

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

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Summary

The silanol $\text{TsiSiMe}_2\text{OH}$ ($\text{Tsi} = (\text{Me}_3\text{Si})_3\text{C}$) has been made by hydrolysis of the iodide $\text{TsiSiMe}_2\text{I}$ in H_2O /dioxane or $\text{H}_2\text{O}/\text{Me}_2\text{SO}$. It has been shown to react with some acid chlorides RCOCl ($\text{R} = \text{Me}$, Et , ClCH_2 , Ph , $4\text{-O}_2\text{NC}_6\text{H}_4$, and $3,5\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3$) and anhydrides $(\text{RCO})_2\text{O}$ ($\text{R} = \text{Me}$, CF_3 , or Ph) to give the carboxylates $\text{TsiSiMe}_2\text{OCOR}$, and with SO_2Cl_2 to give $\text{TsiSiMe}_2\text{OSO}_2\text{Cl}$. The triol TsiSi(OH)_3 has been made by treatment of TsiSiH(OH)I with $\text{H}_2\text{O}/\text{Me}_2\text{SO}$ at 150°C or with a mixture of aqueous AgClO_4 and an organic solvent. The triol has been shown to react with RCOCl ($\text{R} = \text{Me}$, Et , or Ph) or $(\text{RCO})_2\text{O}$ ($\text{R} = \text{Ph}$) to give the corresponding TsiSi(OCOR)_3 , with $(\text{CF}_3\text{CO})_2\text{O}$ to give $\text{TsiSi(OH)}_2(\text{OCOCF}_3)$, and with a mixture of Me_3SiCl and AgClO_4 in benzene or one of Me_3SiI and $(\text{Me}_3\text{Si})\text{NH}$ to give $\text{TsiSi(OSiMe}_3)_3$. The triol is unusually stable, but decomposes at its m.p. of $285\text{--}290^\circ\text{C}$.

Introduction

Some preparations and reactions of the silanol $\text{TsiSiMe}_2\text{OH}$ (I) ($\text{Tsi} = (\text{Me}_3\text{Si})_3\text{C}$) 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. $\text{TsiSiMe}_2\text{OH}$ (I)

It was found that the iodide $\text{TsiSiMe}_2\text{I}$, although reacting only very slowly with MeOH [5], could be converted into the hydroxide I by treatment with 5% H_2O in

dioxane for 16 h under reflux or with 5% H₂O in Me₂SO 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 TsiSiMe₂OCOMe [2], and we have now extended this reaction to the preparation of related TsiSiMe₂OCOR species, with R = Et, ClCH₂, Ph, C₆H₄NO₂-4, and C₆H₃(NO₂)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, ClCH₂, 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 = C₆H₄NO₂-4 was carried out at 100°C (i.e. above the melting point of the chloride) for 4 h, and that for R = C₆H₃(NO₂)₂-3,5 at 150°C for 4 h.

The silanol I was also converted into TsiSiMe₂OCOR with R = Me, CF₃, or Ph by reaction with the corresponding anhydride. The reactions were slower than those with the acyl chloride; for R = Me and R = CF₃ 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 PhSO₂Cl at 130°C for 10 h. The benzenesulphonate TsiSiMe₂OSO₂Ph was made, however, by treating I with MeLi in Et₂O to give TsiSiMe₂OLi and then adding PhSO₂Cl. The benzenesulphonate was found to be less reactive than the iodide TsiSiMe₂I in hydrolysis; no detectable reaction took place when its solution in 2% H₂O in MeCN was kept at 60°C for 24 h.

2. TsiSi(OH)₃ (II)

The starting point for the preparation of II was TsiSiH₃ [6]. This was treated with ICl in CCl₄ to give TsiSiH₂I, which was hydrolysed with 10% H₂O in Me₂SO to give TsiSiH₂(OH). Reaction of the latter with I₂ in CCl₄ 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% H₂O in Me₂SO 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 possibly 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 AgClO₄ 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 ClCH₂COCl for 3 d gave a mixture of TsiSi(OH)_n(OCOCH₂Cl)_{3-n} compounds with *n* = 0-2, and refluxing with (CF₃CO)₂O for 3 d gave a good yield of the mono-trifluoroacetoxy compound TsiSi(OH)₂(OCOCF₃).

