1,3 Silicon to Silicon Migration of the Methoxy Group in Solvolysis of (Bromodiphenylsilyl)(methoxydimethylsilyl)bis(trimethylsilyl)methane. Crystal Structures of (Ethoxydimethylsilyl)(methoxydiphenylsilyl)bis(trimethylsilyl)methane and (Methoxydimethylsilyl)(methoxydiphenylsilyl)bis(trimethylsilylmethane

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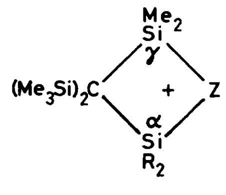
In the reaction of the bromide $(Me_3Si)_2C(SiMe_2OMe)(SiPh_2Br)$ (**1a**) with EtOH the OMe group undergoes a 1,3 Si to Si migration to give exclusively the rearranged product $(Me_3Si)_2C(SiMe_2OEt)(SiPh_2OMe)$ (**2**). (The same product is obtained if $AgClO_4$ is present in the MeOH.) The rate-determining step of the reaction is believed to involve separation of Br^- anchimerically assisted by the γ-OMe group to form a 1,3 methoxy-bridged cation. Because of such assistance the bromide (**1a**) and the related chloride $(Me_3Si)_2C(SiMe_2OMe)(SiPh_2Cl)$ are $>10^8$ times as reactive towards MeOH as the corresponding $(Me_3Si)_3C(SiPh_2X)$ species, but they are somewhat less reactive than the compounds $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2X)$. The reactions of (**1a**) with other alcohols or with water seem also to give rearranged species $(Me_3Si)_2C(SiMe_2OR)(SiPh_2OMe)$ ($R = H, CH_2Ph, CH_2CF_3$).

The structures of $(Me_3Si)_2C(SiMe_2OR)(SiPh_2OMe)$ with R = Me or Et have been determined by *X*-ray diffraction, and shown to involve fairly close Si–O ··· Si interligand contacts.

Compounds of the type $(Me_3Si)_3CSiR_2I$ react with a range of electrophiles, such as silver or mercury salts,[1] ICl,[2] and CF_3CO_2H,[1] to give rearranged products $(Me_3Si)_2C(SiR_2Me)(SiMe_2Y)$, either (*e.g.* R = Ph) exclusively or (*e.g.* R = Et) along with unrearranged products $(Me_3Si)_3C(SiR_2Y)$. It is thought that the methyl-bridged cations of the type (**I**; Z = Me) are initially formed, in the rate-determining step, and then attacked by the nucleophile Y^- at either the α- or γ-silicon atom, attack at the less sterically hindered centre usually being favoured.[1–3] In contrast no rearrangement occurs during methanolysis or hydrolysis of $(Me_3Si)_3CSiEt_2I$ or hydrolysis of $(Me_3Si)_3CSiPh_2I$, and this is taken to indicate that the reactions do not proceed through cations of type (**I**).[4]



(**I**)

The γ-OMe group in compounds of the type $(Me_3Si)_2C(SiMe_2OMe)(SiR_2X)$ is known to provide powerful anchimeric assistance to the leaving of the X group in solvolysis, *e.g.* the chloride $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Cl)$ is $> 10^6$ times as reactive as $(Me_3Si)_3CSiMe_2Cl$ towards MeOH,[5] and this has been associated with powerful bridging by the OMe group in a cation of type (**I**; R = Me, Z = OMe).[5–7] If this is the case, then migration of the OMe group should be observed in such solvolysis, and we present evidence below that this is the case in the ethanolysis of $(Me_3Si)_2C(SiMe_2OMe)(SiPh_2Br)$, (**1a**) [a preliminary report has appeared.[6] Evidence for related migration of the OMe group in the reaction of (**1a**) with $AgBF_4$ was presented recently.[8]]

The reactions of (**1a**) and (**1b**) with MeOH have been shown to be somewhat slower than those of the corresponding compounds $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2X)$.

$(Me_3Si)_2C(SiMe_2OMe)(SiPh_2X)$

(**1**)

a; X = Br
b; X = Cl
c; X = OMe

$(Me_3Si)_2C(SiMe_2OEt)(SiPh_2OMe)$

(**2**)

Results and Discussion

The bromide (**1a**)[8] was found to react readily with MeOH at room temperature (reaction being complete within 5 min), and the product was the expected dimethoxide (**1c**). The reaction with EtOH was also complete within 5 min, and the sole product was judged from its spectra to be either the unrearranged species $(Me_3Si)_2C(SiMe_2OMe)(SiPh_2OEt)$ or the rearranged $(Me_3Si)_2C(SiMe_2OEt)(SiPh_2OMe)$ (**2**). It was impossible to distinguish between these by spectroscopic means, and so an *X*-ray diffraction study was undertaken, and this (see later) showed it to be the rearranged species (**2**). [Because of the slight possibility that the crystal used might have been unrepresentative, and have come from a minor product formed in an amount (<5%) too small for ordinary spectroscopic detection, we examined several crystals, and found them all to be crystallographically identical to that used.] The same product was obtained when (**1a**) was treated with $AgClO_4$ in EtOH, conditions which would be expected to favour rearrangement.[1] The exclusive formation of the rearranged product in the ethanolysis of (**1a**) is consistent with the view that the high reactivity of compounds of the type $(Me_3Si)_2C(SiMe_2OMe)(SiR_2X)$ arises from anchimeric assistance by the γ-OMe group to the leaving of X^- in the rate-determining formation of the cation (**I**; R = Me, Z = OMe). Such assistance is consistent with the observation that in the crystal structure of the chloride (**1b**) the oxygen of the OMe group lies close (at 3.2

Å) to the silicon atom of the $SiPh_2Cl$ group, with an O ••• Si–Cl angle of 168°,[8] *i.e* little movement is needed to reach the transition state associated with loss of Cl^- and formation of (**I**; R = Ph, Z = OMe), since such a conformation can also be expected to be dominant in solution.

