Base Cleavage of R–SiMe$_n$(OMe)$_{3-n}$ Bonds (R = *m*-ClC$_6$H$_4$CH$_2$, PhC≡C, or Cl$_2$CH) and Alkoxy Exchange in RSiMe$_n$(OMe)$_{3-n}$ (R = *m*-ClC$_6$H$_4$CH$_2$)

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The rates of cleavage of R–SiMe$_n$(OMe)$_{3-n}$ bonds (n = 0—3) in NaOMe–MeOH have been measured for R = (i) *m*-ClC$_6$H$_4$CH$_2$, (ii) PhC≡C, and (iii) Cl$_2$CH. The relative reactivities as n is varied in the sequence 3, 2, 1, 0 within each series are: (i) 1, 7.2, 2.7, 0.13; (ii) 1, 27, 24, 5.5; (iii) 1, 38, 93, 29. These reactivity variations are discussed in terms of opposition between the rate-enhancing polar effects of the OMe groups and an unusual type of steric effect which arises on introduction of OMe in place of Me. The rates of replacement of one OMe group of *m*-ClC$_6$H$_4$CH$_2$Me$_n$(OMe)$_{3-n}$ by an OEt group in EtOH containing a base have also been measured; in this case the rates rise progressively with the value of n, the relative reactivities for n = 2, 1, and 0 being 1, 4.4, and 27, respectively.

Much is known about the effects of varying the structure of the leaving group R in cleavage of Me$_3$SiR by base (usually in methanol or aqueous methanol)[1,2] but little information is available on the effects of varying the inert groups R′ in, for example, RSiR′$_3$ or RSiMe$_2$R′ species. Systematic studies seem to have been limited to variation of X in *p*-ClC$_6$H$_4$CH$_2$-SiMe$_2$(C$_6$H$_4$X) and of R′ in *p*-$^-$O$_2$CC$_6$H$_4$CH$_2$SiR′$_3$, in both cases for cleavage by aqueous methanolic alkali.[3] It seemed of interest to examine the effects of much more drastic changes of the inert groups, but a severe limitation on the choice of such groups is imposed by the fact that ligands other than those attached to silicon through carbon will normally be much more readily displaced than the organic ligand by the base. For cleavages in anhydrous methanol a unique opportunity is afforded by use of methoxy compounds such as RSiMe$_n$(OMe)$_{3-n}$, since although exchange of OMe groups with the solvent will take place much more rapidly than the cleavage of the Si–R bond, this exchange will not affect the rate of the cleavage. We recently presented results for the cleavage of RSiMe$_2$(OMe) with R = *m*-ClC$_6$H$_4$CH$_2$ or PhC≡C, and we have now examined the three series RSiMe$_n$(OMe)$_{3-n}$ (n = 0—3) for these same R groups and for R = Cl$_2$CH. For comparison we have also examined the rates of replacement of one OMe group of *m*-ClC$_6$H$_4$CH$_2$SiMe$_n$(OMe)$_{3-n}$ (n = 0—2) by an OEt group in EtOH containing a base.