The triol II was converted into the tris-siloxy compound TsiSi(OSiMe₃)₃ by treatment with Me₃SiCl in the presence of AgClO₄ in PhH or MeCN, the perchlorate Me₃SiOClO₃ presumably being the effective reagent. Triol II reacted slowly

* 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 $\text{TsiSi}(\text{OSiMe}_3)_3$ was also brought about by Me_3SiI in the presence of $(\text{Me}_3\text{Si})_2\text{NH}$.

Compound II is exceptionally thermally stable for a triol. Some triols are known, e.g. $\text{PhSi}(\text{OH})_3$ [9] and $\text{cyclo-C}_6\text{H}_{11}\text{Si}(\text{OH})_3$ [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 $(\text{Me}_3\text{Si})_2\text{-CHSi}(\text{OH})_2\text{OSiMe}_3$ 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 $(\text{Me}_3\text{Si})_2\text{CHSi}(\text{OH})_2\text{OSiMe}_3$ 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 $\text{C}(\text{SiMe}_2\text{OH})_4$ alone [12] or $\text{TsiSiPh}_2\text{OH}$ 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 , $(\text{Me}_3\text{Si})_2\text{CHSi}(\text{OSiMe}_3)_3$ (or an isomer), and $(\text{Me}_3\text{Si})_2\text{CHSi}(\text{OMe})(\text{OH})_2$ (or an isomer). The formation of TsiH is not surprising, in view of the fact that $\text{TsiSiMe}_2\text{H}$ 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 $\text{TsiSi}(\text{OH})_2\text{O}^-$ may be followed by expulsion of Tsi^- (which would then rapidly acquire a proton from the solvent) and transient formation of $(\text{HO})_2\text{Si}=\text{O}$ (cf. ref. 8). The ion $\text{TsiSi}(\text{OH})_2\text{O}^-$ can also be expected to undergo rearrangement to give after protonation $(\text{Me}_3\text{Si})_2\text{CH}(\text{OH})_2\text{OSiMe}_3$, and reaction of the latter with MeOH would ultimately give the species $(\text{Me}_3\text{Si})_2\text{CHSi}(\text{OMe})_n(\text{OH})_{3-n}$, 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 $\text{TsiSiMe}_2\text{OH}$ (I)