The reactions of (**1a**) with water–Me_2CO, $PhCH_2OH$, and CF_3CH_2OH likewise each gave a single product. The ^1H n.m.r. data in each case favour the rearranged product $(Me_3Si)_2C(SiPh_2OMe)(SiMe_2OR)$ (R′ = H, CH_2Ph, or CH_2CF_3), since, like the corresponding compound with R′ = Et, all three have the signal from the OMe protons between δ 3.55 and 3.58, whereas a shift of δ *ca.* 3.40 would be expected for an $SiMe_2OMe$ group [*cf.* δ 3.38 for $(Me_3Si)_3CSiMe_2OMe$ and 3.40 for $(Me_3Si)_2C(SiMe_2OMe)_2$]. In keeping with the reasoning, $(Me_3Si)_2C(SiPh_2OMe)(SiMe_2OMe)$ gives one OMe peak at δ 3.39 that can reasonably be assigned to $SiMe_2O$*Me*, and another at δ 3.60 that can reasonably be assigned to $SiPh_2O$*Me*. Furthermore (but rather lesss reliably) the appearance at δ 1.31 of the ^1H n.m.r. signal from the OH proton of the product from hydrolysis favours its assignment to an $SiMe_2OH$ group [*cf.* δ 1.21 for $(Me_3Si)_3CSiMe_2OH$] rather than an $SiPh_2OH$ group [*cf.* δ 2.02 for $(Me_3Si)_3CSiPh_2OH$].

Rates of Methanolysis (**1a**) *and* (**1b**).—The rates of reaction of (**1a**) and (**1b**) with MeOH were determined so that comparison could be made with those of the related compounds $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2X)$.[7] The structure of the product, $(Me_3Si)_2C(SiMe_2OMe)(SiPh_2OMe)$ (**1c**), was the subject of another *X*-ray diffraction study as described later.

The progress of the reaction of the chloride (**1b**) at 35 °C was monitored by observing the change with time of the relative heights of the signals from the $(Me_3Si)_2C$ groupings in the ^1H n.m.r. spectra of the substrate and product. The data gave a good first-order plot, with $t_{\frac{1}{2}}$ *ca.* 3.2 h, which compares with a value of $t_{\frac{1}{2}}$ of *ca.* 1.7 min for the reaction of $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Cl)$.[5,7] (Even in 4:1 v/v MeOH–dioxane the latter has a half-life of only *ca.* 7.5 min.[7]). It thus seems that substitution of Ph for Me groups at the reaction centre reduces the reactivity by a factor of *ca.* 110. A seemingly obvious explanation of this is that the Ph groups provide additional steric hindrance to the internal nucleophilic attack by the OMe group on the α-Si atom, but this interpretation is not easily reconcilable with the observation that the rearrangement of $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$ to $(Me_3Si)_2CH(SiMe_2OSiPh_2Me)$ in MeOH containing NaOMe is much faster than that of $(Me_3Si)_3C(SiMe_2OH)$ to $(Me_3Si)_2CH(SiMe_2OSiMe_3)$,[9] since the rate-determining step in this rearrangement is thought to involve internal nucleophilic attack by the $Si–O^-$ on γ-Si atom, a process fairly closely analogous to that of a γ-OMe group on the α-Si atom in the reactions of type (**I**) and related species. One difference between this type of rearrangement and that in solvolysis of (**1b**) which may be relevant is that in the former process there is only dispersal of the negative charge on going to the transition state, whereas in the latter there is creation of positive charge, so that steric hindrance to solvation by the Ph groups might be more serious in the solvolysis.

The reaction of the bromide (**1a**) with MeOH was too fast for convenient study, and so a 1:9 MeOH–dioxane mixture was used, as it had been for the reaction of $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Br)$.[7] For the latter the reaction was found not to give a satisfactory first-order plot because of autocatalysis by the formed HBr, but good first-order plots were obtained when NaOMe was present. The reaction of (**1a**) was found to give a satisfactory first-order plot, with $t_{\frac{1}{2}}$ = *ca.* 32 min, up to >80% completion of the reaction, but even so there was presumably some autocatalysis since the half-life was increased to 115 min in the presence of 0.05M-NaOMe. Further increase in the NaOMe concentration caused relatively little change in rate, the values of $t_{\frac{1}{2}}$ being 135 and 150 min, respectively, for 0.10 and 0.22M-NaOMe. The absence of acceleration by base is consistent with the view that the rate-determining step is the formation of the cation (**I**; R = Ph, Z = OMe). The reaction of (**1a**) with MeOH containing 0.05M-NaOMe is only *ca.* 7 times slower than that of $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Br)$, compared with the factor of 110 between the corresponding chlorides. This difference can be associated with the much higher reactivities of the bromides, since it is usual, other things being equal, for substituent effects to be smaller in a more reactive than in a less reactive system, as the transition state is closer to the initial state.

