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Reactions of the sterically hindered organosilicon diol $(Me_3Si)_2C(SiMe_2OH)_2$ and some of its derivatives

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Abstract

The diol $R_2C(SiMe_2OH)_2$ ($R = Me_3Si$) has been shown to react with: SO_2Cl_2 to give $R_2\overline{CSiMe_2OSO_2OSi}Me_2$; $SOCl_2$ to give $R_2C(SiMe_2Cl)_2$; Me_3SiI or Me_3SiCl to give $R_2C(SiMe_2OSiMe_3)_2$; $R'COCl$; ($R' = Me$ or CF_3) to give $R_2C(SiMe_2O_2CR')$-$(SiMe_2Cl)$; $(R'CO)_2O$ ($R' = Me$ or CF_3) to give $R_2C(SiMe_2O_2CR')_2$; with MeOH containing acid to give $R_2C(SiMe_2OMe)_2$; with neutral MeOH to give R_2C-$(SiMe_2OMe)_2$ and probably $R_2\overline{CSiMe_2OSi}Me_2$; MeLi to give $R_2C(SiMe_2OLi)_2$ (and the latter to react with $PhMeSiF_2$ to give $R_2\overline{CSiMe_2OSiMePhOSi}Me_2$). The diacetate $R_2C(SiMe_2O_2CMe)_2$ reacts with CsF in MeCN to give $R_2C(SiMe_2F)_2$; it does not react with NaN_3 or KSCN in MeCN, but the bis(trifluoroacetate) reacts with these salts and with KOCN to give $R_2C(SiMe_2X)_2$ ($X = N_3$, NCS, NCO).

Introduction

Much novel chemistry has emerged from studies of highly sterically hindered compounds of the types $R_3C(SiMe_2X)$ ($R = Me_3Si$ throughout this paper) and $R_2C(SiMe_2Z)(SiMe_2X)$ [1,2]. With the latter species, in which Z and X can be the same, there can be powerful anchimeric assistance by Z to the leaving of X [1–6]. We thus decided to undertake a study of the reactions of the diol $R_2C(SiMe_2OH)_2$ (**1**) [7], which are of interest in themselves and as a source of other $R_2C(SiMe_2X)_2$ species.

$R_2C(SiMe_2OH)_2$ $\quad$ $R = Me_3Si$ throughout
(**1**)

Results and discussion

Reaction of **1** in CH_2Cl_2 with Me_3SiI proceeded readily, and that with Me_3SiCl less readily to give in each case $R_2C(SiMe_2OSiMe_3)_2$. Although in the latter there should not be particularly large steric hindrance to nucleophilic attack on the silicon of the $OSiMe_3$ group, the compound was unaffected by 1 *M* NaOMe/MeOH during 3 h under reflux or by a 9/1 v/v mixture of MeOH and concentrated aqueous sulphuric acid during 18 h at room temperature.

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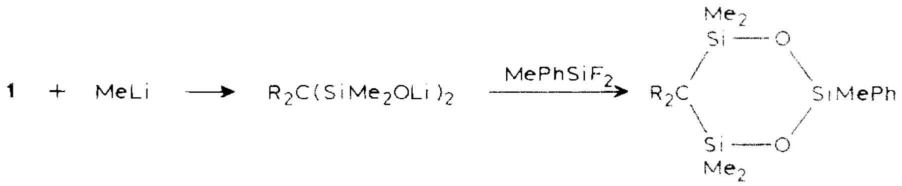
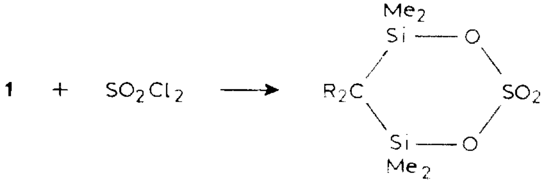
Reaction of **1** with Me_2SiCl_2 in CH_2Cl_2 seemed to give a complex mixture of products, but a simple six-membered ring species was made by treatment of **1** with MeLi followed by addition of $MePhSiF_2$:



The dilithio derivative $R_2C(SiMe_2OLi)_2$ was isolated as a solid, and its ^1H and ^7Li NMR solution spectra were recorded, but attempts to determine its crystal structure by X-ray diffraction studies were unsuccessful, apparently because of extensive disorder.

Reaction **1** with sulphuryl chloride in CH_2Cl_2 also gave a six-membered ring species:



Reaction with thionyl chloride gave the simple dichloride $R_2C(SiMe_2Cl)_2$:

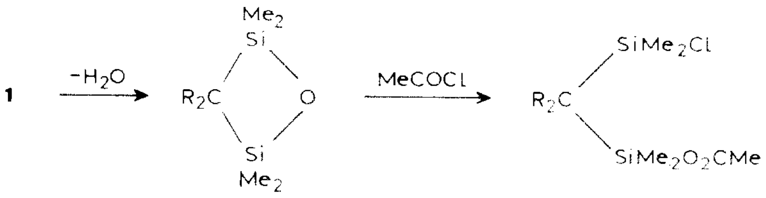
1 + $SOCl_2 \rightarrow R_2C(SiMe_2Cl)_2$