(i) A solution of $\text{TsiSiMe}_2\text{I}$ [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 ($120^\circ\text{C}/0.1\text{ mmHg}$) to give **I** (5.6 g, 95%), m.p. 325°C ; $\delta(\text{H})$ 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%, $[\text{M} - \text{Me}]^+$), 275 (100, $[\text{M} - \text{MeH} - \text{Me}]^+$), 259 (65, $[\text{M} - 2\text{MeH} - \text{Me}]^+$); $\nu(\text{OH})$ 3670 cm^{-1} (Found: C, 47.3; H, 11.1 $\text{C}_{12}\text{H}_{34}\text{OSi}_4$ 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 ($110^\circ\text{C}/0.1\text{ mmHg}$) to give $\text{TsiSiMe}_2\text{OCOME}$ (0.62 g, 92%), m.p. 312°C ; $\delta(\text{H})$ 0.26 (s, 27 H, SiMe_3), 0.52 (s, 6 H, SiMe_2), and 2.0 ppm (s, 3 H, COME); $\nu(\text{C}=\text{O})$ 1723 cm^{-1} ; m/z 333 (100%, $[\text{M} - \text{Me}]^+$), 291 (65, $[\text{M} - \text{CH}_2\text{CO} - \text{Me}]^+$), 275 (75, $[\text{M} - \text{Me}_2\text{CO} - \text{Me}]^+$), 259 (65, $[\text{M} - \text{Me}_2\text{CO} - \text{MeH} - \text{Me}]^+$); m/z (CI), 349 (35%, $[\text{M} + \text{H}]^+$), 333 (100, $[\text{M} - \text{Me}]^+$) (Found: C, 48.0; H, 10.1. $\text{C}_{14}\text{H}_{36}\text{O}_2\text{Si}_4$ calcd.: C, 48.2; H, 10.4%). The ^1H 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 ($120^\circ\text{C}/0.1\text{ mmHg}$) to give $\text{TsiSiMe}_2\text{OCOEt}$ (0.54 g, 90%); m.p. 204°C ; $\delta(\text{H})$ 0.26 (s, 27 H, SiMe_3), 0.54 (s, 6 H, SiMe_2), 1.1 (tr, 3 H, CH_2Me), and 2.25 ppm (q, 2 H, CH_2); $\nu(\text{C}=\text{O})$ 1720 cm^{-1} ; m/z 347 (40%, $[\text{M} - \text{Me}]^+$), 291 (25%, $[\text{M} - \text{CH}_3\text{CHCO} - \text{Me}]^+$), 275 (25, $[\text{M} - \text{MeCOEt} - \text{Me}]^+$), and 73 (100, $[\text{Me}_3\text{Si}]^+$) (Found: C, 49.7; H, 10.8. $\text{C}_{15}\text{H}_{38}\text{Si}_4\text{O}_2$ 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 ($140^\circ\text{C}/0.2\text{ mmHg}$) to give $\text{TsiSiMe}_2\text{OCOCH}_2\text{Cl}$ (0.28 g, 80%), m.p. 252°C ; $\delta(\text{H})$ 0.29 (s, 27 H, SiMe_3), 0.60 (s, 6 H, SiMe_2), and 3.93 ppm (s, 2 H, CH_2); $\nu(\text{C}=\text{O})$ 1745 cm^{-1} ; m/z (EI) 367 (50%, $[\text{M} - \text{Me}]^+$), 289 (25, $[\text{M} - \text{OCOCH}_2\text{Cl}]^+$), 275 (20, $[\text{M} - \text{OCOCH}_2\text{Cl} - \text{Me}]^+$), 201 (20, $[\text{M} - \text{Me}_3\text{SiOCOCH}_2\text{Cl} - \text{Me}]^+$), 73 (100%); m/z (CI) 400 (25, $[\text{M} + \text{H} + \text{NH}_3]^+$), 367 (90, $[\text{M} - \text{Me}]^+$), 306 (100, $[\text{M} - \text{OCOCH}_2\text{Cl} + \text{NH}_3]^+$), 275 (65, $[\text{M} - \text{OCOCH}_2\text{Cl} - \text{Me}]^+$) (Found: C, 44.3; H, 9.4. $\text{C}_{14}\text{H}_{35}\text{ClO}_2\text{Si}_4$ 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 ^1H 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 ($135^\circ\text{C}/0.1\text{ mmHg}$) to give $\text{TsiSiMe}_2\text{OCOPh}$ (0.72 g, 93%), m.p. 139°C ; $\delta(\text{H})$ 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%, $[\text{M} - \text{Me}]^+$), 105 (100, $[\text{COPh}]^+$); m/z (CI) 413 (25%, $[\text{M} - \text{Me} - \text{NH}_4]^+$), 396 (100, $[\text{M} - \text{Me} + \text{H}]^+$), 105 (50) (Found: C, 55.3; H, 9.4. $\text{C}_{19}\text{H}_{38}\text{O}_2\text{Si}_4$ calcd.: C, 55.6; H, 9.3%).

(v) A mixture of **I** (0.21 g) and $4\text{-O}_2\text{NC}_6\text{H}_4\text{COCl}$ (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 $\text{TsiSiMe}_2\text{OCOC}_6\text{H}_4\text{NO}_2$ -4 (0.25 g, 80%), m.p. 97°C; $\delta(\text{H})$ 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); $\nu(\text{C}=\text{O})$ 1705 cm^{-1} ; m/z (CI) 440 (45%, $[\text{M} - \text{Me}]^+$), 275 (20, $[\text{M} - \text{OCOC}_6\text{H}_4\text{NO}_2 - \text{Me}]^+$), 120 (100), 73 (60) (Found: C, 50.1; H, 8.2; N, 3.2. $\text{C}_{19}\text{H}_{37}\text{O}_4\text{NSi}_4$ calcd.: C, 50.1; H, 8.1; N, 3.1%).

