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# Reactions at highly sterically hindered organosilicon centres. Chemistry of $(Me_3Si)_3CSiPhHI$, $(Me_3Si)_3CSiPh(OMe)I$, and related species

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## Abstract

The iodide TsiSiPhHI (Tsi = $(Me_3Si)_3C$) has been shown to react with a range of silver(I) salts, AgY, to give the corresponding species TsiSiPhHY; the reactions with AgOCN give either the isocyanate alone or a mixture of this with the normal cyanate, depending on the conditions. Surprisingly, whereas reaction with $AgBF_4$ in $Et_2O$ gives only TsiSiPhHF, the same reaction in $CH_2Cl_2$ gives a mixture of this with the rearranged $(Me_3Si)_2C(SiPhHMe)(SiMe_2F)$. The reactions of the iodide TsiSiPh(OMe)I with AgY give the unrearranged products TsiSiPh(OMe)Y, except that reaction with $AgO_2CMe$ in $MeCO_2H$ seems also to give some $(Me_3Si)_2C[SiPh(OMe)Me](SiMe_2O_2CMe)$. Treatment of the hydrides TsiSiPhHX (X = OMe, OH, or F) with one molar proportion of ICl in $CCl_4$ gives the iodides TsiSiPhXI, and these react with a further molar proportion of ICl to give the chlorides TsiSiPhXCl. The hydroxide TsiSiPh(OH)H reacted with RCOCl (R = Me or Ph) to give the corresponding carboxylate $TsiSiPh(O_2CR)H$, but prolonged reaction in the case of R = Ph gave the chloride $TsiSiPh(O_2CMe)Cl$, and reaction of $TsiSiMe_2H$ with boiling PhCOCl correspondingly gave the chloride $TsiSiMe_2Cl$.

## Introduction

Much novel chemistry has emerged from studies of reactions of highly sterically hindered organosilicon compounds of the type TsiSiRR′I, (e.g. R = R′ = Me, Et, or Ph; R = Me, R′ = Ph) where Tsi denotes the bulky ligand $(Me_3Si)_3C$ [1,2]. It seemed to us of interest to carry out a study of the reactions of the less sterically hindered species TsiSiPhHI and related compounds of the type TsiSiPhYI, with Y drawn from a range of ligands with differing electronic and steric characteristics. The results are described below.

## Results and discussion

The study began with the iodide TsiSiPhHI, **1**, which was made as described previously [3] by treatment of $TsiSiPhH_2$ with a one molar proportion of ICl.

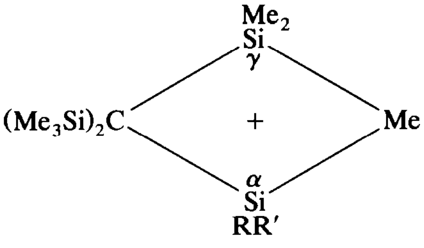
*Reactions of 1 with silver(I) salts*

Reaction of **1** with $AgOCOCF_3$ in refluxing ether gave the expected product $TsiSiPhH(OCOCF_3)$, and reaction with $AgO_2CMe$ in $Et_2O$ or glacial acetic acid correspondingly gave TsiSiPhH(OCOMe). There was no reaction with $AgOSO_2C_6H_4Me$-*p* during 24 h of refluxing in $Et_2O$ or $CH_2Cl_2$, but when a mixture of **1** and the silver salt was kept without a solvent at 120 °C for 30 min conversion into $TsiPhH(OSO_2C_6H_4Me$-*p*) was complete. Similarly, there was no detectable reaction with $AgOSO_2Me$ during 6 h of refluxing in $Et_2O$, but there was complete conversion into $TsiSiPhH(OSO_2Me)$ when a mixture of the neat reagents was kept at 90 °C for 90 min.

In contrast to $TsiSiMe_2I$, which does not react with AgSCN in $CH_2Cl_2$ [4], **1** was found to react with this salt in refluxing $Et_2O$, though fairly slowly, 85 h being required for complete reaction. Complete conversion was achieved in 1 h when a mixture of the neat reagents was kept at 120 °C. The $^1H$ NMR, IR, and mass spectra of the product were consistent with either the normal or the isothiocyanate, but since it was obtained by reaction at 120 °C we are certain that it was the thermodynamically more stable isothiocyanate.

Treatment of **1** with AgOCN in refluxing $Et_2O$ gave exclusively the isocyanate TsiSiPhH(NCO), as judged from the presence of an IR band at 2290 $cm^{-1}$ (cf. ref. 5). However, when the reaction was carried out in $CH_2Cl_2$ at room temperature for 6 h, a solution of the product in $CCl_4$ showed, alongside the band at 2290 $cm^{-1}$, a band of approximately the same height at 2260 $cm^{-1}$, characteristic of a normal cyanate [5]. Since the intensity of the isocyanate absorption is usually markedly higher than that for the cyanate [5] this implies that the normal isomer was the dominant component. After the solution in $CCl_4$ had been kept at room temperature for 6 h the heights of the 2290 and 2260 $cm^{-1}$ bands were in 2:1 ratio, indicating that the cyanate fairly readily undergoes isomerization to the more stable isocyanate, and markedly more readily than the related cyanate $TsiSiMe_2OCN$ [5].

