and two more, with splitting patterns expected for $SiMe_2F$ signals, at −136.8 p.p.m. and −138.6 p.p.m. Linked g.l.c.–mass spectrometry (3% OV 101 on Chromasorb G at 220 °C) revealed three components, (**A**), (**B**), and (**C**), in a ratio of 1:3:6. (**A**) appeared to be the difluoride $(Me_3Si)_2C(SiMe_2F)(SiEt_2F)$ {*m/z* 325 (50%, $[M - Me]^+$), 311 (50, $[M - Et]^+$), 234 (15), 219 (80), 205 (60), 199 (22), 129 (15), 87 (10), 73 (100), 59 (10)}, and (**B**) and (**C**) were isomers, thought to be $(Me_3Si)_2C(SiMe_2F)(SiEt_2CH{=}CH_2)$ and $(Me_3Si)_2C(SiMe_2CH{=}CH_2)(SiEt_2F)$, respectively, *m/z* 333 ($[M - Me]^+$), 321 ($[M - CH{=}CH_2]^+$), 319 ($[M - Et]^+$), 227, 213, 129, 85, 73 (base peak), and 59. The ^{29}Si n.m.r. spectrum showed signals at: (*i*) δ −9.32 (s, $SiMe_2CH{=}CH_2$), −2.08 (s, $SiMe_3$), and 27.1 p.p.m. (d, *J* 284 Hz, $SiEt_2F$) attributed to $(Me_3Si)_2C(SiMe_2CH{=}CH_2)(SiEt_2F)$; (*ii*) −4.34 (s, $SiEt_2CH{=}CH_2$), −2.08 (s, $SiMe_3$), and 26.4 p.p.m. (d, *J* 294.5 Hz, $SiMe_2F$), attributed to $(Me_3Si)_2C(SiMe_2F)(SiEt_2CH{=}CH_2)$; and (*iii*) −2.73 (s, $SiMe_3$), 26.5 (d, *J* 294.5 Hz, $SiMe_2F$), 26.7 p.p.m. (d, *J* 284 Hz, $SiEt_2F$), attributed to $(Me_3Si)_2C(SiMe_2F)(SiEt_2F)$.

When the procedure was repeated, but with CH_2Cl_2 as solvent, the outcome, as judged from the ^{1}H and ^{19}F n.m.r. spectra, was effectively the same.

Reaction of $VsiSiEt_2I$ *with* AgO_2CCF_3.—A mixture of $VsiSiEt_2I$ (0.10 g, 0.22 mmol), AgO_2CCF_3 (0.053 g, 0.24 mmol), and Et_2O (20 cm^3) was stirred for 1 h at room temperature. The solution was filtered and evaporated, and the residue was sublimed (80 °C at 0.1 Torr) to give a white solid, which was judged from its ^{1}H and ^{19}F n.m.r. spectra to contain $VsiSiEt_2$-

O_2CCF_3 and $(Me_3Si)_2C(SiMe_2O_2CCF_3)(SiEt_2CH{=}CH_2)$ in a 1:2 ratio [as indicated by the relative heights of (*i*) the ^1H signals from the $SiMe_3$ groups and (*ii*) the two ^{19}F signals]. For $VsiSiEt_2O_2CCF_3$: δ_H 0.29 (18 H, s, $SiMe_3$), 0.33 (6 H, s, $SiMe_2$), 0.88—1.33 (10 H, m, $SiEt_2$), and 5.06—6.45 (3 H, m, $CH{=}CH_2$); δ_F −70.3 p.p.m. For $(Me_3Si)_2C(SiMe_2O_2CCF_3)$-$(SiEt_2CH{=}CH_2)$: δ_H 0.29 (18 H, s, $SiMe_3$), 0.62 (6 H, s, $SiMe_2$), 0.88—1.33 (10 H, m, $SiEt_2$), and 5.06—6.45 (3 H, m, $CH{=}CH_2$); δ_F −71.05 p.p.m. In addition the ^{19}F n.m.r. spectrum showed two small singlets (with combined heights *ca.* 10% of the combined heights of the main signals) at −71.2 and −70.4, attributable to $(Me_3Si)_2C(SiMe_2O_2CCF_3)(SiEt_2O_2CCF_3)$; Linked g.l.c.-mass spectrometry (3% OV 101 on Chromasorb G) gave only one substantial peak, and the mass spectra of samples from the front and rear sections of this peak had identical mass spectra, assumed to arise from $VsiSiEt_2O_2CCF_3$ and $(Me_3Si)_2C(SiMe_2O_2CCF_3)(SiEt_2CH{=}CH_2)$; *m/z* (main ions only) 427 ($[M-Me]^+$), 415 ($[M-CH{=}CH_2]^+$), 413 ($[M-Et]^+$), 329 ($[M-O_2CCF_3]^+$), 85, and 73 (base peak).

