Silicon–Oxygen and Acyl–Oxygen Bond Cleavage in Reactions of Sterically Hindered Organosilicon Carboxylates

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Because of steric hindrance to attack at the functional silicon centre in $VsiSiMe_2OCOR$ [where Vsi denotes $(Me_3Si)_2(CH_2{=}CHMe_2Si)C$] with R = CF_3 (**1a**) or Me (**1b**), nucleophiles in MeOH can preferentially attack at the carbonyl group to give $VsiSiMe_2OH$, rather than at Si as would be usual for less hindered silicon carboxylates. With CsF or KSCN in MeOH the products are exclusively $VsiSiMe_2F$ and $VsiSiMe_2NCS$, respectively, whereas KOCN gives exclusively $VsiSiMe_2OH$, and NaN_3 gives very predominantly $VsiSiMe_2OH$ along with a little $VsiSiMe_2N_3$. The overall effectiveness of the salts is KOCN > CsF, NaN_3 > KSCN; the sequence of the ease of attack of the nucleophiles at Si is $F^- > SCN^-$ ($>N_3^-$?), and that for attack at carbon is $OCN^- > N_3^- > F^- > SCN^-$. The sequence of ability of various nucleophiles to catalyse cleavage of the SiO–COR bond of (**1a**) in MeOH is RNH_2 (R = H_2N, Me, Et, $HOCH_2CH_2$, or $H_2NCH_2CH_2$), OCN^-, $HO_2^- > MeO^- > N_3^- > Me_2NH > Me_3N > 4\text{-}Me_2NC_5H_4N \gg C_5H_5N > PhNH_2$, and the sequence for reactions of the less reactive (**1b**) is $HO_2^- > H_2NNH_2 > MeO^- > H_2NCH_2CH_2NH_2 > MeNH_2 > HOCH_2CH_2NH_2 > EtNH_2$. Except for the unexpected effectiveness of OCN^-, the sequences are reasonably consistent with those established, for example, for reactions of aryl acetates in water (and also with Ritchie's nucleophilic parameters N_+); it is suggested that, as in the latter reactions, the cleavage of the acyl–oxygen bond is rate-determining. Reactions of (**1a**) with salts MX, namely NaN_3, CsF, KSCN, and KOCN in MeCN, give exclusively the corresponding species $VsiSiMe_2X$. In the representative reactions examined the reactivities of (**1a**) and (**1b**) were very similar to those of the corresponding compounds $(Me_3Si)_3CSiMe_2OCOR$.

Because of the great ease of nucleophilic attack at silicon, organosilicon carboxylates normally react with nucleophiles by displacement of the carboxylate group; for example, in base-catalysed alcoholysis the silicon–oxygen bond is usually cleaved, not the acyl–oxygen bond, so that the reaction proceeds as in equation (1). However, when there is sufficient steric hindrance to attack at silicon the nucleophile can attack the carbonyl carbon, so that the reaction is as shown in equation (2); for example the compounds $TsiSiMe_2OCOR$ [R = Me, CF_3, or Ph; Tsi = $(Me_3Si)_3C$] react with NaOMe in MeOH according to equation (2) to give $TsiSiMe_2OH$.[1] The

$$\geqslant SiOCOR + R'OH \xrightarrow{R'O^-} \geqslant SiOR' + HOCOR \quad (1)$$

$$\geqslant SiOCOR + R'OH \xrightarrow{R'O^-} \geqslant SiOH + R'OCOR \quad (2)$$

availability of such compounds makes possible a study of reactions of silicon carboxylates in which the leaving group is the silanolate ion, including investigation of the effectiveness of various nucleophiles, a topic which has received such attention for other leaving groups (for leading references see ref. 2). We have now examined the reactions of some highly sterically hindered organosilicon carboxylates with some other nucleophiles in MeOH, and also reactions with some salts in MeCN in which acyl–oxygen cleavage does not occur. The carboxylates mainly used were of the type (1), involving the vinyl-containing group $(Me_3Si)_2(CH_2{=}CHMe_2Si)C$, which for convenience we denote by the symbol Vsi. We note that in the reactions concerned the vinyl group plays no significant role, and thus that we could, as it turned out, have reached essentially the same conclusions with the simpler compounds $TsiSiMe_2OCOR$, but the study originated in a general examination of the reactions of $VsiSiMe_2X$ species, in some of which the vinyl group has a powerful influence.[3]

$VsiSiMe_2OCOR$ Vsi = $(Me_3Si)_2(CH_2{=}CHMe_2Si)C$

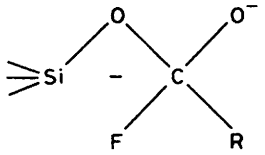
(1) a; R = CF_3
b; R = Me
c; R = Ph

Results and Discussion

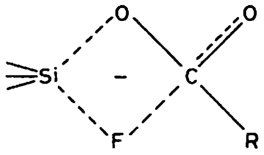
Reactions of (**1a**) *in* MeCN.—We first examined the reactions of the trifluoracetate (**1a**) with NaN_3, CsF, KSCN, and KOCN in MeCN. In all cases there was conversion into the corresponding compounds $VsiSiMe_2Y$ with Y = N_3, F, NCS, or NCO, respectively.

