Absence of Rearrangement in Reactions of the Compounds $(Me_3Si)_3CSiMe(OMe)I$, $(Me_3Si)_3CSiMe(OH)I$, and $(Me_3Si)_3CSi(OMe)_2I$ with Electrophilic Reagents

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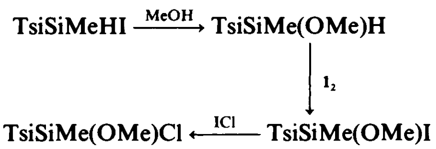
The compounds $TsiSiMe(OMe)I$ and $TsiSi(OMe)_2I$ [$Tsi = (Me_3Si)_3C$] have been prepared and found, unexpectedly, to give only unrearranged products of the type $TsiSiMe(OMe)Z$ and $TsiSi(OMe)_2Z$ ($Z = Cl$ or Y) on treatment with ICl or with silver salts AgY. The hydroxy-iodide $TsiSiMe(OH)I$ likewise gives only $TsiSiMe(OH)Cl$ on treatment with ICl.

It is known that 1,3-migrations of Me groups can occur on treatment of the iodides $TsiSiRR'I$ [$Tsi = (Me_3Si)_3C$; R and R′ = alkyl or aryl] with ICl or silver salts AgY to give the rearranged products $(Me_3Si)_2C(SiRR'Me)(SiMe_2Cl)$ and $(Me_3Si)_2C(SiRR'Me)(SiMe_2Y)$, respectively.[1,2] (Analogous migrations occur in several other types of reaction.[1–3]) Furthermore, the chloro-iodide $TsiSiMeClI$ is known to react analogously with these same reagents to give the rearranged products $(Me_3Si)_2C(SiMe_2Cl)_2$ and $(Me_3Si)_2C(SiMe_2Cl)(SiMe_2Y)$.[2] It thus seemed likely that the methoxy-iodide $TsiSiMe(OMe)I$ would correspondingly give the rearranged products of the type $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Z)$, which are of interest because of their unusually high reactivity, associated with anchimeric assistance by the γ-OMe group to the leaving of Z^-.[4] It turned out, however, that no rearrangements took place, not only in the case of $TsiSiMe(OMe)I$ but also with the related species $TsiSiMe(OH)I$ and $TsiSi(OMe)_2I$.

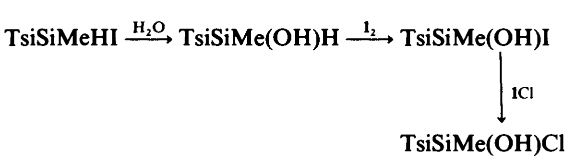
Results and Discussion

The methoxy-iodide $TsiSiMe(OMe)I$ was made from $TsiSiMeHI$ by the route shown in Scheme 1. Treatment with ICl gave only the unrearranged chloride $TsiSiMe(OMe)Cl$, and treatment with silver salts, AgY, likewise gave only $TsiSiMe(OMe)Y$ species ($Y = ONO_2$, $OClO_3$, or OSO_2CF_3). The related hydroxy-iodide $TsiSiMe(OH)I$, prepared as shown in Scheme 2, likewise gave only the unrearranged chloride, $TsiSiMe(OH)Cl$, on treatment with ICl.



$$\begin{tikzcd} TsiSiMeHI \arrow[r, "MeOH"] & TsiSiMe(OMe)H \arrow[d, "I_2"] \\ TsiSiMe(OMe)Cl & TsiSiMe(OMe)I \arrow[l, "ICl"'] \end{tikzcd}$$

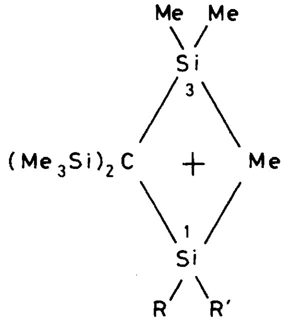
Scheme 1.



$$\begin{tikzcd} TsiSiMeHI \arrow[r, "H_2O"] & TsiSiMe(OH)H \arrow[r, "I_2"] & TsiSiMe(OH)I \arrow[d, "ICl"] \\ & & TsiSiMe(OH)Cl \end{tikzcd}$$

Scheme 2.

The absence of rearrangements in these reactions of $TsiSiMe(OE)I$ species (E = Me or H) is difficult to account for.



