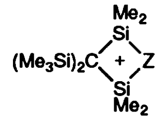
# Anchimeric Assistance by the Acetoxy Group in the Solvolysis of $(Me_3Si)_2C(SiMe_2OCOMe)(SiMe_2X)$, X = Cl, NCS or $N_3$

**Colin Eaborn,* Paul D. Lickiss and Alan D. Taylor**
*School of Chemistry and Molecular Sciences, University of Sussex, Brighton, UK BN1 9QJ*

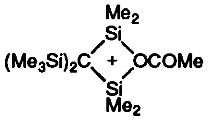
Reaction of the acetoxy chloride $(Me_3Si)_2C(SiMe_2OCOMe)(SiMe_2Cl)$, **1**, at 35 °C with 3:2 v/v MeOH–dioxane containing one equivalent of $Et_3N$ gave exclusively the corresponding methoxide $(Me_3Si)_2C(SiMe_2OCOMe)(SiMe_2OMe)$, **5**, in a pseudo first-order process with a rate constant of $6.5 \times 10^{-3}$ $s^{-1}$. [In the absence of the amine some of the initial product underwent further reaction, catalysed by the generated HCl, to give the dimethoxy compound $(Me_3Si)_2C(SiMe_2OMe)_2$, **8**.] Under similar conditions the reaction of the methoxy chloride, $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Cl)$, to give **8**, was 14 times as slow, and this is taken to indicate that the anchimeric assistance by the acetoxy group in **1** involves the carbonyl oxygen atom, to give the six-membered ring cation **III**. The much less reactive isothiocyanate $(Me_3Si)_2(SiMe_2OCOMe)(SiMe_2NCS)$, **2**, and azide $(Me_3Si)_2C(SiMe_2OCOMe)(SiMe_2N_3)$, **3**, react with MeOH to give solely **5** in the presence of $Et_3N$ but also some **8** in its absence; **3** is *ca.* 21 times as reactive at 50 °C as the corresponding methoxy isothiocyanate **9**, and **3** is >100 times as reactive as the corresponding methoxy azide **10**. The fluoride $(Me_3Si)_2C(SiMe_2OCOMe)(SiMe_2F)$ was found to be unreactive towards MeOH. The chloride **1** was, surprisingly, found to react much less readily with $CF_3CH_2OH$ than with MeOH (possibly because hydrogen bonding between the acidic alcohol $CF_3CH_2OH$ and the carbonyl oxygen inhibits anchimeric assistance through the latter) and the product was not the expected $(Me_3Si)_2C(SiMe_2OCOMe)(SiMe_2OCH_2CF_3)$ but instead the trifluoroethoxy hydroxide $(Me_3Si)_2C(SiMe_2OCH_2CF_3)(SiMe_2OH)$, formed possibly *via* an intermediate oxadisiletane, **13**. In the presence of 1 equiv. of $Et_3N$ some **1** was rapidly converted into the diacetate $(Me_3Si)_2C(SiMe_2OCOMe)_2$ but the subsequent reaction was very slow; the course of the reaction is obscure.

It is well established that appropriate groups Z in compounds of the type $(Me_3Si)_2C(SiMe_2Z)(SiMe_2X)$ can provide anchimeric assistance to the leaving of $X^-$ in solvolysis.[1] For example, Z can be Me,[2] Ph,[3] $CH{=}CH_2$,[4] OMe,[5,6] $N_3$[7] or NCS.[7] The anchimeric assistance is associated with rate-determining formation of a 1,3-bridged cation of type **I**, which can be attacked by a nucleophile, with ring opening, at either the α- or γ-Si atom, that is, 1,3-migration of Z can occur.[1–7]

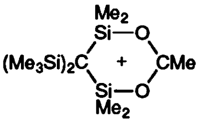
We have shown previously that the acetoxy group, MeOCO, can migrate in this way, and that it can provide anchimeric assistance.[8] In the present study we were concerned to assess the relative abilities of this group and of the OMe group (which is known to provide powerful assistance[6]) to facilitate the leaving of $X^-$, and also to answer the question of whether the bridging in the case of the acetoxy group involves a four-membered ring species **II** or a six-membered species **III**. (The bridging in the latter is analogous to the 1,2-bridging observed in assistance by a β-acetoxy group in solvolysis of some organic compounds.[9]) A preliminary account has appeared.[10]



