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SOME HIGHLY STERICALLY HINDERED ORGANO-SILANOLS AND -SILOXANES

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Summary

Reaction of the iodides $TsiSiMe_2I$ and $TsiSiPh_2I$, (Tsi = $(Me_3Si)_3C$) with $AgClO_4$ in t-BuOH provides a route to the silanols $TsiSiMe_2OH$ and $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$, respectively. $TsiSiMe_2OH$ gives the disiloxane $TsiSiMe_2OSiMe_3$ when treated with either (a) $Me_3SiOClO_3$ (prepared in situ from $AgClO_4$ and Me_3SiCl) in benzene, (b) Me_3SiI (in the presence of a little $(Me_3Si)_2NH$), (c) *O,N*-bis(trimethylsilyl)acetamide, or (d) MeLi followed by Me_3SiCl. It does not react with Me_3SiCl, but with Me_2SiCl_2 gives $TsiSiMe_2OSiMe_2Cl$, and with CH_3COCl gives $TsiSiMe_2OCOCH_3$. The disiloxane is stable to methanolic acid or base, but reacts with KOH in H_2O/Me_2SO and with CF_3COOH to give $TsiSiMe_2OH$. The disiloxane $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OSiMe_3)$ is formed by treatment of $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$ with $Me_3SiI/(Me_3Si)_2NH$. Treatment of $TsiSiPhMeI$ with $AgClO_4$ in t-BuOH gives the silanols $TsiSiPhMeOH$ and $(Me_3Si)_2C(SiPhMe_2)(SiMe_2OH)$ (which with $Me_3SiI/(Me_3Si)_2NH$ give the corresponding disiloxanes) along with some of the t-butoxide $(Me_3Si)_2C(SiPhMe_2)(SiMe_2OBu^t)$.

Introduction

The highly sterically hindered silanols $TsiSiMe_2OH$ (Tsi = 'trisyl' = $(Me_3Si)_3C$) and $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$ have been made previously by treatment of the iodides $TsiSiMe_2I$ and $TsiSiPh_2I$, respectively, with $AgClO_4$ in CH_3CN ('dried' but evidently containing some water) [1,2]. The almost exclusive formation of $TsiSiMe_2OH$ upon solvolysis of the perchlorate $TsiSiMe_2OClO_3$ in MeOH containing 1% of water has also been noted [3], and this silanol has also recently been obtained by treatment of $TsiSiMe_2X$ (X = Br or Cl) in a three-phase mixture with n-Bu_4PCl, KCl, H_2O, and tetradecane at 100°C [4].

We have now found another route to $TsiSiMe_2OH$ and $(Me_3Si)_2C(SiPh_2Me)$-

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($SiMe_2OH$), and have studied some reactions of the former silanol and also the preparation and properties of the disiloxanes $TsiSiMe_2OSiMe_3$ and $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OSiMe_3)$. The results are described below.

Results and discussion

Preparation of the silanols

A new route to $TsiSiMe_2OH$ was discovered during an attempt to make the t-butoxide $TsiSiMe_2OBu^t$ by treatment of $TsiSiMe_2I$ with $AgClO_4$ in dried t-BuOH. Although the t-BuOH had been dried by standard methods, the product was very predominantly the silanol, apparently containing about 5—10% of the t-butoxide; the latter can be converted into the hydroxide by boiling a solution of the product mixture with MeOH containing sulphuric acid. The rearranged hydroxide $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$ was similarly obtained in high yield from $TsiSiPh_2I$ under the same conditions. However, TsiSiPhMeI gave the rearranged t-butoxide $(Me_3Si)_2C(SiPhMe_2)(SiMe_2OBu^t)$ in 14% yield along with unrearranged and rearranged hydroxides (see below). (Hydroxides seem to be formed during the reaction, and not only from initially produced silyl perchlorates during the aqueous work-up; the source of the hydroxides is under study [5].)