A solution of (**1a**) (0.24 mmol) in MeCN (10 cm^3) was refluxed gently with NaN_3 (3.85 mmol) (which remained largely undissolved) and samples were withdrawn at intervals for examination by ^1H n.m.r. spectroscopy. The conversion into $VsiSiMe_2N_3$ was *ca.* 59% complete in 15 min and effectively complete in 1 h. With CsF under similar conditions the conversion into $VsiSiMe_2F$ gave rise to a good first-order plot with $t_{\frac{1}{2}}$ *c.a.* 46 min. (Under identical conditions the value of $t_{\frac{1}{2}}$ for the reaction of $TsiSiMe_2OCOCF_3$ was *ca.* 55 min.) With (**1a**) (0.19 mmol) and KOCN (3.1 mmol) conversion into $VsiSiMe_2NCO$ was *ca.* 60% complete in 45 min and effectively complete in 200 min. The reaction of (**1a**) (0.24 mmol) with KSCN (2.5 mmol) was faster, and so was examined at 60 °C; at this temperature the conversion into $VsiSiMe_2NCS$ was *ca.* 42% complete in 10 min. (With $TsiSiMe_2OCOCF_3$ under identical conditions the reaction was *ca.* 34% complete in 10 min.)

From the results it is evident, after account is taken of differences in temperatures and amounts of salts, that the order of effectiveness of the salts is KSCN > NaN_3 > CsF > KOCN, but this cannot be taken to represent the order of nucleophilicity of the various anions because the salts may not all have been fully dissolved, and this was certainly the case with NaN_3.



(I)



(II)

We did not make direct comparisons of the reactivities of the trifluoroacetate and the corresponding iodide VsiSiMe$_2$I in these reactions, but it seems that they do not differ greatly in reactivity. Thus in the reaction of VsiSiMe$_2$I (0.12 mmol) with KSCN (0.50 mmol) in MeCN (10 cm^3) at 60 °C the reaction was *ca.* half complete in 60 min, whereas with (**1a**) (0.24 mmol) and KSCN (3.85 mmol) reaction was *ca.* 42% complete in 10 min. Again, with VsiSiMe$_2$I (0.12 mmol) and KOCN (2.0 mmol) in MeCN (10 cm^3) at 60 °C the reaction was *ca.* 50% complete in 18 h, whereas with (**1a**) (0.19 mmol) and KOCN (3.1 mmol) under reflux (82 °C) the reaction was *ca.* 60% complete in 45 min.

Reactions in MeOH.—No detectable reaction occurred when solutions of (**1a**), (**1b**), (**1c**), or TsiSiMe$_2$OCOR (R = CF$_3$, Me, or Ph) in MeOH were refluxed for 15 days. [There was also no reaction when a solution of (**1a**) in the more electrophilic solvent CF$_3$CH$_2$OH was kept at 60 °C for 15 days.]

The reaction of 0.024M-(**1**) with 0.25M-KSCN in MeOH at 60 °C gave rise to a good first-order plot, with a half-life of 6 h; the product was exclusively the isothiocyante VsiSiMe$_2$NCS. (The corresponding half-life for the reaction of TsiSiMe$_2$-OCOCF$_3$ was *ca.* 7 h.) In contrast, the corresponding reaction of (**1a**) with 0.24M-KOCN was complete at 35 °C by the time of the first recording of the spectrum (<2 min), and the product was exclusively the hydroxide VsiSiMe$_2$OH. (Conversion of TsiSiMe$_2$OCOCF$_3$ into TsiSiMe$_2$OH was likewise complete in <2 min under similar conditions.)

In the reaction of 0.024M-(**1a**) with 0.25M-CsF in MeOH at 60 °C the product was exclusively the fluoride VsiSiMe$_2$F, and the slope of the first-order plot corresponded with a half-life of *ca.* 31 min. (The corresponding value for conversion of TsiSiMe$_2$OCOCF$_3$ into TsiSiMe$_2$F was *ca.* 26 min, probably not significantly different.) It is of interest that under similar conditions the iodide VsiSiMe$_2$I reacts to give a 19:2 mixture of VsiSiMe$_2$F and VsiSiMe$_2$OMe, the overall reaction having a half-life of *ca.* 7 h, so that the half-life for conversion into the fluoride is *ca.* 7.7 h; (**1a**) is thus *ca.* 15 times as reactive as VsiSiMe$_2$I towards F$^-$ under these conditions, which is surprising, since trifluoroacetate would normally be regarded as a much better leaving group from silicon than iodide. [In solvolysis in MeOH alone VsiSiMe$_2$I is much more reactive than (**1a**).[3]] We tentatively suggest that the initial attack of the fluoride ion on (**1a**) may occur at the carbonyl group to give the intermediate (I), which usually reverts to the starting materials but occasionally breaks down through the transition state (II) by migration of fluoride to silicon and cleavage of the Si–OCOCF$_3$ bond. It is also conceivable that there is direct attack of F$^-$ at silicon assisted by interaction with the carbonyl centre, to give transition state (II), without formation of the intermediate (**I**).