Reaction of **1** with the anhydrides $(CH_3CO)_2O$ and $(CF_3CO)_2O$ gave, as expected, the corresponding dicarboxylates:

1 + $(R'CO)_2O \rightarrow R_2C(SiMe_2O_2CR')_2 \quad (R' = CH_3 \text{ or } CF_3)$

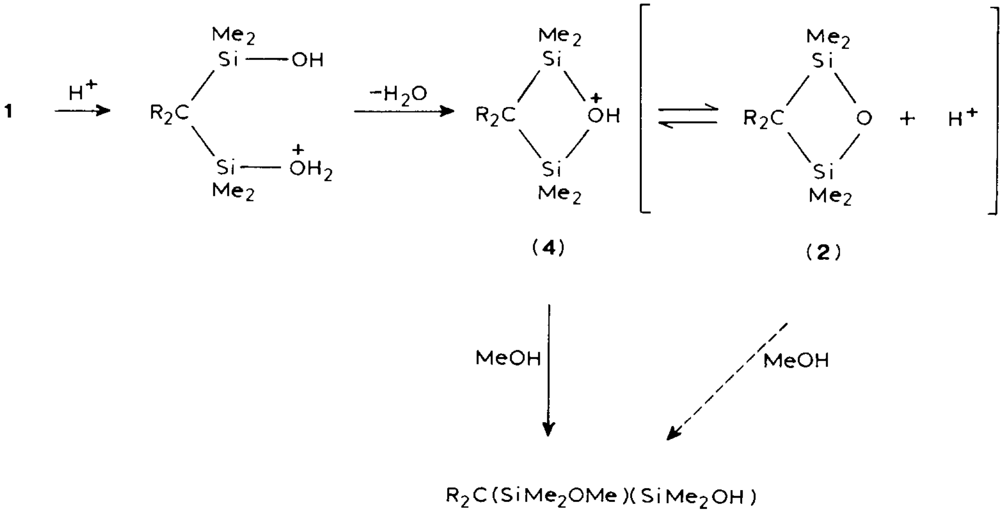
The corresponding reaction also took place with benzoic anhydride, but the product was not isolated pure.

The reaction of **1** with MeCOCl took an unexpected course. Since $R_3C(SiMe_2OH)$ reacts with this chloride to give the acetate $R_3C(SiMe_2O_2CMe)$, we expected to obtain the diacetate $R_2C(SiMe_2O_2CMe)_2$ from **1**, but instead the acetoxy chloride, **3**, was exclusively formed. (Reactions with PhCOCl and $ClCH_2COCl$ apparently proceeded in the same way, but the products could not be isolated pure. There is some evidence suggesting that the diol **1** can, under appropriate conditions, fairly readily lose a molecule of water to give the cyclic disiloxane, **2**, and it is likely that **3** is formed by ring-opening attack of MeCOCl on **2**:



(**2**) (**3**)

Reaction of **1** with a 10/1 v/v mixture of MeOH and concentrated aqueous H_2SO_4 for 5 h at room temperature gave a high yield of the dimethoxide $R_2C(SiMe_2OMe)_2$. It can reasonably be assumed that protonation of one SiOH group of **1**, followed by loss of H_2O assisted by the other OH group (cf. assistance by the γ-OMe group [5]) gives an intermediate cation (**4**), and this (or perhaps its conjugate base (**3**)) is then attacked by MeOH to give $R_2C(SiMe_2OMe)(SiMe_2OH)$. A similar process with assistance by the γ-OMe group will then give $R_2C(SiMe_2OMe)_2$.



Reaction of **1** for 1 h with 1.1 *M* NaOMe/MeOH yielded, after work-up, an oil that was shown by GLC to contain two components in an ca. 20/1 ratio, and from their mass spectra (obtained by GLC-MS) we judged these to be $R_2CH(SiMe_2OMe)$ and $R_2CH(SiMe_2OSiMe_2OMe)$. We had expected rearrangement of the anion $R_2C(SiMe_2OH)(SiMe_2O^-)$ to give $R_2C^-(SiMe_2OSiMe_2OH)$ and hence $R_2CH(SiMe_2OSiMe_2OH)$ (for rearrangements of this general type see ref. 8), and subsequent nucleophilic attack by MeOH at the relatively unhindered silicon centre of the $SiMe_2OH$ group in the latter would give $R_2CH(SiMe_2OSiMe_2OMe)$. The formation of $R_2CH(SiMe_2OMe)$ presumably involves similar nucleophilic attack on the silicon of the C–$SiMe_2O$– system of either $R_2CH(SiMe_2OSiMe_2OH)$ or $R_2CH(SiMe_2OSiMe_2OMe)$; in the latter species, this centre is more hindered than that at the terminal silicon atom, but it is very much less hindered than the corresponding centre in $R_3C(SiMe_2OH)$ or $R_3C(SiMe_2OMe)$.