(vi) A mixture of I (0.25 g) and 3,5-(O_2N) $_2\text{C}_6\text{H}_3\text{COCl}$ (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 $\text{TsiSiMe}_2\text{OCOC}_6\text{H}_3(\text{NO}_2)_2$ -3,5 (0.36 g, 83%), m.p. 109°C; $\delta(\text{H})$ 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); $\nu(\text{C}=\text{O})$ 1715 cm^{-1} ; m/z (EI) 485 (100, $[\text{M} - \text{Me}]^+$) (Found: C, 45.5; H, 7.1; N, 5.7. $\text{C}_{19}\text{H}_{36}\text{N}_2\text{O}_6\text{Si}_4$ calcd.: C, 45.6; H, 7.4; N, 5.6%).

Reactions of I with anhydrides, (RCO) $_2\text{O}$

(i) A mixture of I (0.51 g) and $(\text{MeCO})_2\text{O}$ (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 $\text{TsiSiMe}_2\text{OCOME}$ (0.46 g, 82%), with properties identical to those listed above.

(ii) A mixture of I (0.24 g) and $(\text{CF}_3\text{CO})_2\text{O}$ (2.0 cm^3) was gently refluxed for 4 h. Work-up as in (i) gave $\text{TsiSiMe}_2\text{OCOCF}_3$ (0.27 g, 87%), m.p. 281°C; $\delta(\text{H})$ 0.29 (s, 27 H, SiMe_3) and 0.63 (s, 6H, SiMe_2) ppm; $\nu(\text{C}=\text{O})$ 1770 cm^{-1} ; m/z 387 (60%; $[\text{M} - \text{Me}]^+$), 201 (50, $[\text{M} - \text{Me}_3\text{SiCOCF}_3 - \text{Me}]^+$), 73 (100) (Found: C, 41.4; H, 8.2. $\text{C}_{14}\text{H}_{33}\text{F}_3\text{O}_2\text{Si}_4$ 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 $(\text{PhCO})_2\text{O}$ (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 $\text{TsiSiMe}_2\text{OCOPh}$ (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 $\text{TsiSiMe}_2\text{OSO}_2\text{Cl}$ (0.16 g, 57%); $\delta(\text{H})$ 0.32 (s, 27 H, SiMe_3) and 0.74 ppm (s, 6 H, SiMe_2); m/z (EI) 389 (15%, $[\text{M} - \text{Me}]^+$), 309 (80, $[\text{M} - \text{SO}_3 - \text{Me}]^+$), 275 (50, $[\text{M} - \text{OSO}_2\text{Cl} - \text{Me}]^+$), 73 (100) (Found: C, 35.3; H, 8.0. $\text{C}_{12}\text{H}_{33}\text{ClO}_3\text{SSi}_4$ 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 $\text{TsiSiMe}_2\text{X}$ 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 TsiSiMe₂OSO₂Ph (0.21 g, 57%), m.p. 114°C; δ (H) 0.17 (s, 27 H, SiMe₃), 0.64 (s, 6 H, SiMe₂) and 7.5–8.0 ppm (m, 5 H, C₆H₅); m/z (EI) 431 (100%, [M – Me]⁺), 275 (10 [M – OSO₂Ph – Me]⁺); m/z (CI) 464 (100%, [M + NH₃ + H]⁺), 431 (70, [M – Me]⁺), 291 (80) (Found: C, 48.8; H, 8.8. C₁₈H₃₈O₃SSi₄ 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 CCl₄ (250 cm³) was added dropwise to a solution of TsiSiH₃ [6] (5.0 g, 0.019 mol) in CCl₄ (60 cm³). The solvent was removed under vacuum and the residue was sublimed (130°C/0.1 mmHg) to give TsiSiH₂I (6.6 g, 90%), m.p. 272°C (lit. [6], m.p. 273°C).