In keeping with results described above, when **1** was treated with $AgBF_4$ in refluxing $Et_2O$ the product was exclusively TsiSiPhHF (as judged from the $^1H$ NMR spectrum). However, when the reaction was carried out in $CH_2Cl_2$ at room temperature the product was a 40:60 mixture of TsiSiPhHF with an isomer (as shown by linked GLC-mass spectrometry), and the $^1H$ NMR spectrum of the latter indicated that it was the rearranged species $(Me_3Si)_2C(SiPhHMe)(SiMe_2F)$. Such 1,3-migration of an Me group has been observed frequently in reactions of iodides TsiSiRR'I with electrophiles, and is attributed to the formation as of a Me-bridged cation of type I which is then attacked by a nucleophile either at the original functional silicon centre, $\alpha$-Si, to give an unrearranged product, or at the $\gamma$-Si atom to give the rearranged product [1,2]. The ease of attack is apparently mainly (though not solely, as noted later) determined by the relative degrees of steric hindrance at the $\alpha$-Si and $\gamma$-Si centres, so that for $R = R' = Et$ roughly equal amounts of rearranged and unrearranged products are formed, whereas for $R = R' = Ph$ exclusively rearranged products are normally obtained. The presence of the small hydrogen atom at $\alpha$-Si was expected to lead to exclusive or greatly predominant formation of unrearranged product in reactions of **1** with silver salts, and this was so in all cases except that of reaction with $AgBF_4$ in $CH_2Cl_2$.



(I)

It is not difficult to suggest a possible explanation of the difference between the outcomes of the reactions of **1** with $AgBF_4$ in $Et_2O$ and $CH_2Cl_2$. In $CH_2Cl_2$ the $BF_4^-$ ion liberated from the $Ag^+BF_4^-$ ion pair as the $Ag^+$ attaches to the leaving $I^-$ can be expected to enter the pool of $BF_4^-$ ions, and so, in effect, be free to supply $F^-$ at the $\alpha$-Si or $\gamma$-Si centre (though it is surprising that attack at the more hindered $\gamma$-Si site appears to predominate). In $Et_2O$, when the $BF_4^-$ ion is liberated near the $\alpha$-Si atom it can transfer $F^-$ very rapidly to that atom as the eliminated $BF_3$ is solvated by the $Et_2O$. This still leaves the question of why some rearranged product is obtained from $AgBF_4$ in $CH_2Cl_2$ and not from any of the other silver salts used. The answer may lie in the smallness of the ligand, $F^-$, that becomes attached to silicon, since the smaller the nucleophile the less effectively it will select between two congested sites that do not differ greatly in the degree of steric hindrance. The very great affinity of silicon for fluorine could also play a part in the lower selectivity. The slight possibility that the isomer $(Me_3Si)_2C(SiPhHMe)(SiMe_2F)$ might have been formed by rearrangement of TsiSiPhHF under the action of liberated (and unsolvated) $BF_3$ in $CH_2Cl_2$ was ruled out by the finding that TsiSiPhHF was recovered unchanged when a mixture of it with $Me_3SiCl$ in $CH_2Cl_2$ was treated with $AgBF_4$ to generate $BF_3$ in situ.

### *Reaction of TsiSiPh(OMe)I, **2**, with silver salts*

The methoxy compound TsiSiPh(OMe)H is readily obtained by treatment of the iodide **1** with MeOH [3]. We thought it of interest to examine its reactions with silver salts in the light of the earlier, and surprising, observation that no rearrangement took place in reactions of $TsiSi(OMe)_2I$ with silver salts [8]. Since some rearrangement does, as we have seen, take place in similar reactions of TsiSiPhMeI [3], and since there should be little difference in steric effects of an $\alpha$-Me and an $\alpha$-OMe group, some rearrangement would also be expected in the case of TsiSiPh(OMe)I if the relative ease of attack of a nucleophile at the $\alpha$- and $\gamma$-Si atoms in the intermediate **I** were determined solely by steric effects. In fact, the reactions of **2** with $AgBF_4$ in $Et_2O$ or with $AgOSO_2CF_3$ or AgOCN in $CH_2Cl_2$ gave only unrearranged products, TsiSiPh(OMe)Y ($Y = F$, $O_2SO_2CF_3$, or NCO/OCN). In the case of the reactions with AgOCN, when the reaction was carried out for 90 min under reflux the isolated product was exclusively the isocyanate, TsiSiPh(OMe)(NCO), as indicated by the appearance of a band at 2300 $cm^{-1}$ in the IR spectrum but no band that could be attributed to a normal cyanate [5]. However, when the reaction was carried out for the same time at room temperature the isolated product showed (in $CCl_4$) an additional band at 2265 $cm^{-1}$, attributable to SiOCN, alongside that at 2300 $cm^{-1}$ attributable to SiNCO.

The heights of the isocyanate and cyanate peaks were in 60:40 ratio, implying (see above) that the cyanate was the dominant product.

Unexpectedly in the light of the outcome of the reactions with other silver salts, the reaction of **2** with $AgO_2CMe$ in glacial $MeCO_2H$ appeared to give some of the rearranged acetate $(Me_3Si)_2C[SiPh(OMe)Me](SiMe_2O_2CMe)$ along with the unrearranged $TsiSiPh(OMe)(O_2CMe)$, since the IR spectrum of the product showed two carbonyl bands, at 1735 and 1745 $cm^{-1}$, and the $^1H$ NMR spectrum showed two singlets for the $Me_3Si$ protons, at $\delta$ 0.16 and 0.20, two for the $CH_3CO$ protons, at $\delta$ 2.03 and 1.92, and two for the OMe protons, at $\delta$ 3.40 and 3.30. Comparison of this spectrum with that of an authentic sample of $TsiSiPh(OMe)(O_2CMe)$ (made by treatment of TsiSiPh(OMe)OH with MeCOCl) showed that the $\nu$(CO) band at 1745 $cm^{-1}$ and the $^1H$ NMR signals at $\delta$ 0.16, 2.03, and 3.40 were due to the latter, and so the IR band at 1735 $cm^{-1}$ and the $^1H$ NMR signals at $\delta$ 0.20, 1.92, and 3.30 are tentatively attributed to the rearranged $(Me_3Si)_2C[SiPh(OMe)Me](SiMe_2O_2CMe)$, though some doubt remains since the signals from the $Si\mathit{Me}_2OCOCH_3$ and $SiPh(OMe)\mathit{Me}$ protons were not identified, and unfortunately $^{29}Si$ NMR spectra were not recorded. If the two products were indeed the unrearranged and rearranged acetates, they were, as judged from the heights of the various $^1H$ NMR signals, present in ca. 70:30 ratio.