Somewhat surprisingly, **1** was also found to react with neutral MeOH. When a solution in MeOH was kept in an NMR tube at 60 °C, a complex set of peaks appeared in the δ 0.0–0.4 ppm region of the ^1H NMR spectrum. After 4 days the spectrum seemed to remain fairly constant, and the product was worked-up and appeared from GLC to be a mixture of two components (**A**) and (**B**), which gave mass spectra (by linked GLC-MS) consistent with their being respectively, the cyclic disiloxane **2** and the dimethoxide $R_2C(SiMe_2OMe)_2$. The ^1H NMR spectrum of product **A** showed one larger peak and two smaller closely spaced peaks in 3/1/1 ratio, reasonably attributable to the Me_3Si and Me_2Si protons, the appearance of two peaks for the latter being associated with different locations (roughly axial and equatorial) of the Me groups with respect to the non-planar four-membered ring of **2**.

The formation of the dimethoxide $R_2C(SiMe_2OMe)_2$ is difficult to account for. Direct attack of MeOH on the silicon atom of an SiOH linkage is very unlikely in the absence of acid catalysis, and furthermore, the compound $R_2C(SiMe_2OMe)(SiMe_2OH)$, which would be the product of such attack, was found to be inert to MeOH under the same conditions. On the other hand, there is no obvious way in which the dimethoxide could be formed directly from the cyclic species **2**, since attack of MeOH on the latter should give $R_2C(SiMe_2OMe)(SiMe_2OH)$.

Surprisingly, in view of the reaction with MeOH, no reaction took place when a solution of **1** in CF_3CH_2OH was kept at 60 °C for 3 weeks. In contrast, the closely related $R_2C(SiMe_2OMe)(SiMe_2OH)$ did react with this alcohol, and after work-up after 7 days, GLC analysis indicated the presence of four components (**A**–**D**) (in order of increasing retention time) in an ca. 1.0/6.5/20/7.5 ratio, and linked GLC-MS suggested that these were, respectively, the cyclic disiloxane **2**, $R_2C(SiMe_2OMe)(SiMe_2OCH_2CF_3)$, $R_2C(SiMe_2OCH_2CF_3)(SiMe_2OH)$, and unchanged $R_2C(SiMe_2OMe)(SiMe_2OH)$. The main product, $R_2C(SiMe_2OCH_2CF_3)(SiMe_2OH)$, could have been formed by ring-opening attack of the solvent on **2**.

Reactions of the dicarboxylates $R_2C(SiMe_2O_2CMe)_2$ and $R_2C(SiMe_2O_2CCF_3)_2$ with alkali metal salts MY in MeCN were examined as a potential source of various $R_2C(SiMe_2Y)_2$ species. When a solution of $R_2C(SiMe_2O_2CMe)_2$ in MeCN was kept in contact with an excess of CsF (very little of which was in solution) at 60 °C, monitoring by ^1H NMR spectroscopy showed that a reaction was taking place, and that it was complete after 2 days. Work-up gave exclusively the difluoride $R_2C(SiMe_2F)_2$:

$$R_2C(SiMe_2O_2CMe)_2 + CsF \rightarrow R_2C(SiMe_2F)_2$$

(The same product was obtained from the reaction in MeOH). There was no detectable reaction, however, with KSCN, NaN_3, or KOCN in 3 weeks in MeCN at 60 °C.

The bis(trifluoroacetate) was more reactive, and reacted completely within 2 h with NaN_3, KSCN, or KOCN in refluxing MeCN to give high yields of the corresponding $R_2C(SiMe_2Y)_2$ compounds with $Y = N_3$, NCS, or NCO:

$$R_2C(SiMe_2O_2CCF_3)_2 + Y^- \rightarrow R_2C(SiMe_2Y)_2 \qquad (Y = N_3, NCS, \text{or } NCO)$$

No detectable reaction occurred when a solution of $R_2C(SiMe_2N_3)_2$ or $R_2C(SiMe_2NCO)_2$ in MeOH or CF_3CH_2OH was kept at 60 °C for 4 weeks. The bis(isothiocyanate) $R_2C(SiMe_2NCS)_2$, with its better leaving groups (cf. ref. 9), did react with MeOH at 60 °C, with a half-life of 35 days, to give $R_2C(SiMe_2OMe)_2$, but there was no detectable reaction with CF_3CH_2OH under the same conditions. In the reaction with MeOH, none of the intermediate $R_2C(SiMe_2OMe)(SiMe_2NCS)$ was detected, and this was as expected since anchimeric assistance by the OMe group to the departure of NCS^- [9] makes this compound much more reactive than the bis(isothiocyanate).

Reaction of $R_2C(SiMe_2O_2CMe)(SiMe_2Cl)$ with KSCN or NaN_3 in refluxing MeCN gave $R_2C(SiMe_2O_2CMe)(SiMe_2NCS)$ and $R_2C(SiMe_2O_2CMe)(SiMe_2N_3)$, respectively.

Experimental

General

Solvents were dried by standard methods. Reactions were carried out under dry N_2. Alkali metal salts were dried at 50 °C and 0.1 Torr for 8 h.

For GLC a Pye-Unicam GCD instrument fitted with a column of 3% OV-17 on Chromasorb G and a flame-ionization detector was used. For linked GLC-MS the same packing or (where stated) 5% OV-101 on Chromasorb G was used.

