Base Cleavage of R–Si Bonds of Silanols RSiMe₂OH. A Proposed New Mechanism of Substitution at Silicon

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Cleavage of R–Si bonds has been found to occur unexpectedly rapidly in solutions of $RSiMe_2OMe$ (R = m-$ClC_6H_4CH_2$ or $PhC{\vdots}C$) in 5 vol-% H_2O–MeOH containing relatively small concentrations of NaOMe, but with a levelling off of the rate at high concentrations of the base. The behaviour is attributed to the formation of $RSiMe_2OH$ and hence $RSiMe_2O^-$, and it is suggested that unimolecular dissociation of the silanolate anion $RSiMe_2O^-$ to give R^- and the silanone $Me_2Si{=}O$ (both of which react rapidly with the solvent) plays a significant role. The silanols $RSiMe_2OH$ are roughly estimated to have pK_a values of 11 (R = m-$ClC_6H_4CH_2$) and 9.8 (R = $PhC{\vdots}C$) in water.

The cleavages of R–SiMe₃ bonds by NaOMe–MeOH have been studied for a wide range of R groups.[1] While investigating the effects of variation in the other ligands on silicon we examined the cleavage of m-$ClC_6H_4CH_2Si(OMe)_3$ in NaOMe–MeOH. (Rapid exchange of OMe groups occurs between the substrate and the solvent under these conditions, but this should not cause any complication.) We found that the change of the observed first-order rate constant on variation of the concentration of base showed a most unusual form, which we thought would best be accounted for in terms of the presence of small amounts of water, and the consequent formation of Si–OH bonds and hence silanolate ions, *e.g.* m-$ClC_6H_4CH_2Si(OMe)_2O^-$. To investigate the possible role of such ions we turned to the simpler system involving use of m-$ClC_6H_4CH_2SiMe_2OMe$, with the results described below. A preliminary account has appeared previously.[2]

Results and Discussion

Observed first-order rate constants, k, for the cleavage of m-$ClC_6H_4CH_2SiMe_2OMe$ by 0.05—2.86M-NaOMe in anhydrous MeOH are shown in Table 1, and plotted against the base concentration in Figure 1. Table 2 lists the values of the specific rate constant, k_s ($= k/[NaOMe]$) and of the ratio k_s/k_s°, where k_s° is the specific rate at low base concentrations (in this case 0.05M), and also includes the corresponding values of k_s/k_s° for cleavage of m-$ClC_6H_4CH_2SiMe_3$.[3] It will be seen that the changes in k_s/k_s° are fairly similar for the two compounds, and thus in this medium m-$ClC_6H_4CH_2SiMe_2OMe$ behaves normally. (However, the fact that k_s/k_o is *ca.* 20% larger than might have been expected in 2.86M base suggests that possibly a little silanolate ion is formed under these conditions as a result of the presence of traces of water.) The methoxide is 8.8 times as reactive as m-$ClC_6H_4CH_2SiMe_3$ at 2.00M base concentration, and this increase in reactivity can be attributed to the greater ease of nucleophilic attack at silicon as a result of increased electron withdrawal from this atom.

Very different behaviour was observed when the cleavage of m-$ClC_6H_4CH_2SiMe_2OMe$ was carried out in methanol containing 5 vol-% of water and added NaOMe. (The base in the 5% H_2O–MeOH system is, for convenience, referred to throughout the discussion as NaOMe although some OH^- must be present.) Whereas with NaOMe in 2 or 10% H_2O–MeOH (and thus, it can be assumed, in 5% H_2O–MeOH) the observed first-order rate constant for cleavage of m-$ClC_6H_4CH_2SiMe_3$ varies

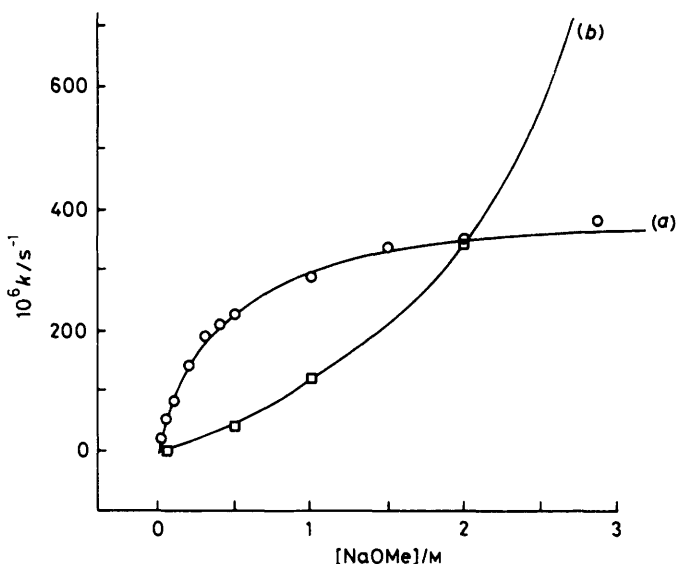**Figure 1.** Plot of observed first-order rate constant, k, against the base concentration for cleavage of m-$ClC_6H_4CH_2SiMe_2OMe$ at 50.0 °C in (*a*) MeOH (□) and (*b*) 5 vol-% H_2O–MeOH (○). The curve in case (*b*) is that generated by equation (8)