The greater tendency towards rearrangement in the reaction with $AgO_2CMe$ in $MeCO_2H$ could reasonably be attributed to the presence of solvent-separated $Ag^+$ and $CH_3CO_2^-$ ions rather than intimate ion pairs in this polar and hydroxylic medium, so that $CH_3CO_2^-$ is not necessarily liberated near the $\alpha$-Si site as the $Ag^+$ ion removes $I^-$, and furthermore any acetate ion liberated near the $\alpha$-Si site is, being strongly solvated and so less reactive, likely to have more time to migrate to carry out attack at the $\gamma$-Si site.

The hydroxy iodide TsiSiPh(OH)I, made by treatment of TsiPh(OH)H with ICl, was found to react with $AgBF_4$ in $Et_2O$ to give exclusively the unrearranged TsiSiPh(OH)F.

*Reaction of the compounds TsiSiPhXH (X = OMe, OH, F, or H) with ICl*

The compounds TsiSiPhXH with X = OMe, OH, or F were found to react normally (see [3,6,7]) with a one molar proportion of ICl in $CCl_4$ to give the corresponding iodide:

$$TsiSiPhXH + ICl \rightarrow TsiSiPhXI \quad (X = OMe, OH, F)$$

The iodides in turn reacted with a further molar proportion of ICl to give the corresponding chlorides:

$$TsiSiPhXI + ICl \rightarrow TsiSiPhXCl \quad (X = OMe, OH, F)$$

This latter type of reaction is thought to proceed through a cationic intermediate of type I [3,6], and the absence of any detectable rearrangement in the present case is in line with the results of the reactions with most silver salts.

When $TsiSiPhH_2$ was treated with a two molar proportion of ICl in $CCl_4$ the product was $TsiSiPhI_2$. Evidently the initially formed TsiSiPhHI reacts preferentially at the Si–H rather than the Si–I bond. Similar behaviour was observed in the case of $TsiSiMeH_2$ [8]. However, it was shown previously that when TsiSiPhHI itself is treated with a one molar proportion of ICl the product is a 35:65 mixture of TsiSiPhClI and $TsiSiPhI_2$ [7]. The different outcome of the reactions of $TsiSiPhH_2$ and TsiSiPhHI may possibly be associated with the fact that in the reaction of the former there is one molar proportion of HCl present as the remaining ICl reacts.

### *Reaction of TsiSiPh(OH)H with MeCOCl and PhCOCl*

Treatment of TsiSiPh(OH)H with neat MeCOCl for 6 h at the reflux temperature or with PhCOCl for 7 h at 120 ° C gave the expected acetates:

$$\text{TsiSiPh(OH)H} + \text{RCOCl} \rightarrow \text{TsiSiPh(OCOCR)Cl}$$

When the mixture of the TsiSiPh(OH)H and neat PhCOCl was stirred at the reflux temperature, after 1 h the $^1H$ NMR spectrum of a sample in $CCl_4$ showed two $(Me_3Si)_3C$ signals, one from starting material and the other from TsiSiPh(OCOPh)H. After 1.5 h the signal from the starting material had disappeared and a new signal had appeared alongside that of TsiSiPh(OCOPh)H, and after 3.5 h the signal from the latter had also disappeared, and only the new signal was present. Work-up showed that complete conversion into TsiSiPh(OCOPh)Cl had occurred.

$$\text{TsiSiPh(OCOPh)H} + \text{PhCOCl} \rightarrow \text{TsiSiPh(OCOPh)Cl}$$

In the light of this observation, the reaction of $TsiSiMe_2H$ with an excess of neat PhCOCl was examined. After 1 h under reflux complete conversion into $TsiSiMe_2Cl$ had taken place.

$$\text{TsiSiMe}_2\text{H} + \text{PhCOCl} \rightarrow \text{TsiSiMe}_2\text{Cl}$$

Conversion of organosilicon hydrides into chlorides by reaction with PhCOCl at high temperature has been observed previously [9], and its occurrence with highly sterically hindered hydrides of the type studied here could find application in synthesis.

The hydroxide TsiSiPh(OMe)(OH) was satisfactorily converted into the acetate $TsiSiPh(OMe)(O_2CMe)$, though fairly slowly, by reaction with neat MeCOCl under reflux.

The preparations of $TsiSiPh(OH)_2$ and TsiSiPh(OMe)OH have been described previously [10]; the latter compound was made by treatment of TsiSiPh(OH)I with 0.25 M NaOMe–MeOH, and the mechanistic significance of the much greater ease of this solvolysis compared with that of TsiSiPh(OMe)I has been noted [11].