Rates of methanolysis of the species $(Me_3Si)_3CSiPh_2X$ (X = Cl or Br) are not available because the reactions are so slow, and even slower than those of the analogous $(Me_3Si)_3CSiMe_2X$ compounds, but it is safe to conclude that they are at least 10^8 times lower than those for (**1a**) and (**1b**), respectively.

Structure of (**2**).—The structure of (**2**), with the atom numbering, is shown in Figure 1, and the list of bond distances and angles is given in Table 1. The structure is closely analogous to that of the chloride (**1b**), which was discussed recently,[8] if the OEt and OMe substituents in (**2a**) are taken as corresponding

Table 1. Intramolecular distances (Å) and angles (°) for (**2**), with estimated standard deviations in parentheses

(a) Bond distances

Si(1)–O(1)	1.668(3)	Si(1)–C(1)	1.897(4)
Si(1)–C(12)	1.896(4)	Si(1)–C(18)	1.881(4)
Si(2)–O(2)	1.650(3)	Si(2)–C(1)	1.887(4)
Si(2)–C(2)	1.869(6)	Si(2)–C(3)	1.864(5)
Si(3)–C(1)	1.933(4)	Si(3)–C(5)	1.870(5)
Si(3)–C(6)	1.878(5)	Si(3)–C(7)	1.866(5)
Si(4)–C(1)	1.925(4)	Si(4)–C(8)	1.879(5)
Si(4)–C(9)	1.848(6)	Si(4)–C(10)	1.860(5)
O(1)–C(11)	1.388(6)	O(2)–C(4)	1.399(6)
C(4)–C(24)	1.476(10)	C(12)–C(13)	1.391(7)
C(12)–C(17)	1.377(6)	C(13)–C(14)	1.387(8)
C(14)–C(15)	1.353(8)	C(15)–C(16)	1.375(8)
C(16)–C(17)	1.387(7)	C(18)–C(19)	1.390(7)
C(18)–C(23)	1.398(6)	C(19)–C(20)	1.377(7)
C(20)–C(21)	1.374(8)	C(21)–C(22)	1.358(5)
C(22)–C(23)	1.372(7)		

(b) Angles

O(1)–Si(1)–C(1)	103.6(2)	O(1)–Si(1)–C(12)	106.7(2)
O(1)–Si(1)–C(18)	107.0(2)	C(1)–Si(1)–C(12)	116.4(2)
C(1)–Si(1)–C(18)	116.2(2)	C(12)–Si(1)–C(18)	106.0(2)
O(2)–Si(2)–C(1)	103.7(2)	O(2)–Si(2)–C(2)	107.4(2)
O(2)–Si(2)–C(3)	108.0(2)	C(1)–Si(2)–C(2)	116.5(2)
C(1)–Si(2)–C(3)	114.9(2)	C(2)–Si(2)–C(3)	106.0(2)
C(1)–Si(3)–C(5)	114.1(2)	C(1)–Si(3)–C(6)	111.4(2)
C(1)–Si(3)–C(7)	115.0(2)	C(5)–Si(3)–C(6)	106.6(2)
C(5)–Si(3)–C(7)	104.5(2)	C(6)–Si(3)–C(7)	104.3(2)
C(1)–Si(4)–C(8)	111.9(2)	C(1)–Si(4)–C(9)	113.8(2)
C(1)–Si(4)–C(10)	113.0(2)	C(8)–Si(4)–C(9)	107.9(2)
C(8)–Si(4)–C(10)	105.7(2)	C(9)–Si(4)–C(10)	103.9(2)
Si(1)–O(1)–C(11)	129.9(3)	Si(2)–O(2)–C(4)	123.9(3)
Si(1)–C(1)–Si(2)	109.8(2)	Si(1)–C(1)–Si(3)	109.6(2)
Si(1)–C(1)–Si(4)	109.9(2)	Si(2)–C(1)–Si(3)	109.7(2)
Si(2)–C(1)–Si(4)	110.4(2)	Si(3)–C(1)–Si(4)	107.5(2)
O(2)–C(4)–C(24)	111.3(5)	Si(1)–C(12)–C(13)	122.0(3)
Si(1)–C(12)–C(17)	121.9(3)	C(13)–C(12)–C(17)	116.0(4)
C(12)–C(13)–C(14)	122.3(5)	C(13)–C(14)–C(15)	119.3(5)
C(14)–C(15)–C(16)	120.9(5)	C(15)–C(16)–C(17)	118.7(5)
C(12)–C(17)–C(16)	122.8(4)	Si(1)–C(18)–C(19)	125.4(3)
Si(1)–C(18)–C(23)	118.9(3)	C(19)–C(18)–C(23)	115.6(4)
C(18)–C(19)–C(20)	122.7(5)	C(19)–C(20)–C(21)	119.6(5)
C(20)–C(21)–C(22)	119.5(5)	C(21)–C(22)–C(23)	120.9(5)
C(18)–C(23)–C(22)	121.7(5)		