Spectra

The ^1H NMR spectra were, unless otherwise stated, recorded with solutions in CCl_4 containing CH_2Cl_2 or $CHCl_3$ as lock and reference. Solutions in CCl_4 containing C_6D_6 as lock were used for ^{19}F NMR spectra (recorded at 75.4 MHz) and shifts are in ppm relative to external $CFCl_3$. Similar solutions were used for ^{13}C (at 90.5 MHz) and ^{29}Si (at 71.5 MHz) NMR spectra, and shifts are in ppm relative to $SiMe_4$. The ^7Li NMR spectra (recorded at 139.9 MHz) were recorded with solutions containing C_6D_6 as lock and external aqueous $LiNO_3$ as reference.

Solutions in CCl_4 were used for IR spectra. Mass spectra were by electron impact (EI) at 70 eV; in most cases only selected significant ions are listed.

Preparation of $R_3C(SiMe_2OMe)$ (cf. ref. 10)

A solution of $AgClO_4$ (5.2 g, 0.025 mol) in MeOH (30 cm^3) was added dropwise to a rapidly stirred mixture of R_3CSiMe_2I (10 g, 0.024 mol), MeOH (60 cm^3), and CH_2Cl_2 (20 cm^3). The mixture was subsequently kept under reflux for 30 min then cooled and filtered. The filtrate was evaporated under reduced pressure, and the residue extracted with hexane. The extract was filtered, then evaporated under reduced pressure to give $R_3C(SiMe_2OMe)$ (7.4 g, 96%); δ(H) 0.23 (27H, s, Me_3Si), 0.27 (6H, s, Me_2Si), and 3.37 (3H, s, OMe).

Preparation of $R_2C(SiMe_2OH)_2$ (1) (cf. ref. 13)

Concentrated sulphuric acid (125 cm^3) was added with stirring during 0.5 h to a solution of R_3SiMe_2OMe (2.50 g) in CH_2Cl_2 (25 cm^3). The mixture was stirred at room temperature for a further 0.5 h, and then very cautiously added dropwise to a stirred ice-water mixture (500 cm^3). Extraction with three 150 cm^3 portions of CH_2Cl_2, followed by washing, drying ($MgSO_4$), filtration, and evaporation of the extract left a solid, which was sublimed at 70 °C under vacuum to give $(Me_3Si)_2C(SiMe_2OH)_2$ (2.0 g, 83%), δ(H) ($CDCl_3$) 0.24 (18H, s, Me_3Si), 0.35 (12H, s, Me_2Si), and 1.86 (2H, br, OH).

Reactions of $R_2C(SiMe_2OH)_2$ (1)

With SO_2Cl_2. Redistilled SO_2Cl_2 (1.04 cm^3, 12.9 mmol) was added to a solution of **1** (1.0 g, 3.25 mmol) in CH_2Cl_2 (15 cm^3). The mixture was refluxed for 3 h then evaporated under reduced pressure. The solid residue was recrystallized from pentane to give 4,4,6,6-tetramethyl-5,5-bis(trimethylsilyl)-1,3-dioxa-2-dioxathia-4,6-disilacyclohexane (1.14 g, 95%), m.p. 170 °C (with decomp.). (Found: C, 35.3; H, 8.2. $C_{11}H_{30}O_4SSi_4$ calc: C, 35.7; H, 8.1%); δ(H) 0.32 (18H, s, $SiMe_3$) and 0.62 (12H, s, $SiMe_2$); *m/z* 355 (30%, $[M - Me]^+$), 290 (20, $[M - SO_3]^+$), 275 (95, $[M - SO_3 - Me]^+$), 261 (20), 203 (20), 187 (80), 129 (45), 73 (100, $[Me_3Si]^+$), 64 (40, $[SO_2]^+$), 59 (30, $[Me_2HSi]^+$), 45 (10, $[MeH_2Si]^+$).

With $SOCl_2$. A mixture of **1**, (0.50 g, 1.62 mmol), CH_2Cl_2 (10 cm^3), and redistilled $SOCl_2$ (1.2 cm^3, 16.2 mmol) was refluxed for 5 h. Evaporation under reduced pressure left a solid, which was sublimed (115 °C at 0.2 Torr) to give $R_2C(SiMe_2Cl)_2$ (cf. ref. 11) (0.46 g, 82%), m.p. > 320 °C: δ(H) 0.36, (18H, s, $SiMe_3$) and 0.70 (12H, s, $SiMe_2$); *m/z* 329 (40%, $[M - Me]^+$), 221 (60, $[M - Me_3SiCl - Me]^+$), 73 (100), 59 (30), and 45 (25).

With Me_3SiI and Me_3SiCl. (*i*) To a solution of **1** (1.0 g, 3.25 mmol) in CH_2Cl_2 (15 cm^3) was added Me_3SiI (0.96 cm^3, 7.14 mmol). The mixture, protected from light, was stirred at room temperature for 2 h, then MeOH (20 cm^3) was added and the mixture was kept overnight at −20 °C. The crystals formed were filtered off, and recrystallized from pentane to give $R_2C(SiMe_2OSiMe_3)_2$ (1.1 g, 75%), m.p. 87 °C (Found: 45.4; H, 10.3. $C_{17}H_{48}O_2Si_6$ calc: C, 45.1; H, 10.6%); δ(H) 0.10 (18H, s, $SiMe_3$), 0.21 (18H, s, $SiMe_3$), and 0.27 (12H, s, $SiMe_2$); *m/z* 437 (100%, $[M - Me]^+$), 349 (10, $[M - Me_4Si - Me]^+$), 275 (5, $[M - Me_3SiOSiMe_3 - Me]^+$).