**I**



**II**



**III**

## Results and Discussion

*Methanolysis of* **1**.—The acetoxy chloride **1** was made by reaction of the diol $(Me_3Si)_2C(SiMe_2OH)_2$ with MeCOCl.[10] When **1** was treated with a 3:2 v/v mixture of MeOH and dioxane at 35 °C, work-up after 30 min gave a solid that was shown by $^1H$ NMR spectroscopy and linked gas-liquid chromatography and mass spectrometry (GLC–MS) to be an 8:1 mixture of the monomethoxy compound **5** and the dimethoxy compound **8**. Recording at appropriate intervals of the ratio of the heights of the signals from the protons of the $SiMe_2$ fragments in the $SiMe_2OCOMe$ group in **1** and $SiMe_2OMe$ groups in **5** gave a good first-order plot for conversion of **1** into **5**, and the formation of the dimethoxy compound being ignored, this yielded a value for the first-order constant of $5.6 \times 10^{-3}$ $s^{-1}$ ($t_{\frac{1}{2}}$ 124 s). An approximate allowance can be made for the formation of **8** by multiplying that rate constant by 9/8, giving a value of *ca.* $6.3 \times 10^{-3}$ $s^{-1}$ ($t_{\frac{1}{2}}$ 110 s) for the disappearance of **1**. To enable a direct comparison to be made the solvolysis of the methoxy chloride **7** was carried out under the same conditions. The sole product after 24 h was **8**, and the good first-order plot yielded a rate constant of $4.8 \times 10^{-4}$ $s^{-1}$ ($t_{\frac{1}{2}}$ 24 min).

The formation of the dimethoxy species **8** from **1** can be attributed to solvolysis at the Si–OCOMe bond of the initial product **5**, catalysed by the generated hydrogen chloride and assisted by nucleophilic participation by the OMe group.[5] This

$(Me_3Si)_2C(SiMe_2OCOMe)(SiMe_2X)$
**1** X = Cl
**2** X = NCS
**3** X = $N_3$
**4** X = F
**5** X = OMe
**6** X = OCOMe

$(Me_3Si)_2C(SiMe_2OMe)(SiMe_2X)$
**7** X = Cl
**8** X = OMe
**9** X = NCS
**10** X = $N_3$

was confirmed when the reaction was carried out in the presence of one molar equivalent of $Et_3N$, the product then being exclusively **5**. A good first-order plot yielded a first-order rate constant of $6.5 \times 10^{-3}$ $s^{-1}$ ($t_{\frac{1}{2}}$ 107 s), in agreement with that derived for the reaction in the absence of the amine. Thus the acetoxy compound **1** is *ca.* 14 times as reactive as the methoxy analogue **7**, and so the anchimeric assistance by the acetoxy group is significantly larger than that by the methoxy group. If the assistance by the acetoxy group involved the ether oxygen, to give the intermediate **II**, the assistance would be expected to be substantially weaker than that by the methoxy group since electron withdrawal by the carbonyl group must greatly reduce the nucleophilicity of the ether oxygen atom. Thus we conclude that the assistance involves attack of the much more strongly nucleophilic oxygen of the carbonyl group, to give the six-membered ring species **III**. The difference observed between the effects of the two groups is reasonably consistent with their relative effects in the ionization of organic compounds.[9]

When a solution of **1** in 1.1 mol $dm^{-3}$ NaOMe–MeOH was kept at 60 °C for 3 h, work-up gave a mixture of two products, identified as $(Me_3Si)_2CH(SiMe_2OMe)$ and $(Me_3Si)_2CH(SiMe_2OSiMe_2OMe)$. These products are known to be formed by the action of NaOMe–MeOH on the methoxy acetate **5**,[12] which would be fully formed from **1** within 1 min under the conditions used.

*Methanolysis of* **2**, **3** *and* **4**.—The isothiocyanate **2** was, as expected, found to be much less reactive than the chloride **1**. Monitoring by $^1H$ NMR spectroscopy of the reaction of **2** with MeOH alone at 50 °C showed that after 70 min the substrate **2** and the products **5** and **8** were present in a *ca.* 1:1:1 ratio. When the reaction was carried out in the presence of a one molar quantity of $Et_3N$ work-up after 6 h gave a solid that was shown to be a mixture of **2** and **5** in a *ca.* 1:6 ratio. A good first-order plot was obtained and yielded a rate constant of $8.1 \times 10^{-5}$ $s^{-1}$ ($t_{\frac{1}{2}}$ 143 min at 50 °C). A half-life of *ca.* 51 h at 50 °C was observed for solvolysis of the methoxy analogue **9** under similar conditions,[6] and so the acetoxy compound is *ca.* 20 times the more reactive.