Results and Discussion

We first examined the compound *m*-ClC$_6$H$_4$CH$_2$SiMe(OMe)$_2$ in 'anhydrous' MeOH–NaOMe, in order to compare the results with those for *m*-ClC$_6$H$_4$CH$_2$SiMe$_2$OMe.[4] To our surprise the variation of the observed (pseudo) first-order rate constant with the base concentration was very abnormal. As can be seen from Table 1, increase in the base concentration from 0.2 to 2.5M caused only a six-fold increase in the observed rate constant, to be compared with an approximately 40-fold increase which would be expected in the case of RSiMe$_3$.[5] In the light of results obtained with *m*-ClC$_6$H$_4$CH$_2$SiMe$_2$(OMe) in MeOH containing H$_2$O,[4] we suspected that this abnormality arose from the presence of traces of water in the MeOH (although the latter had been 'dried' by a standard method), which led to formation of ≡SiO$^-$ (silanolate) anions, and to counteract this we added a large excess of Si(OMe)$_4$. (This will be hydrolysed to give ≡Si-OH species and MeOH; the ≡Si-OH species formed will remove some of the base, but the amount should be insignificant.) In the presence of 0.1M-Si(OMe)$_4$ [with the *m*-ClC$_6$H$_4$CH$_2$Si-Me(OMe)$_2$ in 1.9 × 10^{-3}M concentration], the variation of the rate with the base concentration was fairly normal; *e.g.* there was a 42-fold increase in rate on going from 0.2 to 2.5M-base. The effect of the added Si(OMe)$_4$ was especially large at high base concentrations (at which, of course, there would be the most conversion into silanolate anions); thus at 2.5M base the rate was increased eight-fold by the presence of the Si(OMe)$_4$, and at 5M-base the factor was 47. Importantly, at this highest base concentration, 5.0M, at which the effect of the trace water is greatest, variation in the Si(OMe)$_4$ concentration from 0.1 to 0.5M caused no change in the observed rate constant, indicating that all the water was effectively removed by 0.1M-Si(OMe)$_4$. We therefore measured the rates of cleavage of the whole series of *m*-ClC$_6$H$_4$CH$_2$SiMe$_n$(OMe)$_{3-n}$ compounds by 2.45M-NaOMe in MeOH in the presence of 0.1M-Si(OMe)$_4$; the results (Table 2) show that the relative reactivities of the compounds with n = 3, 2, 1, and 0 are 1.0, 7.2, 2.7, and 0.13, respectively.

Table 1. Observed first-order rate constants in cleavage of *m*-ClC$_6$H$_4$CH$_2$SiMe(OMe)$_2$ in NaOMe–MeOH at 50.0 °C in the absence (k) and in the presence (k') of Si(OMe)$_4$

[MeONa]/M	10^5k/s^{-1}	[Si(OMe)$_4$]/M	$10^5k'$/s^{-1}
0.20	0.50	0.10	0.60
0.50	1.25	0.10	1.80
2.0	2.60		
2.5	3.0	0.10	25.0
5.0	3.9	0.10	185
5.0		0.20	183
5.0		0.50	182

The much more reactive PhC≡CSiMe$_n$(OMe)$_{3-n}$ compounds (*cf.* refs 4 and 6) were next studied, at 30.0 °C and at a much lower concentration (5 × 10^{-3}M) of NaOMe in MeOH containing 0.10M-Si(OMe)$_4$.† The results (Table 3) show that the reactivity again increases on going from the trimethyl to the

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† For these and all the other compounds used in the cleavage studies, variation of the Si(OMe)$_4$ concentration between 0.1 and 0.5M was found to have no significant effect.

Table 2. Cleavage of m-$ClC_6H_4SiMe_n(OMe)_{3-n}$ compounds in NaOMe–MeOH at 50 °C

	With 0.1M-$Si(OMe)_4$			Without $Si(OMe)_4$		
n	[NaOMe]/M	$10^5k/s^{-1}$ [a]	k_{rel} [b]	[NaOMe]/M	$10^5k/s^{-1}$ [a]	k_{rel} [b]
3 [c]	2.45	9.4	1	2.00	3.9	1.0
2	2.45	68	7.2	2.00	34	8.7
1	2.45	25	2.7	2.00	2.6	0.67
0	2.45	1.25	0.13	2.00	0.12	0.030

[a] Observed first-order rate constant. [b] Rate relative to that for $n = 3$. [c] For this compound at this base concentration the rate constant did not change significantly on addition of 0.05, 0.10, or 0.50M-$Si(OMe)_4$.

Table 3. Cleavage of $PhC{\equiv}CSiMe_n(OMe)_{3-n}$ (*ca.* 1.7×10^{-3}M) at 30.0 °C by 5.0×10^{-3}M-NaOMe–MeOH containing 0.10M-$Si(OMe)_4$

n	$10^4k/s^{-1}$ [a]	k_{rel} [b]
3	4.0	1.0
2	108	27
1	95	24
0	22	5.5

[a] Observed first-order rate constant. [b] Rate relative to that for $n = 3$.

monomethoxy compound and then falls as further OMe groups are introduced, the relative reactivities for $n = 3$, 2, 1, and 0 being 1.0, 27, 24, and 5.5, respectively. In spite of the fall in rate in the latter part of the series, the trimethoxy is more reactive than the trimethyl compound, whereas the opposite is the case for the m-chlorobenzyl compounds.