Properties of the silanol $TsiSiMe_2OH$

We first note that, as a result of a transcription error, we previously gave incorrect ^1H NMR data for $TsiSiMe_2OH$ [1], as pointed out by Damrauer [4]; our actual data agree well with those given by Damrauer. We do not, however, agree with him in his observation that the signal from the proton of the OH group is unchanged when a solution of the silanol in CCl_4 is shaken with D_2O. We have confirmed the earlier report [1] that the signal does disappear under these conditions, and quite rapidly (the shaking for 0.5 h which we used previously [1] is unnecessary), and, of course, it reappears on shaking with H_2O *. We have also found, in conflict with the implications of observations by Damrauer (who used BuLi), that $TsiSiMe_2OH$ is converted into $TsiSiMe_2OLi$ by MeLi, since subsequent treatment with Me_3SiCl gives the siloxane $TsiSiMe_2OSiMe_3$, whereas $TsiSiMe_2OH$ itself does not react with Me_3SiCl.

$$TsiSiMe_2OH + MeLi \rightarrow TsiSiMe_2OLi \xrightarrow{Me_3SiCl} TsiSiMe_2OSiMe_3$$

Interestingly, this siloxane was not obtained when $TsiSiMe_2OH$ in benzene was refluxed with potassium and Me_3SiCl then added. The metal dissolved, but the product was $(Me_3Si)_2CHSiMe_2OSiMe_3$, an isomer of the original silanol. It is possible that the added Me_3SiCl played no direct part (though it would serve to quench any organopotassium species present), and that the silanolate ion underwent an intramolecular rearrangement:

$$(Me_3Si)_2C\begin{matrix}SiMe_3\\SiMe_2O^-\end{matrix} \rightarrow (Me_3Si)_2\overline{C}SiMe_2OSiMe_3 \xrightarrow{H^+} (Me_3Si)_2CHSiMe_2OSiMe_3$$

* A collaborative reinvestigation by Dr. Damrauer and ourselves has failed to resolve the discrepancy.

We hope to study this reaction further under more controlled conditions *.

The $TsiSiMe_2OH$ was found to react readily with acetyl chloride, conversion into the acetate $TsiSiMe_2OCOCH_3$ being complete within 20 min at room temperature:

$$TsiSiMe_2OH + CH_3COCl \rightarrow TsiSiMe_2OCOCH_3 + HCl$$

The silanol reacted with an excess of Me_2SiCl_2 under reflux (the 5 h period used may not be necessary) to give $TsiSiMe_2OSiMe_2Cl$, which readily undergoes hydrolysis to give the disiloxane $(TsiSiMe_2OSiMe_2)_2O$:

$$TsiSiMe_2OH + Me_2SiCl_2 \rightarrow TsiSiMe_2OSiMe_2Cl \xrightarrow{H_2O} (TsiSiMe_2OSiMe_2)_2O$$

While the silanol does not react with Me_3SiCl, even on prolonged reflux, it reacts with the more active silylating agents bis(trimethylsilyl)acetamide and Me_3SiI; the latter (used in the presence of a little $(Me_3Si)_2NH$ to take up HI) gave a 92% yield of the expected disiloxane:

$$TsiSiMe_2OH + CH_3C(OSiMe_3)=NSiMe_3 \rightarrow TsiSiMe_2OSiMe_3$$

$$TsiSiMe_2OH + Me_3SiI \rightarrow TsiSiMe_2OSiMe_3$$

This disiloxane can be obtained (in high yield) indirectly from Me_3SiCl and the silanol by bringing the reagents together in the presence of $AgClO_4$ in benzene or CH_3CN, the reaction presumably proceeding through the intermediate formation of the perchlorate $Me_3SiOClO_3$.