The azido compound **3** was, as expected, even less reactive. Again reaction in MeOH alone at 50 °C gave some of the dimethoxy product **8** along with **5**, as a consequence of anchimeric assistance by the azido group (*cf.* ref. 7) to acid-catalysed solvolysis at the Si–OCOMe bond. In the presence of 1 equiv. of $Et_3N$ only **5** was formed, and a good first-order plot yielded a rate constant of $3.5 \times 10^{-6}$ $s^{-1}$ ($t_{\frac{1}{2}}$ 55 h at 50 °C). The methoxy analogue was shown previously not to react detectably with MeOH alone during 20 days at 50 °C, although there was rapid reaction when HBr was present.[6] The difference between the effects of the acetoxy and methoxy groups would be expected to be larger the poorer the leaving-group ability of the departing $X^-$, and the $N_3$ group is an especially poor leaving group from silicon, but the large difference between the reactivities of **3** and **10**, apparently involving a factor of > 100, is somewhat surprising. (This minimum factor is based on the assumption that in the case of the methoxy azide **10**, formation of up to 5% of the expected product during 20 days could have escaped detection,[7] and this corresponds to a maximum rate constant for the solvolysis of *ca.* $3 \times 10^{-8}$ $s^{-1}$.)

Reaction of **1** with $AgBF_4$ in $CH_2Cl_2$ gave a 3:1 mixture of the acetoxy fluoride **4** and the difluoride $(Me_3Si)_2C(SiMe_2F)_2$. When a solution of this mixture was kept in MeOH for 4 days at 50 °C there was no detectable change in the $^1H$ NMR spectrum, and the starting mixture was recovered unchanged. This is in keeping with the absence of any detectable reaction of the methoxy fluoride $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2F)$ with MeOH during 60 days at 50 °C.[6]

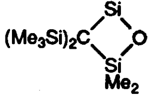
*Reaction of* **1** *with* $CF_3CH_2OH$.—Unexpected behaviour was encountered when **1** was treated with 3:2 v/v $CF_3CH_2OH$–dioxane at 35 °C. The methoxy chloride **7** is known to react much more readily with $CF_3CH_2OH$ than with MeOH, as a consequence, it is thought, of enhanced electrophilic assistance to the leaving of $Cl^-$ by the more acidic $CF_3CH_2OH$.[6] Expecting analogous behaviour for **1**, and to provide a direct comparison with that of **7**, we treated **1** at 35 °C with a 3:2 v/v mixture of $CF_3CH_2OH$ and dioxane, the medium used for **7**. Instead of the very rapid reaction expected (since $t_{\frac{1}{2}}$ for the reaction in 3:2 MeOH–dioxane has a half-life of *ca.* 2 min) we found that after 20 min there was virtually no change in the $^1H$ NMR spectrum. Subsequently a single product was formed, and after work-up this was identified as the trifluoroethoxy hydroxide **11**, not the expected trifluoroethoxide **12**. A good first-order plot was obtained over the range of reaction studied (*ca.* 50% completion) and yielded a rate constant of $2.2 \times 10^{-5}$ $s^{-1}$ ($t_{\frac{1}{2}}$ 8.7 h).

