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PREPARATION AND REACTIONS OF SOME STERICALLY HINDERED SILANOLS, INCLUDING [TRIS(TRIMETHYLSILYL)METHYL]SILANETRIOL

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Summary

The silanol $TsiSiMe_2OH$ ($Tsi = (Me_3Si)_3C$) has been made by hydrolysis of the iodide $TsiSiMe_2I$ in H_2O/dioxane or H_2O/Me_2SO. It has been shown to react with some acid chlorides RCOCl (R = Me, Et, $ClCH_2$, Ph, 4-$O_2NC_6H_4$, and 3,5-$(O_2N)_2C_6H_3$) and anhydrides $(RCO)_2O$ (R = Me, CF_3, or Ph) to give the carboxylates $TsiSiMe_2OCOR$, and with SO_2Cl_2 to give $TsiSiMe_2OSO_2Cl$. The triol $TsiSi(OH)_3$ has been made by treatment of TsiSiH(OH)I with H_2O/Me_2SO at 150°C or with a mixture of aqueous $AgClO_4$ and an organic solvent. The triol has been shown to react with RCOCl (R = Me, Et, or Ph) or $(RCO)_2O$ (R = Ph) to give the corresponding $TsiSi(OCOR)_3$, with $(CF_3CO)_2O$ to give $TsiSi(OH)_2(OCOCF_3)$, and with a mixture of Me_3SiCl and $AgClO_4$ in benzene or one of Me_3SiI and $(Me_3Si)NH$ to give $TsiSi(OSiMe_3)_3$. The triol is unusually stable, but decomposes at its m.p. of 285–290°C.

Introduction

Some preparations and reactions of the silanol $TsiSiMe_2OH$ (I) ($Tsi = (Me_3Si)_3C$) have been described previously [1–4]. We describe below a simpler method of making I and give an account of some reactions of I which involve breaking of the O–H bond (breaking of the Si–O bond being inhibited by severe steric hindrance to nucleophilic attack at silicon). We also describe the first preparation of the triol $TsiSi(OH)_3$ (II) and some of its properties.

Results and discussion

1. $TsiSiMe_2OH$ (I)

It was found that the iodide $TsiSiMe_2I$, although reacting only very slowly with MeOH [5], could be converted into the hydroxide I by treatment with 5% H_2O in

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dioxane for 16 h under reflux or with 5% H_2O in Me_2SO at 130°C for 1 h (cf. ref. 4). This provides the best method of preparing I, which is useful for further syntheses.

It has been shown previously that I reacts with MeCOCl to give $TsiSiMe_2OCOMe$ [2], and we have now extended this reaction to the preparation of related $TsiSiMe_2OCOR$ species, with R = Et, $ClCH_2$, Ph, $C_6H_4NO_2$-4, and $C_6H_3(NO_2)_2$-3,5. The reaction with an excess of neat MeCOCl was found to be complete within 1 h at room temperature; for R = Et, $ClCH_2$, and Ph reactions were carried out under reflux for a few hours (though they may in some cases have been complete in shorter times). The reaction for R = $C_6H_4NO_2$-4 was carried out at 100°C (i.e. above the melting point of the chloride) for 4 h, and that for R = $C_6H_3(NO_2)_2$-3,5 at 150°C for 4 h.

The silanol I was also converted into $TsiSiMe_2OCOR$ with R = Me, CF_3, or Ph by reaction with the corresponding anhydride. The reactions were slower than those with the acyl chloride; for R = Me and R = CF_3 the mixtures of I and an excess of neat $(RCO)_2O$ were refluxed for 10 and 4 h, respectively, while for R = Ph the mixture was kept at 75°C for 12 h.

Somewhat surprisingly, no reaction took place when I was heated with an excess of $PhSO_2Cl$ at 130°C for 10 h. The benzenesulphonate $TsiSiMe_2OSO_2Ph$ was made, however, by treating I with MeLi in Et_2O to give $TsiSiMe_2OLi$ and then adding $PhSO_2Cl$. The benzenesulphonate was found to be less reactive than the iodide $TsiSiMe_2I$ in hydrolysis; no detectable reaction took place when its solution in 2% H_2O in MeCN was kept at 60°C for 24 h.