(b) A solution of TsiSiH₂I (6.6 g) in a mixture of Me₂SO (66.5 cm³) and H₂O (3.5 cm³) 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 cm³) followed by washing, drying (MgSO₄), and evaporation of the extract, and sublimation of the residue (120°C/0.2 mmHg) gave TsiSiH₂OH (3.2 g, 82%), m.p. 298°C; δ 0.23 (s, 27 H, SiMe₃) 1.43 (br s, 1 H, SiOH) and 4.78 ppm (s, 2H, SiH₂); 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. C₁₀H₃₀OSi₄ calcd.: C, 43.2; H, 10.8%).

(c) A mixture of TsiSiH₂OH (7.0 g, 0.025 mol) and I₂ (7.8 g, 0.031 mol) in CCl₄ (100 cm³) was stirred at room temperature for 3 h. The solvent was removed under vacuum and the solid residue was shaken with aqueous NaHSO₃. Extraction with CH₂Cl₂, 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, SiMe₃), 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 + 2NH₃]⁺ (?)), 422 (25, [M + NH₃ + H]⁺), 277 (100), [M – I]⁺) (Found: C, 30.0; H, 7.3. C₁₀H₂₉IOSi₄ calcd.: C, 29.7; H, 7.2%).

(d) A solution of TsiSiH(OH)I (10 g) in a mixture of Me₂SO (490 cm³) and H₂O (10 cm³) 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 CHCl₃, followed by washing, drying (MgSO₄), 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, SiMe₃) and 4.30 (br s, 3 H, OH); ν (OH) 3425(br) cm^{–1}; m/z (EI) 295 (10%, [M – Me]⁺), 277 (100, [M – H₂O – Me]⁺); m/z (CI) 328 (100, [M + NH₃ + H]⁺), 295 (15), 277 (55) (Found: C, 38.6; H, 9.4. C₁₀H₃₀O₃Si₄ calcd.: C, 38.7; H, 9.6%).

(e) A mixture of TsiSiH(OH)I (3.0 g, 7.4 mmol) and AgClO₄ (1.6 g, 7.7 mmol) in light petroleum (b.p. 30–40°C) (80 cm³) was shaken vigorously for 5 min, then washed with water. Dioxane (100 cm³) was added and the petroleum was distilled off under vacuum. Water (3 cm³) was added, the mixture was stirred for 30 min at room temperature, then an excess of water was added. Extraction with CHCl₃, followed by washing, drying (MgSO₄) 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 AgClO₄ 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 cm³) 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; $\delta(\text{H})$ 0.30 (s, 27 H, SiMe₃) and 2.10 ppm (s, 9 H, CMe); $\nu(\text{C}=\text{O})$ 1752 cm⁻¹; m/z (EI), 421 (100%, [M - Me]⁺), 379 (80, [M - COMe - Me]⁺), 337 (95, [M - 2COMe - Me]⁺); 277 (95, [M - 2COMe - O₂CMe - Me]⁺); m/z (CI) 456 (5%, [M + NH₃ + H]⁺), 437 (100, [M + H]⁺), 421 (30) (Found: C, 44.0; H, 8.0. C₁₆H₃₆O₆Si₄ calcd.: C, 44.0; H, 8.2%).

(ii) A mixture of II (0.20 g) and (MeCO)₂O (15 cm³) 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; $\delta(\text{H})$ 0.28 (s, 27 H, SiMe₃), 1.1 (t, 9 H, CCH₃) and 2.4 ppm (q, 6 H, CH₂); $\nu(\text{C}=\text{O})$ 1750 cm⁻¹; m/z (EI) 463 (100%, [M - Me]⁺), 407 (65, [M - COEt - Me]⁺) (Found: C, 48.0; H, 8.3. C₁₉H₄₂O₆Si₄ calcd.: C, 47.8; H, 8.7%).