(1)

We previously interpreted the rearrangement which takes place on reactions of $TsiSiRR'I$ species, where R and R′ are alkyl or aryl groups, with ICl or AgY in terms of a methyl-bridged species (1), with the relative extents of attack of Cl^- or Y^- on Si(1) or Si(3) determined by the relative steric hindrance at the two centres, and on this basis some, if not exclusive, rearrangement would be expected for R = Me, R′ = OMe. In the discussion of the rearrangement which occurs on treatment of $TsiSiMeICl$ with ICl or silver salts, it was suggested that repulsion by the lone pairs of the Cl ligand on Si(1) in the cation (1; R = Me, R′ = Cl) might divert the nucleophile towards Si(3),[2] but if this were the case a similar, though smaller, effect would be expected for the OMe group. In isolation we could rationalize the absence of rearrangement with the methoxy and hydroxy compounds in terms of electron withdrawal by the OE group in the intermediate (1; R = Me, R′ = OH or OMe) which would, by decreasing the electron density at Si(1), favour attack there rather than at Si(3), but if this were the case a similar, larger, effect would be expected for the Cl ligand.† It is evident that interpretation of the degree of rearrangement in reactions of $TsiSiRR'X$ species in terms of steric effects, which has so far been adequate for cases in which R and R′ are alkyl, aryl, or hydride ligands,[1–3] is not satisfactory when R or R′ (or both) are electronegative groups.

In view of the unexpected behaviour of $TsiSiMe(OMe)I$ we also prepared the dimethoxy compound $TsiSi(OMe)_2I$ by iodination of $TsiSi(OMe)_2H$. We had planned to make the latter by methanolysis of $TsiSiHI_2$, which we thought would be

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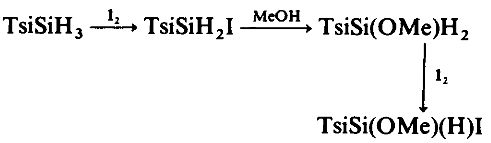
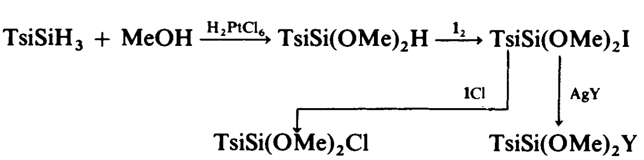
† In principle the OE groups might, by conjugative electron release, so stabilize the Si(1) cation that bridging would be unnecessary; if this were the case, however, $TsiSi(OMe)_2I$ would be more reactive than $TsiSiMe_2I$ towards silver salts, whereas the opposite is true (E. Chaffin, personal communication).

produced by iodination of $TsiSiH_3$, but even with an excess of iodine and prolonged reflux in CCl_4 only the monoiodide $TsiSiH_2I$ was formed (and use of ICl gave a mixture of silicon chlorides and iodides). The monoiodide was, however, converted into TsiSi(OMe)(H)I by the route shown in Scheme 3;



Scheme 3.

this iodide would no doubt give $TsiSi(OMe)_2H$ on treatment with MeOH, but this route was abandoned when we found that $TsiSiH_3$ reacted directly with MeOH in the presence of chloroplatinic acid to give the dimethoxy-hydride $TsiSi(OMe)_2H$, which reacted with iodine to give the required $TsiSi(OMe)_2I$. In keeping with the behaviour of the monomethoxy compound, $TsiSi(OMe)_2I$ reacted with ICl and with silver salts (see Scheme 4) to give unrearranged products of the type $TsiSi(OMe)_2Y$ ($Y = OSO_2CF_3$ from AgO_3SCF_3; Y = F from $AgBF_4$).



Scheme 4.

The stability of the hydroxy-iodide TsiSiMe(OH)I, which has an iodide and a hydroxide ligand on the same silicon atom, is noteworthy, since in the absence of steric hindrance, nucleophilic attack by a hydroxy group of one molecule at the Si–I bond of another would normally give rise rapidly to polysiloxanes. The compound was purified by sublimation, and melted sharply at 296 °C. We previously reported the existence of the related compound TsiSiPh(OH)I as a stable species,[5] and the compounds $Bu^t_2Si(OH)X$ (X = Br or Cl) were subsequently isolated.[6]

Experimental

The ^1H n.m.r. spectra are for CCl_4 solutions at 60 or 90 MHz. The i.r. data are for Nujol mulls. For m.p. determinations samples were sealed in capillaries.