2. *$TsiSi(OH)_3$ (II)*

The starting point for the preparation of II was $TsiSiH_3$ [6]. This was treated with ICl in CCl_4 to give $TsiSiH_2I$, which was hydrolysed with 10% H_2O in Me_2SO to give $TsiSiH_2(OH)$. Reaction of the latter with I_2 in CCl_4 gave TsiSiH(OH)I *, which we planned to convert into $TsiSi(OH)_2H$, and hence into $TsiSi(OH)_2I$ and then $TsiSi(OH)_3$. In the event, however, reaction of TsiSiH(OH)I with 5% H_2O in Me_2SO at 150°C for 10 min gave not the expected $TsiSi(OH)_2H$ but the required $TsiSi(OH)_3$. This abnormally high reactivity of the Si–H bond in (presumably) $TsiSi(OH)_2H$ may possible be related to that of the Si–I bond in TsiSiPh(OH)I [8].

The triol II was also obtained when a solution of TsiSiH(OH)I was treated with a mixture of aqueous $AgClO_4$ and an organic solvent.

II was converted into the tris-carboxylates $TsiSi(OCOR)_3$, with R = Me, Et, and Ph, by the appropriate RCOCl under reflux. The tris-acetoxy compound was also obtained by refluxing II with $(MeCO)_2O$, and $TsiSi(OCOPh)_3$ by treating II with $(PhCO)_2O$ for 20 h at 80°C (i.e. above the melting point of the anhydride). Refluxing of II with $ClCH_2COCl$ for 3 d gave a mixture of $TsiSi(OH)_n(OCOCH_2Cl)_{3-n}$ compounds with n = 0–2, and refluxing with $(CF_3CO)_2O$ for 3 d gave a good yield of the mono-trifluoroacetoxy compound $TsiSi(OH)_2(OCOCF_3)$.

The triol II was converted into the tris-siloxy compound $TsiSi(OSiMe_3)_3$ by treatment with Me_3SiCl in the presence of $AgClO_4$ in PhH or MeCN, the perchlorate $Me_3SiOClO_3$ presumably being the effective reagent. Triol II reacted slowly

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* The stability of this species, which has an iodine atom and hydroxyl group bonded to the same silicon, is noteworthy (cf. ref. 7).

with an excess of neat Me_3SiCl under reflux, but after 20 d several products were present. Conversion of II into $TsiSi(OSiMe_3)_3$ was also brought about by Me_3SiI in the presence of $(Me_3Si)_2NH$.

Compound II is exceptionally thermally stable for a triol. Some triols are known, e.g. $PhSi(OH)_3$ [9] and cyclo-$C_6H_{11}Si(OH)_3$ [10], and the crystal structure of the latter has been determined by X-ray diffraction at low temperature [11], but they readily undergo condensation by formation of disiloxane linkages. Triol II has shown no tendency to decompose on normal handling, but breakdown, with gas evolution (presumably H_2O) take place at the melting point, 285–290°C. When a sample was kept for 1 h at 315°C, analysis by GLC/MS indicated that three main products were formed; one was probably TsiH, another appeared to be $(Me_3Si)_2$-$CHSi(OH)_2OSiMe_3$ or an isomer of it, and the third was not identified. The formation of TsiH could involve attack of base dissolved from the glass by water formed in the initial decomposition. (Compare the reaction with NaOMe/MeOH, below.) The compound $(Me_3Si)_2CHSi(OH)_2OSiMe_3$ could be formed by a 1,3-migration of an Me_3Si group from C to O, a rearrangement [3] of the type observed, for example, on heating $C(SiMe_2OH)_4$ alone [12] or $TsiSiPh_2OH$ in MeOH [13] (cf. ref. 12).

The triol II also decomposed on treatment with 1.5 *M* NaOMe in MeOH at 50°C for 3 d. Analysis by GC/MS indicated the presence of five main products, three of which appeared to be TsiH, $(Me_3Si)_2CHSi(OSiMe_3)_3$ (or an isomer), and $(Me_3Si)_2CHSi(OMe)(OH)_2$ (or an isomer). The formation of TsiH is not surprising, in view of the fact that $TsiSiMe_2H$ also gives this cleavage product on treatment with 2 *M* MeONa in MeOH, although $TsiSiMe_3$ is inert under these conditions [14]. Presumably the attack by MeO^- on the silicon atom is less sterically hindered than in the case of $TsiSiMe_3$, and may, moreover, be facilitated by electron-withdrawal by the OH groups. Alternatively, formation of the silanolate ion $TsiSi(OH)_2O^-$ may be followed by expulsion of Tsi^- (which would then rapidly acquire a proton from the solvent) and transient formation of $(HO)_2Si{=}O$ (cf. ref. 8). The ion $TsiSi(OH)_2O^-$ can also be expected to undergo rearrangement to give after protonation $(Me_3Si)_2CH(OH)_2OSiMe_3$, and reaction of the latter with MeOH would ultimately give the species $(Me_3Si)_2CHSi(OMe)_n(OH)_{3-n}$, which would account for two of the assumed products (those with $n = 1$ and 3).