Comparisons of the Reactivities of $VsiSiMe_2X$ *and* $TsiSiMe_2X$ *Compounds.* (1) *Solvolysis.*—For reactions in MeOH, CF_3CH_2OH, CF_3CO_2H, or MeOH (sometimes containing NaOMe or H_2O), H_2O–Me_2SO, or H_2O–DMF, usually about 5—10 mg of the organosilicon compound was dissolved in a drop (*ca.* 0.01 cm^3) of CCl_4 in an n.m.r. tube, then the appropriate solvent (0.5—1.0 cm^3) was added, and the tube was capped, shaken briefly, then placed either in the probe of the spectrometer or (for reactions at temperatures above 35 °C) in a thermostat bath, from which it was removed at intervals for recording of the spectrum. The progress of the reaction was monitored by determining the ratio of the height of a suitable ^1H n.m.r. signal from the starting material [usually from $(Me_3Si)_3C$ or $(Me_3Si)_2C$ protons] to that of the analogous signal from the product.

For reactions in H_2O–MeCN, a solution of 0.25 mmol of the organosilane (initially dissolved in a drop of CCl_4) in 25 cm^3 of H_2O–MeCN was kept in a stoppered vessel in a thermostat bath, and samples (*ca.* 2 cm^3) were withdrawn at intervals and quickly evaporated to dryness under reduced pressure. The residue was dissolved in CCl_4, the solution was filtered, and its n.m.r. spectrum recorded.

A solution described as containing x% v/v of water consisted of a mixture of x vol of water with (100 − x) vol of the solvent. Unless otherwise indicated, the identities of the products were established by comparison of their ^1H n.m.r. spectra with those of similar solutions of authentic samples.

(*a*) *Methanolysis of the iodides* (**1**) *and* (**2**). Reactions were at 49 °C. For reactions in MeOH or 0.05M-NaOMe–MeOH the Me_3Si peaks of the starting material and products were used. For reactions of (**1**) in 0.10—0.40M-NaOMe–MeOH the ratio of the heights of the Me_3Si signals of the starting material to the combined heights of the corresponding peaks of the products $VsiSiMe_2OMe$ and $(Me_3Si)_2CHSiMe_2OMe$ were used; the final ratios of these products were *ca.* 6:1, 4:1, and 2:1 in 0.10, 0.20, and 0.40M-NaOMe–MeOH respectively. Good first-order plots were obtained up to >80% completion of the reactions, and the values of the rate constants are shown in Table 2.

(*b*) *Methanolysis of* $VsiSiMe_2O_3SCF_3$. The MeOH or NaOMe–MeOH was preheated to 35 °C before addition to the organosilane. The sole product in each case was $VsiSiMe_2OMe$. Good first-order kinetics were obtained up to >90% completion of the reaction. The values of the rate constants are shown in Table 2.

(*c*) *Hydrolysis of* (**1**) *and* (**2**). The sole product in each case was the corresponding hydroxide. Good first-order plots were obtained up to >80% completion of the reaction, and the values of the half-lives are shown in Table 3.

(*d*) *Solvolysis of* (**1**) *and* (**2**) in CF_3CH_2OH. When a solution of (**1**) in CF_3CH_2OH was kept at 50 °C, the approximate extents of reaction at various times were: 15%, 45 min; 42%, 120 min; 57%, 180 min; and 71%, 270 min; thus the reaction was 50% complete in *ca.* 2.5 h. After 8 h the solvent was evaporated off, to give $(Me_3Si)_2C(SiMe_2OCH_2CF_3)_2$, m.p. 68 °C; δ_H 0.22 (18 H, s, $SiMe_3$), 0.32 (12 H, s, $SiMe_2$), and 3.68—3.98 (4 H, q, OCH_2); δ_F −68.3 p.p.m.; *m/z* 457 (57%, $[M-Me]^+$), 373 (10, $[M-OCH_2CF_3]^+$), 357 (20), 297 (53), 275 (25), 255 (60), and 73 (100). (These properties are identical to those of an authentic sample.)