(*ii*) A similar procedure (without protection from light) but with Me_3SiCl, 6 h reflux, and recrystallization from MeOH, gave $R_2C(SiMe_2OSiMe_3)_2$, with properties identical to those above.

With MeLi and then $MePhSiF_2$. (*i*) A 1.1 *M* solution of MeLi (1.24 cm^3, 1.36 mmol) was added with stirring to a solution of **1** (0.20 g, 0.65 mmol) in THF (10 cm^3). Gas was evolved. The solution was stirred for 3 h (probably unnecessarily) then a sample was removed and the ^1H and ^7Li NMR spectra of the solution were recorded: δ(H) 0.03 (12H, s, $SiMe_2$) and 0.23 (18H, s, $SiMe_3$): (there was no detectable signal from residual MeLi at δ(H) −2.40); δ(Li) (with 10% C_6D_6 added) −0.219 (br).

(*ii*) A solution of $R_2C(SiMe_2OLi)_2$ (1.62 mmol), prepared as above from **1** (0.50 g) in THF (20 cm^3), was added to a solution of $MePhSiF_2$ (0.26 g, 1.62 mmol) in THF (20 cm^3). The mixture was refluxed for 1 h then allowed to cool, and the solvent was removed under reduced pressure. The solid residue was extracted with hexane, and the extract was filtered and evaporated to give a solid, which was recrystallized from MeOH (10 cm^3) at −10 °C and then sublimed (60 °C at 0.2 Torr) to give 2,4,4,6,6-pentamethyl-5,5-bis(trimethylsilyl)-2-phenyl-1,3-dioxa-2,4,6-trisilacyclohexane (0.42 g, 60%), m.p. 63°C (Found: C, 50.3; H, 8.5. $C_{18}H_{38}O_2Si_5$ calc: C, 50.6; H, 8.9%); δ(H) (10/1 v/v CCl_4/C_6D_6; 360 MHz) 0.163 (9H, s, $SiMe_3$), 0.274 (6H, s, $SiMe_2$), 0.339 (12H, s, $SiMe_3$ + Si*Me*Ph), 0.444 (6H, s, $SiMe_2$), and 7.3–7.65 (5H, m, Ph); ν(SiOSi) (CCl_4) 1010 cm^{-1}; *m/z* 411 (100%, $[M - Me]^+$), 395 (15, $[M - MeH - Me]^+$), 135 (35, $[Me_2PhSi]^+$), 73 (85).

With MeOH. *(i) In the presence of H_2SO_4.* Concentrated sulphuric acid (1.5 cm^3) was added to a solution of **1** (0.20 g) in MeOH (15 cm^3) and the mixture was stirred for 5 h then added to a mixture of pentane (20 cm^3) and water (20 cm^3). Vigorous shaking followed by separating, washing, drying ($MgSO_4$) and evaporation of the organic layer gave $R_2C(SiMe_2OMe)_2$ (0.19 g, 87%), m.p. 269 °C (lit. [12], m.p. 270 °C): δ(H) 0.21 (s, $SiMe_3$), 0.26 (s, $SiMe_2$), 3.38 (s, OMe).

(ii) In the presence of NaOMe. A solution of **1** (0.50 g) in 1.1 *M* NaOMe/MeOH (20 cm^3) was refluxed for 1 h. The solvent was then removed under reduced pressure, and the residue extracted to leave an oil. Analysis by GLC showed the presence of two components in a 20/1 ratio, and from linked GLC-MS these were judged to be respectively $R_2CH(SiMe_2OMe)$ (*m/z* 233 (100%, $[M-Me]^+$), 129 (50, $[M-Me_3SiOMe-Me]^+$), and $R_2CH(SiMe_2OSiMe_2OMe)$ (*m/z* 307 (70%, $[M-Me]^+$)), 73 (100)).

(iii) MeOH alone. A solution of **1** (10 mg) in MeOH (0.5 cm^3) was sealed in an NMR tube and kept at 60 °C. Monitoring of the ^1H NMR spectrum revealed the appearance of a complex set of overlapping peaks in the δ 0.0–0.4 ppm region, but after 4 days the spectrum seemed to remain constant and the mixture was worked up. Analysis by GLC indicated the presence of two components **A** and **B**, in an ca. 1/1.6 ratio. Linked GLC-MS gave mass spectra consistent with the formulation **2** for **A** (*m/z* 290 (15%, $[M]^+$), 275 (10, $[M-Me]^+$), 187 (30), 73 (100)) and $R_2C(SiMe_2OMe)_2$ for **B** (*m/z* (100%, $[M-Me]^+$), 217 (55, $[M-Me_3SiOMe-Me]^+$), 201 (65), 187 (15), 73 (45)). The ^1H NMR spectrum in CH_2Cl_2 containing 10% of C_6D_6 was consistent with the presence of these two species in 1/1.7 ratio; a set of peaks at δ 0.36 (18H, s, $SiMe_3$), 0.54 (6H, s, $SiMe_2$), and 0.56 (6H, s, $SiMe_2$) was assigned to **A**, and a set at δ 0.48 (18H, s, $SiMe_3$), 0.51 (12H, s, $SiMe_2$), and 3.56 (6H, s, OMe) to **B**. It should be noted that these shifts recorded in CH_2Cl_2/C_6D_6, with the normal shift of δ 5.23 assumed for the CH_2Cl_2 used as reference, are significantly different from those in CCl_4: an authentic sample of $R_2C(SiMe_2OMe)_2$ in a similar but not identical medium gave shifts close to those recorded for **B**.

