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Anchimeric assistance in the reactions of the crowded organosilicon iodide $(Me_3Si)_2(Ph_2MeSi)CSiMe_2I$ with electrophiles[†]

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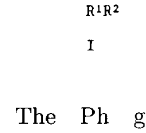
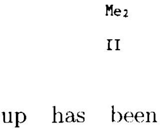
Summary – The relative reactivities of the iodides $(Me_3Si)_2(Ph_2MeSi)CSiMe_2I$, **1**, $(Me_3Si)_2(PhMe_2Si)CSiMe_2I$, **2**, $(Me_3Si)_3CSiPhMeI$ **3**, $(Me_3Si)_3CSiPh_2I$, **4**, and $(Me_3Si)_3CSiMe_2I$, **5**, towards silver salts or ICl have been studied and the results support the proposal that for **1** and **2** the rate-determining step involves generation of a Ph-bridged cation, and so anchimeric assistance by a Ph group to the departure of I^-. Thus the fall in reactivity in the sequence **1** > **2** > **5** reflects the presence of two γ-Ph groups in **1** and one in **2** able to provide such assistance. Towards $AgO_3SC_6H_4Me$-p in CH_2Cl_2 **1** is > 50 times as reactive as **5**, but in the reactions with $AgNO_3$ in MeOH the effects of the assistance are smaller, and the relative reactivities of **1**, **2** and **5** are *ca* 7:2:1. In the reaction with ICl in CCl_4 the corresponding ratio is *ca* 150:70:1. In the reactions of **1** there is little if any formation of rearranged products arising from migration of a Ph group to the α-Si, the lower steric hindrance at the α-site in the Ph-bridged cation favouring attack there. Because of the anchimeric assistance, even the chloride $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Cl$ reacts in CH_2Cl_2 with AgO_3SCF_3, towards which $(Me_3Si)_3CSiMe_2Cl$ is inert. The reactivity ratio for reaction of $(Me_3Si)_3CSiPh_2I$, $(Me_3Si)_3CSiPhMeI$, and **5** with ICl in CCl_4 is *ca* 6:1.5:1, indicating that α-Ph groups can give some help to formation of a Me-bridged cation.

silicon / anchimeric assistance / steric hindrance / reaction mechanism

It is thought that appropriate groups Z in compounds of the type $(Me_3Si)_2(ZMe_2Si)CSiR^1R^2X$ can provide anchimeric assistance to the leaving of X^-, usually I^-, in reactions with some electrophiles, including Ag(I) salts, ICl, CF_3CO_2H and CF_3CH_2OH [1-7]. For example, Z can be Me [2], Ph [3], CH=CH$_2$ [4], OMe [5,6], N_3 [7] or NCS [7]. The anchimeric assistance is associated with rate-determining formation of a 1,3-bridged cation of type I, which can be attacked by a nucleophile, with ring opening, at either the α- or the γ-Si atom; that is, 1,3-migration of Z can occur [1-7].



I



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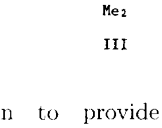

III

The Ph group has been shown to provide substantial assistance in reactions of the iodide $(Me_3Si)_2(PhMe_2Si)CSiMe_2I$ with CF_3CH_2OH, the intermediate cation in this case having the form II [3]. We thus thought it of interest to examine the behaviour of the related diphenyl compound $(Me_3Si)_2(Ph_2MeSi)CSiMe_2I$, **1**, which has two Ph groups potentially available to provide assistance, and so, if the above interpretation of the assistance is correct, should be even more reactive but only by a small factor, since only one of the Ph groups can be directly involved in each ionization process. (In contrast, if, for example, the function of a Ph group were to provide conjugative stabilization of a positive charge developed at the silicon atom to which it is attached then the effect of a second such group would be expected to be comparable with that of the first.)

It was also of interest to find out whether some of the attack of the nucleophile on the intermediate cation, III, might take place at the γ-position, to yield the rearranged product of the type $(Me_3Si)_2(PhMeSi)CSiPhMeY$. The proportion of attack at the γ-position in the intermediate cations is often (but by no means always [8,9]) determined largely by the relative degrees of steric hindrance at the α- and γ-centres, and thus in the reaction of $(Me_3Si)_3CSiPhMeI$, **2**, with AgO_2CMe in $MeCO_2H$, involving the cation I, R^1 = Ph, R^2 = Me, attack at the γ-site to give rearranged product dominates, but *ca* 25% of the product is the unrearranged $(Me_3Si)_3CSiPhMeO_2CMe$, resulting from attack at the α-centre, which bears a Ph and an Me group [2a]. Con-

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[†] Dedicated to Professor R Calas, a distinguished organometallic chemist and a true gentleman.

[*] Correspondence and reprints

sequently, in reactions of the iodide **1**, a minor but significant proportion of the attack on the cation III might take place at the γ-centre to give the rearranged species.

To provide information about the behaviour of **1** we examined its reactions with Ag(I) salts and with ICl. We also examined the reaction of the corresponding chloride, $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Cl$, with AgO_3SCF_3 and that of the α-diphenyl derivate $(Me_3Si)_3CSiPh_2I$ with $AgBF_4$. The results provide additional support for the previously proposed mechanisms.

Results and discussion

Preparation of **1** *and its reactions with silver salts*

The iodide **1** was made by treatment of the corresponding hydride $(Me_3Si)_2(Ph_2MeSi)CSiMe_2H$ with iodine in CCl_4 in the presence of an excess of $PhSiMe_3$; in the absence of the latter the generated HI cleaves the Si-Ph bonds.