$$Me_3SiCl + AgClO_4 \rightarrow Me_3SiOClO_3 + AgCl$$

$$TsiSiMe_2OH + Me_3SiOClO_3 \rightarrow TsiSiMe_2OSiMe_3 + HClO_4$$

The disiloxane $TsiSiMe_2OSiMe_3$ has a low reactivity; the serious steric hindrance would be expected to inhibit any nucleophilic attack at the silicon atom of the $TsiSiMe_2$ group, leading to cleavage of the Si—$OSiMe_3$ bond, but attack on the $SiMe_3$ group, with cleavage of the O—$SiMe_3$ bond, would not necessarily be prohibited (although models reveal that it might be difficult to attach 5 groups to the silicon of the Me_3Si group in a transition state, and even protonation of the oxygen atom would increase the already serious crowding). No reaction was observed when $TsiSiMe_2OSiMe_3$ was treated with (a) 2.5 *M* HCl in MeOH for 24 h at room temperature; (b) 1 *M* NaOMe in MeOH under reflux for 3 h; (c) KF/18-crown-6 in CH_2Cl_2 under reflux for 7 h; or (d) KF in MeOH under reflux for 3 days. However, the siloxane was cleaved by (a) anhydrous CF_3CO_2H, which quite rapidly gave $TsiSiMe_2OH$ (and presumably $Me_3SiO_2CCF_3$, i.e. the Me_3Si—O bond is broken, but not the $TsiSiMe_2$—O bond), and (b) KOH in 1/9 v/v H_2O/Me_2SO. In this powerfully basic medium there was also some Si—C bond cleavage, some TsiH being formed along with the predominant product $TsiSiMe_2OH$.

$$TsiSiMe_2OSiMe_3 + CF_3CO_2H \rightarrow TsiSiMe_2OH + Me_3SiO_2CCF_3$$

$$TsiSiMe_2OSiMe_3 + KOH/H_2O/Me_2SO \rightarrow TsiSiMe_2OH$$

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* Rearrangement does occur when $TsiSiMe_2OH$ is refluxed with NaOMe/MeOH [5].

Preparations of $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OSiMe_3)$, $TsiSiPhMeOSiMe_3$, $(Me_3Si)_2C(SiPhMe_2)(SiMe_2OSiMe_3)$, and $(Me_3Si)_2C(SiPhMe_2)(SiMe_2OBu^t)$

Treatment of the silanol $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$ with $Me_3SiI/(Me_3Si)_2NH$ gave a high yield of the expected disiloxane:

$$(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH) + Me_3SiI \rightarrow (Me_3Si)_2C(SiPh_2Me)(SiMe_2OSiMe_3)$$

After treatment of TsiSiPhMeI with $AgClO_4$ in t-BuOH, GLC gave two peaks in ca. 4/1 ratio. Preparative TLC then gave two components; the first was judged from its ^1H NMR spectrum to be a mixture of the unrearranged and rearranged silanols TsiSiPhMeOH and $(Me_3Si)_2C(SiPhMe_2)(SiMe_2OH)$, and treatment of the mixture with $Me_3SiI/(Me_3Si)_2NH$ and subjection of the product to preparative GLC gave the corresponding disiloxanes $(Me_3Si)_3CSiPhMeOSiMe_3$ and $(Me_3Si)_2C(SiPhMe_2)(SiMe_2OSiMe_3)$. The second component from the TLC was shown to be the rearranged t-butoxide $(Me_3Si)_2C(SiPhMe_2)(SiMe_2OBu^t)$, which was isolated in 14% yield.

Experimental

^1H NMR Spectra. These were recorded at 90 MHz using CCl_4 solution containing CH_2Cl_2 as reference and lock.

Materials. The iodides $TsiSiMe_2I$, $TsiSiPh_2I$ and TsiSiPhMeI were prepared as previously described [6]. t-Butanol was dried by refluxing over CaO, followed by distillation from CaH_2. Silver perchlorate (supplied as 'anhydrous') was dried over P_2O_5 for 48 h at 1 mmHg.

Preparation of $TsiSiMe_2OH$ and $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$

(a) A solution of $TsiSiMe_2I$ (0.50 g, 1.2 mmol) and $AgClO_4$ (0.30 g, 1.47 mmol) in t-BuOH (20 cm^3) was refluxed for 0.5 h. The solution was then cooled, hexane was added, the solution was decanted from the silver iodide, shaken several times with water, then evaporated to leave $TsiSiMe_2OH$ (0.35 g, 98%, if pure); ^1H NMR, δ(ppm) 0.23 (s, 27 H, Me_3Si), 0.31 (s, 6 H, Me_2Si), and 1.34 (s, 1 H, OH). The presence of small signals in the region δ ca. 1.39 indicated that 5—10% of butoxide product was present. The impurity was removed by refluxing the product for 1 h with MeOH containing 10% v/v of concentrated aqueous sulphuric acid.