Preparation and Reactions of TsiSiMe(OMe)X (X = I, Cl, ONO_2, OSO_2CF_3, OMe *or* OH).—(*a*) A solution of TsiSiMe(OMe)H (0.75 g, 2.5 mmol)[7] and I_2 (0.65 g, 2.6 mmol) in CCl_4 (10 cm^3) was stirred for 18 h. Removal of solvent and I_2 under vacuum gave a solid, which was sublimed (100 °C at 0.1 Torr) to give *[iodo(methoxy)methylsilyl]tris(trimethylsilyl)-methane* (1.04 g, 98%), m.p. >320 °C (Found: C, 33.3; H, 7.7. $C_{12}H_{33}IOSi_4$ requires C, 33.3; H, 7.7%); δ_H 0.33 (s, 27 H, $SiMe_3$), 1.02 (s, 3 H, SiMe), and 3.44 (s, 3 H, OMe).

(*b*) A (1M) solution of ICl (1.0 mmol) in CCl_4 (1 cm^3) was added dropwise to a stirred solution of TsiSiMe(OMe)I (0.20 g, 0.46 mmol) in CCl_4 (5 cm^3). The solution was subsequently stirred for 30 min, then evaporated. The residue was washed with a little cold MeOH, dried, and sublimed (90 °C at 0.2 Torr) to give *[chloro(methoxy)methylsilyl]tris(trimethylsilyl)methane* (0.080 g, 51%), m.p. >320 °C (Found: 42.1; H, 9.6. $C_{12}H_{33}ClOSi_4$ requires C, 42.2; H, 9.8%); δ_H 0.27 (s, 27 H, $SiMe_3$), 0.60 (s, 3 H, SiMe), and 3.51 (s, 3 H, OMe).

(*c*) A mixture of TsiSiMe(OMe)I (0.050 g, 0.12 mmol) and $AgNO_3$ (0.034 g, 0.20 mmol) in MeCN (10 cm^3) was kept under reflux for 8 h. Removal of the solvent under vacuum left a solid, which was extracted with hot light petroleum (b.p. 60—80 °C). Filtration and evaporation of the extract left a solid, which was judged from its ^1H n.m.r. spectrum to be exclusively $TsiSiMe(OMe)(ONO_2)$; δ_H 0.28 (s, 27 H, $SiMe_3$), 0.64 (s, 3 H, SiMe), and 3.68 (s, 3 H, OMe).

(*d*) A mixture of TsiSiMe(OMe)I (0.080 g, 0.19 mmol) and AgO_2CCF_3 (0.080 g, 0.36 mmol) in CH_2Cl_2 (10 cm^3) was stirred for 1 h. Filtration followed by removal of the solvent left a solid, which was sublimed (80 °C at 0.2 Torr) to give *[methoxy-(methyl)trifluoroacetoxysilyl]tris(trimethylsilyl)methane*. (0.055 g, 71%) (Found: C, 40.2; H, 8.1. $C_{14}H_{33}F_3O_3Si_4$ requires C, 40.2; H, 7.9%); δ_H 0.27 (s, 27 H, $SiMe_3$), 0.60 (s, 3 H, SiMe), and 3.64 (s, 3 H, OMe); ν(C=O) 1 765 cm^{-1}.

(*e*) A refluxing mixture of TsiSiMe(OMe)I (1.00 g, 2.3 mmol) and AgO_3SCF_3 (0.60 g, 2.3 mmol) in CH_2Cl_2 (10 cm^3) was stirred for 2 h. Work up as in (*d*), but with sublimation at 100 °C and 0.2 Torr, gave *[methoxy(methyl)trifluoromethylsulphonyl-oxysilyl]tris(trimethylsilyl)methane* (0.62 g, 59%) (Found: C, 34.1; H, 7.4. $C_{13}H_{33}F_3O_4SSi_4$ requires C, 34.3; H, 7.3%); δ_H 0.28 (s, 27 H, $SiMe_3$), 0.68 (s, 3 H, SiMe), and 3.67 (s, 3 H, OMe); δ_F(CCl_4, rel. to $CFCl_3$) −77.4 p.p.m. (s, CF_3); *m/z* 439 ($[M - Me]^+$), 335 ($[M - Me - Me_3SiOMe]^+$), 275 ($[M - Me - MeSO_3CF_3]^+$), and 73 ($[Me_3Si]^+$).

(*f*) A solution of $TsiSiMe(OMe)OSO_2CF_3$ (0.10 g) in MeOH (5 cm^3) was kept at 60 °C for 48 h, then cooled and diluted with water. Extraction with light petroleum followed by washing and evaporation of the extract left a solid, which was judged to be exclusively *[dimethoxy(methyl)silyl]tris(trimethylsilyl)-methane*; δ_H 0.19 (s, 27 H, $SiMe_3$), 0.28 (s, 3 H, SiMe), and 3.52 (s, 6 H, OMe); *m/z* 321 ($[M - Me]^+$), 305 ($[M - OMe]^+$), 233 ($[M - Me - Me_4Si]^+$), 217 ($[M - Me - Me_3SiOMe]^+$), 201 ($[M - OMe - Me_3SiOMe]^+$), 105 ($[(MeO)_2MeSi]^+$), and 73 ($[Me_3Si]^+$).