When the procedure was repeated but in the presence of Et_3N (0.024 mmol), the reaction was *ca.* 50% complete in 2.4 h, and the product was $VsiSiMe_2OCH_2CF_3$, m.p. 135 °C; δ_H 0.24 (18 H, s, $SiMe_3$), 0.30 (6 H, s, $SiMe_2$), 0.35 (6 H, s, $SiMe_2O$), 3.88—4.22 (2 H, q, OCH_2), and 5.5—6.6 (3 H, m, $CH{=}CH_2$); δ_F −70.9 p.p.m. (t); *m/z* 385 (100%, $[M-Me]^+$), 373 (20, $[M-CH{=}CH_2]^+$), 305 (85), 301 (20, $[M-OCH_2CF_3]^+$), 243 (20), 187 (30), 213 (100, $[M-Me_3SiOCH_2CF_3-Me]^+$), 201 (70, $[M-CH_2{=}CHMe_2SiOCH_2CF_3-Me]^+$), 155 (20), 129 (30), 85 (20), 73 (100), and 59 (20).

When (**2**) was used in place of (**1**) in the first procedure described above (*i.e.* in the absence of Et_3N), there was no detectable reaction in 5 days.

(*e*) *Solvolysis of* (**1**) *and* (**2**) *in* CF_3CO_2H. When a solution of (**1**) in CF_3CO_2H was kept at 50 °C the final product was $(Me_3Si)_2C(SiMe_2O_2CCF_3)_2$, but during the reaction $VsiSiMe_2O_2CCF_3$ appeared and then disappeared. The ratios of (**1**), the intermediate, and the final product, respectively, at various times were: 5 min, 65:15:20; 10 min, 45:20:35; 15 min, 20:25:55; and 20 min, 10:25:65. After 50 min only the bis(trifluoroacetate) was present.

When the procedure was repeated but in the presence of one equivalent of Et_3N, the final product was $VsiSiMe_2O_2CCF_3$, and the half-life was *ca.* 8 min. The reaction of (**2**) with CF_3CO_2H alone gave a good first-order plot with a half-life of *ca.* 235 h.

(2) *Reactions with Silver Salts.*—Usually a mixture of the relevant organosilicon halide (0.25 mmol) with the appropriate silver salt (0.25 mmol) in CH_2Cl_2 (20 cm^3) was stirred at room temperature (*ca.* 21 °C). Samples were removed at intervals and filtered through cotton wool into an n.m.r. tube, the ^1H n.m.r. spectra were recorded, and the ratio of starting material to product was estimated from the heights of the Me_3Si peaks.

In some specified cases, a mixture of (**1**) and (**2**) was used with a deficiency of the silver salt.

(*a*) A mixture of (**1**) (0.25 mmol), (**2**) (0.25 mmol), and $AgO_3SC_6H_4Me$-*p* (0.25 mmol) was used. After 3 min *ca.* 40% of (**1**) had been converted into $VsiSiMe_2O_3SC_6H_4Me$-*p*, after 13 min *ca.* 60%, and after 27 min *ca.* 85%. After 45 min only $VsiSiMe_2O_3SC_6H_4Me$-*p* and unchanged (**2**) were present in solution.

(*b*) When a mixture of (**2**) (0.25 mmol) and $AgO_3SC_6H_4Me$-*p* was used, the reaction was half-complete in *ca.* 15 h.

(*c*) When a mixture of (**1**) (0.25 mmol), $VsiSiMe_2Br$ (0.25 mmol), and $AgO_3SC_6H_4Me$-*p* (0.50 mmol) in CH_2Cl_2 (25 cm^3) was used, after 3 min *ca.* 40% of (**1**) and no detectable amount of $VsiSiMe_2Br$ had reacted. After 60 min all of (**1**) and *ca.* 55% of $VsiSiMe_2Br$ had reacted, and after 240 min only $VsiSiMe_2$-$O_3SC_6H_4Me$-*p* was present in solution.

(*d*) No reaction occurred under similar conditions between $TsiSiMe_2Br$ (0.25 mmol) and $AgO_3SC_6H_4Me$-*p* (0.25 mmol) during 48 h.

(*e*) When a mixture of (**1**) (0.25 mmol), (**2**) (0.25 mol), AgSCN (0.50 mmol), and CH_2Cl_2 was used, no detectable reaction of (**2**) took place, and the approximate amounts of (**1**) which had reacted at various times were: 8 min, 25%; 20 min, 50%; 34 min, 70%; 55 min, 85%; 70 min, 90%; and 120 min, 100%. After 48 h only $VsiSiMe_2NCS$ and $TsiSiMe_2I$ were present in solution.