$(Me_3Si)_2C(SiMe_2OCH_2CF_3)(SiMe_2OH)$

**11**

$(Me_3Si)_2C(SiMe_2OCOMe)(SiMe_2OCH_2CF_3)$

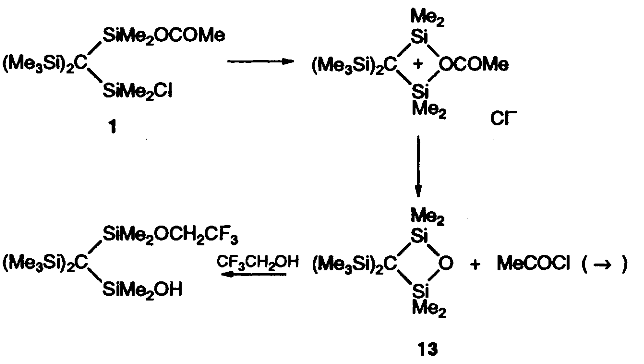
**12**



**13**

The most important aspect of this result is that the observed reaction is *ca.* 290 times as slow as that of the methanolysis under similar conditions. Thus (since formation of 10% of **12** would not have escaped detection) any direct solvolysis to give **12** must be > 2000 times slower than the corresponding methanolysis. It seems very likely that this must be attributed to inhibition of the anchimeric assistance in this medium, and we tentatively suggest that this involves hydrogen bonding between the carbonyl group and the acidic alcohol, which could substantially lower the nucleophilicity of the carbonyl oxygen. (If this suggestion is correct, then anchimeric assistance by β-acetoxy and related groups in reactions of organic compounds should be similarly inhibited in $CF_3CH_2OH$, but we have been unable to find any reports of relevant studies.)

A further significant feature is that although **1** is much less reactive towards $CF_3CH_2OH$ than towards MeOH, it is still much more reactive than the related chloride $(Me_3Si)_3CSiMe_2Cl$ or acetate $(Me_3Si)_3CSiMe_2OCOMe$, which are inert towards both alcohols even under prolonged reflux. Thus it seems that either the acetoxy group still provides some assistance to the leaving of chloride ion or the chloride ligand assists leaving of the acetate ion (facilitated by hydrogen bonding to the solvent). If the latter process operated, however, to give a cation **I** with Z = Cl, the initial product would be $(Me_3Si)_2C(SiMe_2OCH_2CF_3)(SiMe_2Cl)$, which would be expected to go to the bis(trifluoromethoxide) $(Me_3Si)_2C(SiMe_2OCH_2CF_3)_2$, though it is conceivable that selective reaction with traces of water in the solvent could give the observed hydroxide **11**. Moreover, departure from first-order kinetics would be expected as a result of catalysis by liberated HCl, as observed in the methanolysis of the methoxy chloride **7**.[6] We thus think it more likely that assistance by the ether oxygen of the acetoxy group in some way gives rise to the oxadisiletane **13**, which appears to be readily formed [*e.g.* from $(Me_3Si)_2C(SiMe_2OH)_2$ in MeOH[11]] and to participate in a range of reactions, but which we have been unable to isolate.[12] Ring-opening attack by the solvent on this intermediate would give the observed product **11**. One conceivable route is shown in Scheme 1.



**Scheme 1** Possible course of the reaction of **1** with $CF_3CH_2OH$

When the reaction of **1** with 3:2 v/v $CF_3CH_2OH$–dioxane [containing $(Me_3Si)_3CH$ as internal standard] was repeated with 1 equiv. of $Et_3N$ present remarkably different behaviour was observed. Recording of the $^1H$ NMR spectrum as soon as possible after dissolution of the substrate (*i.e.* after *ca.* 1 min) indicated that a second species was present, and from its spectrum this appeared to be the diacetate **6** (as confirmed by addition of an authentic sample to a second reaction mixture). From the heights of the peaks from the Si*Me*$_2$OCOMe protons in the product and those from the Si*Me*$_2$OCOMe and $SiMe_2Cl$ peaks in the substrate, the latter and **6** appeared to be present in a *ca.* 2:1 ratio, but this is impossible unless one or more other products are present but hidden, since reaction of 33% of **1** could give only 16.5% of **6**, and in any case formation of **6** must give rise to a second product.* The amount of **1** remaining (as indicated by reference to the internal standard) fell by *ca.* 15% in the next 20 min, with the ratio of **1** to **6** effectively constant, but there was little further change during 24 h except for the growth of small additional peaks at the expense of those from **6**. After work-up, analysis by GLC revealed the presence of four compounds in the ratio 1.0:19:2.0:8, and examination by GLC–MS indicated that these were respectively the oxadisiletane **13**, the starting material **1**, the trifluoroethoxy hydroxide **11** and the diacetate **6**. The formation of small amounts of **13** and **11** upon prolonged reaction is not surprising since they are known to be formed slowly from the diacetate in $CF_3CH_2OH$ at 60 °C.[12] The seeming presence of **1** and **6** in a *ca.* 2:1 ratio presents the same anomaly as that arising from the spectroscopic analysis.