(*g*) A solution of $TsiSiMe(OMe)(OSO_2CF_3)$ (0.10 g) in MeCN (5 cm^3) containing a few percent of water was kept under reflux for 4 h, then evaporated to give a solid. This was sublimed (80 °C at 0.2 Torr) to give *[hydroxy(methoxy)methylsilyl]-tris(trimethylsilyl)methane*, m.p. 291 °C (Found: C, 44.9; H, 10.5. $C_{12}H_{34}O_2Si_4$ requires C, 44.6; H, 10.6%); δ_H 0.22 (s, 27 H, $SiMe_3$), 0.25 (s, 3 H, SiMe), 1.7 (br s, 1 H, OH), and 3.46 (s, 3 H, OMe); ν(OH) 3 690 and 3 600—3 300 cm^{-1}.

Preparation of TsiSiMe(OH)X (X = H, I, *or* Cl).—(*a*) A solution of TsiSiMeHI (0.81 g) in a mixture of acetone (25 cm^3) and H_2O (25 cm^3) was kept under reflux for 30 min. The solvent was evaporated off, and the residue was dissolved in light petroleum (20 cm^3). The solution was washed with aqueous $NaHSO_3$ then with H_2O, dried ($MgSO_4$), and evaporated. The residue was sublimed (100 °C at 0.2 Torr) to give *[hydroxy-(methyl)silyl]tris(trimethylsilyl)methane* (0.52 g, 88%), m.p. 286 °C (Found: C, 45.3; H, 10.8. $C_{11}H_{32}OSi_4$ requires C, 45.1; H, 11.0%); δ_H 0.21 (s, 27 H, $SiMe_3$), 0.40 (d, 3 H, SiMe), 1.3 (br s, 1 H, OH), and 4.86 (q, 1 H, SiH); ν(OH) 3 690 and 3 600—3 300; ν(SiH) 2 120 cm^{-1}.

(*b*) A mixture of TsiSiMe(OH)H (0.28 g, 0.96 mmol) and I_2 (0.50 g, 2.0 mmol) in CCl_4 (10 cm^3) was stirred for 15 min. The solvent was removed to leave a solid, which was dissolved in light petroleum. The solution was washed with aqueous $NaHSO_3$ then with water, dried ($MgSO_4$), and evaporated to leave a solid, which was sublimed (90 °C at 0.2 Torr) to give *[hydroxy(iodo)(methyl)silyl]tris(trimethylsilyl)methane* (0.35 g, 87%), m.p. 296 °C (Found: C, 32.6; H, 7.7. $C_{11}H_{31}IOSi_4$ requires C, 31.9; H, 7.5%); δ_H 0.36 (s, 27 H, $SiMe_3$), 1.10 (s, 3 H, SiMe), and 2.4 (br s, 1 H, OH); ν(OH) 3 690 and 3 600—3 300 cm^{-1}.

(*c*) A (1M) solution of ICl (0.2 mmol) in CCl_4 (0.2 cm^3) was added dropwise to a stirred solution of TsiSiMe(OH)I (0.058 g, 0.14 mmol) in CCl_4 (3 cm^3). After a further 5 min of stirring the solvent and residual halogen were taken off in vacuum, and the residue was sublimed (100 °C at 0.2 Torr) to give [*chloro*(*hydroxy*)(*methyl*)*silyl*]*tris*(*trimethylsilyl*)*methane* (0.030 g, 80%), m.p. >320 °C (Found: C, 40.3; H, 9.3. $C_{11}H_{31}ClOSi_4$ requires C, 40.4; H, 9.6%); δ_H 0.31 (s, 27 H, $SiMe_3$), 0.65 (s, 3 H, SiMe), and 2.4 (br s, 1 H, OH); ν(OH) 3 690 and 3 600—3 300 cm^{-1}.

Preparation and Reactions of $TsiSiIH_2$, TsiSi(OMe)HX (X = H, I, *or* OMe), *and* $TsiSi(OMe)_2Y$ (Y = H, I, Cl, F, *or* OSO_2CF_3).—(*a*) A stirred mixture of $TsiSiH_3$ (0.50 g, 1.9 mmol),[1] I_2 (2.42 g, 9.5 mmol), and heptane (25 cm^3) was kept under reflux for 17 h. Removal of the solvent and residual I_2 under vacuum left a solid, which was sublimed (80 °C at 0.2 Torr) to give $TsiSiH_2I$ (0.59 g, 80%), m.p. 270 °C (lit.,[1] 273 °C) (Found: C, 30.6; H, 7.75. Calc. for $C_{10}H_{29}ISi_4$: C, 30.9; H, 7.75%); δ_H 0.26 (s, 27 H, $SiMe_3$) and 4.38 (s, 2 H, SiH_2); ν(SiH) 2 150 cm^{-1}.