(*f*) In the reaction of (**1**) (0.25 mmol) with AgO_2CMe (0.25 mmol) in CH_2Cl_2 (25 cm^3) the approximate extents of conversion of (*1*) into $VsiSiMe_2O_2CMe$ at various times were: 4 min, 30%; 9 min, 45%; 16 min, 60%; 30 min. 80%; and 80 min, 100%.

With (**2**) under similar conditions the corresponding results were: 8 h, 20%; 17 h, 35%; 25 h, 45%; 40 h, 55%; and 80 h, 80%.

(3) *Reactions with Alkali Metal Salts.*—Reactions were monitored by ^1H n.m.r. spectroscopy, the relative heights of corresponding peaks (usually those from Me_3Si but sometimes those from Me_2Si protons) in starting materials and products being used as the measure of the extent of reaction. Good first-order plots were obtained in all cases.

Reactions in MeCN.—Solutions were kept in a bath at 60 °C, and samples were removed at various times and rapidly evaporated under reduced pressure. The residue was extracted with CCl_4 containing acetone (5%) as reference and the ^1H n.m.r. spectrum of the extract was recorded.

(*a*) In the reaction of (**1**) (0.125 mol) with 0.50M-KSCN (0.50 mmol) in MeCN (10 cm^3) the approximate extents of conversion into $VsiSiMe_2NCS$ at various times were: 10 min, 15%; 20 min, 22%; 40 min, 40%; 60 min, 50%; 95 min, 65%; 106 min, 70%; and 150 min, 82%. The value of $t_{\frac{1}{2}}$ was *ca.* 61 min.

(*b*) When (**2**) was used in the procedure described under (*a*) the corresponding data were: 20 min, 20%; 28 min, 27%; 40 min, 35%; 50 min, 40%; 75 min, 52%; 90 min, 60%; 106 min, 68%; and 150 min, 80%. The value of $t_{\frac{1}{2}}$ was *ca.* 66 min.

(*c*) The procedure described under (*a*) but with 0.10M-KSCN resulted in a good first-order plot with $t_{\frac{1}{2}}$ *ca.* 30 min, and with 0.20M-KSCN $t_{\frac{1}{2}}$ was *ca.* 15.5 min.

(*d*) When (**1**) and 2.0M-KOCN in MeCN were used in the procedure described above, $t_{\frac{1}{2}}$ for the conversion into $VsiSiMe_2NCO$ was *ca.* 18 h. In a similar procedure but with (**2**), $t_{\frac{1}{2}}$ was *ca.* 21 h.

(*e*) When (**1**) and 2.0M-NaN_3 were used $t_{\frac{1}{2}}$ was *ca.* 11 h. For (**2**), $t_{\frac{1}{2}}$ was *ca.* 13 h.

Reactions in MeOH.—The organosilane (0.023 mmol) was dissolved in a drop of CCl_4 (*ca.* 0.01 cm^3) in an n.m.r. tube and an 0.25M-solution (1 cm^3) of the salt in MeOH was added. The tube was capped, shaken, kept in a bath at 60 °C, and transferred at intervals to the n.m.r. spectrometer. Good first-order plots were obtained in all cases up to $>80\%$ completion of the reaction.

(*a*) For reaction of (**1**) or (**2**) with NaN_3, values of $t_{\frac{1}{2}}$ were 5.5 and 6.5 h, respectively. The products were exclusively the corresponding azides.

(*b*) In the reaction of (**1**) with CsF, the fluoride $VsiSiMe_2F$ and the methoxide $VsiSiMe_2OMe$ were formed, and their ratio during the reaction averaged *ca.* 10:1. The value of $t_{\frac{1}{2}}$ for disappearance of (**1**) was *ca.* 7 h. When (**2**) was used the ratio of fluoride to methoxide was *ca.* 18:1, and the corresponding value of $t_{\frac{1}{2}}$ was *ca.* 9 h.

(*c*) In the reaction of $VsiSiMe_2Br$ with CsF the ratio of methoxide to fluoride product was *ca.* 12:1, and $t_{\frac{1}{2}}$ for disappearance of the bromide was *ca.* 14 h. In a similar procedure with $TsiSiMe_2Br$ the corresponding ratio was *ca.* 17:1 and $t_{\frac{1}{2}}$ *ca.* 24 h.

(*d*) In the reactions of $VsiSiMe_2Cl$ and $TsiSiMe_2Cl$ with CsF, the corresponding fluorides were the only products, and the values of $t_{\frac{1}{2}}$ were 29 and 35 h, respectively.

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