in a very similar way to that observed for reactions in MeOH alone (see Table 2),[2] in the case of the methoxy compound the rate in 5% H_2O–MeOH initially rises much more steeply, to values markedly higher than those observed in MeOH alone, but then starts to level off, ultimately (above 2.1M base) becoming lower than that in the latter medium (see Table 3 and Figure 1).

We suggest that this behaviour in the water-containing medium is caused by the formation from the initial methoxide, $RSiMe_2OMe$ (R = m-$ClC_6H_4CH_2$), of some hydroxide $RSiMe_2OH$ and hence, in the presence of base, some silanolate ion $RSiMe_2O^-$, the proportions of the various species being controlled by the equilibrium constants for reactions (1) and (2).† It can safely be assumed that the silanolate ion would,

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† It is possible that a little of the disiloxane $(RMe_2Si)_2O$ is also present, but this would have no significant effect. (Its Si–R bonds should be cleaved at a very similar rate to those of $RSiMe_2OMe$.) The disiloxane was found to be converted fairly slowly into RMe_2SiO^- in 5% H_2O–MeOH containing 1.5M-NaOMe (see Experimental section).

Table 1. Apparent first-order rate constants, k, for cleavage of $RSiMe_2X$ by NaOMe in MeOH or 5 vol-% H_2O–MeOH[a]

					$10^5k/s^{-1}$	
R	X	$10^4[RSiMe_2X]/M$	$\theta_c/°C$	[MeONa]/M	5% H_2O–MeOH	MeOH
m-$ClC_6H_4CH_2$	Me	3.0	50	2.00	4.80	3.90[b]
m-$ClC_6H_4CH_2$	OMe	46	50	0.02	2.20	
				0.05	5.0	0.40
				0.50	22.9	4.20
				1.01	28.8	12.2
				2.00	35.0	34.0
				2.86	39.0	82.4
$PhC\overset{\cdot}{:}C$	Me	45	30	0.05	975	642
$PhC\overset{\cdot}{:}C$	OMe	50	30	0.001	1 000	234
				0.01	7 200	2 200
				0.03	13 600	6 630
				0.05	17 000	11 000

[a] For simplicity the base is referred to as NaOMe although some hydroxide ion must be present in the H_2O–MeOH. [b] Lit.,[3] 3.95×10^{-5} s^{-1}.

Table 2. Values of k_s/k_o for cleavage of m-$ClC_6H_4CH_2SiMe_2X$ by NaOMe in MeOH or H_2O–MeOH at 50.0 °C[a]

	$k_s/k_s^{o\,b}$			
	Me		OMe	
[MeONa]/M	MeOH[c]	10% H_2O–MeOH[c]	MeOH	5% H_2O–MeOH
0.05	1.00	1.00	1.00	1.00
0.50	1.02	1.03	1.05	0.42
1.0	1.20	1.31	1.52	0.26
2.0	2.00	1.88	2.12	0.16
2.86	3.11	3.02	3.60	0.12

[a] The concentrations of m-$ClC_6H_4CH_2SiMe_2X$ were as shown in Table 1. [b] $k_s = k/[NaOMe]$, where k is the observed first-order rate constant; k_s^o is the value of k_s at very low base concentrations. [c] Ref. 3.
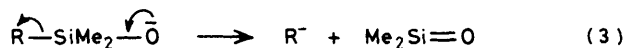
Table 3. Cleavage of m-$ClC_6H_4CH_2SiMe_2OMe$ by NaOMe in 5 vol-% H_2O–MeOH at 50.0 °C[a]

[NaOMe]/M	$10^6k/s^{-1\,b}$	r^c
0.020	22	0.05
0.050	50	0.11
0.10	84	0.20
0.20	142	0.33
0.30	192	0.43
0.40	212	0.50
0.50	229	0.56
1.00	288	0.71
1.50	337	0.79
2.00	350	0.83
2.86	390	0.88

[a] For initial concentration of $RSiMe_2OMe$ see Table 1; see also footnote a to Table 1. [b] Observed first-order rate constant. [c] Fraction of $RSiMe_2OMe$ converted into $RSiMe_2O^-$, assuming half conversion at 0.40M-base.