Experimental

General. The ^1H NMR spectra were recorded at 60 or 90 MHz; solutions in CCl_4, containing CH_2Cl_2 or PhH as reference, were used unless otherwise stated. Mass spectra were by electron impact (EI) at 70 eV or by chemical ionization (CI) in the presence of NH_3; only ions especially significant for identification are given.

For GLC and GC/MS, columns of OV101 on 100–120 mesh Chromosorb G were used.

For melting points, samples were sealed in capillaries.

Preparation of $TsiSiMe_2OH$ (I)

(i) A solution of $TsiSiMe_2I$ [6] (8.0 g, 0.019 mol) in a mixture of dioxane (95 cm^3) and water (5 cm^3) was refluxed and the progress of the reaction was monitored by ^1H NMR spectroscopy. Reaction was complete after 16 h, and the solution was then cooled to room temperature and added to an excess of water. Extraction with $CHCl_3$, followed by separation, washing, drying ($MgSO_4$), and evaporation of the extract left a solid residue, which was sublimed (120°C/ 0.1 mmHg) to give I (5.6 g, 95%), m.p. 325°C; δ(H) 0.23 (s, 27 H, $SiMe_3$), 0.31 (s, 6 H, $SiMe_2$), 1.35 ppm (br s, 1 H, SiOH); m/z 291 (80%, $[M-Me]^+$), 275 (100, $[M-MeH-Me]^+$), 259 (65, $[M-2MeH-Me]^+$); ν(OH) 3670 cm^{-1} (Found: C, 47.3; H, 11.1 $C_{12}H_{34}OSi_4$ calcd.: C, 47.1; H, 11.1%).

(ii) A similar procedure to that described under (i), but with a mixture of Me_2SO (95 cm^3) and H_2O (5 cm^3) as solvent, a reaction time of 1 h at 130°C, and washing of the chloroform extract with aqueous $NaHSO_3$ to remove free I_2, gave I in 92% yield.

Reactions of I with acyl halides, RCOCl

(i) A mixture of I (0.60 g, 1.96 mmol) and MeCOCl (15 cm^3) was kept at room temperature (ca. 21°C) for 1 h. The remaining MeCOCl was evaporated off under vacuum, and the residue was sublimed (110°C/0.1 mmHg) to give $TsiSiMe_2OCOMe$ (0.62 g, 92%), m.p. 312°C; δ(H) 0.26 (s, 27 H, $SiMe_3$), 0.52 (s, 6 H, $SiMe_2$), and 2.0 ppm (s, 3 H, COMe); ν(C=O) 1723 cm^{-1}; m/z 333 (100%, $[M-Me]^+$), 291 (65, $[M-CH_2CO-Me]^+$), 275 (75, $[M-Me_2CO-Me]^+$), 259 (65, $[M-Me_2CO-MeH-Me]^+$); m/z (CI), 349 (35%, $[M+H]^+$), 333 (100, $[M-Me]^+$) (Found: C, 48.0; H, 10.1. $C_{14}H_{36}O_2Si_4$ calcd.: C, 48.2; H, 10.4%). The ^{1}H NMR data agree with those previously reported [15,16].

(ii) A mixture of I (0.42 g) and EtCOCl (12 cm^3) was refluxed for 3 h. Volatile materials were then removed under vacuum, and the residue was sublimed (120°C/0.1 mmHg) to give $TsiSiMe_2OCOEt$ (0.54 g. 90%); m.p. 204°C; δ(H) 0.26 (s, 27 H, $SiMe_3$), 0.54 (s, 6H, $SiMe_2$), 1.1 (tr, 3 H, CH_2Me), and 2.25 ppm (q, 2 H, CH_2); ν(C=O) 1720 cm^{-1}; m/z 347 (40%, $[M-Me]^+$), 291 (25%, $[M-CH_3CHCO-Me]^+$), 275 (25, $[M-MeCOEt-Me]^+$), and 73 (100, $[Me_3Si]^+$) (Found: C, 49.7; H, 10.8. $C_{15}H_{38}Si_4O_2$ calcd.: C, 49.6; H, 10.6%).