In the case of the $Cl_2CHSiMe_n(OMe)_{3-n}$ compounds the rates cannot be measured spectrophotometrically, as they were for the other series, and samples were analysed by g.l.c. Thus it was necessary to use a considerably higher concentration (0.18M) of the substrate, and since solutions of these compounds generated small amounts of acid in MeOH, equivalent to only a few percent of the substrate but to a substantial fraction of the appropriate concentration of NaOMe, it was not sufficient simply to dissolve the substrate in an NaOMe–MeOH solution of known molarity. Thus the rate for each of the compounds in a given solution was directly compared with that of $PhC{\equiv}CSiMe_2(OMe)$ measured spectrophotometrically in the same reaction solution, *i.e.* the solution contained both $PhC{\equiv}CSiMe_2OMe$ and the relevant $Cl_2CHSiMe_n(OMe)_{3-n}$ compound. Again the reactivities go through a maximum as the number of OMe groups is increased, the relative rates for $n = 3$, 2, 1, and 0 being 1, 38, 93, and 29 (Table 4), but the maximum in this case is at the dimethoxy compound, not the monomethoxy as in the other series, and the trimethoxy is markedly more reactive than the trimethyl compound. From the rate in each solution for $PhC{\equiv}CSiMe_2OMe$ the effective concentration of NaOMe in each case can be deduced, and so specific rate constants can be derived for the $Cl_2CHSiMe_n(OMe)_{3-n}$ compounds, as shown in Table 4, but this is not necessary for the estimation of the relative reactivities.

The cleavage of $Cl_2CHSiMe_n(OMe)_{3-n}$ compounds with n = 0—2 was also studied in MeOH containing Me_3N and HCl in 4:1 molar ratio and also 0.50M-$Si(OMe)_4$ (see Table 5). (In this medium the effective concentration of methoxide ion was estimated to be 6.7×10^{-6}M from measurement of the rate of cleavage of $PhC{\equiv}CSiMe_2OMe$, so that values of k_s could be derived for the dichloromethyl compounds.) The relative rates for the compounds with $n = 2$, 1, and 0 were 1, 2.3, and 0.78, respectively, in excellent agreement with the corresponding values of 1, 2.4, and 0.77 observed for cleavage in NaOMe–MeOH.

The increase in reactivity on going from $RSiMe_3$ to $RSiMe_2OMe$ species was expected, since replacement of an Me ligand on silicon by an electron-withdrawing OMe ligand would be expected to stabilize a pentaco-ordinate transition state more or less close to the (possibly hypothetical) intermediate $[RSiMe_n(OMe)_{4-n}]^-$.[*] Moreover, since the R group is leaving, as R^-, in the rate-determining transition state,[1,2] the better the leaving group, *i.e.* the greater the reactivity of $RSiMe_3$, the closer the transition state should be to the intermediate and so the greater the degree of negative charge on the silicon atom, and the greater the influence of the electron withdrawal by the OMe group, in line with the bigger increases for R = Cl_2CH and $PhC{\equiv}C$ than for R = $ClC_6H_4CH_2$ on going from $n = 3$ to $n = 2$. However, if this were the only effect operating, the reactivity would be expected to increase progressively (though not additively) as the number of OMe ligands is increased further, and there is evidently some other effect (or possibly more than one) acting in the opposite direction. An obvious possibility is a steric effect, and if OBu^t ligands were being successively introduced the additional steric hindrance (which would increase more steeply as the number of large ligands was increased) would be expected to outweigh the inductive effects, to give just such a maximum as we have observed for OMe ligands [but probably with a much greater fall in reactivity on going to the $RSi(OBu^t)_3$ species]. At first sight it might seem unlikely that replacement of Me by OMe ligands would introduce sufficient hindrance to account for the observed results, especially since we have found that the diethyl compound m-$ClC_6H_4CH_2SiEt_2OMe$ is only six times less reactive than the corresponding dimethyl compound.[†] [The first-order rate constant k for cleavage of the diethyl compound at 50 °C in 0.215M-MeOH–MeONa in the presence of 0.1M-$Si(OMe)_4$ was 3.3×10^{-6} s^{-1}, corresponding to a specific rate constant, k_s (k/[NaOMe]), of 1.5×10^{-5} l mol^{-1} s^{-1}. The corresponding value of k_s for the dimethyl compound under the same conditions was 8.8×10^{-5} l mol^{-1} s^{-1}.] However, the nature of the charged transition state may be such as to require orientations of the OMe groups which would maximize intramolecular interactions. For example, there could be serious crowding and unfavourable repulsions between lone pairs if the OMe groups were oriented with their lone pairs as far away as possible from the negatively charged leaving group. The effect could then be greatest for the poorest leaving group, m-$ClC_6H_4CH_2$, on which the charge would be most fully developed in the transition state, in keeping with the greater