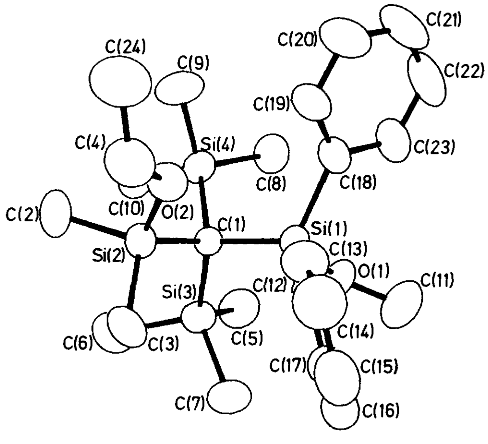


Figure 1. Crystal structure of $(Me_3Si)_2C(SiMe_2OEt)(SiPh_2OMe)$ (**2**) showing the atom numbering scheme

to the OMe and Cl substituents, respectively, in (**1b**). In particular the Si(Et)O $\cdots$ Si–OMe distance is 3.18 Å, significantly below the sum (3.60 Å) of the van der Waals radii, and the related O $\cdots$ Si–O angle is 163°, and these facts would be consistent with a definite but very weak O $\cdots$ Si bonding interaction. (Ebsworth and his colleagues have interpreted intermolecular O $\cdots$ Si distances of 3.1—3.3 Å associated with O–Si $\cdots$ O angles of 173—177° in terms of weak directionally specific secondary bonding that influences the crystal packing, and have drawn a parallel between $O\text{–}SiH_2 \cdots O$ and O–H $\cdots$ O bonding.[10]) However, doubt is cast on the reality of such an interaction in (**2**) by the fact that the oxygen atom of the OMe group approaches even more closely (3.08 Å) to Si(3), which bears three Me groups.

These close non-bonded O $\cdots$ Si approaches are associated with small C(1)–Si(1)–O(1) and C(1)–Si(2)–O(2) angles [103.6(2) and 103.7(2)°, respectively], which contrast markedly with the related C(1)–Si(1)–Ph and C(1)–Si(2)–Me angles [mean 115.7(11) and 116.3(2)°, respectively]. Similar effects were noted in $(Me_3Si)_2C(SiMe_2OMe)(SiPh_2Cl)$.[8]

Other features of the structure, which also parallel those in $(Me_3Si)_2C(SiMe_2OMe)(SiPh_2Cl)$, are as follows:

(a) The $C(1)\text{–}SiMe_3$ bonds [mean 1.929(6)°] are significantly longer than the $C\text{–}SiPh_2OMe$ and $C\text{–}SiMe_2OEt$ bonds [1.897(4) and 1.887(4)°, respectively].

(b) Within the $(Me_3Si)_3C$ system the peripheral Si–Me bonds [mean 1.867(11)] are significantly shorter than the central $C\text{–}SiMe_3$ bonds [mean 1.929(6)°], and the strain is mainly accommodated by opening of the C–Si–Me angles [mean 113.2(14)°] and the corresponding closing of the Me–Si–Me angles [mean 105.5(15)°]. Such effects have been noted previously for a range of related compounds (for references see ref. 8).

(c) There is a significant closing of the Ph–Si–Ph angle [106.0(2)°], but this is somewhat less marked than in $(Me_3Si)_2C(SiMe_2OMe)(SiPh_2Cl)$ [104.6(2)°].

The structure determined for (**1c**) (see Figure 2 and Table 2) is very similar to that of (**2**), but the bond lengths and angles are much less precise. Since the structural features match so closely those noted for (**2**), no detailed analysis is required. The only additional noteworthy feature of significance is that the close approach of the $SiMe_2OMe$ and $SiPh_2OMe$ group involves the alignment $SiMe_2(Me)O \cdots SiPh_2\text{–}OMe$ rather than the possible alternative $SiPh_2(Me) \cdots OSiMe_2\text{–}OMe$, but the significance to be attached to this is limited by the observation that the Si $\cdots$ O distance involved (3.17 Å) is apparently longer than the $Ph_2Si(Me)O \cdots Si(3)Me_3$ distance (3.08 Å).

Table 2. Intramolecular distances (Å) and angles (°) for (**1c**), with estimated standard deviations in parentheses