Reaction of 0.024M-(**1a**) with 0.25M-NaN$_3$ in MeOH at 60 °C appeared from the change in the ^{1}H n.m.r. spectrum to give exclusively the hydroxide VsiSiMe$_2$OH, with a half-life of *ca.* 25 min. However, analysis of the product at the end of the reaction by g.l.c.–mass spectrometry showed that VsiSiMe$_2$OH and the azide VsiSiMe$_2$N$_3$ were present in 98:2 ratio. If this ratio is accurate the half-life for conversion into VsiSiMe$_2$N$_3$ would be *ca.* 21 h, but this could easily be in error by a factor of two.

It is evident that OCN$^-$ is by far the most effective of the nucleophiles towards (**1a**), but it reacts exclusively at the carbonyl carbon atom with cleavage of the SiO–COCF$_3$ bond. The reactions with CsF and NaN$_3$ have similar overall rates, but the former involves substitution only at silicon whereas the latter involves very predominant attachment to the carbonyl group with cleavage of the SiO–C bond. The slowest reaction was with KSCN, which gave exclusive substitution at silicon.

It seems that for substitution at silicon the order of effectiveness of the nucleophiles is F$^-$ > SCN$^-$ (>N$_3$$^-$), and that for attack at carbon with breaking of the SiO–C bonds is OCN$^-$ > N$_3$$^-$ > F$^-$ > SCN$^-$.

Reactions with NaOMe, HO$_2$$^-$, *or Amines in* MeOH.—Reaction of the trifluoroacetate (**1a**) with 0.20M-NaOMe in MeOH at room temperature was complete by the time (<1 min) the spectrum could be recorded. The product was exclusively VsiSiMe$_2$OH. The reaction of TsiSiMe$_2$OCOCF$_3$ was similarly rapid.

Reaction of the acetate (**1b**) with 0.20M-NaOMe was much slower; 50% of (**1b**) disappeared in *ca.* 9 h at 35 °C, seemingly to give only VsiSiMe$_2$OH, but after 60 h, when reaction was effectively complete, the product was found to be a mixture of VsiSiMe$_2$OH and its isomer (Me$_3$Si)$_2$CHSiMe$_2$OSiMe$_2$-CH=CH$_2$ in *ca.* 7:3 ratio. (The formation of this isomer can be attributed to a 1,3-migration of the SiMe$_2$CH=CH$_2$ group from carbon to oxygen within the silanolate ion, in a previously observed type of rearrangement.[4]) Under the same conditions TsiSiMe$_2$OCOMe underwent 50% reaction in *ca.* 8 h; after this time only TsiSiMe$_2$OH seemed to be formed, as judged from the ^{1}H n.m.r. spectrum.

The reaction of the benzoate (**1c**) under similar conditions at 60 °C was 50% complete after about 12 days, a mixture of VsiSiMe$_2$OH and (Me$_3$Si)$_2$CHSiMe$_2$OSiMe$_2$CH=CH$_2$ then being present in *ca.* 3:1 ratio.

It is evident that in all these cases the solvolysis of the esters involves cleavage of the SiO–C bond, and that the reactivity sequence is (**1a**) > (**1b**) > (**1c**), paralleling that for the corresponding compounds TsiSiMe$_2$OCOR.[1]

When (**1b**) was treated with a solution of H$_2$O$_2$ (0.24M) in 0.10M-NaOMe in MeOH at 35 °C, conversion into VsiSiMe$_2$OH was *ca.* 35% complete after 10 min and 80% after 30 min.

When (**1a**) was treated at 35 °C with a 0.2M-solution of RNH$_2$ (R = NH$_2$, Me, Et, HOCH$_2$CH$_2$, or H$_2$NCH$_2$CH$_2$) in MeOH, conversion into VsiSiMe$_2$OH was complete within 1 min in all cases. (In the case of the reaction with MeNH$_2$ the non-organosilicon product was isolated and shown to be the expected CF$_3$CONMeH.) The corresponding reactions of TsiSiMe$_2$OCOCF$_3$ were likewise complete within 1 min.