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[*] The inductive electron withdrawal by an OMe group from silicon is commonly assumed to be opposed by electron-releasing $(p \longrightarrow d)_\pi$ bonding, but the overall effect is one of electron withdrawal. It is likely that interplay of the inductive and π-bonding effects is one of the factors affecting rate variations in the $RSiMe_n(OMe)_{3-n}$ series, but it could not in itself account for the existence of a maximum in the reactivity as the number of OMe groups is increased.

[†] This result is consistent with the fall in reactivity for p-$^-O_2CC_6H_4CH_2SiR'_3$ species on going from R′ = Me to R′ = Et.[3] It is noteworthy, however, that $PhC{\equiv}CSiEt_3$ is 280 times less reactive than $PhC{\equiv}CSiMe_3$ in H_2O–MeOH–NaOH.[6]

Table 4. Cleavage of $Cl_2CHSiMe_n(OMe)_{3-n}$ compounds (0.18M) at 25.0 C in NaOMe–MeOH containing 0.10M-$Si(OMe)_4$ and $PhC{\equiv}CSiMe_2OMe$ (A) (5×10^{-3}M)

n	$10^3k/s^{-1}$ [a]	$10^3k/s^{-1}$ for (A) [b]	10^4[MeONa]/M [c]	10^2k_s/l mol^{-1} s^{-1} [d]	k_{rel} [e]
3	0.086	8.4	61	1.4	1
2	3.05	7.8	57	53	38
1	10.4	11.0	80	130	93
0	1.64	5.3	40	41	29

[a] Observed rate constant for $Cl_2CHSiMe_n(OMe)_{3-n}$. Observed rate constant for $PhC{\equiv}CSiMe_2OMe$. [c] Concn. of MeONa derived from k_s value of 1.37 l mol^{-1} s^{-1} for $PhC{\equiv}CSiMe_2OMe$ (based on values of 10^3 times the observed rate constants of 6.8, 9.6, and 11.0 for cleavage in 0.0050, 0.0070, and 0.0080M-NaOMe, respectively). [d] Specific rate constant, given by k/[NaOMe]. [e] Rate relative to that for $n = 3$.

Table 5. Cleavage of $Cl_2CHSiMe_n(OMe)_{3-n}$ compounds (0.16M) at 30 °C in MeOH containing Me_3N (0.16M), HCl (0.040M), and $Si(OMe)_4$ (0.50M)

n	$10^5k/s^{-1}$ [a]	k_s/l mol^{-1} s^{-1} [b]
2	1.58	2.4
1	3.7	5.5
0	1.23	1.8

[a] Observed first-order rate constant. [b] Specific rate constant, $k/[OMe^-]$, based on an effective concentration of OMe^- of 6.7×10^{-6}M, as calculated from first-order rate constant of 1.45×10^{-5} s^{-1} observed for $PhC{\equiv}CSiMe_2(OMe)$ in the same medium.