$$RSiMe_2OMe + H_2O \rightleftharpoons RSiMe_2OH + MeOH \quad (1)$$

$$RSiMe_2OH + OMe^- \rightleftharpoons RSiMe_2O^- + MeOH \quad (2)$$

because of its negative charge and high electron density at the silicon atom, be cleaved at a negligible rate by direct attack of the base anion at silicon. We suggest, however, that there may be a significant contribution to the observed rate by the internal nucleophilic displacement shown in equation (3), which gives R^- and the silanone $RSiMe_2=O$, both of which react rapidly with the solvent, as shown in equations (4) and (5).* The

$$R\overset{\frown}{—}SiMe_2\overset{\frown}{—}O \longrightarrow R^- + Me_2Si=O \quad (3)$$

$$Me_2Si=O + MeOH \longrightarrow Me_2Si(OMe)OH \quad (4)$$

$$R^- + MeOH \longrightarrow RH + OMe^- \quad (5)$$

observed rate constant at a given base concentration would then be made up of contributions from (a) decomposition of the anion, and (b) the cleavage of $RSiMe_2OMe$ and $RSiMe_2OH$ by direct attack of base at silicon. For simplicity, in the initial discussion below we assume that $RSiMe_2OMe$ and $RSiMe_2OH$ have the same reactivity, and the observed rate constant k at a

* There is also the possibility that R^- is never free, but acquires a proton from the solvent as it separates.

given base concentration is then given by equation (6), where r

$$k = k_{s(AX)}(1 - r)[NaOMe] + rk_A^- \quad (6)$$

is the fraction of the initial $RSiMe_2OMe$ (subsequently frequently denoted by AMe) present as the anion $RSiMe_2O^-$ (frequently denoted by A^-), $k_{s(AX)}$ is the second-order (specific) rate constant for $RSiMe_2OMe$ (AMe) and $RSiMe_2MeOH$ (AH), and k_A^- the first-order rate constant for the decomposition of the $RSiMe_2O^-$ species. Since (a) the proportion of $RSiMe_2O^-$ (A^-) present is given by the value of the equilibrium constant K, where $K = ([A^-])/[AMe + AH]$-[NaOMe], and (b) $[A^-]/[AMe + AH] = r/(1 - r)$, equation (6) can be re-expressed as in equation (7), which shows that the observed rate constant should be linearly related to the fraction of the $RSiMe_2OMe$ present as $RSiMe_2O^-$, i.e. to r.

To test the validity of equation (7) we need to know the value

$$k = \{(k_{s(AX)}/K) + k_A^-\}r \quad (7)$$

of K. This could not be determined directly for m-$ClC_6H_4CH_2SiMe_2OMe$ because of the cleavage, and so we turned to $PhCH_2SiMe_2OMe$. For the latter, u.v. spectroscopy indicated that (at room temperature) the conversion of the methoxide into the silanolate ion is half complete in 0.45M-NaOMe (see Experimental section). Since m-$ClC_6H_4CH_2$-$SiMe_2OH$ will be slightly more acidic than $PhCH_2Me_2SiOH$, we arbitrarily assume that conversion of m-$ClC_6H_4CH_2Me_2$-$SiOMe$ would be half complete at 0.40M base. (The degree of
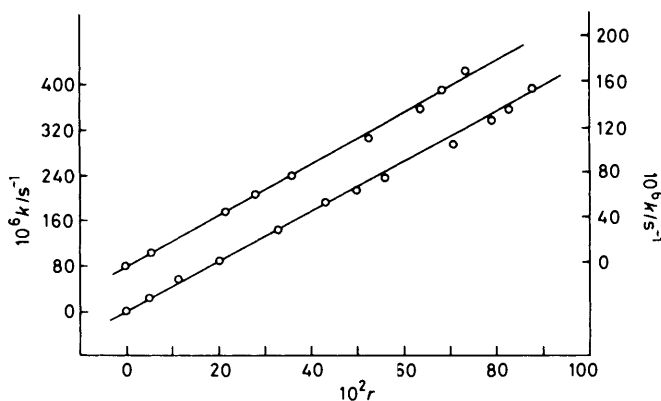
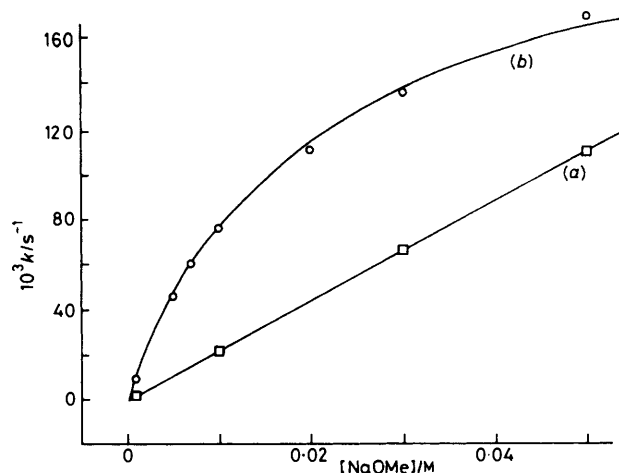**Figure 2.** Plot of observed first-order rate constant, k, for cleavage of $RSiMe_2OMe$ [(a) R = m-$ClC_6H_4CH_2$; lower line and left-hand vertical axis; (b) R = PhC≡C; upper line and right-hand vertical axis] against r, the fraction of $RSiMe_2OMe$ present as $RSiMe_2O^-$