In the reaction of (**1a**) with 0.24M-Me$_2$NH in MeOH at 35 °C the conversion was 50% complete in *ca.* 57 min. With Me$_3$N the corresponding half-life was *ca.* 4.5 h, and with 4-Me$_2$NC$_5$H$_4$N it was *ca.* 18 h; with 0.48 and 0.96M-4-Me$_2$NC$_5$H$_4$N the half-lives were 9.3 and 4.4 h, respectively, indicating that the reaction was, as expected, of first-order in the amine. [The half-life for TsiSiMe$_2$OCOCF$_3$ with 0.24M-4-Me$_2$NC$_5$H$_4$N was the same as that for (**1a**).] With 0.24M-C$_5$H$_5$N the half-life was *ca.* 8 days even at 60 °C, and with PhNH$_2$ there was only 11% reaction in 44 days at 60 °C.

From the foregoing results it appears that the order of effectiveness of the various nucleophiles in reactions with (**1a**) is RNH$_2$ (R = H$_2$N, Me, Et, HOCH$_2$CH$_2$, H$_2$NCH$_2$CH$_2$), OCN$^-$, HO$_2$$^-$, OMe$^-$ > N$_3$$^-$ > Me$_2$NH > Me$_3$N > 4-Me$_2$NC$_5$H$_4$N $\gg$ C$_5$H$_5$N > PhNH$_2$. Insofar as there is overlap in the nucleophiles used, this sequence is generally consistent with those for reactions of organic esters in water[5] [for example, the sequence for p-$O_2NC_6H_4OCOMe$, is $HO_2^- > MeO^- > EtNH_2 > H_2NCH_2CH_2NH_2 > NH_2NH_2 > N_3^- > C_5H_5N > PhNH_2 > OCN^-$, and that for 2,4-$(NO_2)_2C_6H_3OCOMe$ is $HO_2^- > MeO^- > H_2NNH_2 > EtNH_2 > H_2NCH_2CH_2NH_2 > C_5H_5N > N_3^-$] except that N_3^- is rather more, and OCN^- much more, reactive towards (**1a**) than would be expected from the results for the organic esters. The sequence for (**1a**) is in even better agreement with Ritchie's nucleophilic parameters N_+ for reactions in water, *viz.* $HO_2^- > N_3^- > MeO^- > H_2NNH_2 > H_2NCH_2CH_2NH_2 > EtNH_2 > C_5H_5N > PhNH_2$.[6]

The powerful effect of OCN^- prompts the speculation that this anion might initially attach to the carbonyl carbon through nitrogen and then migrate to attach to silicon through oxygen, to give the cyanate $VsiSiMe_2OCN$, which would be rapidly hydrolysed to the silanol by traces of water present (*cf.* ref. 7). Direct attack on silicon seems unlikely, since OCN^- is significantly less effective than N_3^- in nucleophilic attack on $TsiSiMe_2I$ in MeOH,[8] and in that reaction gives the isocyanate, $TsiSiMe_2NCO$, which is very resistant to solvolysis.

The spread of rates for the reactions of the amines $PhNH_2$, C_5H_5N, and 4-$Me_2NC_5H_4N$ with (**1a**) in MeOH, associated with rate ratios of 1:62:340, is much greater than that in the reactions with CH_3COCl in H_2O at 22 °C, in which the corresponding ratios are 1:15:17,[2] and this is consistent with the view that in the reactions of (**1a**) the rate-determining step is probably the departure of the leaving group whereas in the reactions of CH_3COCl with these particular amines it is the formation of the tetrahedral intermediate.[2,5]

In order to establish the reactivity sequence for those amines which reacted too rapidly with (**1a**), the reactions with (**1b**) were examined. Reaction of (**1b**) with 0.24M-H_2NNH_2 in MeOH at 35 °C was 50% complete in *ca.* 3 h. [Since the reaction of (**1a**) under similar conditions was complete in <2 min, (**1a**) must be at least 500 times as reactive as (**1b**).] Reaction of (**1b**) with 0.24M-$MeNH_2$ in MeOH had a half-life of *ca.* 7 h at 60 °C. (The product was shown to be exclusively $VsiSiMe_2OH$.) With $H_2NCH_2CH_2NH_2$ the half-life was again *ca.* 7 h, with $HOCH_2CH_2NH_2$ it was *ca.* 17 h, and with $EtNH_2$ *ca.* 6 days. If account is taken of results described earlier for HO_2^- and MeO^-, the order of effectiveness of the nucleophiles is $HO_2^- > H_2NNH_2 > MeO^- > H_2NCH_2CH_2NH_2 > MeNH_2 > HOCH_2CH_2NH_2 > EtNH_2$. When it is remembered that such sequences vary even for reactions of some closely related organic esters, the observed sequence for (**1b**) must be regarded as reasonably consistent with that observed, for example, for reactions of 2,4-$(O_2N)_2C_6H_3OCOMe$ in water, *viz.* $HO_2^- > MeO^- > H_2NNH_2 > EtNH_2 > H_2NCH_2CH_2NH_2$.[5] It is also fairly consistent with that for reactions of CH_3COCl in H_2O, *viz.* $HO_2^- > N_2H_4 > EtNH_2 > H_2NCH_2CH_2NH_2 > HOCH_2CH_2NH_2$,[2] and with the sequence of Ritchies's N_+ values (see earlier discussion).