## Experimental

### *Solvents and reagents*

Silver salts, AgY, either purchased from the Aldrich Chemical Company (Y = $BF_4$, $OSO_2CF_3$, $OSO_2C_6H_4Me$-*p*) or freshly made (Y = $OCOCF_3$, AgOCN, AgSCN, $AgOSO_2Me$) were dried by prolonged warming under vacuum. Solvents were dried by standard methods, except for glacial acetic acid which was used as purchased. Acetyl chloride and benzoyl chloride were distilled immediately before use. The iodide TsiSiPhHI, **1**, was made as previously described [3].

### *Spectra*

The $^1H$ NMR spectra were recorded on a Perkin Elmer R12 spectrometer at 60 MHz or a Perkin Elmer R32 spectrometer at 90 MHz, with $CCl_4$ as solvent and

$CH_2Cl_2$ or $SiMe_4$ as internal standard. The IR spectra were recorded with solutions in $CCl_4$ on a Perkin Elmer 157G spectrometer. Mass spectra (electron impact) were obtained at 70 eV. Only certain selected significant peaks are shown; where relevant, isotope patterns were as expected. Suggested identities of ions are not meant to indicate possible fragmentation pathways. For linked GLC-mass spectrometry a column of 3% OV-101 was used with a flame ionization detector.

*Reactions of TsiSiPhHI, 1, with silver salts*

(a) A stirred mixture of **1** (0.69 g, 1.49 mmol) and $AgBF_4$ (0.31 g, 1.59 mmol) in $Et_2O$ (25 $cm^3$) was refluxed for 30 min and the solvent then evaporated off. The residue was extracted several times with boiling pentane, the extract was filtered and evaporated, and the residue was recrystallized from EtOH to give TsiSiPhHF (0.49 g, 92%); m.p. 76–77 °C (Found: C, 53.4; H, 9.7. $C_{16}H_{33}FSi_4$ calc.: C, 53.9, H, 9.3%); $\delta$(H) 0.22 (s, 27H, $Me_3Si$), 5.29 (d, 1H, SiH), 7.2–7.9 (m, 5H, arylH); $\nu$(SiH) 2150 $cm^{-1}$; $m/z$ 341 (80%, $[M-Me]^+$), 249 (10, $[M-Me-Me_3SiF]$), 247 (25, $[M-Me-HF-Me_3SiF]^+$), 187 (15, $[M-Ph-Me_3SiF]$, 175 (40), 135 (35, $[SiPhMe_2]^+$), 77 (15, $[Ph]^+$), 73 (100, $[Me_3Si]^+$), 59 (15, $[Me_2SiH]^+$).

(b) A mixture of **1** (0.116 g, 0.25 mmol) and $AgBF_4$ (0.060 g, 0.31 mmol) in $CH_2Cl_2$ (15 ml) was stirred at room temperature (ca. 21 °C) for 45 min then the solvent was evaporated off under reduced pressure. The residue was extracted several times with pentane and the extract filtered then evaporated to leave a solid, the IR spectrum of which (in $CCl_4$) showed two $\nu$(SiH) bands, at 2130 and 2150 $cm^{-1}$, in a height ratio 60:40. The band at 2150 $cm^{-1}$ coincided with that for an authentic sample of TsiSiPhHF (see above). Separation by TLC on alumina with n-heptane as eluent gave two compounds; the $^1H$ NMR spectrum of one was identical with that of TsiSiPhHF (see above), and that of the other, judged to be $(Me_3Si)_2C(SiMe_2F)(SiPhMeH)$, showed peaks at $\delta$ 0.11 (s, 18H, $Me_3Si$), 0.18 (d, 6H, $Me_2SiF$), 0.41 (d, 3H, Me), 4.50 (q, 1H, SiH), and 7.11–7.58 (m, 5H, arylH). The IR spectrum of the second product had the $\nu$(SiH) band at 2130 $cm^{-1}$, and its mass spectrum was essentially identical to that of TsiSiPhHF (above). The GLC peaks for the two products were in a ca. 60:40 area ratio.

(c) A mixture of **1** (0.69, 1.49 mmol) and $AgO_2CCF_3$ (0.34 g, 1.54 mmol) in $Et_2O$ (25 $cm^3$) was stirred under reflux for 45 min. The solvent was evaporated off and the residue extracted several times with pentane. The pentane extract was filtered, then evaporated to leave a solid, which was sublimed to give $TsiSiPhH(O_2CCF_3)$ (0.51 g, 76%), m.p. 43 °C (Found: C, 48.6, H, 7.6. $C_{18}H_{33}F_3O_2Si_4$ calc.: C, 48.0; H, 7.3%); $\delta$(H) 0.26 (s, 27H, $Me_3Si$), 5.43 (s, 1H, SiH), 7.06–7.68 (m, 5H, arylH); $\nu$(SiH) 2190, $\nu$(CO) 1780 $cm^{-1}$; $m/z$ 435 (25%, $[M-Me]^+$), 337 (65 $[M-CF_3CO_2]^+$), 279 (25), 175 (30), 135 (30), 77 (15), 73 (100).

(d) A procedure similar to that described in (c) above, with $Et_2O$ as solvent, but with AgOCN, reflux for 6 h, and recrystallization from EtOH in place of sublimation, gave TsiSiPhH(NCO) (0.28 g, 75%), m.p. 85–87 °C (Found: C, 53.5, H, 8.8. $C_{17}H_{33}NOSi_4$ calc.: C, 53.8; H, 8.7%); $\delta$(H) 0.25 (s, 27H, $Me_3Si$), 4.97 (s, 1H, SiH), 6.96–7.56 (m, 5H, arylH); $\nu$(SiH) 2160, $\nu$(NCO) 2290 $cm^{-1}$; $m/z$ 364 (65%, $[M-Me]^+$), 337 (10, $[M-NCO]^+$), 321 (55, $[M-Me-HNCO]^+$), 175 (20), 135 (35), 77 (5), 73 (100), 59 (15).