(a) Bond distances			
Si(1)–O(1)	1.691(10)	Si(1)–C(1)	1.888(13)
Si(1)–C(2)	1.871(13)	Si(1)–C(8)	1.880(14)
Si(2)–C(1)	1.930(13)	Si(2)–C(19)	1.83(2)
Si(2)–C(20)	1.91(2)	Si(2)–C(21)	1.92(2)
Si(3)–C(1)	1.959(13)	Si(3)–C(16)	1.89(2)
Si(3)–C(17)	1.905(14)	Si(3)–C(18)	1.91(2)
Si(4)–O(2)	1.698(12)	Si(4)–C(1)	1.855(14)
Si(4)–C(14)	1.89(2)	Si(4)–C(15)	1.93(2)
O(1)–C(22)	1.41(2)	O(2)–C(23)	1.38(2)
C(2)–C(3)	1.38(2)	C(2)–C(7)	1.44(2)
C(3)–C(4)	1.40(2)	C(4)–C(5)	1.41(2)
C(5)–C(6)	1.38(2)	C(6)–C(7)	1.43(2)
C(8)–C(9)	1.44(2)	C(8)–C(13)	1.37(2)
C(9)–C(10)	1.46(2)	C(10)–C(11)	1.43(3)
C(11)–C(12)	1.32(2)	C(12)–C(13)	1.42(2)
(b) Angles			
O(1)–Si(1)–C(1)	104.4(5)	O(1)–Si(1)–C(2)	105.3(5)
O(1)–Si(1)–C(8)	107.3(6)	C(1)–Si(1)–C(2)	116.6(6)
C(1)–Si(1)–C(8)	117.1(6)	C(2)–Si(1)–C(8)	105.1(6)
C(1)–Si(2)–C(19)	113.1(6)	C(1)–Si(2)–C(20)	112.7(7)
C(1)–Si(2)–C(21)	113.5(6)	C(19)–Si(2)–C(20)	107.7(8)
C(19)–Si(2)–C(21)	103.3(7)	C(20)–Si(2)–C(21)	105.8(7)
C(1)–Si(3)–C(16)	114.0(6)	C(1)–Si(3)–C(17)	113.4(6)
C(1)–Si(3)–C(18)	111.7(7)	C(16)–Si(3)–C(17)	104.8(8)
C(16)–Si(3)–C(18)	104.6(7)	C(17)–Si(3)–C(18)	107.8(8)
O(2)–Si(4)–C(1)	102.1(5)	O(2)–Si(4)–C(14)	108.6(7)
O(2)–Si(4)–C(15)	108.8(8)	C(1)–Si(4)–C(14)	114.9(7)
C(1)–Si(4)–C(15)	116.7(7)	C(14)–Si(4)–C(15)	105.3(8)
Si(1)–O(1)–C(22)	130(1)	Si(4)–O(2)–C(23)	120(1)
Si(1)–C(1)–Si(2)	109.7(6)	Si(1)–C(1)–Si(3)	108.4(6)
Si(1)–C(1)–Si(4)	111.2(7)	Si(2)–C(1)–Si(3)	106.5(6)
Si(2)–C(1)–Si(4)	111.0(7)	Si(3)–C(1)–Si(4)	109.8(6)
Si(1)–C(2)–C(3)	122.5(9)	Si(1)–C(2)–C(7)	119(1)
C(3)–C(2)–C(7)	118(1)	C(2)–C(3)–C(4)	123(1)
C(3)–C(4)–C(5)	120(1)	C(4)–C(5)–C(6)	118(1)
C(5)–C(6)–C(7)	123(1)	C(2)–C(7)–C(6)	118(1)
Si(1)–C(8)–C(9)	115(1)	Si(1)–C(8)–C(13)	126(1)
C(9)–C(8)–C(13)	118(1)	C(8)–C(9)–C(10)	118(1)
C(9)–C(10)–C(11)	119(2)	C(10)–C(11)–C(12)	120(2)
C(11)–C(12)–C(13)	122(2)	C(8)–C(13)–C(12)	122(1)

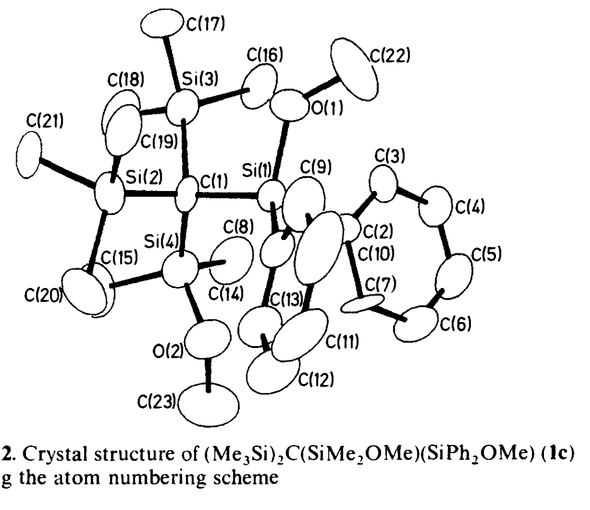


Figure 2. Crystal structure of $(Me_3Si)_2C(SiMe_2OMe)(SiPh_2OMe)$ (**1c**) showing the atom numbering scheme

Experimental

Solvents.—These were dried as previously described.[8]

Spectra.—The ^1H n.m.r. spectra were recorded at 90 MHz with solutions in CCl_4 containing CH_2Cl_2 as lock and reference.

For ^{19}F n.m.r. spectra, CCl_4 solutions containing $CDCl_3$ were used with a Bruker WP80SY spectrometer operated at 75.4 MHz, and shifts are relative to external $CFCl_3$ in $CDCl_3$.

Mass spectra were by electron impact at 70 eV. Only more significant peaks are listed

Reactions of (**1a**) *with Alcohols and with Water*.—(*a*) *With* MeOH. A solution of (**1a**)[8] (0.50 g, 0.98 mmol) in MeOH (10 cm^3) was kept at room temperature for 5 min then the solvent was removed under reduced pressure. The solid residue was sublimed (100 °C at 0.2 Torr) to give *(methoxydimethylsilyl)(methoxydiphenylsilyl)bis(trimethylsilyl)methane* (**1c**) (0.40 g, 88%), m.p. 186 °C (Found: C, 59.7; H, 8.5. $C_{23}H_{40}O_2Si_4$ requires C, 60.0; H, 8.7%); δ_H 0.05 (6 H, s, $SiMe_2$), 0.18 (18 H, s, $SiMe_3$), 3.39 (3 H, s, $SiMe_2O\mathit{Me}$), 3.60 (3 H, s, $SiPh_2O\mathit{Me}$), and 7.2—7.95 (10 H, m, $SiPh_2$); *m/z* 445 (55%, $[M - Me]^+$), 383 (25, $[M - 2(OMe) - Me]^+$), 341 (70, $[M - Me_3SiOMe - Me]^+$), 247 (30, $[M - SiPh_2OMe]^+$), 135 (90), 89 (100, $[SiMe_2OMe]^+$), 73 (90, $[Me_3Si]^+$), and 59 (20, $[SiMe_2H]^+$).