Since triorganosilanols are similar in acidity to phenols,[9] $VsiSiMe_2OCOMe$ could be expected to show behaviour somewhat similar to that of aryl acetates in reactions of the type under consideration. We found that the reaction of PhOCOMe with 0.24M-H_2NNH_2 in MeOH at 35 °C was complete within 1 min, that with $EtNH_2$ half complete in *ca.* 2 min, and that with $H_2NCH_2CH_2NH_2$ half complete in *ca.* 6 min. From the last result it appears that PhOCOMe is roughly 400 times as reactive as $VsiSiMe_2OCOMe$, but it is likely that steric hindrance by the very bulky $VsiSiMe_2$ group to formation of the tetrahedral intermediate and to solvation reduces the reactivity of (**1b**) below that which could be expected for $Me_3SiOCOMe$ if the appropriate reactions of the latter could be studied. The rate-determining step in the reactions of (**1a**) and (**1b**) (and of $TsiSiMe_2OCOCF_3$ and $TsiSiMe_2OCOMe$) very probably involves the departure of the siloxy group, corresponding to rate-determining separation of PhO^- in reactions of PhOCOMe in water.[2,5]

Experimental

Starting Materials.—The compounds $TsiSiMe_2OCOR$, with R = Me, CF_3, or Ph, were prepared as described previously.[1] The corresponding compounds $VsiSiMe_2OCOR$ were made analogously, as will be described in a forthcoming publication. Authentic samples of $(Me_3Si)_2CHSiMe_2OSiMe_2CH{=}CH_2$ and of $VsiSiMe_2X$ and $TsiSiMe_2X$ species with X = OH, F, OCN, or N_3 were available.

Metal salts were dried by heating at 150 °C under vacuum. The amines used were commercial products, and were purified by standard methods. Methanol was dried over $Mg(OMe)_2$ and stored over molecular sieves (3 Å). 2,2,2-Trifluoroethanol was refluxed over and distilled from CaH_2 then stored over molecular sieves (4 Å).

Reactions of (**1a**) *with* NaN_3, KSCN, *or* KOCN *in* MeCN.—(*a*) A mixture of (**1a**) (0.16 g, 0.037 mmol) and KOCN (0.50 g, 6.2 mmol) in MeCN (15 cm^3) was refluxed for 8 h, then the solvent was evaporated off under vacuum and hexane was added to the residue, followed by water. Separation, washing, drying ($MgSO_4$), and evaporation of the hexane layer left a solid, which was recrystallized from pentane to give (*isocyanatodimethylsilyl*)(*vinyldimethylsilyl*)*bis*(*trimethylsilyl*)-*methane* (0.09 g, 70%), m.p. 225 °C; δ_H (CCl_4) 0.28 (18 H, s, $SiMe_3$), 0.35 (6 H, s, $SiMe_2CH{=}CH_2$), 0.48 (6 H, s, $SiMe_2NCO$), and 5.5—6.7 (3 H, m, $CH{=}CH_2$); ν(SiNCO)(in CCl_4) 2 245 cm^{-1}; m/z 343 (30%, $[M]^+$), 328 (100, $[M - Me]^+$), and 316 (30, $[M - CH{=}CH_2]^+$) (Found: C, 48.7; H, 9.7. $C_{14}H_{33}NOSi_4$ requires C, 49.0; H, 9.6%).

(*b*) A mixture of (**1a**) (0.10 g, 0.24 mmol) and NaN_3 (0.25 g, 3.85 mmol) in MeCN (10 cm^3) was refluxed gently. Samples were withdrawn at intervals for recording of the ^1H n.m.r. spectra, which showed that conversion into $VsiSiMe_2N_3$ was *ca.* 26% complete in 5 min, 59% in 15 min, 78% in 25 min, and 88% in 35 min. After 90 min, addition of hexane then of water to the residual solution, followed by separation, drying ($MgSO_4$), and evaporation of the hexane layer, left a solid with properties identical with those described under (*a*).

(*c*) In the procedure described under (*b*), but with (**1a**) (0.19 mmol) and KOCN (3.10 mmol), conversion into $VsiSiMe_2NCO$ was *ca.* 60% complete in 45 min and complete within 4 h.

(*d*) In the procedure described under (*b*) but with (**1a**) (0.24 mmol) and CsF (3.85 mmol), conversion into $VsiSiMe_2F$ was *ca.* 10% complete in 8 min, 21% in 15 min, 51% in 45 min, 74% in 85 min, and 89% in 140 min. The data gave a good first-order plot with a slope corresponding to a half-life of 46 min.