(iii) A mixture of I (0.28 g) and $ClCH_2COCl$ (10 cm^3) was refluxed for 3 h. Volatile materials were removed under reduced pressure, and the residue was sublimed (140°C/0.2 mmHg) to give $TsiSiMe_2OCOCH_2Cl$ (0.28 g, 80%), m.p. 252°C; δ(H) 0.29 (s, 27 H, $SiMe_3$), 0.60 (s, 6 H, $SiMe_2$), and 3.93 ppm (s, 2H, CH_2); ν(C=O) 1745 cm^{-1}; m/z (EI) 367 (50%, $[M-Me]^+$), 289 (25, $[M-OCOCH_2Cl]^+$), 275 (20, $[M-OCOCH_2Cl-Me]^+$), 201 (20, $[M-Me_3SiOCOCH_2Cl-Me]^+$), 73 (100%); m/z (CI) 400 (25, $[M+H+NH_3]^+$), 367 (90, $[M-Me]^+$), 306 (100, $[M-OCOCH_2Cl+NH_3]^+$), 275 (65, $[M-OCOCH_2Cl-Me]^+$) (Found: C, 44.3; H, 9.4. $C_{14}H_{35}ClO_2Si_4$ calcd.: C, 43.9; H, 9.2%).

(iv) A mixture of I (0.58 g) and PhCOCl (15 cm^3) was stirred for 5 h at room temperature. The ^{1}H NMR spectrum showed that no reaction had taken place, so the mixture was refluxed for 6 h. Volatile material was distilled off under vacuum, and the residue was sublimed (135°C/0.1 mmHg) to give $TsiSiMe_2OCOPh$ (0.72 g, 93%), m.p. 139°C; δ(H) 0.35 (s, 27 H, $SiMe_3$), 0.70 (s, 6 H, $SiMe_2$), and 7.39–8.12 ppm (m, 5 H, C_6H_5); m/z (EI), 395 (20%, $[M-Me]^+$), 105 (100, $[COPh]^+$); m/z (CI) 413 (25%, $[M-Me-NH_4]^+$), 396 (100, $[M-Me+H]^+$), 105 (50) (Found: C, 55.3; H, 9.4. $C_{19}H_{38}O_2Si_4$ calcd.: C, 55.6; H, 9.3%).

(v) A mixture of I (0.21 g) and $4\text{-}O_2NC_6H_4$ COCl (4 g) was kept at 100°C for 4 h, then cooled and stirred with an excess of aqueous $NaHCO_3$. Extraction with light petroleum (b.p. 60–80°C), followed by drying ($MgSO_4$) and evaporation of the extract left a solid, which was sublimed (100°C/0.1 mmHg) to give $TsiSiMe_2OCOC_6H_4NO_2$-4 (0.25 g, 80%), m.p. 97°C; δ(H) 0.34 (s, 27 H, $SiMe_3$), 0.70 (s, 6 H, $SiMe_2$), and 8.2–8.4 ppm (m, 4H, C_6H_4); ν(C=O) 1705 cm^{-1}; m/z (CI) 440 (45%, $[M-Me]^+$), 275 (20, $[M-OCOC_6H_4NO_2-Me]^+$, 120 (100), 73 (60) (Found: C, 50.1; H, 8.2; N, 3.2. $C_{19}H_{37}O_4NSi_4$ calcd.; C, 50.1; H, 8.1; N, 3.1%).

(vi) A mixture of I (0.25 g) and 3,5-$(O_2N)_2C_6H_3COCl$ (0.8 g) was kept at 150°C for 4 h. Work up as in (v), but with sublimation at 130°C/0.2 mmHg, gave $TsiSiMe_2OCOC_6H_3(NO_2)_2$-3,5 (0.36 g, 83%), m.p. 109°C; δ(H) 0.37 (s, 27 H, $SiMe_3$), 0.74 (s, 6 H, $SiMe_2$), and 9.23–9.42 ppm (m, 3 H, C_6H_3); ν(C=O) 1715 cm^{-1}; m/z (EI) 485 (100, $[M-Me]^+$) (Found: C, 45.5; H, 7.1; N, 5.7. $C_{19}H_{36}N_2O_6Si_4$ calcd.: C, 45.6; H, 7.4: N, 5.6%).

Reactions of I with anhydrides, $(RCO)_2O$

(i) A mixture of I (0.51 g) and $(MeCO)_2O$ (10 cm^3) was refluxed. Monitoring by ^1H NMR spectroscopy indicated that 10 h were required for complete reaction. Volatile material was removed under reduced pressure, and the residue was sublimed (115°C/0.1 mmHg) to give $TsiSiMe_2OCOMe$ (0.46 g, 82%), with properties identical to those listed above.