(e) The reaction described in (d) was carried out but with $CH_2Cl_2$ as solvent and 6 h stirring at room temperature. After evaporation of the solvent under reduced pressure the residue was extracted with $CCl_4$. The filtered extract showed IR peaks of about the same height at 2290 and 2260 $cm^{-1}$. After 6 h at room temperature the solution showed the same peaks in a 2:1 height ratio.

(f) A similar procedure to that described under (d), with $Et_2O$ as solvent, but with AgSCN and reflux for 85 h, gave TsiSiPhH(NCS), m.p. 80–81 °C (Found: C, 51.2; H, 8.1; N, 3.3. $C_{17}H_{33}NSSi_4$ calc.: C, 51.6; *H*, 8.35; *N*, 3.5%); $\delta$(H) 0.27 (s, 27H, $Me_3Si$), 5.04 (s, 1H, SiH), 7.04–7.60 (m, 5H, arylH); $\nu$(SiH) 2165, $\nu$(NCS) 2085 $cm^{-1}$; $m/z$ 380 (100%, $[M-Me]^+$), 337 (10, $[M-NCS]^+$, 321 (95, $[M-Me-HNCS]^+$), 249 (30), 247 (65), 175 (35), 135 (15), 73 (20), 59 (5).

(g) (*i*) A stirred temperature of **1** (0.46 g, 0.99 mmol) and $AgOSO_2C_6H_4Me$-*p* (0.35 g, 1.25 mmol) in $CH_2Cl_2$ (15 $cm^3$) was warmed to evaporate off all the $CH_2Cl_2$ and the residue was kept at 120 °C for 30 min then cooled and extracted several times with $CCl_4$. The extract was filtered and evaporated and the residue recrystallized from pentane to give TsiSiPhH($OSO_2C_6H_4Me$-*p*) (0.47 g, 91%), m.p. 130–131 °C (Found: C, 54.3; H, 7.9. $C_{23}H_{40}O_3SSi_4$ calc.: C, 54.3; H, 8.1%); $\delta$(H) 0.18 (s, 27H, $Me_3Si$), 2.27 (s, 3H, arylMe), 5.18 (s, 1H, SiH), 6.68–7.48 (m, 9H, arylH); $\nu$(SiH) 2190, $\nu(SO_3)$ 1365, 1185 $cm^{-1}$; $m/z$ 493 (65%, $[M-Me]^+$), 337 (10, $[M-OSO_2C_6H_4Me]^+$), 249 (30), 247 (15), 187 (20), 175 (20), 155 (25, $[SO_2C_6H_4Me]^+$), 135 (40), 91 (100, $C_6H_4Me$), 73 (95).

(*ii*) A mixture of the same amounts of reagents as in (i) above, but with 25 $cm^3$ of $CH_2Cl_2$ or $Et_2O$ as solvent, was refluxed for 24 h. The solvent was then evaporated off and the residue extracted several times with pentane. The extract was evaporated to leave a solid, which was shown by its $^1H$ NMR spectrum to be unchanged **1**.

(h) (*i*) A mixture of **1** (0.46 g, 0.99 mmol) and $AgOSO_2Me$ (0.22 g, 1.08 mmol) in $Et_2O$ (15 $cm^3$) was warmed in an open vessel until all the ether had evaporated. The residue was kept at 90 °C for 90 min then cooled and extracted with pentane. The extract was filtered and evaporated and the residue sublimed to give TsiSiPhH($OSO_2Me$) (0.40 g, 93%), m.p. 123–124 °C (Found: C, 47.1, H, 8.1. $C_{17}H_{36}O_3SSi_4$ calc.: C, 47.2, H, 8.3%); $\delta$(H) 0.20 (s, 27H, $Me_3Si$), 2.31 (s, 3H, $OSO_2Me$), 5.11 (s, 1H, SiH), 6.94–7.60 (m, 5H, arylH); $\nu$(SiH) 2200, $\nu(SO_3)$, 1190 and 1370 $cm^{-1}$; $m/z$ 417 (70%, $[M-Me]^+$), 343 (25, $[M-Me-Me_3SiH]^+$), 337 (10), 321 (40, $[M-Me-HOSO_2Me]^+$), 249 (40), 247 (25), 187 (20), 175 (35), 135 (50), 73 (100), 59 (30).

(*ii*) A mixture of **1** (0.46 g, 0.99 mmol) and $AgOSO_2Me$ (0.22 g, 1.08 mmol) in 25 ml of $CH_2Cl_2$ or $Et_2O$ was refluxed for 6 h. The solvent was evaporated off and the residue extracted several times with pentane. The extract was filtered, and evaporated to leave a solid, which was shown by its $^1H$ spectrum to be unchanged **1**.