With CF_3CH_2OH. In a procedure identical to that used for the reaction with MeOH, a solution of **1** in CF_3CH_2OH was found to have an unchanged ^1H NMR spectrum after 3 weeks at 60 °C.

With acyl halides. (*i*) Redistilled MeCOCl (2.0 cm^3) was added to a solution of **1** (0.50 g) in CH_2Cl_2 (20 cm^3) and the mixture was refluxed for 5 h. Evaporation under reduced pressure left a solid, which was recrystallized from pentane then sublimed (120 °C at 0.4 Torr) to give $R_2C(SiMe_2O_2CMe)(SiMe_2Cl)$ (0.46 g, 77%), m.p. 234 °C (Found: C, 42.3; H, 8.9. $C_{13}H_{33}ClO_2Si_4$ calc: C, 42.3; H, 8.9%); δ(H) 0.30 (18H, s, $SiMe_3$), 0.58 (6H, s, $SiMe_2$), 0.62 (6H, s, $SiMe_2Cl$), and 2.05 (3H, s, O_2CMe); ν(C=O) (CCl_4) 1725 cm^{-1}; *m/z* 353 (50%, $[M-Me]^+$), 311 (20, $[M-COCH_2-Me]^+$), 275 (100, $[M-MeCOCl-Me]^+$), 244 (10), 187 (25), 73 (30). The isotope patterns for chlorine-containing ions were as expected.

The product is somewhat moisture sensitive and was stored under dry N_2 at −10 °C.

(*ii*) A solution of **1** (0.10 g), in PhCOCl (10 cm^3) was kept at 50 °C for 5 h. The ^1H NMR spectrum showed that complete reaction had occurred, apparently to give $R_2C(SiMe_2O_2CPh)(SiMe_2Cl)$, δ(H) (in PhCOCl) 0.25 (18H, s, $SiMe_3$), 0.52 (6H, s, $SiMe_2Cl$), and 0.61 (6H, s, $Si\mathit{Me}_2O_2CPh$). Attempts to remove the excess of PhCOCl completely were unsuccessful.

(*iii*) A solution of **1** (0.10 g), in $ClCH_2COCl$ (15 cm^3) was refluxed for 4 h. The ^1H NMR spectrum of the solution suggested the presence of two components in an ca. 1/9 ratio, the minor one **1**, δ 0.25 and 0.33, and the latter presumably $R_2C(SiMe_2O_2CCH_2Cl)(SiMe_2Cl)$, δ 0.31 (18H, s, $SiMe_3$), 0.55 (6H, s, $SiMe_2Cl$), and 0.61 (6H, s, $Si\mathit{Me}_2O_2CCH_2Cl$). Attempts to isolate the product were unsuccessful.

With $(MeCO)_2O$. A solution of **1** (0.50 g) in $(MeCO)_2O$ (25 cm^3) was refluxed gently for 30 min. Volatile materials were removed during 2 days under vacuum (0.2 Torr), and the residue was sublimed (120 ° C at 0.2 Torr) to give $R_2C(SiMe_2O_2CMe)_2$ (0.52 g, 87%), m.p. > 360 ° C (lit. [3] m.p. > 360 ° C); δ(H) 0.29 (18H, s, $SiMe_3$), 0.55 (12H, s, $SiMe_2$), and 2.05 (6H, s, CO_2Me); ν(CO) (CCl_4) 1750 cm^{-1}.

With $(CF_3CO)_2O$. A procedure identical to that described immediately above, but with $(CF_3CO)_2O$, gave $R_2C(SiMe_2O_2CCF_3)_2$ (0.68 g, 84%), m.p. 107 ° C (lit. [3], 108–110 ° C); δ 0.32 (18H, s, $SiMe_3$) and 0.66 (12H, s, $SiMe_2$); ν(CO) (CCl_4) 1765 cm^{-1}.

Reactions of $R_2C(SiMe_2O_2CMe)_2$ *and* $R_2C(SiMe_2O_2CCF_3)_2$

(*i*) A solution of $R_2C(SiMe_2O_2CMe)_2$ (10 mg, 0.026 mmol) in MeCN (0.75 cm^3 was placed in an NMR tube containing CsF (39 mg, 0.26 mmol). The tube was shaken, then placed in a bath at 60 ° C and removed at intervals for recording of the ^1H NMR spectrum, which revealed that reaction was complete within 2 days. The solvent was evaporated off under reduced pressure and the residue extracted with hexane. The extract was filtered and evaporated to leave exclusively $R_2C(SiMe_2F)_2$ (cf. ref. 12); δ(H) 0.29 (18H, s, $SiMe_3$) and 0.45 (12H, d, ^3J(H–F) 8 Hz, $SiMe_2F$); *m/z* 297 (85%, $[M - Me]^+$) and 205 (100, $[M - Me_3SiF - Me]^+$).