(*b*) *With* EtOH. A procedure similar to that described in (*a*), but with EtOH in place of MeOH, gave *(ethoxydimethylsilyl)(methoxydiphenylsilyl)bis(trimethylsilyl)methane* (**2**) (0.40 g, 88%, after sublimation), m.p. 168 °C (Found: C, 60.7; H, 8.9. $C_{24}H_{42}O_2Si_4$ requires 60.8; H, 8.9%); δ_H 0.10 (6 H, s, $SiMe_2$), 0.18 (18 H, s, $SiMe_3$), 1.32 (3 H, t, CH_2Me), 3.55 (3 H, s, OMe), 3.65 (2 H, q, OCH_2), and 7.2—8.0 (10 H, m, $SiPh_2$); *m/z* 459 (100%, $[M - Me]^+$), 428 (25, $[M - OMe - Me]^+$), 398 (10, $[M - OMe - OEt]^+$), 381 (25, $[M - PhH - Me]^+$), 73 (20), and 59 (5). The structure was established by an *X*-ray diffraction study.

(*c*) *With* EtOH *containing* $AgClO_4$. To a solution of $AgClO_4$ (0.20 g, 0.97 mmol) in EtOH was added (**1a**) (0.10 g, 0.20 mmol). The mixture was stirred for 5 min at room temperature then the solvent was removed under reduced pressure. The mixture was extracted with pentane, and the extract was filtered then evaporated. The ^1H n.m.r. spectrum of the residue was identical to that described under (*b*).

(*d*) *With* $PhCH_2OH$. A solution of (**1a**) (0.25 g, 0.49 mmol) in a mixture of CCl_4 (10 cm^3)–$PhCH_2OH$ (0.1 cm^3) was kept at room temperature for 5 min then added to water. The organic layer was separated, dried ($MgSO_4$), and evaporated, and the residue was sublimed (100 °C at 0.2 Torr) to give a solid, m.p. 106 °C, which from its ^1H n.m.r. spectrum appeared to be a single product, and is assumed to be *(benzyloxydimethylsilyl)(methoxydiphenylsilyl)bis(trimethylsilyl)methane* $(Me_3Si)_2C(SiMe_2OCH_2Ph)(SiPh_2OMe)$(0.20 g, 76%) but could conceivably be the isomeric (benzyloxydiphenylsilyl)(methoxydimethylsilyl)bis(trimethylsilyl)methane $(Me_3Si)_2C(SiMe_2OMe)(SiPh_2OCH_2Ph)$ (Found: C, 64.7; H, 8.4. $C_{29}H_{44}O_2Si_4$ requires C, 64.9; H, 8.2%); δ_H 0.15 (6 H, s, $SiMe_2$), 0.18 (18 H, s, $SiMe_3$), 3.58 (3 H, s, OMe), 4.58 (2 H, s, OCH_2Ph), and 6.8—8.2 (15 H, m, $SiPh_2$); *m/z* 521 (20%, $[M - Me]^+$), 505 (10, $[M - O7e]^+$), 429 (25, $[M - OCH_2Ph]^+$), 459 (10, $[M - Ph]^+$), 135 (60), 73 (60), and 59 (10).

(*e*) *With* CF_3CH_2OH. A solution of (**1a**) (0.25 g, 0.49 mmol) in a mixture of CH_2Cl_2 (1 cm^3)–CF_3CH_2OH (0.5 cm^3)–Et_3N (1 cm^3) was stirred at room temperature for 0.5 h. The solvent was then removed under reduced pressure, and the residue was extracted with pentane. The extract was filtered then evaporated, and the residue was sublimed (100 °C at 0.1 Torr) to give what appeared to be a single product, m.p. 104 °C, which was assumed to be *(trifluoroethoxydimethylsilyl)(methoxydiphenylsilyl)bis(trimethylsilyl)methane* (0.20 g, 77%) [but could conceivably be the isomeric *(trifluoroethoxydiphenylsilyl)(methoxydimethylsilyl)bis(trimethylsilyl)methane*] (Found: C, 54.6; H, 7.7. $C_{24}H_{39}F_3O_2Si_4$ requires C, 54.5; H, 7.4%); δ_H 0.20 (6 H, s, $SiMe_2$), 0.22 (18 H, s, $SiMe_3$), 3.55 (3 H, s, SiOMe), 3.80 (2 H, q, CH_2CF_3), and 7.2—8.05 (10 H, m, $SiPh_2$); δ_F −75.3 (t, *J* 9.03 Hz); *m/z* 513 (35%, $[M - Me]^+$), 435 (35, $[M - Ch_2CF_3]^+$), 414 (20, $[M - OCH_2CF_3 - Me]^+$), 399 (75), 353 (40), 135 (100, $[SiMe_2Ph]^+$), 89 (15), and 73 (30).