(i) A mixture of **1** (0.20 g, 0.43 mmol) and $AgO_2CMe$ (0.10 g, 0.60 mmol) in glacial acetic acid (10 $cm^3$) was refluxed for 20 min. The solvent was then evaporated off under reduced pressure and the residue extracted several times with pentane. The extract was filtered and evaporated and the residue sublimed to give TsiSiPhH($O_2CMe$) (0.16 g, 96%), m.p. 92–94 °C (lit. [3], m.p. 96 °C) (Found: C, 53.8, H, 9.0. $C_{18}H_{36}O_2Si_4$ calc.: C, 54.4; H, 9.1%); $\delta$(H) 0.27 (s, 27H, $Me_3Si$), 2.05 (s, 3H, COMe), 5.51 (s, 1H, SiH), 7.29–8.07 (m, 5H, arylH); $\nu$(SiH) 2180, $\nu$(C=O) 1740 $cm^{-1}$; $m/z$ 381 (80, $[M-Me]^+$), 337 (100, $[M-CO_2Me]^+$), 321 (65,

$[M - Me - MeCO_2H]^+$), 261 (80), 249 (80), 47 (45), 187 (65), 175 (55), 135 (15), 73 (75), 59 (15), 43 (35, $[CH_3CO]^+$).

*Reaction of TsiSiPh(OMe)I, 2, with silver salts*

(a) A mixture of **2** (0.25 g, 0.51 mmol) and $AgBF_4$ (0.11 g, 0.66 mmol) in $Et_2O$ (20 $cm^3$) was stirred under reflux for 30 min. The solvent was evaporated off, and the residue extracted with pentane. The extract was filtered and evaporated, and the residue was recrystallized from MeOH to give TsiSiPh(OMe)F (0.17 g, 93%), m.p. 135–136 °C (Found: C, 52.9; H, 9.3. $C_{17}H_{35}FOSi_4$ calc.: C, 52.85; H, 9.1%); δ(H) 0.20 (s, 27H, $Me_3Si$), 3.22 (s, 3H, OMe), 6.96–7.60 (m, 5H, arylH); *m/z* 371 (100%, $[M - Me]^+$), 355 (10, $[M - OMe]^+$), 339 (15, $[M - Me - MeOH]^+$), 279 (20), 247 (19), 175 (20), 147 (75), 135 (10), 73 (20), 59 (5).

(b) (*i*) The procedure described under (a) was used, but with **2** (0.51 mmol) and AgOCN (0.67 mmol) in $CH_2Cl_2$ (20 $cm^3$) and with reflux for 90 min and purification by sublimation instead of by recrystallization; this gave TsiSiPh(OMe)(NCO) (88%), m.p. 192–193 °C (Found: C, 52.6; H, 8.7; N, 3.2. $C_{18}H_{35}NO_2Si_4$ calc.: C, 52.8; H, 8.6; N, 3.4%); δ(H) 0.17 (s, 27H, $Me_3Si$), 3.28 (s, 3H, OMe), 6.9–7.5 (m, 5H, arylH); ν(NCO) 2300 $cm^{-1}$; *m/z* 394 (100% $[M - Me]^+$), 362 (40, $[M - Me - MeOH]^+$), 351 (20, $[M - Me - HNCO]^+$), 291 (20), 279 (15), 263 (20), 247 (15), 175 (25), 135 (25), 91 (80, $[SiMeOH(OMe)]^+$?), 73 (25), 59 (10).

(*ii*) The reaction described in (*i*) was repeated but with stirring at room temperature for 15 h at room temperature (ca. 21 °C) instead of under reflux, and the solvent was evaporated off at room temperature under reduced pressure. The residue was extracted with $CCl_4$, and the filtered extract showed IR bands at 2300 and 2265 $cm^{-1}$ in a ca. 60:40 height ratio.

(c) The procedure described under (a), but with $AgOSO_2CF_3$, stirring for 45 min at room temperature, and purification by sublimation instead of recrystallization, gave TsiSiPh(OMe)($OSO_2Me$) (0.23 g, 87%), m.p. 110–112 °C (Found: C, 42.4; H, 7.3. $C_{18}H_{35}F_3O_4SSi_4$ calc.: C, 41.9; H, 6.8%); δ(H) 0.28 (s, 27H, $SiMe_3$), 3.88 (s, 3H, OMe), 7.25–7.78 (m, 5H, arylH).

(d) A mixture of **2** (0.12 g, 0.24 mmol) and $AgO_2CMe$ (0.07 g, 0.42 mmol) in glacial acetic acid (10 $cm^3$) was stirred under reflux for 30 min then the solvent was evaporated off under reduced pressure. The residue was extracted with pentane and the extract filtered then evaporated. A solution of the residue in $CCl_4$ gave a $^1H$ NMR spectrum that showed $Me_3Si$ singlets at δ 0.16 and 0.20, two $CH_3CO$ singlets, at δ 1.92 and 2.03, and two OMe singlets, at δ 3.30 and 3.40, along with the aryl proton multiplet at δ 6.94–7.58. Integration showed that singlets at δ 0.16 and 0.20 together corresponded to 45 H, those at δ 1.92 and 2.03 together to 6 H, those at δ 3.30 and 3.40 together to 6 H, and the arylH multiplet to 10 H. The signals at δ 0.16, 2.03, and 3.40 were shown to coincide with those from an authentic sample of TsiSiPh(OMe)($O_2CMe$) (see below), and so those at δ 0.20, 1.92, and 3.30 are assumed to be from $(Me_3Si)_2C[SiMe_2(O_2CMe)][SiPh(OMe)Me]$. The heights of the two sets of signals indicated that the two products were present in a ca. 70:30 ratio.

The IR spectrum of the mixture showed a ν(C=O) band at 1745 $cm^{-1}$, (coinciding with that for an authentic sample of TsiSiPh(OMe)($O_2CMe$)) and a smaller, overlapping, band at 1735 $cm^{-1}$.