Figure 3. Plot of observed first-order rate constant, k, against the base concentration for cleavage of PhC≡CSiMe$_2$OMe at 30.0 °C in (a) MeOH (□) and (b) 5 vol-% H_2O-MeOH (○). The curve in case (b) is that generated by the equation $k = 3.3(1 - r)[NaOMe] + (160\ r \times 10^{-3})$ (see text)

uncertainty in this figure would have no significance in the subsequent discussion.) This leads to the values of r shown in Table 3, and use of these gives the plot of k against r shown in Figure 2, which is satisfactorily linear. It can reasonably be concluded that the form of the relationship between k and [NaOMe], as depicted in Figure 1, is attributable to the formation of $RSiMe_2O^-$.

From the plot in Figure 2 it can be seen that the observed rate constant at the point at which $r = 0.5$, i.e. at [NaOMe] = 0.40M, is 215×10^{-6} s^{-1}, and the value at which the observed rate constant should level off is 430×10^{-6} s^{-1}.

The problem now is to estimate the relative contributions of the components of the overall process. We first note that the observed variation of k with [NaOMe], and the linearity of the plot of k against r, would be found even if the contribution of either of the two proposed processes were zero. If the decomposition of the silanolate ion made no significant contribution, this would imply a value of $k_{s(AX)}$ of 10.7×10^{-4} l mol^{-1} s^{-1} {given by $k = 2.15 \times 10^{-4}$ s^{-1} = 0.5 $k_{s(AX)}$[NaOMe] at 0.40M-NaOMe}. We can estimate with some confidence the value of k_s for the direct bimolecular cleavage of $RSiMe_2OMe$ in the 5% H_2O-MeOH medium by noting that at a 1.0M base concentration the cleavage of $RSiMe_3$ in this medium is 1.3 times as fast as that in NaOMe-MeOH [3] (in the present work a factor of 1.24 was observed for 2.0M base), and applying this factor to the value of k_s for $RSiMe_2OMe$ in MeOH at a low base concentration (viz. 8×10^{-5} l mol^{-1} s^{-1} at 0.05M) gives a k_s value of ca. 10×10^{-5} l mol^{-1} s^{-1} at such concentrations in 5% H_2O-MeOH, i.e. about one-eleventh of the value of $k_{s(AX)}$ derived above on the assumption that k_A is zero. Thus if effectively all the $RSiMe_2OMe$ were converted into $RSiMe_2OH$ in the medium used then the value of k_s for $RSiMe_2OH$ would have to be ca. 11 times as large as that for $RSiMe_2OMe$. If, as is more likely, the $RSiMe_2OH$:$RSiMe_2OMe$ ratio is in the region of 1:4 (see later), then the value of k_s for $RSiMe_2OH$ would have to be ca. 50 times as large as that for $RSiMe_2OMe$. Since there is a fairly small increase in k_s on going from $RSiMe_3$ to $RSiMe_2OMe$ (the factor is 8.8) it seems unlikely that there would be a large increase on going from $RSiMe_2OMe$ to $RSiMe_2OH$, and thus it is probable that there is a substantial contribution to the observed rate from the decomposition of the silanolate ion.

If we return to the simplifying assumption that the values of k_s for $RSiMe_2OMe$ and $RSiMe_2OH$ are similar, then $k_{s(AX)} = 100 \times 10^{-6}$ l mol s^{-1} and the value of k_A is 390×10^{-6} s^{-1}, with the value of k (in s^{-1}) at any base concentration then given

by equation (8). (Of the limiting value of 430×10^{-6} s^{-1} for k,

$$10^6 k = 100(1 - r)[NaOMe] + 390r \qquad (8)$$

the bimolecular cleavage would contribute 40×10^{-6} s^{-1} and the unimolecular decomposition of the silanolate 390×10^{-6} s^{-1}.) The line drawn in Figure 1 for the variation of k with [NaOMe] for m-$ClC_6H_4CH_2SiMe_2OMe$ in 5% H_2O-MeOH is actually that generated by equation (8). On this basis, the unexpectedly high rate of cleavage observed for $RSiMe_2OMe$ in the aqueous medium arises predominantly from the high rate of decomposition of the silanolate anion.