(ii) A mixture of I (0.24 g) and $(CF_3CO)_2O$ (2.0 cm^3) was gently refluxed for 4 h. Work-up as in (i) gave $TsiSiMe_2OCOCF_3$ (0.27 g, 87%), m.p. 281°C; δ(H) 0.29 (s, 27 H, $SiMe_3$) and 0.63 (s, 6H, $SiMe_2$) ppm; ν(C=O) 1770 cm^{-1}; m/z 387 (60%, $[M-Me]^+$), 201 (50, $[M-Me_3SiCOCF_3-Me]^+$), 73 (100) (Found: C, 41.4; H, 8.2. $C_{14}H_{33}F_3O_2Si_4$ calcd.: C, 41.7; H, 8.2%). The properties agree satisfactorily with those reported previously [15].

(iii) A mixture of I (0.52 g) and $(PhCO)_2O$ (4 g) was kept at 75°C for 18 h, then cooled and stirred with an excess of aqueous $NaHCO_3$ for 6 h. Extraction with light petroleum (b.p. 60–80°C), followed by washing, drying ($MgSO_4$), and evaporation of the extract left a solid, which was shown to be exclusively $TsiSiMe_2OCOPh$ (0.63 g, 91%) by comparison of its properties with those of an authentic sample.

Reactions of I with SO_2Cl_2 and $PhSO_2Cl$

(i) A solution of I (0.21 g) in SO_2Cl_2 (10 cm^3) was refluxed gently and its ^1H NMR spectrum was examined at intervals. After 4 h ca. 50% of I remained and a single new product had appeared. After 20 h reaction was effectively complete, and volatile material was removed under vacuum to leave a solid, which was sublimed (125°C/0.1 mmHg) to give $TsiSiMe_2OSO_2Cl$ (0.16 g, 57%); δ(H) 0.32 (s, 27 H, $SiMe_3$) and 0.74 ppm (s, 6 H, $SiMe_2$); m/z (EI) 389 (15%, $[M-Me]^+$), 309 (80, $[M-SO_3-Me]^+$), 275 (50, $[M-OSO_2Cl-Me]^+$), 73 (100) (Found: C, 35.3; H, 8.0. $C_{12}H_{33}ClO_3SSi_4$ calcd.: C, 35.6; H, 8.2%).

(ii) When a mixture of I (0.23 g) and $PhSO_2Cl$ (5 cm^3) was kept at 130°C for 16 h the ^1H NMR spectrum of the solution indicated that no reaction had occurred.

A solution of I (0.25 g, 0.82 mmol) in Et_2O (5 cm^3) was treated with MeLi (1.3 mmol) in Et_2O (1 cm^3). The mixture was refluxed for 3 h (probably unnecessarily) then $PhSO_2Cl$ (0.5 cm^3) was added dropwise. The mixture was stirred for 30 min then filtered, and the filtrate was evaporated under reduced pressure to leave an oil, which solidified when kept under high vacuum for 3 d. The ^1H NMR spectrum of the product indicated that it contained I and another $TsiSiMe_2X$ species in ca. 1/4 ratio. The solid was washed with a minimum of cold MeOH to dissolve out the silanol, and the residue was dried under vacuum and then sublimed to give $TsiSiMe_2OSO_2Ph$ (0.21 g, 57%), m.p. 114°C; δ(H) 0.17 (s, 27 H, $SiMe_3$), 0.64 (s, 6 H, $SiMe_2$) and 7.5–8.0 ppm (m, 5 H, C_6H_5); m/z (EI) 431 (100%, $[M-Me]^+$), 275 (10 $[M-OSO_2Ph-Me]^+$); m/z (CI) 464 (100%, $[M+NH_3+H]^+$), 431 (70, $[M-Me]^+$), 291 (80) (Found: C, 48.8; H, 8.8. $C_{18}H_{38}O_3SSi_4$ calcd.: C, 48.4; H, 8.5%).

Preparation of $TsiSi(OH)_3$ *(II)*

(a) A solution of ICl (3.2 g, 0.019 mol) in CCl_4 (250 cm^3) was added dropwise to a solution of $TsiSiH_3$ [6] (5.0 g, 0.019 mol) in CCl_4 (60 cm^3). The solvent was removed under vacuum and the residue was sublimed (130°C/0.1 mmHg) to give $TsiSiH_2I$ (6.6 g, 90%), m.p. 272°C (lit. [6], m.p. 273°C).

(b) A solution of $TsiSiH_2I$ (6.6 g) in a mixture of Me_2SO (66.5 cm^3) and H_2O (3.5 cm^3) was stirred at room temperature for 15 min and an excess of water was then added. Extraction with light petroleum (b.p. 40–60°C) (100 cm^3) followed by washing, drying ($MgSO_4$), and evaporation of the extract, and sublimation of the residue (120°C/0.2 mmHg) gave $TsiSiH_2OH$ (3.2 g, 82%), m.p. 298°C; δ 0.23 (s, 27 H, $SiMe_3$) 1.43 (br s, 1 H, SiOH) and 4.78 ppm (s, 2H, SiH_2); ν(SiH) 2125 cm^{-1}, ν(SiOH) 3680 cm^{-1}; m/z (EI) 263 (75; $[M-Me]^+$), 261 (100, $[M-OH]^+$) (Found: C, 42.8; H, 10.5. $C_{10}H_{30}OSi_4$ calcd.: C, 43.2; H, 10.8%).