*Reaction of TsiSiPh(OH)I with $AgBF_4$*

A mixture of TsiSiPh(OH)I (0.24 g, 0.50 mmol) and $AgBF_4$ (0.10 g, 0.51 mmol) in $Et_2O$ (25 $cm^3$) was stirred for 30 min at room temperature. The usual work-up involving evaporation, extraction of the solid with pentane, evaporation of the extract, and purification of the residue by sublimation, gave TsiSiPh(OH)F (0.16 g, 86%), m.p. 74–76 °C (Found: C, 51.7; H, 8.6. $C_{16}H_{33}FOSi_4$ calc.: C, 51.6; H, 8.9%); $\delta$(H) 0.26 (s, 27H, $SiMe_3$), 1.30 (s, 1H, OH), 7.20–7.70 (m, 5H, arylH); $\nu$(OH) 3680 $cm^{-1}$; $m/z$ 357 (100%, $[M-Me]^+$), 341 (15, $[M-OMe]^+$), 339 (15, $[M-Me-H_2O]^+$), 337 (15), 295 (30), 279 (45), 187 (10), 175 (10), 135 (15), 73 (35), 59 (5).

*Reactions of the compounds TsiSiPhHX (X = OMe, F, H) with ICl*

(a) A solution of ICl (0.33 g, 2.03 mmol) in $CCl_4$ (40 $cm^3$) was added dropwise to a stirred solution of TsiSiPh(OMe)H (0.74 g, 2.01 mmol) in $CCl_4$ (20 $cm^3$) at room temperature. Volatile materials were then evaporated off under reduced pressure, and the residue was recrystallized from EtOH to give TsiSiPh(OMe)I. (90%), m.p. 254–255 °C (Found: C, 41.4; H, 7.2. $C_{17}H_{35}IOSi_4$ calc.: C, 41.3; H, 7.1%); $\delta$(H) 0.28 (s, 27H, $Me_3Si$), 3.48 (s, 3H, OMe), 7.30–7.85 (m, 5H, arylH); $m/z$ 479 (20%, $[M-Me]^+$), 447 (20, $[M-Me-MeOH]^+$), 367 (100, $[M-I]^+$), 351 (25, $[M-Me-HI]^+$), 337 (25), 335 (30), 279 (20), 249 (15), 247 (35), 175 (30), 135 (25), 73 (45), 59 (10).

(b) A solution of ICl (0.23 g, 1.42 mmol) in $CCl_4$ (10 $cm^3$) was added dropwise with stirring to one of TsiSiPh(OMe)I (0.25 g, 0.51 mmol) in $CCl_4$ (5 $cm^3$) at room temperature. The volatile materials were then evaporated off under reduced pressure, and the residue was recrystallized from MeOH to give TsiSiPh(OMe)Cl (0.18 g, 91%), m.p. 212–213 °C (Found: C, 50.2; H, 8.8. $C_{17}H_{35}ClOSi_4$ calc.: C, 50.1; H, 8.7%); $\delta$(H) 0.24 (s, 27H, $Me_3Si$), 3.36 (s, 3H, OMe), 6.92–7.66 (m, 5H, arylH); $m/z$ 387 (100%, $[M-Me]^+$), 371 (10, $[M-OMe]^+$), 355 (35), 279 (15), 247 (15), 175 (25), 135 (15), 73 (30), 53 (20).

(c) A similar procedure to that described for the reaction of TsiSiPh(OMe)I under (a) above, but starting from TsiSiPhFH and culminating in recrystallization from MeOH, gave TsiSiPhFI (0.67 g, 93%), m.p. 172–173 °C (Found: C, 40.1; H, 6.7. $C_{16}H_{32}FISi_4$ calc.: C, 39.8; H, 6.6%); $\delta$(H) 0.31 (s, 27H, $Me_3Si$), 7.0–7.65 (m, 5H, arylH); $m/z$ 467 (5%, $[M-Me]^+$), 355 (100, $[M-I]^+$), 339 (35, $[M-Me-HI]^+$), 263 (15), 247 (20), 175 (25), 135 (15), 73 (20), 59 (5).

(d) A solution of ICl (0.18 g, 1.11 mmol) in $CCl_4$ (2 $cm^3$) was added in one portion to a stirred solution of $TsiSiPhH_2$ (0.17 g, 0.50 mmol) in $CCl_4$ (1 cm) at room temperature. Evaporation under reduced pressure left a solid, which was recrystallized from EtOH to give $TsiSiPhI_2$ (0.25 g, 85%), m.p. 305 °C (Found: C, 32.8; H, 5.6. $C_{16}H_{32}I_2Si_4$ calc.: C, 32.5; H, 5.4%); $\delta$(H) 0.32 (s, 27H, $Me_3Si$), 6.98–7.98 (m, 5H, arylH) (lit. [7], $\delta$ 0.34 and 7.25–8.35); $m/z$ 575 (25%, $[M-Me]^+$), 486 (15), 462 (40, $[M-HI]^+$), 446 (30), 335 (90, $[M-I-HI]^+$), 247 (45), 175 (30), 135 (35), 73 (100), 59 (15).