We have assumed above that the value of k_s for $RSiMe_2OMe$ remains constant over the whole range of base concentration, and since k_2 values actually increase significantly with this concentration at 1M and above (see Table 2 and ref. 3) some justification of our procedure is needed. The observed rate constant, k, for cleavage of $RSiMe_3$ species in NaOMe-MeOH (and in other media) shows a linear dependence on the h_- acidity function (given by $H_- = -\log h_-$, where H_- is the more commonly used acidity function [3-5]). The ratio [A$^-$]/[AMe + AH] should, by the definition of h_- (and H_-), be proportional to h_- rather than [NaOMe], and so at fairly high degrees of conversion of AMe into A$^-$, [AMe + AH] should be approximately inversely proportional to h_-. Thus a change in base concentration which leads to a doubling of k for AMe and AH will at the same time reduce the proportion of [AMe + AH] to about one-half, and so the contribution by AMe and AH will be approximately the same as if k_s were independent of, and the ratio [A$^-$]/[AMe + AH] determined solely by, the base concentration. (In the case of the cleavage of PhC≡CSiMe$_3$ considered below, the data refer to low base concentrations, at which k_s should remain constant over the whole range.)

We next turned to the cleavage of PhC≡CSiMe$_2$OMe. We chose this knowing that it would be cleaved at a convenient rate at very low base concentrations, at which, we thought, there might be little conversion into the anion PhC≡CSiMe$_2O^-$, so that the dependence of the observed rate constant on the base concentration might be similar to that for $RSiMe_3$ species. In fact, although this is the case in MeOH (k being directly proportional to [NaOMe]; see Table 1), for 5% H_2O-MeOH the plot of k (at 30 °C) against [NaOMe] (see Figure 3) has a rather similar shape to that of the earlier portion of the

corresponding plot for $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{SiMe}_2\text{OMe}$ (at 50 °C). The implication is that $\text{PhC}\vdots\text{CSiMe}_2\text{OH}$ is markedly more acidic than $m\text{-ClC}_6\text{H}_4\text{SiMe}_2\text{OH}$, and a satisfactorily linear plot of k against r is obtained if it is assumed that $\text{PhC}\vdots\text{CSiMe}_2\text{OMe}$ is half converted into $\text{PhC}\vdots\text{CSiMe}_2\text{O}^-$ at a base concentration of ca. 0.018M (see Figure 2).

From the plot in Figure 2 it can be seen that k has a value of 110×10^{-3} s^{-1} for $r = 0.5$, i.e. in 0.018M base, and the limiting value of k would be 220×10^{-3} s^{-1}. If the cleavage were exclusively through the bimolecular process (i.e. direct attack on $\text{PhC}\vdots\text{CSiMe}_2\text{OMe}$ and $\text{PhC}\vdots\text{CSiMe}_2\text{OH}$) the value of $k_{\text{s(AX)}}$ for this would be 12 l mol^{-1} s^{-1}. A value of ca. 3.3 l mol^{-1} s^{-1} can be estimated for k_s for base cleavage of $\text{PhC}\vdots\text{CSiMe}_2\text{OMe}$ in 5% $\text{H}_2\text{O–MeOH}$ (at 30 °C) by multiplying the value of 2.2 l mol^{-1} s^{-1} observed in NaOMe–MeOH by 1.5, the factor which applies to the k_s value for $\text{PhC}\vdots\text{CSiMe}_3$ for this change of medium (Table 1). Thus to account for the observed rate of cleavage in 5% $\text{H}_2\text{O–MeOH}$, $\text{PhC}\vdots\text{CSiMe}_2\text{OH}$ would have to be cleaved ca. 3.6 times as readily in the direct attack as $\text{PhC}\vdots\text{CSiMe}_2\text{OMe}$ if effectively all of the latter were converted into the hydroxide in the medium used. The corresponding factor would be ca. 18 if, as is more likely, the ratio of methoxide to hydroxide is about 4:1. In this case, however, since there is an 18-fold increase in k_s on going from $\text{PhC}\vdots\text{CSiMe}_3$ to $\text{PhC}\vdots\text{CSiMe}_2\text{OMe}$, a further substantial increase on going to $\text{PhC}\vdots\text{CSiMe}_2\text{OH}$ cannot be ruled out, and it is possible that the decomposition of the silanolate plays only a minor role. If we nevertheless assume, for comparison, that the value of k_s at 30 °C for $\text{PhC}\vdots\text{CSiMe}_2\text{OH}$ is the same as that for $\text{PhC}\vdots\text{CSiMe}_2\text{OMe}$, viz. 3.3 l mol^{-1} s^{-1}, then the value of k_{A}^- for decompostion of the anion would be ca. 160×10^{-3} s^{-3}, and this would be the contribution of this process to the limiting rate of 220×10^{-3} s^{-1} at high base concentrations, with the bimolecular process contributing ca. 60×10^{-3} s^{-1}. The upper curve in Figure 3 is that generated by the equation $k = 3.3 (1 - r)[\text{NaOMe}] + (160r \times 10^{-3})$.
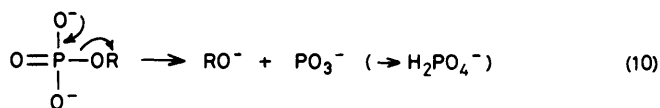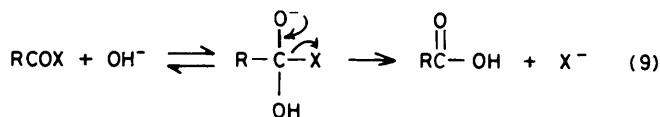
If the assumption is valid that in both cases the value of k_s for the bimolecular cleavage of the hydroxide is similar to that for the methoxide, then it would follow that $\text{PhC}\vdots\text{CSiMe}_2\text{O}^-$ undergoes unimolecular decomposition in 5% $\text{H}_2\text{O–MeOH}$ at 30 °C some 430 times as rapidly as $m\text{-ClC}_6\text{H}_4\text{CH}_2\text{SiMe}_2\text{O}^-$ at 50 °C. Assuming a 3-fold decrease in the rate constant for the latter compound for each 10 °C fall in temperature, the reactivity ratio would be ca. 4 000 at 30 °C.