(iv) A solution of II (0.23 g) in ClCH₂COCl (10 cm³) was refluxed for 3 d then the solvent was removed. The residue crystallized upon addition of CH₂Cl₂, 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(OCOCH₂Cl), m/z (EI) 371 (100%, [M - Me]⁺), 277 (75, [M - OCOCH₂Cl - OH]⁺); TsiSi(OH)(OCOCH₂Cl)₂, m/z 447 (100%, [M - Me]⁺); TsiSi(OCOCH₂Cl)₃, m/z 523 (100%, [M - Me]⁺).

(v) A solution of II (0.21 g) in (CF₃CO)₂O (2.5 cm³) 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(OCOCF₃) (0.26 g, 86%), m.p. 141°C; $\delta(\text{H})$ 0.31 (s, 27 H, SiMe₃) and 3.44 ppm (br s, 2 H, OH); m/z (EI) 391 (35%, [M - Me]⁺), 277 (100, [M - CF₃CO₂H - Me]⁺); m/z (CI), 424 (100%, [M + NH₃ + H]⁺), 391 (80), 277 (95).

(vi) A solution of II (0.30 g) in PhCOCl (10 cm³) 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; $\delta(\text{H})$ 0.45 (s, 27 H, SiMe₃) and 7.35 - 8.2 ppm (m, 15 H, C₆H₅); $\nu(\text{C}=\text{O})$ 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. C₃₁H₄₂O₆Si₄ 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 NaHCO₃. The mixture was stirred for 4 h then extracted with light petroleum (b.p. 60-80°). The extract was washed, dried (MgSO₄), 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(OSiMe₃)₃

(i) A mixture of II (0.2 g) and Me₃SiCl (15 cm³) 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 Me₃SiCl 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 AgClO₄ (0.89 g, 4.3 mmol) in PhH (20 cm³) was added to a solution of II (0.20 g, 0.64 mmol) in Me₃SiCl (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 H₂O, dried (MgSO₄), and evaporated under vacuum. The solid residue was recrystallized from n-pentane then sublimed (115°C/0.2 mmHg) to give TsiSi(OSiMe₃)₃ (0.29 g, 85%), m.p. 305°C; δ(H) (CDCl₃) 0.47 (s, 27 H, SiMe₃), 0.48 (s, 27 H, SiMe₃); *m/z* (EI) 511 (40%, [*M* - Me]⁺), 147 (20, [Me₃SiOSiMe₂]⁺), 73 (100) (Found: C, 43.0; H, 9.9. C₁₉H₅₄O₃Si₇ calcd.: C, 43.3; H, 10.2%).

(iii) A solution of II (50 mg) in Me₃SiI (2 cm³) containing (Me₃Si)₂NH (ca. 0.4 cm³) 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(OSiMe₃)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 (Me₃Si)₃CH), *m/z* 217 (100%, [*M* - Me]⁺), 129 (60, [*M* - Me₄Si - Me]⁺), 73 (50); (b) ((Me₃Si)₂CHSi(OH)₂(OSiMe₃) or an isomer), *m/z* 296 (25%, [*M* - Me]⁺), 279 (100, [*M* - MeH - Me]⁺), 205 (40, [*M* - Me₃SiOH - 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 cm³) 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 (MgSO₄), 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* - SiMe₄ - Me]⁺), 73 (75); (B) ((Me₃Si)₂CHSi(OMe)₃ or an isomer), 265 (20%, [*M* - Me]⁺), 219 (100, [*M* - Me₂O - Me]⁺); (C) ((Me₃Si)₂CHSi(OH)₂(OMe) or an isomer), 237 (15%, [*M* - Me]⁺), 219 (100, [*M* - H₂O - Me]⁺), 205 (60, [*M* - Me₂O - 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 TsiSiMe₂OSO₂Ph

A solution of TsiSiMe₂OSO₂Ph (10 mg) in 2% H₂O in MeCN (1 cm³) in an NMR

tube was kept at 60°C for 24 h. The ^1H NMR spectrum indicated that no reaction had taken place.

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