Since methanolysis of the acetate $(Me_3Si)_2C(SiMe_2CH{=}CH_2)(SiMe_2OCOMe)$ by cleavage of the O–COMe bond to give the corresponding hydroxide has been shown to be powerfully catalysed by amines (as is hydrolysis of alkyl esters),[13] it is reasonable to assume that the remarkably large effect of $Et_3N$ on the reaction of **1** with $CF_3CH_2OH$ arises from attachment of the amine to the carbonyl carbon atom (though we note that the amine has little effect on the rate of reaction of **1** with MeOH). This attachment would greatly increase the nucleophilicity of the carbonyl oxygen, and thus its ability to assist leaving of chloride ion, but we can suggest no plausible way in which this would lead to formation of the diacetate. Alternatively the attachment could result in cleavage of the SiO–C bond to give the hydroxy chloride $(Me_3Si)_2C(SiMe_2OH)(SiMe_2Cl)$, but again there is no obvious route from this to the diacetate. Neither can we account for the fact that the main reaction stops (or reaches an equilibrium) after the initial consumption of less than half of the substrate, though, of course, the effect of the amine would be expected to tail off as it is taken up by interaction with liberated HCl. A more detailed study would be required to establish the course of the reaction, and this we are not in a position to undertake.

## Experimental

*Solvents.*—Methanol was dried by refluxing with, and distillation from, $Mg(OMe)_2$, and stored over 3 Å molecular sieves. 2,2,2-Trifluoromethanol and MeCN were dried similarly over $CaH_2$ and stored over 4 Å molecular sieves. Dioxane was refluxed with, and distilled from, sodium and stored over 4 Å molecular sieves.

*Instrumentation.*—The $^1H$ NMR spectra were normally recorded at 80 MHz on a Bruker WP80FT spectrometer; unless otherwise indicated solutions were in $CCl_4$ containing $CH_2Cl_2$ or $CHCl_3$ as reference. However, for continuous monitoring of the spectrum of a reaction mixture a Perkin-Elmer R32 instrument (90 MHz) was used. Mass spectra were obtained at 70 eV with a Kratos MS25 spectrometer, and for GLC–MS this was linked to a 2 m column of 3% OV-17 or 5% OV-101 on Gas Chrom G (100–200 mesh). Ordinary GLC analyses were carried out with a Pye-Unicam GCD chromatograph fitted with a flame-ionization detector; the packing was 3% OV-17 on Chromosorb G.

*Starting Materials.*—Compound **1** was made as previously described.[11] The salts KSCN and $NaN_3$ were dried at 60 °C/0.1 Torr† for 8h.

*Preparations of the Compounds* $(Me_3Si)_2C(SiMe_2OCOMe)(SiMe_2X)$ *with* X = NCS **2**, $N_3$ **3** *or* F **4**.—(*a*) X = NCS. A mixture of **1** (0.30 g, 0.81 mmol) and KSCN (0.39 g, 4.07 mmol) in MeCN (25 cm$^3$) was boiled under reflux for 1 h. The solvent was removed under vacuum, the residue extracted with pentane (20 cm$^3$), the extract filtered, and the filtrate evaporated to leave a solid. This was sublimed (120 °C/0.2 Torr) to give (acetoxydimethylsilyl)(isothiocyanatodimethylsilyl)bis(trimethylsilyl)methane (0.27 g, 85%), 212 °C (Found: C, 43.1; H, 8.5; N, 3.3. $C_{14}H_{33}NO_2SSi_4$ requires C, 42.9; H, 8.5; N, 3.6%); $\delta_H$ 0.30 (18 H, s, $SiMe_3$), 0.52 (6 H, s, $SiMe_2NCS$), 0.59 (6 H, s, Si*Me*$_2$OCOMe) and 2.05 (3 H, s, OCOMe); *m/z* 376 (90%, M − Me), 334 (70), 333 (90, M − Me − COMe), 318 (20, M − Me − NCS), 275 (100), 245 (20), 187 (15), 73 (80), 59 (10) and 43 (25).