(b) A similar procedure starting from $TsiSiPh_2I$ (1.0 g, 1.85 mmol), $AgClO_4$ (0.45 g, 2.2 mmol) and t-BuOH (30 cm^3) gave $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$ (0.75 g, 95%), ^1H NMR δ(ppm) 0.16 (s, Me_2Si), 0.20 (s, Me_3Si), 0.96 (s, $SiPh_2\mathit{Me}$), 1.71 (br. s, OH), 7.2—8.1 (m, Ph). Signals indicating the possible presence of a small amount of butoxide products disappeared upon recrystallization.

Treatment of $TsiSiMe_2OH$ and $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$ with Me_3SiCl

A mixture of $TsiSiMe_2OH$ (0.10 g) and Me_3SiCl (10 cm^3) was refluxed for 6 h. The Me_3SiCl was then distilled off, and the residue was kept under vacuum (ca. 1 mmHg) for some time to ensure complete removal of the Me_3SiCl. The solid thus obtained was shown by its ^1H NMR spectrum and GLC retention time to be unchanged $TsiSiMe_2OH$.

Identical results were obtained in similar experiments involving various reflux times up to 48 h.

Similar experiments with $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$, but with reflux for up to 7 days, gave unchanged starting material.

Reaction of $TsiSiMe_2OH$ with N,O-bis(trimethylsilyl)acetamide (BSA)

A solution of $TsiSiMe_2OH$ (0.18 g, 0.58 mmol) and BSA (0.25 g, 1.23 mmol) in anhydrous $CHCl_3$ (10 cm^3) was refluxed for 48 h with exclusion of moisture, small additional amounts of BSA being added from time to time. The solvent and other volatile materials were removed in vacuo. (The $CH_3CONHSiMe_3$ sublimed out rapidly at 50°C under 0.2 mmHg pressure.) GLC examination of the residue showed two peaks, in the ratio of ca. 2/3, and the two components were separated by preparative GLC (2 m 20% OV101 on 80—100 mesh Chromosorb P at 200°C with N_2 as carrier gas). The minor component was shown to be unchanged $TsiSiMe_2OH$, and the other was identified as $TsiSiMe_2OSiMe_3$, m.p. 53°C, ^1H NMR, δ(ppm): 0.08 (s, 9 H, $SiMe_3$), 0.19 (s, 27 H, Me_3Si), 0.27 (s, 6 H, Me_2Si) (Found: C, 47.5; H, 10.6. $C_{15}H_{42}OSi_5$ calcd.: C, 47.6; H, 11.1%). The mass spectrum showed the expected strong $(M - Me)^+$ peak at *m/e* 363 (with relative intensity of 85), and other prominent ions appeared at 275 (17, $(M - Me - SiMe_4)^+$) 147 (15) and 73 (100).

Reaction of $TsiSiMe_2OH$ with $Me_3SiI/(Me_3Si)_2NH$

A mixture of $TsiSiMe_2OH$ (0.10 g, 0.32 mmol), Me_3SiI (3 cm^3) and $(Me_3Si)_2NH$ (0.3 cm^3) was refluxed for 2 h. The Me_3SiI was then distilled off, and other volatile materials (including $(Me_3Si)_2O$) were pumped off to leave $TsiSiMe_2OSiMe_3$ (0.11 g, 92%), with properties identical to those listed above.

Reaction of $TsiSiMe_2OH$ with $Me_3SiOClO_3$

(a) A solution of $AgClO_4$ (0.91 g, 4.4 mmol) in benzene (10 cm^3) was added to a solution of $TsiSiMe_2OH$ (0.30 g, 0.98 mmol) and Me_3SiCl (0.52 g, 4.9 mmol) in benzene (10 cm^3), and the mixture was stirred at room temperature for 10 min. The benzene solution was decanted from the AgCl, then shaken several times with water. The solvent and any other volatile materials were removed (finally under vacuum) to give $TsiSiMe_2OSiMe_3$ (0.32 g, 87%), with properties identical to those listed above.