(*b*) A solution of $TsiSiH_2I$ (0.42 g) in a mixture of CH_2Cl_2 (2 cm^3) and MeOH (10 cm^3) was kept for 15 min, then evaporated to leave a solid. This was sublimed (100 °C at 0.2 Torr) to give $TsiSi(OMe)H_2$ (0.29 g, 92%), m.p. 226 °C (lit.,[1] 228 °C) (Found: C, 45.0; H, 10.7. Calc. for $C_{11}H_{32}OSi_4$: C, 45.1; H, 11.0%); δ_H 0.15 (s, 27 H, $SiMe_3$), 3.46 (s, 3 H, OMe), and 4.55 (s, 2 H, SiH_2); ν(SiH) 2 100 cm^{-1}.

(*c*) A stirred mixture of $TsiSi(OMe)H_2$ (0.10 g, 0.34 mmol) and I_2 (0.20 g, 0.79 mmol) in CCl_4 (10 cm^3) was kept under reflux for 30 min. Removal of the solvent and residual I_2 under vacuum left a solid, which was judged from its ^{1}H n.m.r. spectrum to be exclusively TsiSi(OMe)HI; δ_H 0.33 (s, 27 H, $SiMe_3$), 3.46 (s, 3 H, OMe), and 5.83 (s, 1 H, SiH).

(*d*) A solution of $TsiSiH_3$ (1.00 g) in MeOH (40 cm^3) was treated with 10 drops of 0.04M-H_2PtCl_6 in EtOH, then stirred under reflux for 16 h. Removal of the solvent followed by sublimation of the residue gave (*dimethoxysilyl*)*tris*(*trimethylsilyl*)*methane* (1.1 g, 90%), m.p. 262 °C (Found: C, 44.4; H, 10.4. $C_{12}H_{34}O_2Si_4$ requires C, 44.6; H, 10.6%); δ_H 0.19 (s, 27 H, $SiMe_3$), 3.66 (s, 6 H, OMe), and 4.62 (s, 1 H, SiH); ν(SiH) 2 105 cm^{-1}.

(*e*) A mixture of $TsiSi(OMe)_2H$ (0.90 g, 2.8 mmol) and I_2 (1.50 g, 2.9 mmol) in CCl_4 (10 cm^3) was stirred for 18 h. Removal of the solvent left a brown solid, which was extracted with light petroleum. The extract was washed with aqueous $NaHSO_3$ then with water, dried ($MgSO_4$), and evaporated. The residue was sublimed to give [*iodo*(*dimethoxy*)*silyl*]*tris*(*trimethylsilyl*)*methane* (0.95 g, 76%), m.p. > 320 °C (Found: C, 32.8; H, 7.2. $C_{12}H_{33}IO_2Si_4$ requires C, 32.1; H, 7.4%); δ_H 0.29 (s, 27 H, $SiMe_3$) and 3.54 (s, 6 H, OMe).

(*f*) A 1M-solution of ICl in CCl_4 (1.0 cm^3) was added dropwise to a stirred solution of $TsiSi(OMe)_2I$ (0.19 g, 0.42 mmol) in CCl_4 (10 cm^3). The solution was stirred for 1 h then evaporated under vacuum to leave a solid, which was judged from its ^{1}H n.m.r. spectrum to be $TsiSi(OMe)_2Cl$; δ_H 0.22 (s, 27 H, $SiMe_3$) and 3.59 (s, 6 H, OMe).

(*g*) A mixture of $TsiSi(OMe)_2I$ (0.10 g, 0.22 mmol) and $AgBF_4$ (0.06 g, 0.31 mmol) in CH_2Cl_2 (5 cm^3) was stirred for 45 min. The solution was filtered then evaporated to leave a solid, which was judged from its ^{1}H n.m.r. spectrum to be $TsiSi(OMe)_2F$; δ_H 0.18 (s, 27 H, $SiMe_3$) and 3.63 (s, 6 H, OMe).

(*h*) The procedure described under (*g*), but with AgO_3SCF_3 in place of $AgBF_4$, gave a solid which was judged to be $TsiSi(OMe)_2(OSO_2CF_3)$; δ_H 0.23 (s, 27 H, $SiMe_3$) and 3.80 (s, 6 H, OMe).

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