(*b*) X = $N_3$. A solution of **1** (0.50 g, 1.36 mmol) in MeCN was refluxed with $NaN_3$ (0.44 g, 6.78 mmol) in MeCN (35 cm$^3$) for 6 h. Work-up as in (*a*) but with two sublimations (105 °C/0.2 Torr) gave (acetoxydimethylsilyl)(azidodimethylsilyl)bis(trimethylsilyl)methane (0.42 g, 82%) (Found: C, 41.5; H, 8.9; N, 10.8. $C_{13}H_{33}N_3O_2Si_4$ requires C, 41.6; H, 8.9; N, 11.2%); $\delta_H$ 0.30 (18 H, s, $SiMe_3$), 0.50 (6 H, s, $SiMe_2N_3$), 0.55 (6 H, s, Si*Me*$_2$OCOMe) and 2.01 (3 H, s, OCOMe); $\nu(CCl_4)$/cm$^{-1}$ 2140 ($SiN_3$); *m/z* 360 (20%, M − Me), 317 (10), 275 (100), 259 (10), 245 (15), 213 (20), 187 (10), 75 (45), 59 (15) and 43 (10).

(*c*) X = F. To a solution of **1** (0.20 g, 0.54 mmol) in $CH_2Cl_2$ (20 cm$^3$) was added anhydrous $AgBF_4$ (0.21 g, 1.08 mmol). The mixture was stirred for 30 min and the solvent then removed. Extraction with $CCl_4$ (20 cm$^3$) followed by filtration gave a solution whose $^1H$ NMR spectrum corresponded to a 3:1 mixture of **4** with $(Me_3Si)_2C(SiMe_2F)_2$. For **4**, $\delta_H$ 0.30 (18 H, s, $SiMe_3$), 0.50 [6 H, d, $^3J$(H–F) 8 Hz, $SiMe_2F$], 0.58 (6 H, s, $SiMe_2O$) and 2.05 (3 H, s, OCOMe), and for $(Me_3Si)_2$-

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* A 2:1 ratio of **1** to **6** could in principle arise from disproportionation of 50% of **1** to give 25% of **6** and 25% of the dichloride $(Me_3Si)_2C(SiMe_2Cl)_2$, but it is very unlikely that the latter would escape detection, especially by GLC–MS, unless it reacted to give several products in small amounts.

† 1 Torr = 133.332 Pa.

$C(SiMe_2F)_2$ (an authentic sample of which was available) $\delta_H$ 0.29 ($SiMe_3$) and 0.43 [d, $^3J$(H–F) 8 Hz, $SiMe_2F$). The heights of the peaks at $\delta$ 0.30 and 0.29 were in the approximate ratio 3:1. Removal of the solvent left a white solid, which was sublimed at 140 °C/0.5 Torr. The sublimate gave a $^1H$ NMR spectrum in $CCl_4$ virtually identical with that of the initial product solution. Analysis by GLC showed that two components were present in a *ca.* 3:1 ratio, and the GLC–MS data for the separate components confirmed that they were respectively **4** [*m/z* 337 (50%, M – Me), 295 (100), 279 (50), 245 (10), 203 (30), 187 (60), 73 (80), 59 (10) and 43 (40)] and $(Me_3Si)_2C(SiMe_2F)_2$ [*m/z* 297 (30%, M – Me), 205 (25), 73 (100) and 59 (10)]. The mixture was used for the attempted methanolysis.

*Rate Studies.*—A sample of the substrate (*ca.* 10 mg, giving a *ca.* 0.05 mol $dm^{-3}$ solution) was placed in a dry NMR tube and the relevant solvent (*ca.* 0.5 $cm^3$) (prewarmed to the reaction temperature in the case of short half-lives), alone or containing the appropriate additive, was added. The tube was capped immediately, sealed with Parafilm, shaken briefly and either placed in the probe of the spectrometer at the required temperature or (for reactions with $t_{\frac{1}{2}} > 3$ h) kept in a thermostat bath. The progress of the reaction was monitored by determining at appropriate intervals the relative heights of a suitable signal from the substrate and either the corresponding signal from the product or that from the $Me_3Si$ protons of $(Me_3Si)_3CH$ added as an internal standard. From the ratios a first-order plot was generated in the usual way. At the end of the reaction the solvent was removed under vacuum and the residue taken up in $CCl_4$ (*ca.* 0.5 $cm^3$) for recording of the $^1H$ NMR spectrum and the analysis by GLC and/or GLC–MS. Rate constants were reproducible to within *ca.* 5%, and are thought to be accurate to within *ca.* ± 10%.