Table 6. Replacement of MeO groups of m-$ClC_6H_4CH_2SiMe_n(OMe)_{3-n}$ compounds (0.26M) by EtO groups at 50.0 °C in EtOH containing Me_3N (2.0M) and HCl (0.10M), in the absence or in the presence of $Si(OMe)_4$ (0.50M)

	$10^5k/s^{-1}$ [a]	
n	Without $Si(OMe)_4$	With $Si(OMe)_4$
2	0.28	0.68
1	1.43	3.0
0	15.0	18.5

[a] Observed first-order rate constant for disappearance of m-$ClC_6H_4CH_2SiMe_n(OMe)_{3-n}$.

dominance of the rate-reducing effect in the m-$ClC_6H_4CH_2SiMe_n(OMe)_{3-n}$ series.

Similar patterns of reactivity have been observed in analogous reactions of alkoxysilicon hydrides. Thus in reactions of $RSiH_3$ species with alcohols, including MeOH, with or without a base catalyst, the rates of the successive steps of the sequence $RSiH_3 \longrightarrow RSi(OR')H_2 \longrightarrow RSi(OR')_2H \longrightarrow RSi(OR')_3$ correspond with the reactivity sequence $RSiH_3 > RSi(OR')H_2 > RSi(OR')_2H$.[7,8] In these cases, however, the small hydride ligands are being replaced by the alkoxide ligands, and so interpretation of the pattern in terms of opposing polar and steric effects[8] is readily acceptable. More relevant to our observations is the finding by Heftlejš *et al.* that the relative reactivities of $HSiPr_n(OEt)_{3-n}$ species with EtOH containing NaOEt are: (n =) 3,1; 2, 688; 1, 6 860; 0, 1 490.[9] On the basis of their assumption that the Pr and the OEt groups would have similar steric effects, the authors concluded that their results could not be interpreted in terms of such effects along with polar effects, and they proposed that the lone pairs of the OEt groups repelled the approaching ethoxide ion. This explanation is not, in our view, acceptable as it was presented, since (a) there is no obvious reason why the importance of such effects relative to those of the rate-enhancing polar effects should increase markedly with the number of such groups, and (b) the transition state for hydride solvolysis has been shown to have the base anion fully (if the reaction is a two-step process) or almost fully (if the reaction is a single-step process) attached to the silicon atom on the transition state, so that little of the original charge is, in fact, left on the incoming group.[10] If, however, the interaction between the lone pairs and the leaving hydride ion orientates the OR groups to maximize steric crowding, then the observed pattern can be readily understood.

In the light of the foregoing results and our suggested interpretation, we turned to a study of the base-catalysed replacement of one of the OMe groups of m-$ClC_6H_4SiMe_n(OMe)_{3-n}$ species by OEt groups in EtOH containing NaOEt. We did so because this much faster reaction, involving the much better leaving group OMe^-, can be expected to have a transition state much closer to the (possibly hypothetical) intermediate of the type $[RSiMe_n(OMe)_{3-n}(OEt)]^-$, which is closely analogous to the corresponding intermediate in the cleavage of $RSiMe_n(OMe)_{3-n}$ species discussed above. Thus the polar effects of the (inert) OMe groups, which should stabilize the intermediate, should dominate.

The reactions were monitored by g.l.c. analysis, which gave the amount of unchanged m-$ClC_6H_4CH_2SiMe_n(OMe)_{3-n}$ (relative to an internal standard). A very low concentration of base had to be used to give a measurable rate, and this was obtained by using EtOH containing 2.0M-Me_3N along with 0.1M-$Me_3N{\cdot}HCl$ in the presence of 0.1M-$Si(OMe)_4$. The effect of the $Si(OMe)_4$ can be seen from Table 6. That it was base-catalysed exchange which was observed under these conditions was confirmed by the observation that reaction occurred only very slowly, if at all, when 0.1M- was used in place of 2.0M-Me_3N in the mixture. In this medium the exact concentration of methoxide ion was unknown, but the same medium was used for all three m-$ClC_6H_4CH_2SiMe_n(OMe)_{3-n}$ species; the relative rates for n = 2, 1, and 0 were 1, 4.4, and 27, respectively, but after allowance for the numbers of OMe ligands available for replacement the reactivity ratios become 1:2.2:9. The progressive increase in reactivity is in contrast with the pattern observed in the cleavages, but is in line with our expectation.