The validity of our view that unimolecular decompositon of silanolate ions may play a significant part depends on the validity of the assumption that RSiMe$_2$OH species are not much more readily cleaved than RSiMe$_2$OMe species in the bimolecular process. This would not be a satisfactory position if there were no independent indication of the existence of a silanolate ion decomposition process. Such an indication is, in fact, available from studies of the methanolysis of TsiSiPhRX species [Tsi = (Me$_3$Si)$_3$C], in which steric hindrance very strongly inhibits attack of nucleophiles on silicon.[6] It is known that the methanolysis of TsiSiPhHI and the more hindered TsiSiMe$_2$I is not catalysed by NaOMe,[7,8] that the latter undergoes solvolysis only very slowly in refluxing NaOMe–MeOH,[8] and, consistently, TsiSiPh(OMe)I undergoes no detectable reaction with 0.5M-NaOMe–MeOH in 2 h under reflux. In sharp contrast, TsiSiPh(OH)I, which did not react with MeOH alone in 24 h under reflux, was found to be completely converted into TsiSiPh(OH)(OMe) within 5 min at room temperature in an initially 0.17M solution of the iodide in 0.25M-NaOMe in MeOH (i.e., with only a 0.08M excess of the base).[2] Since the methanolysis of the much less hindered species TsiSiPhHI is not significantly accelerated by base,[8] it is extremely unlikely that the abnormal reactivity of TsiSiPh(OH)I arises from bimolecular attack of the methoxide ion at silicon, and much more probable that it involves a process analogous to

that depicted in equations (3) and (4) but with iodide ion as the leaving group.

It seems likely that unimolecular decomposition of a silanolate ion to a silanone (of the type $-\text{SiR}_2\text{OSiR}_2\text{O}^- \rightarrow -\text{SiR}_2\text{O}^- + \text{R}_2\text{Si=O}$) also plays a role in base-catalysed processes leading to polysiloxane polymers.[9]

The proposed silanolate ion to silanone decomposition is, of course, analogous to well established processes in carbonyl chemistry (in which, however, the doubly bonded species is formed in a fast rather than a rate-determining step); e.g. in the hydrolysis of esters and acyl halides [equation (9)]. There are also analogues in phosphorus chemistry;[10] e.g. in the hydrolysis of phosphoric monoester dianions [equation (10)].

$$\text{RCOX} + \text{OH}^- \rightleftharpoons \text{R}-\underset{\underset{\text{OH}}{|}}{\overset{\overset{\text{O}^-}{|}}{\text{C}}}-\text{X} \longrightarrow \text{RC}-\overset{\text{O}}{\overset{||}{}}\text{OH} + \text{X}^- \quad (9)$$

$$\text{O}=\underset{\underset{\text{O}^-}{|}}{\overset{\overset{\text{O}^-}{|}}{\text{P}}}-\text{OR} \longrightarrow \text{RO}^- + \text{PO}_3^- \quad (\rightarrow \text{H}_2\text{PO}_4^-) \quad (10)$$

We should emphasize that, whatever the mechanisms involved, the results presented in this paper reveal that the presence of a hydroxy group on silicon can greatly facilitate the removal of an organic group from the same silicon atom by dilute base. This observation could be of value in organic sysntheses in which at some stage a silyl protecting group has to be removed from an organic centre under basic conditions; e.g. there could be an advantage in using, rather than RSiR$'_3$ species, RSiR$'_2$OMe species in which the OMe group is readily replaced by OH in weakly basic, partly aqueous media.