Details for particular runs were as follows. (*a*) For the reaction of **1** with a 3:2 v/v mixture of MeOH and dioxane at 35 °C the relative heights of the signals from the protons of the $SiMe_2Cl$ group in **1** and the Si*Me*$_2$OCOMe group in the major product **5** were monitored. After 30 min work-up gave a solid which was shown by $^1H$ NMR spectroscopy and GLC analysis to be a *ca.* 8:1 mixture of **5** and **8**. (Authentic samples were available.) When the procedure was repeated but with 1.0 molar equivalents of anhydrous $Et_3N$ present, only one product appeared, and work-up after 5 h showed that only **5** was present. For the reaction of **7** in 3:1 v/v MeOH–dioxane alone the peaks from the $Me_3Si$ protons of **7**, at $\delta$ 0.28, and the sole product **8**, at $\delta$ 0.18, were used.

Good first-order plots were obtained in all three cases.

(*b*) For the reaction of the isothiocyanate **2** with MeOH the NMR tube containing the solution was kept at a bath maintained at 50 ± 0.1 °C and transferred to the spectrometer every 15 min for recording of the $^1H$ NMR spectrum. This showed that after 70 min the substrate **2** and the products **5** and **7** were present in *ca.* 1:1:1 ratio as judged from the heights of the signals from the $Me_3Si$ protons at $\delta$ 0.30, 0.23 and 0.18, respectively. When a 1.0 molar equivalent of $Et_3N$ was present the relative heights of the signals from the $SiMe_2NCS$ group in **2**, at $\delta$ 0.52, and the Si*Me*$_2$OCOMe group of the sole product **5**, at $\delta$ 0.47 were used. A good first-order plot was obtained for the range studied (up to 75% completion). After 10 h work-up gave a mixture that was shown from its spectrum to be a *ca.* 6:1 mixture of **2** and **5**.

(*c*) In the reaction of the azide **3** in MeOH alone at 50 °C the procedure described under (*b*) revealed that both **5** and **8** were formed, and after 24 h **3**, **5** and **8** were present in a *ca.* 1:1:0.4 ratio, as indicated by the heights of the signals from the $Me_3Si$ group in **3**, at $\delta$ 0.30, **5**, at $\delta$ 0.23, and **8**, at $\delta$ 0.18. When a 1.0 molar equivalent of $Et_3N$ was present only **5** was formed, and use of the relative heights of signals from the $Me_3Si$ protons in **3** and **5** gave a good first order plot.

(*d*) For the reaction of **1** (0.10 g) with 3:2 v/v $CF_3CH_2OH$–dioxane at 35 °C $(Me_3Si)_3CH$ (*ca.* 2 $mm^3$) was added to serve as an internal standard. The relative heights of the peaks from the $SiMe_2Cl$ group in **1** and those from the $Me_3Si$ groups of the standard were monitored. A good first-order plot was obtained for the disappearance of **1**, and gave a rate constant of $2.2 \times 10^{-5}$ $s^{-1}$ ($t_{\frac{1}{2}}$ 520 min). The spectrum of the mixture indicated that only one product was formed, and work-up after 24 h gave a solid that from its $^1H$ NMR spectrum and GLC–MS analysis (which gave only one peak) was shown to be the hydroxide **11**; $\delta_H$ 0.27 (18 H, s, $SiMe_3$) 0.30 (6 H, s, Si*Me*$_2$OH), 0.35 (6 H, s, Si*Me*$_2$OCH$_2$CF$_3$), 1.35 (1 H, br s, SiMe$_2$O*H*) and 3.85–4.15 (2 H, q, SiMe$_2$OC*H*$_2$CF$_3$); *m/z* 375 (15%, M – Me), 275 (100), 187 (15), 129 (10), 73 (70), 59 (15) and 45 (10).