(*ii*) When the procedure described under (i) was repeated, but with KSCN, NaN_3, or KOCN in place of CsF, the ^1H NMR showed no detectable change during 3 weeks at 60 ° C and the $R_2C(SiMe_2O_2CMe)_2$ was recovered unchanged.

(*iii*) A mixture of $R_2C(SiMe_2O_2CCF_3)_2$ (0.50 g, 1.0 mmol), NaN_3 (0.65 g, 10.0 mmol) and MeCN (30 cm^3) was refluxed for 2 h, then the solvent was removed under reduced pressure. The residue was extracted with CCl_4 and the extract was filtered and evaporated to leave a solid, which was sublimed to give $R_2C(SiMe_2N_3)_2$ (0.29 g, 81%), m.p. 215 ° C (Found: C, 36.5; H, 8.6; N, 21.7; $C_{11}H_{30}N_6Si_4$ calc: C, 36.8; H, 8.4; N, 23.4%); δ(H) 0.29 (18H, s, $SiMe_3$) and 0.54 (12H, s, $SiMe_2$); $\nu(SiN_3)$ (CCl_4) 2150 cm^{-1}; *m/z* 342 (10%), 316 (70, $[M - N_3]^+$), 100 (35, $[Me_2SiN_3]^+$), 73 (100).

(*iv*) A similar procedure but with KSCN gave a solid, which was sublimed (125 ° C at 0.2 Torr) and shown to be $R_2C(SiMe_2NCS)_2$ (0.30 g, 77%), m.p. 195 ° C (Found: C, 39.7; H, 7.8; N, 6.8. $C_{13}H_{30}N_2S_2Si_4$ calc: C, 39.9; H, 7.8; N, 7.2%); δ(H) 0.35 (18H, s, $SiMe_3$) and 0.55 (12H, s, $SiMe_2$); ν(SiNCS) (CCl_4) 2080 cm^{-1}; *m/z* 375 (70%, $[M - Me]^+$), 332 (25, $[M - NCS]^+$), 244 (50, $[M - Me_3SiNCS - Me]^+$), 73 (100).

(*v*) A similar procedure but with KOCN gave a solid, which was sublimed (110 ° C at 0.3 Torr) to give $R_2C(SiMe_2NCO)_2$ (0.28 g, 78%), m.p. 264 ° C (Found: C, 43.7; H, 8.1; N, 8.0. $C_{13}H_{30}N_2O_2Si_4$ calc: C, 43.6; H, 8.4; N, 7.8%); δ(H) 0.30 (18H, s, $SiMe_3$) and 0.49 (12H, s, $SiMe_2$); ν(SiNCO) (CCl_4) 2285 cm^{-1}; *m/z* 343 (100%, $[M - Me]^+$), 228 (45, $[M - Me_3SiNCO - Me]^+$), 73 (100).

Reactions of $R_2C(SiMe_2O_2CMe)(SiMe_2Cl)$ *with KSCN and* NaN_3

(*i*) A mixture of $R_2C(SiMe_2O_2CMe)(SiMe_2Cl)$ (0.30 g, 0.81 mmol), KSCN (0.39, 4.07 mmol), and MeCN (25 cm^3) was refluxed for 1 h. The solvent was evaporated under vacuum and the residue extracted with pentane. The extract was filtered and evaporated, and the residue sublimed (120 ° C at 0.2 Torr) to give $R_2C(SiMe_2O_2CMe)(SiMe_2NCS)$ (0.27 g, 85%), m.p. 212 ° C (Found: C, 43.1; H, 8.5; N, 3.3,

$C_{14}H_{33}NO_2SSi_4$ calc: C, 42.9; H, 8.4; N, 3.6%); δ(H) 0.30 (18H, s, $SiMe_3$), 0.52 (6H, s, $SiMe_2NCS$), 0.59 (6H, s, $Si\mathit{Me}_2O_2CMe$), and 2.05 (3H, s, $SiMe_2O_2C\mathit{Me}$); ν(SiNCS) (CCl_4) 2050 cm^{-1}; m/z 376 (100%, $[M-Me]^+$), 334 (70 $[M-COCH_2-Me]^+$), 333 (90, $[Me-COMe-Me]^+$), 318 (20, $[M-NCS-Me]^+$), 275 (90), 245 (20, $[M-Me_3SiNCS-Me]^+$), 73 (80).