(c) A mixture of $TsiSiH_2OH$ (7.0 g, 0.025 mol) and I_2 (7.8 g, 0.031 mol) in CCl_4 (100 cm^3) was stirred at room temperature for 3 h. The solvent was removed under vacuum and the solid residue was shaken with aqueous $NaHSO_3$. Extraction with CH_2Cl_2, followed by evaporation of the extract and sublimation (130°C/0.1 mmHg) gave TsiSiH(OH)I (8.7 g, 86%), m.p. 231°C; δ(H) 0.25 (s, 27 H, $SiMe_3$), 1.46 (br s, 1 H, OH) and 4.68 ppm (s, 1H, SiH); m/z (EI) 403 (5, $[M-H]^+$), 387 (10, $[M-OH]^+$), 277 (85, $[M-I]^+$), 261 (90, $[M-HI-Me]^+$), 73 (100); m/z (CI) 438 (85, $[M+2NH_3]^+$ (?)), 422 (25, $[M+NH_3+H]^+$), 277 (100), $[M-I]^+$) (Found: C, 30.0; H, 7.3. $C_{10}H_{29}IOSi_4$ calcd.: C, 29.7; H, 7.2%).

(d) A solution of TsiSiH(OH)I (10 g) in a mixture of Me_2SO (490 cm^3) and H_2O (10 cm^3) was kept at 150°C for 10 min. It was allowed to cool to room temperature and an excess of water was added. Extraction with $CHCl_3$, followed by washing, drying ($MgSO_4$), and evaporation of the extract left a residue, which was recrystallized from n-hexane then sublimed (130°C/0.1 mmHg) to give $TsiSi(OH)_3$ (6.9 g, 93%), m.p. 285–290°C (decomp; δ(H) 0.28 (s, 27 H, $SiMe_3$) and 4.30 (br s, 3 H, OH); ν(OH) 3425(br) cm^{-1}; m/z (EI) 295 (10%, $[M-Me]^+$), 277 (100, $[M-H_2O-Me]^+$); m/z (CI) 328 (100, $[M+NH_3+H]^+$), 295 (15), 277 (55) (Found: C, 38.6; H, 9.4. $C_{10}H_{30}O_3Si_4$ calcd.: C, 38.7; H, 9.6%).

(e) A mixture of TsiSiH(OH)I (3.0 g, 7.4 mmol) and $AgClO_4$ (1.6 g, 7.7 mmol) in light petroleum (b.p. 30–40°C) (80 cm^3) was shaken vigourously for 5 min, then washed with water. Dioxane (100 cm^3) was added and the petroleum was distilled off under vacuum. Water (3 cm^3) was added, the mixture was stirred for 30 min at room temperature, then an excess of water was added. Extraction with $CHCl_3$, followed by washing, drying ($MgSO_4$) and evaporation of the extract, left a solid, which was recrystallized from hexane then sublimed (120°C/0.1 mmHg) to give $TsiSi(OH)_3$ (2.2 g, 95%) with properties identical to those described above.

(*Note.* This elaborate procedure may be unnecessary; it would probably be sufficient to treat TsiSiH(OH)I with $AgClO_4$ in dioxane containing water.)

Reactions of $TsiSi(OH)_3$ with RCOCl and $(RCO)_2O$

(i) A solution of II (0.4 g) in MeCOCl (20 cm^3) was refluxed for 2 h. The MeCOCl was distilled off and the residue was kept under vacuum for 0.5 h then sublimed (120°C/0.1 mmHg) to give $TsiSi(OCOMe)_3$ (0.54 g, 95%), m.p. 281°C; δ(H) 0.30 (s, 27 H, $SiMe_3$) and 2.10 ppm (s, 9 H, CMe); ν(C=O) 1752 cm^{-1}; *m/z* (EI), 421 (100%, $[M-Me]^+$, 379 (80, $[M-COMe-Me]^+$), 337 (95, $[M-2COMe-Me]^+$); 277 (95, $[M-2COMe-O_2CMe-Me]^+$); *m/z* (CI) 456 (5%, $[M+NH_3+H]^+$), 437 (100, $[M+H]^+$), 421 (30) (Found: C, 44.0; H, 8.0. $C_{16}H_{36}O_6Si_4$ calcd.: C, 44.0; H, 8.2%).