(b) A solution of $TsiSiMe_2OH$ (0.10 g, 0.32 mmol) in CH_3CN (2 cm^3) was added to a mixture of Me_3SiCl (0.048 g, 0.45 mmol) and $AgClO_4$ (0.086 g, 0.42 mmol) (in this case the commercially supplied "anhydrous" salt was used as supplied) in CH_3CN (3 cm^3). The mixture was refluxed for 2 h, then cooled. Addition of water was followed by extraction with hexane. The hexane layer was shaken several times with water then evaporated to leave $TsiSiMe_2OSiMe_3$ (0.099 g, 82%), with properties identical to those described above.

Treatment of $TsiSiMe_2OH$ with MeLi then Me_3SiCl

The $TsiSiMe_2OH$ (0.20 g, 0.65 mmol) was refluxed with 1.3 *M* MeLi (prepared from MeCl or MeBr) in Et_2O (6 cm^3) for 3 h. An excess of Me_3SiCl (2 cm^3) was added and the mixture was refluxed for 1 h. (This refluxing may not be necessary.) Additional ether was added and the solution was then washed

several times with water. The solvent and other volatile material were then removed to leave $TsiSiMe_2OSiMe_3$ (0.18 g, 72%), with properties identical to those described above.

Reaction of $TsiSiMe_2OH$ with potassium

A mixture of $TsiSiMe_2OH$ (1.0 g, 3.30 mmol), potassium (0.30 g, 7.6 mmol), and anhydrous benzene (15 cm^3) was refluxed under dry N_2 for 5 h, during which a substantial amount of the metal disappeared and the mixture became violet. An excess of Me_3SiCl (5 cm^3) was added and the mixture was stirred at room temperature for 12 h. Water was then cautiously added followed by some additional benzene, and the benzene layer was shaken several times with water and evaporated. Analysis of the residue by GLC indicated that there was a major product representing about 85% of the mixture, along with small quantities of several other materials. The major product was isolated as a liquid by preparative GLC (2.5 m 20% OV101 on 80—100 mesh Chromosorb P at 110—250°C with N_2 as carrier gas) and shown to be $(Me_3Si)_2CH(SiMe_2OSiMe_3)$; ^1H NMR, δ(ppm) −0.06 (s, 1 H, CH), 0.06 (s, 9 H, $SiMe_3$), 0.08 (s, 18 H, Me_3Si), 0.16 (s, 6 H, Me_2Si) (Found: C, 47.05; H, 10.8. $C_{12}H_{34}OSi_4$ calcd.: C, 47.05; H, 11.1%). The mass spectrum showed the expected $(M - Me)^+$ ion as the base peak at *m/e* 291, with other prominent ions at *m/e* 203 (16) and 73 (52).

Reaction of $TsiSiMe_2OH$ with Me_2SiCl_2

The $TsiSiMe_2OH$ (0.10 g, 0.32 mmol) was refluxed with Me_2SiCl_2 (5 cm^3) for 5 h. The Me_2SiCl_2 was then distilled off, and the residue kept under vacuum for 0.5 h; its ^1H NMR spectrum, δ(ppm) 0.42 (s, 27 H, Me_3Si), 0.56 (s, 6 H, $CSiMe_2O$), and 0.63 (s, 6 H, $SiMe_2Cl$), was consistent with the formulation $TsiSiMe_2OSiMe_2Cl$. Hexane was added, and the solution was shaken several times with water. Evaporation of the hexane left a solid, which was sublimed to give $(TsiSiMe_2OSiMe_2)_2O$, m.p. 96—97°C; ^1H NMR spectrum, δ(ppm) 0.12 (s, 12 H, $OSiMe_2O$), 0.23 (s, 54 H, Me_3Si), 0.33 (s, 12 H, $CSiMe_2O$) (Found: C, 45.0; H, 10.5. $C_{28}H_{78}O_3Si_{10}$ calcd.: C, 45.3; H, 10.5%).

Reaction of $TsiSiMe_2OH$ with CH_3COCl

The $TsiSiMe_2OH$ (0.2 g) was stirred with an excess of CH_3COCl (ca. 5 cm^3) at room temperature for 20 min. Hexane was then added, the solution was washed several times with water. The solvent and other volatile material were evaporated off to leave pure $TsiSiMe_2OAc$, which was identified by comparison of its spectroscopic properties with those of an authentic sample [6].