We should draw attention to a rather unusual feature of our proposals, namely our postulate that introduction of a substituent lowers the energy of the pentaco-ordinate intermediate but raises that of the transition state on the way from it (or to it). Such a situation can be envisaged, however, when there is a geometrical restriction in the transition state which is absent from the intermediate and the initial or final states, as we suggest.

Experimental

N.m.r. spectra were determined at 60 MHz for solutions in CCl_4.

Synthesis.—(*a*) The m-$ClC_6H_4CH_2SiMe_nCl_{3-n}$ and hence the m-$ClC_6H_4CH_2SiMe_n(OMe)_{3-n}$ (n = 0—2) compounds were prepared by the methods described previously for the corresponding $PhCH_2SiMe_nX_{3-n}$ (X = Cl or OMe) compounds.[11] The m-$ClC_6H_4CH_2SiMe_nCl_{3-n}$ compounds had b.p.s of 142 °C at 30 mmHg ($n = 0$), 138 °C at 24 mmHg ($n = 1$), and 131 °C at 24 mmHg ($n = 2$). The m-$\mathrm{ClC_6H_4CH_2SiMe}_n\mathrm{(OMe)}_{3-n}$ compounds had physical properties as follows: (i) $n = 0$, b.p. 126 °C at 10 mmHg (Found: C, 48.6; H, 6.1. $\mathrm{C_{10}H_{15}ClO_3Si}$ requires C, 48.7; H, 6.1%); δ_H 1.98 (2 H, s, $\mathrm{CH_2Si}$), 3.35 (9 H, s, OMe), and 6.78—7.04 (4 H, m, aryl H); m/z 246 (M^+); (ii) $n = 1$, b.p. 120 °C at 10 mmHg (Found: C, 51.8; H, 6.7. $\mathrm{C_{10}H_{15}ClO_2Si}$ requires C, 52.0; H, 6.55%); δ_H −0.08 (3 H, s, SiMe), 1.98 (2 H, s, $\mathrm{CH_2Si}$), 3.33 (6 H, s, OMe), and 6.6—7.1 (4 H, m, aryl H); m/z 230 (M^+); (iii) $n = 2$, b.p. 109 °C at 10 mmHg (Found: C, 55.9; H, 7.2. $\mathrm{C_{10}H_{15}ClOSi}$ requires C, 55.9; H, 7.0%); δ_H −0.07 (6 H, s, $\mathrm{SiMe_2}$), 1.97 (2 H, s, $\mathrm{CH_2Si}$), 3.30 (3 H, s, OMe), and 6.6—7.05 (4 H, m, aryl H); m/z 214 (M^+).

(*b*) For the preparation of the $\mathrm{PhC{\equiv}CSiMe}_n\mathrm{(OMe)}_{3-n}$ (n = 0—2) compounds, the corresponding $\mathrm{PhC{\equiv}CSiMe}_n\mathrm{Cl}_{3-n}$ compounds were first made from $\mathrm{PhC{\equiv}CMgBr}$ and the appropriate $\mathrm{Me}_n\mathrm{SiCl}_{4-n}$ species as previously described;[12] yields and b.p.s were: $n = 0$, 32%, 95 °C at 5 mmHg (lit.,[13] 132—135 °C at 26 mmHg); $n = 1$, 34%, 93 °C at 4 mmHg (lit.,[12] 71 °C at 1 mmHg); $n = 2$, 30%, 104 °C at 4 mmHg (lit.,[8] 96 °C at 2 mmHg). These halides were then treated with MeOH containing $\mathrm{Et_3N}$, as described for the preparation of $\mathrm{PhCH_2SiMe}_n\mathrm{(OMe)}_{3-n}$ compounds,[11] to give the $\mathrm{PhC{\equiv}CSiMe}_n\mathrm{(OMe)}_{3-n}$ compounds, with yields and physical constants as follows: (i) $n = 0$, 48%, b.p. 98 °C at 2 mmHg (lit.,[14] 95 °C at 1.5 mmHg), δ_H 3.51 (9 H, s, Me) and 7.0—7.45 (5 H, m, Ph); m/z 222 (M^+), (ii) $n = 1$, 52%, b.p. 103 °C at 6 mmHg (Found: C, 64.1; H, 6.8. $\mathrm{C_{11}H_{14}O_2Si}$ requires C, 64.0; H, 6.8%); δ_H 0.21 (3 H, s, SiMe), 3.48 (6 H, s, OMe), and 7.0—7.45 (5 H, m, aryl H); m/z 206 (M^+); $n = 2$, 42%, b.p. 89 °C at 5 mmHg (Found: C, 69.4; H, 5.8. $\mathrm{C_{11}H_{14}OSi}$ requires C, 69.4; H, 5.8%); δ_H 0.28 (6 H, s, SiMe), 3.41 (3 H, s, OMe), and 7.0—7.45 (5 H, m, aryl H); m/z 190 (M^+).