(ii) A mixture of II (0.20 g) and $(MeCO)_2O$ (15 cm^3) was refluxed for 4 h. The $(MeCO)_2O$ was then distilled off, and the residue was sublimed (125°C/0.1 mmHg) to give exclusively $TsiSi(OCOMe)_3$, which had properties identical to those listed above.

(iii) A procedure similar to that described under (i) above, but starting from EtCOCl, and with reflux for 8 h and final sublimation at 130°C/0.1 mmHg, gave exclusively $TsiSi(OCOEt)_3$, m.p. 165°C; δ(H) 0.28 (s, 27 H, $SiMe_3$), 1.1 (t, 9 H, CCH_3) and 2.4 ppm (q, 6 H, CH_2); ν(C=O) 1750 cm^{-1}; *m/z* (EI) 463 (100%, $[M-Me]^+$), 407 (65, $[M-COEt-Me]^+$) (Found: C, 48.0; H, 8.3. $C_{19}H_{42}O_6Si_4$ calcd.: C, 47.8; H, 8.7%).

(iv) A solution of II (0.23 g) in $ClCH_2COCl$ (10 cm^3) was refluxed for 3 d then the solvent was removed. The residue crystallized upon addition of CH_2Cl_2, and was sublimed (140°C/0.01 mmHg). The ^1H NMR spectrum of the product showed only one peak in the SiMe region, but the IR spectrum showed three CO bands, at 1710, 1750, and 1780 cm^{-1} (as well as a broad OH band at 3400 cm^{-1}), indicating that it was a mixture. Analysis by GC/MS indicated that it was a mixture of three components in 4/2/1 ratio; these were, respectively: $TsiSi(OH)_2(OCOCH_2Cl)$, *m/z* (EI) 371 (100%, $[M-Me]^+$), 277 (75, $[M-OCOCH_2Cl-OH]^+$); $TsiSi(OH)(OCOCH_2Cl)_2$, *m/z* 447 (100%, $[M-Me]^+$); $TsiSi(OCOCH_2Cl)_3$, *m/z* 523 (100%, $[M-Me]^+$).

(v) A solution of II (0.21 g) in $(CF_3CO)_2O$ (2.5 cm^3) was refluxed gently for 3 d. The solvent was removed under vacuum, and the residue was recrystallized from n-pentane then sublimed (130°C/0.01 mmHg) to give $TsiSi(OH)_2(OCOCF_3)$ (0.26 g, 86%), m.p. 141°C; δ(H) 0.31 (s, 27 H, $SiMe_3$) and 3.44 ppm (br s, 2 H, OH); *m/z* (EI) 391 (35%, $[M-Me]^+$), 277 (100, $[M-CF_3CO_2H-Me]^+$); *m/z* (CI), 424 (100%, $[M+NH_3+H]^+$), 391 (80), 277 (95).

(vi) A solution of II (0.30 g) in PhCOCl (10 cm^3) was refluxed gently and its ^1H NMR spectrum was recorded at intervals. This showed that reaction was complete after 10 h, and the excess of PhCOCl was distilled off; the residue was kept under high vacuum for 2 h then sublimed (130°C/0.01 mmHg) to give $TsiSi(OCOPh)_3$ (0.53 g, 87%), m.p. 167°C; δ(H) 0.45 (s, 27 H, $SiMe_3$) and 7.35 – 8.2 ppm (m, 15 H, C_6H_5); ν(C=O) 1725 cm^{-1}; *m/z* (EI) 607 (80%, $[M-Me]^+$), 381 (15, $[M-(PhCO)_2O-Me]^+$), 105 (100, $[COPh]^+$) (Found: C, 59.5; H, 6.9. $C_{31}H_{42}O_6Si_4$ calcd.: C, 59.8; H, 6.8%).

(vii) A mixture of II (0.21 g) and $(PhCO)_2O$ (3 g) was kept at 80°C for 20 h, then added to an excess of aqueous $NaHCO_3$. The mixture was stirred for 4 h then extracted with light petroleum (b.p. 60–80°). The extract was washed, dried ($MgSO_4$), and evaporated under vacuum, to leave exclusively $TsiSi(OCOPh)_3$, with properties identical to those listed above.

Conversion of $TsiSi(OH)_3$, (II), into $TsiSi(OSiMe_3)_3$

(i) A mixture of II (0.2 g) and Me_3SiCl (15 cm^3) was refluxed and its ^1H NMR spectrum was recorded at intervals. After 24 h the signal from II at δ 0.26 ppm was still present, along with three new signals at δ 0.24, 0.21 and 0.18 ppm. After 4 d these four peaks were present in 3/4/1/1 height ratio. After 20 d the Me_3SiCl was distilled off and the residue was kept under vacuum for 12 h. The ^1H NMR spectrum then showed the three signals at 0.24, 0.21, and 0.18 ppm in 4/1/2 ratio.