(*e*) When $TsiSiMe_2OCOCF_3$ was used in place of (**1a**) in the procedure described under (*d*), the reaction was (as judged from the heights of the respective Me_3Si peaks at δ 0.28 and 0.23) *ca.* 12% complete in 10 min, 18% in 15 min, 43% in 45 min, 67% in 85 min, and 83% in 140 min; the first-order plot had a slope corresponding to a half-life of 55 min.

(*f*) When a solution of (**1a**) (0.24 mmol) and KSCN (3.8 mmol) in MeCN (10 cm^3) was kept at 60 °C, analysis as in (*b*) showed that conversion into $VsiSiMe_2NCS$ was 18% complete in 4 min, 42% in 10 min, and 84% in 32 min.

(*g*) The procedure described in (*e*) but with $TsiSiMe_2OCOCF_3$, showed that conversion into $TsiSiMe_2NCS$ was *ca.* 14% complete in 4 min, 34% in 10 min, and 79% in 42 min. [The $SiMe_2$ peaks at δ 0.62 ($SiMe_2OCOCF_3$) and 0.50 ($SiMe_2NCS$) were used.]

Treatment of $TsiSiMe_2OCOR$ *and* $VsiSiMe_2OCOR$ *with* MeOH *or* CF_3CH_2OH *Alone.*—(*a*) A solution of $TsiSiMe_2$-

OCOR or $VsiSiMe_2OCOR$ (R = Me, CF_3, or Ph) (0.12 mmol) in MeOH (10 cm^3) was refluxed for 15 days. Removal of the MeOH left unchanged starting material in each case.

(*b*) When a solution of $VsiSiMe_2OCOR$ (R = Me, CF_3, or Ph) (20 mg) in CF_3CH_2OH (1 cm^3) was kept in an n.m.r. tube at 60 °C for 15 days there was no change in the ^1H n.m.r. spectrum.

Reactions of (**1a**) *with* 0.20M-NaOMe *in* MeOH.—A sample of (**1a**) (0.024 mmol) was dissolved in a small drop (*ca.* 0.01 cm^3) of CCl_4 in an n.m.r. tube, 0.2M-NaOMe in MeOH (1 cm^3) at room temperature was added, and the tube was capped, shaken, and placed in the spectrometer. The ^1H spectrum in the SiMe region recorded within 1 min of mixing was that of $VsiSiMe_2OH$ (singlets at δ 0.22 and 0.30 in 3:2 ratio).

Reactions of $VsiSiMe_2OCOMe$ *and* $TsiSiMe_2OCOMe$ *with* 0.20M-NaOMe *in* MeOH.—(*a*) To a solution of (**1b**) (0.028 mmol) in a drop (*ca.* 0.01 cm^3) of CCl_4 contained in an n.m.r. tube was added 0.20M-NaOMe in MeOH (1 cm^3) The tube was capped and shaken then placed in the spectrometer at 35 °C. After 9 h the spectrum showed that *ca.* 50% of the starting material had been converted into $VsiSiMe_2OH$, as indicated by the relative heights of the singlets from the Me_3Si protons at δ 0.33 (starting material) and 0.22 (silanol). After 70 h the spectrum indicated that almost all the starting material had been converted into a mixture of $VsiSiMe_2OH$ and its isomer $(Me_3Si)_2CHSiMe_2OSiMe_2CH{=}CH_2$ in *ca.* 7:3 ratio, as indicated by the relative heights of the Me_2Si peaks at δ 0.22 and 0.16, respectively.

(*b*) When $TsiSiMe_2OCOMe$ was used in a similar procedure, *ca.* 50% had reacted after 8 h, and after 70 h only $TsiSiMe_2OH$ could be detected. (The relevant Me_3Si peaks for starting material and silanol were at δ 0.27 and 0.23, respectively.)

Reaction of $VsiSiMe_2OCOPh$ *with* 0.20M-NaOMe *in* MeOH.—A solution of (**1c**) (0.025 mmol) in a drop of CCl_4 (*ca.* 0.01 cm^3) in an n.m.r. tube was diluted with 0.20M-NaOMe in MeOH (1 cm^3). The tube was capped and shaken then kept in a bath at 60 °C and removed at intervals for the recording of the ^1H n.m.r. spectrum. After 12 days *ca.* 50% of the starting material had been converted into $VsiSiMe_2OH$ and $(Me_3Si)_2CHSiMe_2OSiMe_2CH{=}CH_2$ in *ca.* 4:1 ratio, as indicated by the heights of the Me_2Si proton signals at δ 0.28, 0.22, and 0.16, respectively. After 40 days only $VsiSiMe_2OH$ and $(Me_3Si)_2CHSiMe_2OSiMe_2CH{=}CH_2$, in *ca.* 3:1 ratio, could be detected.