(*c*) For the preparations of the $\mathrm{Cl_2CHSiMe}_n\mathrm{(OMe)}_{3-n}$ compounds (n = 0—2), the corresponding $\mathrm{Cl_2CHSiMe}_n\mathrm{Cl}_{3-n}$ compounds were made by vapour-phase chlorination of the corresponding $\mathrm{Me}_{n+1}\mathrm{SiCl}_{4-n-1}$ compounds as previously described.[15] Treatment of the chlorides with MeOH containing $\mathrm{Et_3N}$ (*cf.* ref. 11) then gave the $\mathrm{Cl_2CHSiMe}_n\mathrm{(OMe)}_{3-n}$ compounds, with properties as follows: (i) $n = 0$, b.p. 78 °C at 10 mmHg (lit.,[16] 55 °C at 2 mmHg); δ_H 3.71 (9 H, s, OMe) and 5.20 (1 H, s, CH); m/z 121 ($[M - \mathrm{CHCl_2}]^+$ 100%); $n = 1$, b.p. 68 °C at 20 mmHg (lit.,[17] 63 °C at 17 mmHg); δ_H 0.30 (3 H, s, SiMe), 3.61 (6 H, s, OMe), and 5.20 (1 H, s, CH); m/z 105 ($[M - \mathrm{CHCl_2}]^+$, 100%); $n = 2$, b.p. 51 °C at 20 mmHg (Found: C, 27.7; H, 5.7. $\mathrm{C_4H_{10}ClOSi}$ requires C, 27.7; H, 5.8%); δ_H 0.30 (6 H, s, SiMe), 3.50 (3 H, s, OMe), and 5.21 (1 H, s, CH); m/z 89 ($[M - \mathrm{CHCl_2}]^+$, 100%).

Treatment of $\mathrm{Cl_2CHSiMe_2Cl}$ with MeMgBr gave $\mathrm{Cl_2CHSiMe_3}$, b.p. 133—135 °C (lit.,[18] 133 °C at 730 mmHg).

(*d*) The compound m-$\mathrm{ClC_6H_4CH_2SiEt_2(OMe)}$ was prepared from $\mathrm{Et_2Si(OMe)_2}$ and m-$\mathrm{ClC_6H_4CH_2MgBr}$ by standard procedures; it had b.p. 116 °C at 1 mmHg (Found: C, 59.4; H, 7.8. $\mathrm{C_{12}H_{19}ClOSi}$ requires C, 59.3; H, 7.8%); δ_H 0.46—1.04 (10 H, m, Et), 2.07 (2 H, s, $\mathrm{CH_2Si}$), 3.33 (3 H, s, OMe), and 6.8—7.1 (4 H, m, aryl H).