(*e*) When the reaction described under (*d*) was repeated with 1 equiv. of $Et_3N$ present, and again with $(Me_3Si)_3CH$ as internal standard, the $^1H$ NMR spectrum recorded after *ca.* 1 min showed that seemingly a single product was formed, with peaks consistent with its being the diacetate **6** and addition of an authentic sample of the latter to a second reaction mixture appeared to confirm this. The height of the peak at $\delta$ 0.54 from the Si*Me*$_2$OCOMe protons of the product was approximately equal to each of those from the Si*Me*$_2$OCOMe ($\delta$ 0.57) and $SiMe_2Cl$ ($\delta$ 0.61) protons of the substrate. The amount of **1** present [as judged from the relative heights of the signal from the $SiMe_2Cl$ protons in **1** and the $Me_3Si$ protons in $(Me_3Si)_3CH$] fell by *ca.* 15% in the next 20 min, but there was then little further change during 24 h except that the height of the peak at $\delta$ 0.54 decreased slightly as new small peaks grew up in the region $\delta$ 0.2–0.35. Work-up gave a solid with a complex spectrum in the latter region, but again the height of the signals from the Si*Me*$_2$OCOMe protons in the diacetate and the $SiMe_2Cl$ protons in the substrate were approximately equal, implying that **1** and **6** were present in a 2:1 molar ratio. Analysis by GLC revealed four components in an approximate ratio of 1.0:19:2.0:8, and GLC–MS indicated that these were respectively the oxadisiletane **13** [*m/z* 290 (10%, $M^+$), 275 (100, M – Me), 187 (20), 73 (60), 59 (10) and 45 (10)], the substrate **1** [*m/z* 353 (50%, M – Me), 311 (15), 275 (100), 244 (10), 187 (30), 117 (15), 73 (65), 59 (12) and 43 (45)], the hydroxide **11** [*m/z* 375 (10%, M – Me), 275 (100), 187 (10), 73 (45) and 59 (10)], and the diacetate **6** [*m/z* 377 (60%, M – Me), 335 (10), 275 (100), 187 (20), 177 (10), 73 (65), 59 (10) and 43 (60).

Treatment of $(Me_3Si)_2C(SiMe_2OCOMe)(SiMe_2F)$, **4**, with MeOH—a solution in MeOH of the 4:1 mixture (0.01 g) of **4** with $(Me_3Si)_2C(SiMe_2F)_2$ obtained as described earlier was kept in an NMR tube at 35 °C. No change in the $^1H$ NMR spectrum was observed during 4 days, and the starting mixture was recovered unchanged.

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## References

1 A. R. Bassindale and P. G. Taylor, in *The Chemistry of Organosilicon Compounds*, eds. S. Patai and Z. Rappoport, Wiley, Chichester, 1989, pp. 880–886.

2 C. Eaborn, D. A. R. Happer, S. P. Hopper and K. D. Safa, *J. Organomet. Chem.*, 1980, **188**, 179; C. Eaborn and S. P. Hopper, *J. Organomet. Chem.*, 1980, **192**, 27; C. Eaborn, in *Organosilicon and Bioorganosilicon Chemistry*, ed. H. Sakurai, Ellis Horwood, Chichester, 1985, pp. 123–130.

3 C. Eaborn, K. L. Jones and P. D. Lickiss, *J. Chem. Soc., Chem. Commun.*, 1985, 595; C. Eaborn, K. L. Jones and P. D. Lickiss, *J. Chem. Soc., Perkin Trans. 2*, 1992, 489; C. Eaborn, P. D. Lickiss, S. T. Najim and W. A. Stańczyk, *J. Chem. Soc., Perkin Trans. 2*, 1993, 59.

4 G. A. Ayoko and C. Eaborn, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1047.

5 C. Eaborn, P. D. Lickiss, S. T. Najim and M. N. Romanelli, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1754.

6 C. Eaborn and M. N. Romanelli, *J. Chem. Soc., Perkin Trans. 2*, 1987, 657.

7 C. Eaborn and M. N. Romanelli, *J. Organomet. Chem.*, 1993, **451**, 45.

8 C. Eaborn and S. P. Hopper, *J. Organomet. Chem.*, 1979, **170**, C51.

9 E. M. Kosower, *An Introduction to Physical Organic Chemistry*, Wiley, New York, 1968, pp. 103–110.

10 C. Eaborn, P. D. Lickiss and A. D. Taylor, *J. Organomet. Chem.*, 1988, **338**, C27.

11 C. Eaborn, P. D. Lickiss and A. D. Taylor, *J. Organomet. Chem.*, 1988, **340**, 283.

12 A. D. Taylor, D. Phil. Thesis, University of Sussex, 1986.

13 G. A. Ayoko and C. Eaborn, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1357.

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