(*f*) *With water*. A solution of (**1a**) (0.25 g, 0.49 mmol) in a mixture of acetone (5 cm^3)–water (0.1 cm^3) was stirred at room temperature for 5 min, then the solvent was removed under reduced pressure. The residue was sublimed (115 °C at 0.3 Torr) to give a solid, m.p. 80 °C, which appeared to be a single product and is assumed to be *(hydroxydimethylsilyl)(methoxydiphenylsilyl)bis(trimethylsilyl)methane* [but which could conceivably be the isomeric *(hydroxydiphenylsilyl)(methoxydimethylsilyl)bis(trimethylsilyl)methane*] (Found: C, 58.8; H, 8.1. $C_{22}H_{38}O_2Si_4$ requires C, 59.2; H, 8.5%); δ_H 0.15 (18 H, s, $SiMe_3$), 0.25 (6 H, s, $SiMe_2$), 1.31 (1 H, br s, OH), 3.55 (3 H, s, OMe), and 7.3—7.75 (10 H, m, $SiPh_2$); *m/z* 446 (5%, $[M]^+$), 431 (5, $[M - Me]^+$), 415 (30, $[M - OMe]^+$), 400 (75, $[M - OMe - Me]^+$), 354 (50, $[M - Ph - Me]^+$), 322 (20), 135 (90), 73 (100), and 59 (20).

Kinetic Studies.—*Methanolysis*. (i) A sample of (**1a**) (0.026 g) was dissolved in dioxane (0.90 cm^3) in an n.m.r. tube, and MeOH (0.10 cm^3) was added. The tube was shaken then capped, then placed in the n.m.r. spectrometer at 35 °C, and the ^1H n.m.r. spectrum was recorded at intervals. The relative heights of the signals from the Me_3Si protons, at δ 0.30 and δ 0.18, respectively, for (**1a**) and the product (**1c**) were used to monitor the progress of the reaction, and the data gave a good first-order plot up to >80% completion of the reaction, with a slope corresponding with a first-order rate constant, *k*, of 3.6×10^{-4} s^{-1} and $t_{\frac{1}{2}}$ of 32 min. The n.m.r. spectrum of the product was identical with that of authentic (**1c**).

(ii) When the procedure described under (i) was used, but with MeONa–MeOH instead of MeOH, again good first-order plots were obtained, and the values of $t_{\frac{1}{2}}$ for 0.50, 1.0, and 2.2M-NaOMe–MeOH were *ca.* 115, 136, and 152 min, respectively. (Note that the base concentrations are those in the NaOMe–MeOH taken; those in the dioxane–MeOH mixture were *ca.* 0.05, 0.10, and 0.22M).

(iii) A sample of the chloride (**1b**)[8] (0.025 g) was dissolved in a drop (*ca.* 0.02 cm^3) of CCl_4 and MeOH (1.0 cm^3) was added. The procedure described under (i) was followed, and a good first-order plot was obtained up to 90% completion of the reaction; the rate constant was *ca.* 6.0×10^{-5} s^{-1} ($t_{\frac{1}{2}}$ *ca.* 3.2 h).

Structure Determinations. $(Me_3Si)_2C(SiMe_2OEt)$ $(SiPh_2OMe)$ (**2**).—*Crystal data*. $C_{24}H_{42}O_2Si_4$, *M* = 474.9. Monoclinic, *a* = 9.610(3), *b* = 11.973(5), *c* = 24.444(2) Å, β = 94.31(5), *U* = 2 804.8 $Å^3$, *Z* = 4, D_c = 1.13 g cm^{-3}, *F*(000) = 516, monochromated Mo-K_α radiation, λ = 0.710 69 Å, μ = 2.23 cm^{-1}, space group $P2_1/c$.

Data were measured on an Enraf-Nonius diffractometer with a crystal of dimensions *ca.* 0.25 × 0.35 × 0.4 mm, obtained by recrystallization from pentane. Preliminary cell dimensions were found using the SEARCH and INDEX routines of the CAD4, and final values were calculated from the setting angles of 25 reflections with $\theta \approx 13°$. Intensities for $h \pm k \pm l$ reflections with $2 < \theta < 23°$ were measured by a $\theta/2\theta$ scan with a width $\Delta\theta = (0.8 + 0.35 \tan\theta)$. The scan rate for each reflection was determined by a rapid prescan at 10° min^{-1}, when any reflection with $I < \sigma(I)$ was coded as unobserved. The remaining reflections were measured at such a speed as to give a minimum value of $\sigma I/I$ of 0.05 subject to a maximum scan time of 60 s. Two standard reflections monitored every hour showed no significant variation. Data were corrected for Lorentz-polarization (Lp) effects but not for absorption, and after averaging of the equivalent reflections 2 723 reflections with $|F^2| > \sigma(F)$ were used in the structure refinement. The values of $\sigma(F^2)$ were calculated as $[\sigma^2(I) + (0.021I)^2]^{\frac{1}{2}}/\mathrm{Lp}$.