Rate Measurements.—(*a*) The procedure used for the cleavage of m-$\mathrm{ClC_6H_4CH_2SiR}_n\mathrm{(OMe)}_{3-n}$ and $\mathrm{PhC{\equiv}CSiMe}_n\mathrm{(OMe)}_{3-n}$ compounds was as previously described. The initial concentration of the substrates was *ca.* 5×10^{-3}M in each case. The wave lengths (in nm) used to monitor the reactions were: for m-$\mathrm{ClC_6H_4CH_2SiMe}_n\mathrm{OMe)}_{3-n}$, 279.5 ($n = 3$), 279 ($n = 2$), and 278.5 ($n = 1$ and 0); for m-$\mathrm{ClC_6H_4CH_2SiEt_2OMe}$, 283; for $\mathrm{PhC{\equiv}CSiMe}_n\mathrm{(OMe)}_{3-n}$, 273. Good first-order plots were obtained in all cases, and the final spectra corresponded with those of the expected cleavage products m-$\mathrm{ClC_6H_4CH_3}$ and $\mathrm{PhC{\equiv}CH}$.

(*b*) For the cleavage of the $\mathrm{Cl_2CHSiMe}_n\mathrm{(OMe)}_{3-n}$ compounds catalysed by NaOMe, a methanolic solution of the $\mathrm{Cl_2CHSiMe}_n\mathrm{(OMe)}_{3-n}$ compound, $\mathrm{PhC{\equiv}CSiMe_2(OMe)}$, and the internal standard (n-octane) was mixed with one containing NaOMe and $\mathrm{Si(OMe)_4}$. The concentrations of the component solutions were such that after mixing they were $\mathrm{Cl_2CHSiMe}_n\mathrm{(OMe)}_{3-n}$; *ca.* 0.18M; n-$\mathrm{C_8H_{18}}$, *ca.* 0.08M; $\mathrm{PhC{\equiv}SiMe_2OMe}$, 5×10^{-3}M; $\mathrm{Si(OMe)_4}$, 0.10M; the concentration of NaOMe in the mixture would have been *ca.* 0.01M if it had all remained unchanged, but the actual concentration (see text and Table 4) was 0.004—0.008M. Samples (0.3 μl) were removed at appropriate times and analysed by direct injection into a g.l.c. column (3 m × 0.4 cm; 20% LAC 296 on GasChrom Q at 75 °C; injection temp., 100 °C; flame ionization detector at 100 °C). The peak areas for $\mathrm{CH_2Cl_2}$ and n-$\mathrm{C_8H_{18}}$ were determined, and a previously constructed calibration curve was used to derive the concentration of the $\mathrm{CH_2Cl_2}$. Occasionally the concentrations of $\mathrm{Cl_2CHSiMe}_n\mathrm{(OMe)}_{3-n}$ were determined throughout a run; the derived rate constants did not differ significantly from those based on the concentration of $\mathrm{CH_2Cl_2}$.

For the cleavage in the $\mathrm{Me_3N}$–HCl buffer a similar procedure was used, except that the basic solution used to make up the reaction mixture contained amounts of $\mathrm{Me_3N}$, HCl, and $\mathrm{Si(OMe)_4}$ such that after mixing these were present in 0.16, 0.0040, and 0.50M concentration, respectively. In the case of $\mathrm{Cl_2CHSiMe(OMe)_2}$, variation of the concentration of $\mathrm{Si(OMe)_4}$ from 0.10 to 0.50 to 1.00M caused no significant change in the rate constant.

(*c*) For the exchange of m-$\mathrm{ClC_6H_4CH_2SiMe}_n\mathrm{(OMe)}_{3-n}$ compounds with EtOH, a stock solution of 2.2M-$\mathrm{Me_3N}$, 0.1M-HCl, n-undecane (0.22M), and $\mathrm{Si(OMe)_4}$, (0.55M) was prepared. To 0.90 cm^3 of this solution at 50 °C, 0.10 cm^3 of the organosilane was added from a syringe through a rubber seal and the mixture was shaken and placed in the thermostat. At appropriate times 0.3 μl samples were removed and analysed by g.l.c. [see details under (*b*)] to give the concentration of m-$\mathrm{ClC_6H_4CH_2SiMe}_n\mathrm{(OMe)}_{3-n}$; the initial concentration of the latter was 0.26M. Use of $\mathrm{Si(OEt)_4}$ in place of $\mathrm{Si(OMe)_4}$ did not affect the rate constants significantly.

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