Reaction of $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$ with $Me_3SiI/(Me_3Si)_2NH$

A mixture of $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$ (0.30 g, 0.69 mmol), Me_3SiI (5 cm^3) and $(Me_3Si)_2NH$ (0.5 cm^3) was refluxed under dry N_2 for 2 h. Volatile materials were removed, and the residue was taken up in hexane. The solution was shaken several times with water then evaporated to leave a solid. GLC analysis showed that there was a very dominant product, which constituted about 95% of the mixture, along with small amounts of other products. The major product was purified by TLC (silica gel, hexane) and shown to be $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OSiMe_3)$, m.p. 100—102°C, ^1H NMR, δ(ppm) 0.20

(s, Me_3Si) and 0.24 (s, Me_3Si + Me_2Si) (these two singlets together equivalent to 33 H), 0.93 (s, 3 H, MeSi), and 7.1—8.0 (m, 10 H, aryl-H) (Found: C, 59.8; H, 8.9. $C_{25}H_{46}OSi_5$ calcd.: C, 59.8; H, 9.2%).

The mass spectrum showed the expected $(M - Me)^+$ ion at 487 (relative intensity 35), and other prominent ions at 409 (27, $(M - Me - PhH)^+$) 290 (19), 197 (38), 147 (23), 135 (62), and 73 (100).

Reaction of TsiSiPhMeI with $AgClO_4$ in t-BuOH

A mixture of TsiSiPhMeI (1.0 g, 2.09 mmol), $AgClO_4$, (0.51 g, 2.51 mmol), and t-BuOH (30 cm^3) was refluxed for 0.5 h. The solution was decanted from the AgI, and water and hexane were added. The hexane layer was shaken several times with water then evaporated. Examination of the residue by GLC (2 m, 5% OV101 on 100—120 mesh Chromosorb P at 220°C) showed two peaks A and B (in order of increasing retention time) in the ratio of ca. 4/1. These two components were separated by preparative TLC (silica gel, hexane).

The ^1H NMR spectrum suggested that A (0.63 g, 62%) was a mixture of TsiSiPhMeOH and $(Me_3Si)_2C(SiPhMe_2)(SiMe_2OH)$: δ(ppm), 0.22 (s, $SiMe_2OH$), 0.24 (s, Me_3Si), 0.26 (s, Me_3Si) (all three peaks together equivalent to 51 H), 0.58 (s, $SiMe_2$ + SiMe, 9 H), 1.45 (broad s, 2 H, OH), 7.2—7.9 (m, 10 H, aryl-H); the signal at δ 1.45 ppm disappeared when the solution in CCl_4 was shaken for 5 min with D_2O. A sample of the mixture A was sublimed (125°C/0.1 mmHg) to provide an analytical sample (Found: C, 55.4; H, 9.8. $C_{17}H_{36}OSi_4$ calcd.: C, 55.4; H, 9.8%); the mass spectrum showed the expected $(M - Me)^+$ ion at 353 (relative intensity 75), with other prominent ions at 337 (50), 275 (75), 135 (50), 73 (100). Component B was identified as $(Me_3Si)_2C(SiPhMe_2)(SiMe_2OBu^t)$ (0.14 g, 14%), m.p. 73—75°C; ^1H NMR, δ(ppm) 0.25 (s, 18 H, Me_3Si), 0.34 (s, 6 H, $SiMe_2O$), 0.60 (s, 6 H, $SiMe_2$), 1.34 (s, 9 H, OBu^t), 7.2—7.9 (m, 5 H, aryl-H) (Found: C, 59.5; H, 10.6. $C_{21}H_{44}OSi_4$ calcd.: C, 59.4; H, 10.4%). The mass spectrum showed a weak $(M - Me)^+$ peak at *m/e* 409 (relative intensity 2), with a base peak at 353 ($M - Me - CH_2{=}CMe_2$?), and other significant peaks at 351 (5, $M - OBu$?), 337 (30), 335 (20), 275 (25), 135 (20) and 73 (40).