*Preparation of $TsiSiPhF_2$*

A solution of $PhSiF_3$ (2.90 g, 17.9 mmol) and TsiLi (18 mmol) in THF (42 $cm^3$) was refluxed for 10 min and the solvent then evaporated off under reduced pressure. The residue was repeatedly extracted with pentane, and the extract was filtered then evaporated. The residue was recrystallized from MeOH to give $TsiSiPhF_2$ (5.4 g, 86%), m.p. 90 °C (Found: C, 51.3; H, 8.9. $C_{16}H_{32}F_2Si_4$ calc.: C, 51.3; H, 8.6%); $\delta$(H) 0.17 (s, 27H, $Me_3Si$), 6.95–7.55 (m, 5H, arylH); *m/z* 359 (100%, $[M - Me]^+$), 282 (10, $[M - Me_3SiF]^+$), 267 (25, $[M - Me - Me_3SiF]^+$), 205 (60, $[M - Ph - Me_3SiF]^+$), 175 (25), 135 (20), 73 (20), 59 (5).

### *Reactions of TsiSiPh(OH)H and TsiSiPh(OMe)(OH) with MeCOCl or PhCOCl*

(a) A mixture of TsiSiPh(OH)H (0.13 g, 0.37 mmol) and MeCOCl (10 $cm^3$) was heated under reflux and small samples were removed at intervals for recording of the $^1H$ NMR spectrum. After 6 h the $Me_3Si$ signal of the starting material had disappeared and the volatile materials were distilled off under reduced pressure. The residue was sublimed to give $TsiSiPh(O_2CMe)H$ (0.13 g, 89%). The physical properties were as given above for the sample obtained from TsiSiPhHI and AgOAc.

(b) (*i*) A mixture of TsiSiPh(OH)H (20 g, 0.56 mmol) and PhCOCl (10 $cm^3$) was kept on oil bath at 120 °C and small samples were removed from time to time for recording of the $^1H$ NMR spectrum. The starting material had disappeared after 7 h and the PhCOCl was then removed under reduced pressure. The residue was sublimed to give $TsiSiPhH(O_2CPh)$ (0.24 g, 92%), m.p. 93–95 °C (Found: C, 60.0; H, 8.7. $C_{23}H_{38}O_2Si_4$ calc.: C, 60.3, H, 8.3%); $\delta$(H) 0.26 (s, 27H, $Me_3Si$), 5.55 (s, 1H, SiH), 7.0–8.0 (m, 10H, arylH); $\nu$(SiH) 2190, $\nu$(CO) 1730 $cm^{-1}$; *m/z* 443 (65%, $[M - Me]^+$), 337 (65, $[M - O_2CPh]^+$), 323 (15), 227 (50), 175 (10), 135 (20), 105 (100), $[COPh]^+$) 77 (45, $[Ph]^+$) 73 (35), 59 (5).

(*ii*) A mixture of TsiSiPh(OH)H (0.35 g) and PhCOCl (10 $cm^3$) was stirred under reflux and the progress of the reaction monitored by withdrawal of small samples for recording of the $^1H$ NMR spectrum. After 1 h two $Me_3Si$ signals were present, one from starting material and the other from $TsiSiPh(O_2CPh)H$. After 1.5 h the signal from the starting material had disappeared but a new signal had appeared alongside that from $TsiSiPh(O_2CPh)H$, and after 3.5 h only this new signal was present. The PhCOCl was distilled off under reduced pressure and the sticky residue was stirred with MeOH to give a solid, which was filtered off and sublimed, to give $TsiSiPh(O_2CPh)Cl$ (0.39 g, 79%), m.p. 106–107 °C (Found: C, 56.1; H, 7.8. $C_{23}H_{37}ClO_2Si_4$ calc.: C, 56.0; H, 7.5%); $\delta$(H) 0.24 (s, 27H, $Me_3Si$), 6.88–7.78 (m, 10H, arylH); $\nu$(CO) 1735 $cm^{-1}$; *m/z* 477 (65%, $[M - Me]^+$), 457 (10, $[M - Cl]^+$), 389 (15), 369 (20), 337 (20), 249 (35), 187 (35), 175 (25), 135 (40), 121 (10, $[O_2CPh]^+$), 105 (100, $[COPh]^+$), 77 (75, $[Ph]^+$), 73 (70), 59 (25).

### *Reaction of $TsiSiMe_2H$ with PhCOCl*

A mixture of $TsiSiMe_2H$ (0.15 g) and PhCOCl (5 $cm^3$) was refluxed for 1 h then the residual PhCOCl was distilled off under reduced pressure. The $^1H$ NMR spectrum of the residue showed that all the $TsiSiMe_2H$ had been converted into $TsiSiMe_2Cl$, an authentic sample of which [3] was available.

### *Reaction of TsiSiPh(OH)(OMe) with MeCOCl*

A mixture of TsiSiPh(OH)(OMe)H (0.13 g) and MeCOCl (10 $cm^3$) was refluxed and small samples were removed at intervals for recording of the $^1H$ NMR spectrum. Reaction was judged to be complete after 26 h and the volatile materials were distilled off under reduced pressure. The residue was sublimed to give

TsiSiPh(OMe)($O_2$CMe), m.p. 187–189 °C (Found: C, 53.5; H, 9.4. $C_{19}H_{38}O_3Si_4$ calc.: C, 53.5; H, 9.9%); $\delta$(H) 0.16 (s, 27H, $Me_3Si$), 2.03 (s, 3H, COMe), 3.40 (s, 3H, OMe), 6.94–7.40 (s, 5H, arylH); $\nu$(CO) 1745 $cm^{-1}$; $m/z$ 411 (55%, $[M - Me]^+$), 353 (20, $[M - Me_3Si]^+$), 337 (50), 291 (100, $[M - Me - MeOH - Me_4Si]^+$), 249 (20), 189 (20), 187 (20), 175 (15), 147 (100), 135 (25), 73 (45), 59 (15), 28 (100, $[CO]^+$).

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