The Acidities of $\text{PhCH}_2\text{SiMe}_2\text{OH}$ *and* $\text{PhC}\vdots\text{CSiMe}_2\text{OH}$.— From the base concentration at which half of the initial AMe (RSiMe$_2$OMe) is converted into A$^-$ (RSiMe$_2$O$^-$), we could calculate the concentration at which the ratio [A$^-$]/[AH] (AH = RSiMe$_2$OH) would be unity if we knew the [AMe]/[AH] ratio in the medium used. In this medium MeOH and H$_2$O are present in a molar ratio of 8.2:1, and if we assume that the equilibrium constant for reaction (1) is statistically determined, and allow for the fact that two OH groups are available in each water molecule, this implies a value of 4 for the ratio [AMe]/[AH]. Thus for A = $\text{PhCH}_2\text{SiMe}_2\text{O}$, since [A$^-$]/[AMe + AH] = 1 at ca. 0.45M base, [A$^-$]/[AH] = 5 at this concentration, and would be 1 at ca. 0.09M base. The corresponding base concentration for A = $\text{PhC}\vdots\text{CSiMe}_2\text{O}^-$ is 0.0036M, and thus $\text{PhC}\vdots\text{CSiMe}_2\text{OH}$ is 25 times as acidic as $\text{PhCH}_2\text{SiMe}_2\text{OH}$. [This same factor is obtained from the ratio of the base concentrations at which the respective AMe species are half converted into A$^-$; the value of the factor does not depend on the value of the equilibrium constant for reaction (1), but its validity depends on the accuracy of the assumption that this constant is the same in both cases.]

Examination of the u.v. spectrum of phenol in 5% H$_2$O–MeOH containing varying concentrations of base indicated that the conversion into phenolate was half complete for ca. 0.005M base, and we conclude that, very roughly, the acidity of $\text{PhC}\vdots\text{CSiMe}_2\text{OH}$ is close to that of PhOH (which has a pK_a of 9.89 in water), which is 18 times as acidic as $\text{PhCH}_2\text{SiMe}_2\text{OH}$. Thus, as a rough estimate, $\text{PhC}\vdots\text{CSiMe}_2\text{OH}$ and $\text{PhCH}_2\text{SiMe}_2\text{OH}$ would have pK_a values of 9.8 and 11, respectively, in water. The acidities of these silanols are unexpectedly high in view of an observation that trialkylsilanols are much weaker acids than phenols in pyridine, but the same study showed that

Table 4. Cleavage of PhC⫶CSiMe$_2$OMe by NaOMe in 5 vol-% H$_2$O–MeOH at 30.0 °C[a]

[NaOMe]/M	$10^3 k/s^{-1}$[b]	r[c]
0.0010	10	0.05
0.0050	47	0.20
0.0070	62	0.28
0.010	76	0.36
0.020	110	0.53
0.030	136	0.64
0.040	154	0.69
0.050	170	0.74

[a,b] As in Table 3. [c] Fractions of RSiMe$_2$OMe converted into RSiMe$_2$O$^-$ assuming half conversion at 0.018M base.

in this solvent triphenylsilanol appears to be somewhat less acidic than p-methoxyphenol (pK_a 10.20 in water) but more acidic than p-nitroaniline (pK_a 11.96 in water).[11]

The substantial shift in the u.v. spectrum on going from PhCH$_2$SiMe$_2$OMe to PhCH$_2$SiMe$_2$O$^-$ can be attributed to the increase in hyperconjugative electron release into the aromatic ring from the CH$_2$–Si bond.[12]

We note finally that (as for PhC⫶CSiMe$_2$OH) in suitable cases the variation of the rate of replacement of X with the base concentration in appropriate media could be used to derive an approximate measure of the acidity of silanols of the type XSiR$_2$OH where direct measurement is impracticable.

Experimental

Materials.—Methanol was dried as previously described.[13] Solutions of NaOMe were prepared by dissolution of sodium.