(*ii*) A mixture of $R_2C(SiMe_2O_2CMe)(SiMe_2Cl)$ (0.50 g, 1.36 mmol), NaN_3 (0.44 g, 6.8 mmol), and MeCN (35 cm^3) was refluxed for 6 h. Work-up as in (i) gave $R_2C(SiMe_2O_2CMe)(SiMe_2N_3)$ (0.53 g, 82%) (Found: C, 41.5; H, 8.9; N, 11.0. $C_{13}H_{33}N_3O_2Si_4$ calc: C, 41.6; H, 8.8; N, 11.2%); δ(H) 0.30 (18H, s, $SiMe_3$), 0.50 (6H, s, $SiMe_2N_3$), 0.55 (6H, s, $Si\mathit{Me}_2O_2CMe$), and 2.01 (3H, s, $SiMe_2O_2CMe$); $\nu(SiN_3)$ (CCl_4) 2140 cm^{-1}; m/z 360 (20%, $[M-Me]^+$), 317 (10, $[M-Me-HN_3]^+$), 275 (100, $[M-HN_3-COCH_2-Me]^+$), 245 (15, $[M-Me_3SiN_3-Me]^+$).

Treatment of $R_2C(SiMe_2OMe)(SiMe_2OH)$ with MeOH or CF_3CH_2OH

(*i*) A solution of $R_2C(SiMe_2OMe)(SiMe_2OH)$ [7] (10 mg) in MeOH (0.5 cm^3) in an NMR tube was kept at 60 °C. The ^1H NMR spectrum was unchanged after 8 days, and removal of the solvent left unchanged starting material.

(*ii*) In a similar procedure but with CF_3CH_2OH as solvent, a complex set of peaks in the δ 0.1–0.5 range had appeared within 1 day. Evaporation of the solvent under reduced pressure left a solid, which from analysis by GLC seemed to contain four components, (**A**–**D**) (in order of elution) in the ca. ratio 1.0/6.5/20/7.5. From the mass spectra, obtained by linked GLC-MS, these appeared to be: (**A**) the cyclic disiloxane **2** (m/z 290 (15%, $[M]^+$), 275 (100, $[M-Me]^+$); (**B**) $R_2C(SiMe_2OMe)(SiMe_2OCH_2CF_3)$ (m/z 389 (100%, $[M-Me]^+$), 357 (10, $[M-MeOH-Me]^+$), 309 (25), 275 (20, $[M-MeOCH_2CF_3-Me]^+$), 201 (35), 73 (80); (**C**) $R_2C(SiMe_2OCH_2CF_3)(SiMe_2OH)$ (m/z 375 (25%, $[M-Me]^+$), 275 (100, $[M-CF_3CH_2OH-Me]^+$), 73 (45); (**D**) unchanged $R_2C(SiMe_2OMe)(SiMe_2OH)$ (m/z 307 (25%, $[M-Me]^+$), 307 (25%, $[M-Me]^+$), 290 (10, $[M-MeOH]^+$), 275 (100, $[M-MeOH-Me]^+$), 187 (25), 73 (50).

Treatment of $R_2C(SiMe_2OSiMe_3)_2$ with MeOH/NaOMe and with MeOH/H_2O/H_2SO_4

(*i*) A solution of **1** (0.25 g) in 1.0 *M* NaOMe/MeOH (20 cm^3) was refluxed for 3 h then added to a mixture of hexane (25 cm^3) and sufficient 2 *M* HNO_3 to neutralize the base. The mixture was shaken and the organic layer then separated, washed, dried ($MgSO_4$), and evaporated to leave exclusively unchanged starting material.

(*ii*) A solution of $R_2C(SiMe_2OSiMe_3)_2$ (0.15 g) in CH_2Cl_2 was mixed with MeOH (18 cm^3) containing concentrated aqueous H_2SO_4 (2 cm^3). The mixture was stirred overnight then worked up as above (but with water in place of the aqueous HNO_3) to give exclusively unchanged starting material.

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References

1 C. Eaborn, J. Organomet. Chem., 239 (1982) 93.
2 C. Eaborn, in H. Sakurai (Ed.), Organosilicon and Bioorganosilicon Chemistry, Ellis Horwood, Chichester, 1985, pp. 123–130.
3 C. Eaborn and S.P. Hopper, J. Organomet. Chem., 170 (1979) C51.
4 C. Eaborn and D.E. Reed, J. Chem. Soc., Chem. Commun., (1983) 495.
5 C. Eaborn, P.D. Lickiss, S.T. Najim, and M.N. Romanelli, J. Chem. Soc., Chem. Commun., (1985) 1754.
6 G.A. Ayoko and C. Eaborn, J. Chem. Soc., Chem. Commun., (1986) 630.
7 A.I. Al-Wassil, C. Eaborn, and M.N. Romanelli, J. Chem. Soc., Perkin Trans. 2, (1986) 1363.
8 R. Damrauer, C. Eaborn, D.A.R. Happer, and A.I. Mansour, J. Chem. Soc., Chem. Commun., (1983) 348.
9 C. Eaborn and M.N. Romanelli, J. Chem. Soc., Perkin Trans. 2, (1987) 657.
10 C. Eaborn, D.A.R. Happer, and K.D. Safa, J. Organomet. Chem., 191 (1980) 355.
11 C. Eaborn and S.P. Hopper, J. Organomet. Chem., 192 (1980) 27.
12 C. Eaborn and D.E. Reed, J. Chem. Soc., Perkin Trans. 2, (1985) 1687.
13 C. Eaborn, P.D. Lickiss, and N.A. Ramadan, J. Chem. Soc., Perkin Trans. 2, (1984) 267.