Reactions of $TsiSiMe_2OCOCF_3$ *and* $VsiSiMe_2OCOCF_3$ *with Salts in* MeOH.—(i) A 0.20M-solution of KOCN in MeOH (1 cm^3) was added to (**1a**) (0.024 mmol) dissolved in a drop (*ca.* 0.01 cm^3) of CCl_4 in an n.m.r. tube at 35 °C. The ^1H n.m.r. spectrum in the SiMe region was recorded within 2 min of mixing and was identical with that of $VsiSiMe_2OH$. The identity of the product was confirmed by g.l.c.-mass spectrometry, which revealed only one component, with *m/z* 303 (100%), $[M - Me]^+$) and 287 (25, $[M - CH{=}CH_2]^+$).

(*ii*) A similar procedure starting from $TsiSiMe_2OCOCF_3$ showed that formation of $TsiSiMe_2OH$ was complete within 2 min.

(*iii*) A 0.25M-solution of KSCN in MeOH (1 cm^3) was added to a solution of (**1a**) (0.024 mmol) in CCl_4 (*ca.* 0.01 cm^3) in an n.m.r. tube. The tube was capped and shaken, then kept in a bath at 60 °C and removed at intervals for recording of the ^1H n.m.r. spectrum. Conversion into $VsiSiMe_2NCS$ was *ca.* 22% complete in 2 h, 46% in 5 h, 62% in 8 h and 90% in 19 h. At the end of the reaction the solvent was removed and the residue extracted with CCl_4, to give a solution with a ^1H n.m.r. spectrum identical to that of an authentic sample of $VsiSiMe_2NCS$.

(iv) The procedure described under (iii) was repeated with $TsiSiMe_2OCOCF_3$. The product was exclusively $TsiSiMe_2NCS$, and the reaction was *ca.* 28% complete in 3.5 h, 57% in 11 h, and 86% in 19 h.

(v) The procedure described under (iii) was repeated but with 0.25M-CsF in place of KSCN. The sole product was $VsiSiMe_2F$, and reaction was *ca.* 26% complete in 8 min, 58% in 30 min, 77% in 60 min, and 85% in 75 min.

(vi) The procedure described under (v) was repeated with $TsiSiMe_2OCOCF_3$. The sole product was $TsiSiMe_2F$, and reaction was *ca.* 24% complete in 10 min, 57% in 32 min, 75% in 55 min, and 88% in 80 min.

(vii) The procedure described under (iii) was repeated but with 0.25M-NaN_3. From the ^1H n.m.r. spectrum in the SiMe region the product appeared to be exclusively $VsiSiMe_2OH$, and from the heights of the Me_3Si peaks of the starting material (δ 0.31) and product (δ 0.22) the conversion was judged to be *ca.* 80% complete after 1 h. After 4 h, removal of the solvent and extraction of the residue with CCl_4 gave a solution with ^1H n.m.r. spectrum seemingly identical with that of an authentic sample of $VsiSiMe_2OH$, but g.l.c.-mass spectrometry indicated that the silanol and $VsiSiMe_2N_3$ were present in *ca.* 98:2 ratio.

Methanolysis of $VsiSiMe_2OCOR$ *and* $TsiSiMe_2OCOR$ (R = CF_3 *or* Me) *Catalysed by Amines or Peroxide Ion.*—(*a*) A solution of (**1a**) (0.024 mmol) in MeOH (1 cm^3) at 35 °C was added to $EtNH_2$ (0.24 mmol) in an n.m.r. tube. The tube was capped, shaken, and placed in the spectrometer at 35 °C. The ^1H n.m.r. spectrum recorded within 1 min of mixing showed that complete conversion into $VsiSiMe_2OH$ had occurred. (Addition of a little authentic silanol enhanced the spectrum.) Identical results were obtained when N_2H_4, $MeNH_2$, $HOCH_2CH_2NH_2$, or $H_2NCH_2CH_2NH_2$ was used in place of $EtNH_2$. Complete conversion within 1 min was also observed in each case with all the amines when $TsiSiMe_2OCOCF_3$ was used in place of (**1a**).

(*b*) A solution of (**1a**) (0.024 mmol) in MeOH (10 cm^3) containing $MeNH_2$ (2.4 mmol) was kept for 10 min at room temperature then added to water. Extraction with diethyl ether followed by separation, washing, drying ($MgSO_4$), and evaporation of the extract left a solid, which was shown to be $VsiSiMe_2OH$ by comparison with an authentic sample (m.p., i.r., ^1H n.m.r.). The aqueous layer was evaporated to leave a solid, which was shown to be $CF_3CONHMe$ by comparison with an authentic sample.