Preparation of $TsiSiPhMeOSiMe_3$ and $(Me_3Si)_2C(SiPhMe_2)(SiMe_2OSiMe_3)$

The mixture A (0.20 g, 0.54 mmol) from the preceding experiment was treated with $(Me_3Si)_2NH$ (0.4 cm^3) and Me_3SiI (3 cm^3). After 2 h reflux volatile material was distilled off, and hexane was added. The solution was washed several times with water, and the solvent was then removed to leave a semi-solid. GLC showed that this contained two components C and D (in order of increasing retention time) in the approximate ratio 3/7. These were separated by preparative GLC (2.5 m 5% OV101 on 80—100 mesh Chromosorb P at 250°C with N_2 as carrier gas). Component A was a solid, m.p. 124—126°C, and was identified as $TsiSiPhMeOSiMe_3$; ^1H NMR, δ(ppm) 0.06 (s, 9 H, Me_3Si), 0.21 (s, 27 H, Me_3Si), and 0.65 (s, 3 H, MeSi) (Found: C, 54.5; H, 9.8. $C_{20}H_{44}OSi_5$ calcd.: C, 54.5; H, 10.0%). Component D was a liquid, identified as $(Me_3Si)_2C(SiPhMe_2)(SiMe_2OSiMe_3)$, ^1H NMR, δ(ppm) 0.17 (s, 9 H, Me_3Si), 0.20 (s, $SiMe_2O$) and 0.21 (s, $SiMe_3$) (together corresponding to 24 H), 0.55 (s, 6 H, $SiPhMe_2$), and 7.2—7.9 (m, 5 H, aryl-H) (Found: C, 54.7; H, 10.0. $C_{20}H_{44}OSi_5$ calcd.: C, 54.5; H, 10.0%).

Treatment of $(Me_3Si)_2C(SiPhMe_2)(SiMe_2OBu^t)$ with CF_3COOH in MeOH

A solution of $(Me_3Si)_2C(SiPhMe_2)(SiMe_2OBu^t)$ (ca. 0.1 g) in MeOH (5 cm^3) containing 1 *M* CF_3CO_2H was kept at 50° C for 1 h. (The ^1H NMR spectrum of the solution after this time showed that no benzene had been formed.) The usual work-up gave only unchanged starting material.

Reaction of $TsiSiMe_2OSiMe_3$ with CF_3CO_2H

A solution of $TsiSiMe_2OSiMe_3$ in CF_3CO_2H was kept in an NMR tube at room temperature. After 20 min the ^1H NMR spectrum was recorded and showed that complete conversion into $TsiSiMe_2OH$ had occurred. The usual work-up gave only $TsiSiMe_2OH$.

Reaction of $TsiSiMe_2OSiMe_3$ with KOH in 1/9 v/v H_2O/Me_2SO

The $TsiSiMe_2OSiMe_3$ (0.10 g) was dissolved in mixture of 0.1 *M* KOH (0.2 cm^3) with Me_2SO (1.8 cm^3), and the solution was kept at 75° C for 4 h. Hexane was added, and the organic layer was washed several times with water and then evaporated. The residue was analysed by GLC, which, on the basis of the retention times, indicated the presence of TsiH (21%), $TsiSiMe_2OH$ (50%), and unchanged $TsiSiMe_2OSiMe_3$ (9%).

Treatment of $TsiSiMe_2OSiMe_3$ with various reagents

The disiloxane was recovered unchanged, after the following procedures:

(a) A solution in (i) MeOH containing 2.5 *M* HCl or (ii) dioxane containing 1.7 *M* HCl was kept at room temperature for 24 h.

(b) A solution in MeOH containing 1 *M* NaOMe was refluxed for 3 h.

(c) A solution in MeOH (5 cm^3) containing anhydrous KF (0.20 g) was refluxed for 3 days.

(d) A solution (0.37 g) in CH_2Cl_2 (7 cm^3) was added to CH_2Cl_2 (10 cm^3) containing KF (63 mg) and 18-crown-6 (0.26 g) and the mixture was refluxed for 7 h. (Some NaCl was added before the washing with water in the usual work-up).

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