Organosilicon compounds were prepared as follows.

m-ClC$_6$H$_4$CH$_2$SiMe$_2$OMe was prepared as previously described.[14]

PhC⫶CSiMe$_2$OMe.—Phenylacetylene (51 g, 0.55 mol) was added to the Grignard reagent made from EtBr (55 g, 0.51 mol) in Et$_2$O (200 cm^3). The mixture was refluxed for 4 h then cooled and added dropwise to a stirred mixture of Me$_2$SiCl$_2$ (64.5 g, 0.50 mol) and Et$_2$O (50 cm^3). The mixture was subsequently refluxed for 6 h then filtered under nitrogen, the Et$_2$O and any residual Me$_2$SiCl$_2$ were distilled off under reduced pressure, and the residue was fractionated to give PhC⫶CSiMe$_2$Cl (31 g, 30%), b.p. 104 °C at 4 mmHg (lit.,[15] 96 °C at 2 mmHg). The product was dissolved in Et$_2$O (300 cm^3), and a solution of MeOH (5.8 g, 0.18 mol) and Et$_3$N (18 g, 0.18 mol) in Et$_2$O (50 cm^3) was added dropwise with stirring. The mixture was refluxed for 3 h, then light petroleum (b.p. 60—80 °C; 300 cm^3) was added, followed by ice-cold water (200 cm^3). The organic layer was separated, washed, and dried (CaCl$_2$), and the solvents were distilled off under slightly reduced pressure. The residue was distilled at lower pressure to give PhC⫶CSiMe$_2$OMe (13.1 g, 42%), b.p. 89 °C at 5 mmHg: δ(CCl$_4$) 0.28 (6 H, s, Me), 3.41 (3 H, s, OMe), and 7—7.5 (5 H, m, Ph). The mass spectrum was as expected, with a strong [M − Me]$^+$ peak at m/z 175.

(PhCH$_2$SiMe$_2$)$_2$O.—The methoxide PhSiMe$_2$OMe (2 g) was dissolved in a mixture of methanol (15 cm^3) and 1M-aqueous HCl (2 cm^3). After some hours an excess of CH$_2$Cl$_2$ was added, followed by water. The organic layer was separated, washed several times with water, and dried (MgSO$_4$). Removal of the solvent and distillation of the residue gave (PhCH$_2$SiMe$_2$)$_2$O (0.8 g, 51%), b.p. 140 °C at 4 mmHg (lit.,[16] 150—151 °C at 5.5 mmHg); δ(CCl$_4$) −0.035 (6 H, s, Me), 2.00 (2 H, s, CH$_2$), and 6.1—7.1 (5 H, m, Ph). Examination by g.l.c. (5% OV-101) revealed <0.5% of impurity.

Rate Measurements.—The rates were measured spectrophoto-

metrically as previously described (with the solution contained in a thermostatted cell).[14] Wavelengths used to monitor the progress of the reactions were: 279.5 (m-ClC$_6$H$_4$CH$_2$SiMe$_3$), 279 (m-ClC$_6$H$_4$CH$_2$SiMe$_2$OMe), and 273 nm (PhC⫶CSiMe$_3$ and PhC⫶CSiMe$_2$OMe). The u.v. spectrum of the product was identical in all cases with that of an authentic sample of m-ClC$_6$H$_4$CH$_3$ or PhC⫶CH, and good first-order kinetics were observed. Rate constants were reproducible to within ±3%.

The [A$^-$]/[AH + AMe] *Ratio for* A = PhCH$_2$SiMe$_2$O *in* 5% H$_2$O–MeOH–MeONa.—The u.v. spectra of 2.5 × 10^{-3}M-solutions of PhCH$_2$SiMe$_2$OMe in 5% H$_2$O–MeOH containing various concentrations of NaOMe were recorded at room temperature. There was a shift in the spectrum of ca. 3 nm towards the visible on going from the neutral solution to 2.4M base (e.g. the peaks at 262, 268, and 275 nm were shifted to 265, 271, and 278 nm), with some increase in the optical density. The optical densities (1 cm cell) at 278 nm at the base concentrations (M) in parentheses were 0.07 (0.00), 0.15 (0.10), 0.19 (0.18), 0.28 (0.27), 0.31 (0.38), 0.35 (0.50), 0.41 (0.82), 0.50 (1.52), and 0.55 (2.40), and it was estimated that the conversion into PhCH$_2$SiMe$_2$O$^-$ was half complete in ca. 0.45M base.

Behaviour of (PhCH$_2$SiMe$_2$)$_2$O *in* 5% H$_2$O–MeOH.—The u.v. spectrum of a 1.25 × 10^{-3}M-solution of (PhCH$_2$SiMe$_2$)$_2$O in 5% H$_2$O–MeOH was very similar to that of a 2.5 × 10^{-3}M-solution of PhCH$_2$SiMe$_2$OMe. In the presence of 1.5M-NaOMe the spectrum changed relatively slowly at room temperature, to reach an equilibrium position after about 5 h, at which it was virtually identical with that obtained from PhCH$_2$SiMe$_2$OMe under similar conditions, i.e. most of the disiloxane had been converted into PhCH$_2$SiMe$_2$O$^-$.

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