(*c*) A solution of (**1a**) (0.024 mmol) and Me_2NH (0.24 mmol) in MeOH (1 cm^3) was made up as described under (*a*), the n.m.r. tube was placed in the spectrometer at 35 °C, and the spectrum was recorded at intervals. This showed that conversion into $VsiSiMe_2OH$ was *ca.* 50% complete after 57 min, and effectively complete after 200 min.

With Me_3N in place of Me_2NH the reaction was 26% complete in 2 h, 46% in 4 h, and 80% in 10 h.

(*d*) The procedure described under (*c*) was repeated starting with (**1a**) (0.012 mmol) and 4-$Me_2NC_5H_4N$ (0.12 mmol) in MeOH (0.5 cm^3) at 35 °C. Conversion into $VsiSiMe_2OH$ was 21% complete in 4 h, 44% in 14 h, 58% in 21 h, 74% in 33 h, 79% in 40 h, 90% in 58 h, 95% in 79 h, and effectively 100% complete in 200 h. The data gave a good first-order plot corresponding to a half-life of 18 h.

(*e*) The procedure described under (*c*) was repeated but with $TsiSiMe_2OCOCF_3$. The data gave a good first-order plot with a slope corresponding to a half-life of 18 h.

(*f*) A solution of (**1a**) (0.024 mmol) and pyridine (0.24 mmol) in MeOH (1 cm^3) in an n.m.r. tube was kept in a bath at 60 °C. The ^1H n.m.r. spectra showed that conversion into $VsiSiMe_2OH$ was *ca.* 48% complete in 7 days and 80% in 19 days.

When aniline was used in place of pyridine, reaction was only *ca.* 11% complete after 44 days.

(*g*) Procedures similar to those described above, but starting with (**1b**), gave the following results: (i) with N_2H_4 as catalyst at 35 °C, *ca.* 52% conversion into VsiSiMe$_2$OH in 3 h, 89% in 10 h, and >95% in 15 h; (ii) with MeNH$_2$ as catalyst at 60 °C, 50% conversion in 7 h and 90% in 24 h; (iii) with EtNH$_2$ as catalyst at 60 °C, 50% conversion in 6 days and 89% in 20 days; (iv) with $HOCH_2CH_2NH_2$ catalyst at 60 °C, 50% conversion in 17 h; (v) with $H_2NCH_2CH_2NH_2$ as catalyst at 60 °C, 50% conversion in 7 h.

(*h*) A solution of (**1b**) (0.024 mmol) in MeOH (1 cm^3) at 35 °C was added to H_2O_2 (0.24 mmol) in an n.m.r. tube, which was then placed in the spectrometer at 35 °C. Conversion into VsiSiMe$_2$OH was *ca.* 31% complete in 10 min, 54% in 20 min, and effectively 100% complete in 100 min.

(*i*) In the procedure described under (*h*), but with TsiSiMe$_2$OCOMe as starting material, conversion was *ca.* 28% complete in 10 min and 86% in 50 min.

(*j*) In the procedure described under (*h*), but with N_2H_4 in place of H_2O_2, conversion was 52% complete in 3 h, 89% in 12 h, and effectively 100% complete after 15 h.

(*k*) In the procedure described under (*h*), but with MeNH$_2$ as catalyst and the tube was kept in a bath at 60 °C, conversion was *ca.* 50% complete in 7 h and 90% in 23 h.

(*l*) A solution of (**1b**) (0.24 mmol) and MeNH$_2$ (2.4 mmol) in MeOH (10 cm^3) was kept at room temperature for 12 days, then hexane was added followed by water. The organic layer was separated, washed, dried, and evaporated, to leave a solid, which was shown by its m.p. and ^{1}H and mass spectra to be VsiSiMe$_2$OH.

(*m*) In the procedure described under (*h*), but with EtNH$_2$ as catalyst at 60 °C, conversion was *ca.* 50% complete in 6 days and 90% in 20 days. With $HOCH_2CH_2NH_2$ or $H_2NCH_2CH_2NH_2$ as catalyst the reactions were *ca.* 50% complete in 17 h and 7 h, respectively.

Methanolysis of PhOCOMe.—(*a*) A solution (prewarmed to 35 °C) of PhOCOMe (0.024 mmol) in MeOH (1 cm^3) containing Me$_4$Si (0.01 mmol) was added to $H_2NCH_2CH_2NH_2$ (0.24 mmol) in an n.m.r. tube, which was capped, shaken, and placed in the spectrometer at 35 °C. From the height of the OCOMe peak (δ 2.4) relative to that of the Me$_4$Si peak, conversion into PhOH was judged to be *ca.* 50% complete 2 min after mixing. The spectrum in the aromatic region upon completion of the reaction was identical with that of PhOH.

(*b*) In the procedure described under (*a*), but with EtNH$_2$ as catalyst, reaction was *ca.* 50% complete in 6 min.

(*c*) In the procedure described under (*a*), but with H_2NNH_2 as catalyst, reaction was complete within 1 min.

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