(ii) A solution of $AgClO_4$ (0.89 g, 4.3 mmol) in PhH (20 cm^3) was added to a solution of II (0.20 g, 0.64 mmol) in Me_3SiCl (0.50 g, 4.8 mmol). The mixture was refluxed gently with stirring for 6 h, then the solution was decanted from the AgCl, shaken several times with H_2O, dried ($MgSO_4$), and evaporated under vacuum. The solid residue was recrystallized from n-pentane then sublimed (115°C/0.2 mmHg) to give $TsiSi(OSiMe_3)_3$ (0.29 g, 85%), m.p. 305°C; δ(H) ($CDCl_3$) 0.47 (s, 27 H, $SiMe_3$), 0.48 (s, 27 H, $SiMe_3$); *m/z* (EI) 511 (40%, $[M-Me]^+$), 147 (20, $[Me_3SiOSiMe_2]^+$), 73 (100) (Found: C, 43.0; H, 9.9. $C_{19}H_{54}O_3Si_7$ calcd.: C, 43.3; H, 10.2%).

(iii) A solution of II (50 mg) in Me_3SiI (2 cm^3) containing $(Me_3Si)_2NH$ (ca. 0.4 cm^3) was kept at 52°C for 3 d. The solvent was then removed under vacuum, and the residue sublimed (110°C/0.2 mmHg) to give exclusively $TsiSi(OSiMe_3)_3$, with properties identical to those listed above.

Other reactions of $TsiSi(OH)_3$ (II)

(i) When a sample of II in an open capillary tube was heated in a melting point apparatus, melting took place at 285–290°C with vigorous evolution of gas. The sample was kept at 300°C for 3 min then cooled to room temperature. It did not solidify.

(ii) A sample of II was kept at 315°C in a sealed capillary tube for 1 h then cooled to room temperature. When the tube was opened gas was evolved. The ^1H NMR spectrum of the oily residue showed that three major components were present: (a) (apparently $(Me_3Si)_3CH$), *m/z* 217 (100%, $[M-Me]^+$), 129 (60, $[M-Me_4Si-Me]^+$), 73 (50); (b) ($(Me_3Si)_2CHSi(OH)_2(OSiMe_3)$ or an isomer), *m/z* 296 (25%, $[M-Me]^+$), 279 (100, $[M-MeH-Me]^+$), 205 (40, $[M-Me_3SiOH-Me]^+$), 73 (35); (c) (unidentified), *m/z* 367 (30%), 295 (15), 279 (80), 207 (40), 147 (30), 73 (100).

(iii) A solution of II (0.4 g) in 1.5 *M* NaOMe in MeOH (5 cm^3) was kept at 52°C for 3 d then cooled to room temperature. Hexane was added, followed by an excess of water. The organic layer was separated, washed, dried ($MgSO_4$), and evaporated under vacuum to leave an oil, the ^1H NMR spectrum of which showed a large somewhat broad peak at δ 0.12 ppm and other substantial peaks at δ 0.30 and 3.52 ppm. Analysis by GC/MS showed that the oil contained five major compounds A, B, C, D, and E in ca. 3/4/2/2/2 ratio, and with *m/z*: (A) (apparently TsiH), 217 (100%, $[M-Me]^+$), 129 (50, $[M-SiMe_4-Me]^+$), 73 (75); (B) ($(Me_3Si)_2CHSi(OMe)_3$ or an isomer), 265 (20%, $[M-Me]^+$), 219 (100, $[M-Me_2O-Me]^+$); (C) ($(Me_3Si)_2CHSi(OH)_2(OMe)$ or an isomer), 237 (15%, $[M-Me]^+$), 219 (100, $[M-H_2O-Me]^+$), 205 (60, $[M-Me_2O-Me]^+$); (D) 325 (25%), 309 (40), 293 (25), 277 (100), 248 (25), 219 (50), 189 (50), 129 (40), 73 (95); (E) 382 (100%), 277 (25), 219 (10), 73 (75).

Attempted hydrolysis of $TsiSiMe_2OSO_2Ph$

A solution of $TsiSiMe_2OSO_2Ph$ (10 mg) in 2% H_2O in MeCN (1 cm^3) in an NMR tube was kept at 60°C for 24 h. The ^{1}H NMR spectrum indicated that no reaction had taken place.

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