Table 3. Fractional atomic co-ordinates (× 10⁴) for (**2**) with estimated standard deviations in parentheses

	x	*y*	*z*
Si(1)	6 667(1)	1 706(1)	6 117(10)
Si(2)	9 337(1)	2 892(1)	6 608(1)
Si(3)	6 745(1)	2 709(1)	7 301(1)
Si(4)	6 649(1)	4 294(1)	6 290(1)
O(1)	5 144(3)	1 397(2)	6 365(1)
O(2)	9 695(3)	2 684(3)	5 967(1)
C(1)	7 369(4)	2 892(3)	6 573(2)
C(2)	10 223(5)	4 216(5)	6 844(2)
C(3)	10 186(5)	1 757(4)	7 036(2)
C(4)	11 049(5)	2 600(6)	5 797(2)
C(5)	4 888(5)	3 123(4)	7 363(2)
C(6)	7 830(6)	3 560(5)	7 819(2)
C(7)	6 862(6)	1 256(5)	7 576(2)
C(8)	4 745(5)	4 200(4)	6 056(2)
C(9)	7 584(6)	4 849(4)	5 715(2)
C(10)	6 787(5)	5 434(4)	6 809(2)
C(11)	4 289(5)	472(5)	6 271(3)
C(12)	7 731(4)	372(4)	6 141(2)
C(13)	8 719(5)	155(4)	5 767(2)
C(14)	9 446(6)	−845(5)	5 762(2)
C(15)	9 210(6)	−1 637(4)	6 139(2)
C(16)	8 248(5)	−1 468(4)	6 520(2)
C(17)	7 523(5)	−465(4)	6 512(2)
C(18)	6 293(4)	2 047(4)	5 369(2)
C(19)	7 281(5)	2 371(5)	5 013(2)
C(20)	6 949(6)	2 571(5)	4 464(2)
C(21)	5 596(6)	2 435(5)	4 250(2)
C(22)	4 605(6)	2 107(5)	4 584(2)
C(23)	4 933(5)	1 918(4)	5 132(2)
C(24)	11 252(7)	3 354(8)	5 332(3)

Table 4. Fractional atomic co-ordinates (× 10⁴) for (**1c**) with estimated standard deviations in parentheses

	x	*y*	*z*
Si(1)	1 757(4)	1 915(3)	1 083(1)
Si(2)	1 778(4)	4 514(3)	1 161(2)
Si(3)	1 871(5)	3 081(4)	2 244(2)
Si(4)	4 518(4)	3 136(4)	1 483(2)
O(1)	171(9)	1 666(8)	1 381(4)
O(2)	4 851(11)	2 813(10)	811(4)
C(1)	2 529(14)	3 147(10)	1 479(5)
C(2)	2 778(13)	574(11)	1 145(5)
C(3)	2 489(14)	−222(11)	1 542(6)
C(4)	3 213(14)	−1 246(12)	1 579(6)
C(5)	4 227(17)	−1 522(13)	1 180(7)
C(6)	4 580(16)	−721(13)	793(7)
C(7)	3 825(13)	312(13)	736(6)
C(8)	1 379(14)	2 104(11)	315(6)
C(9)	−84(16)	1 900(13)	128(7)
C(10)	−415(21)	1 922(15)	−471(8)
C(11)	679(19)	2 225(15)	−844(7)
C(12)	1 999(19)	2 431(15)	−652(6)
C(13)	2 358(15)	2 410(13)	−72(6)
C(14)	5 397(16)	2 049(15)	1 951(8)
C(15)	5 477(18)	4 523(15)	1 672(9)
C(16)	1 972(20)	1 644(13)	2 564(6)
C(17)	−78(14)	3 525(13)	2 310(6)
C(18)	3 018(20)	3 993(15)	2 734(7)
C(19)	−127(17)	4 423(12)	958(7)
C(20)	2 789(19)	4 984(15)	523(7)
C(21)	1 852(15)	5 749(11)	1 668(7)
C(22)	−740(20)	726(16)	1 337(9)
C(23)	6 244(17)	2 754(22)	636(10)

The structure was solved by direct methods using the MULTAN[11] program. Refinement of the non-hydrogen atoms with anisotropic temperature factors was by block diagonal least-squares. Hydrogen atoms were located on a difference map and included in the refinement with a fixed isotropic temperature factor of $B = 6.0$. Refinement converged at $R = 0.051$, $R' = 0.065$, when the maximum shift/error was <0.45 and the weighting scheme was $w = 1/\sigma^2(F)$. A final difference map was everywhere featureless. The structure solution and refinement were carried out on PDP11/34 computer using the Enraf-Nonius Structure Determination Package. Scattering factors for neutral atoms were taken from ref. 12. The final non-hydrogen atom co-ordinates are listed in Table 3.

$(Me_3Si)_2C(SiMe_2OMe)(SiPh_2OMe)$ (**1c**).—*Crystal data.* $C_{23}H_{40}O_2Si_4$, $M = 460.9$. Monoclinic, space group $P2_1/c$, $a = 9.327(4)$, $b = 11.990(3)$, $c = 24.028(7)$ Å, $\beta = 91.87(3)°$, $U = 2\,685.6$ Å^3, $Z = 4$, $D_c = 1.14$ g cm^{-3}, $F(000) = 1\,000$, monochromated Mo-K_α radiation, λ 0.710 69Å, $\mu = 2.3$ cm^{-1}.

A crystal of *ca.* 0.4 × 0.3 × 0.4 mm, obtained by recrystallization from pentane, was used. The data collection and refinement were as described for (**2**) above, except for the following variations: (i) 25 reflections with $\theta \approx 14°$ were used; (ii) 2 580 reflections were used in the structure refinement; (iii) no attempt was made to include hydrogen atoms. Refinement converged at $R = 0.14$, $R' = 0.18$, when the maximum shift/error was 0.5 and the weighting scheme was $w = 1/\sigma^2(F)$. A final difference map had peaks of up to 1.2 e Å^{-3}. The poor R and R' values are thought to arise from interference from the presence of a very small second crystal attached to the main one. The final non-hydrogen atom co-ordinates are listed in Table 4.

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