$(Me_3Si)_2(Ph_2MeSi)CSiMe_2I$
1

$(Me_3Si)_2(PhMe_2Si)CSiMe_2I$
2

$(Me_3Si)_3CSiPhMeI$
3

$(Me_3Si)_3CSiPh_2I$
4

$(Me_3Si)_3CSiMe_2I$
5

When we treated the iodide **1** with $AgBF_4$ in CH_2Cl_2 (a solvent that favours rearrangement) the ^1H NMR spectrum of the solution indicated that only the unrearranged fluoride $(Me_3Si)_2(Ph_2MeSi)CSiMe_2F$ was formed (though a little of the rearranged fluoride could have escaped detection), and this was isolated in *ca* 90% yield after recrystallization. Identical behaviour was observed when the reaction was carried out in Et_2O. A similar result was obtained for the reaction with AgO_2CCF_3 in CH_2Cl_2. Likewise only the unrearranged products $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Y$ were isolated 'in 80-93% yields' from the reactions in CH_2Cl_2 with AgY = NO_3 or O_3SCF_3. It is apparent that although these reactions of **1** do involve formation of the Ph-bridged cation III (see later), there is little, if any, migration of a Ph group, attack of the nucleophile at the less hindered α-Si centre being strongly favoured.

Relative reactivities of the iodides **1**, **2** *and* **5** *towards silver salts*

The reactions with silver tosylate $AgO_3SC_6H_4Me$-p, AgOTs, were first examined. When an equimolar mixture of **1** and **5** in CH_2Cl_2 was treated during 1 h at room temperature with a one molar proportion of AgOTs (*ie* sufficient to react with half of the combined amount of the iodides) all of iodide **1** was converted into the tosylate $(Me_3Si)_2(Ph_2MeSi)CSiMe_2OTs$, and none of the tosylate $(Me_3Si)_3CSiMe_2OTs$ could be detected. Thus **1** must be $>$ 50 times as reactive as **5**. When we treated an equimolar solution of **1** and **5** in MeOH with a half-molar proportion of $AgNO_3$ (*ie* sufficient to react with 25% of the combined amount of the iodides), the products were the expected methoxides $(Me_3Si)_2(Ph_2MeSi)CSiMe_2OMe$ and $(Me_3Si)_3CSiMe_2OMe$ in a ratio of *ca* 85:15 (as judged from the relative heights of the signals from the respective OMe protons), implying that **1** is the more reactive by a factor of *ca* 7. When a mixture of **2** and **5** was used under similar conditions the ratio of the corresponding methoxides was *ca* 65:35, *ie* **1** is *ca* twice as reactive as **2**. It is not surprising that the anchimeric assistance by the γ-Ph groups is less effective in the reaction in MeOH since $AgNO_3$ is very reactive in this medium, in which it will be at least partly dissociated, and so there is less demand on the assistance, and solvation of the forming cation by the hydroxylic solvent will further reduce the need for anchimeric assistance.

It is evident that in the reactions of **1** the γ-Ph groups can provide substantial anchimeric assistance, and somewhat more effectively than does the single γ-Ph group in **2**. More striking evidence for such assistance was obtained when the chloride $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Cl$ was treated with AgO_3SCF_3 in CH_2Cl_2. After 6 days at room temperature *ca* 60% of the chloride had been converted into the trifluoromethanesulfonate $(Me_3Si)_2(Ph_2MeSi)CSiMe_2O_3SCF_3$ and, in a separate experiment, after 3 days under reflux only the latter was present, whereas $(Me_3Si)_3CSiMe_2Cl$ undergoes no reaction under such conditions. Since Cl^- is a much poorer leaving group than I^- from silicon, its departure makes a greater demand on the anchimeric assistance.

Before leaving the investigation of the relative reactivities of the iodides we treated an equimolar mixture of **4** and **5** with a one molar proportion of AgOTs in CH_2Cl_2. After 1 h at room temperature workup gave a 7:3 mixture of $(Me_3Si)_2(Ph_2MeSi)CSiMe_2OTs$ and $(Me_3Si)_3CSiMe_2OTs$, implying that **4** is roughly 3 times as reactive as **5**, and that in this reaction α-Ph groups can also slightly assist formation of the intermediate cation. However, in an earlier competition reaction between the two iodides and $AgNO_3$ in MeOH, the two iodides were found to show almost equal reactivities [2a] and again the lower selectivity in this medium can be attributed to the higher reactivity of the silver salt and better solvation of the transition state.

Relative reactivities of the iodides **1-5** *towards ICl in* CCl_4

In each case the iodide (0.018 mmol) was dissolved in 0.50 cm^3 of an 0.50 mol dm^{-3} solution of ICl (a 14-fold excess) in an NMR tube, which was then securely capped, quickly shaken, and transferred to the probe of the spectrometer maintained at 35°C. In the case of the most reactive iodide, **1**, the reaction was *ca* 80% complete after *ca* 50 s, the time of the first measurement, and was complete within 2 min, implying a half-life in the region of 20 s (and somewhat shorter if account is taken of the time needed for the mixture to warm to 35°C). With the somewhat less reactive iodide **2**, reaction was *ca* 70% complete after 2 min, implying a half-life of roughly 60 s (the warm-up time again being ignored). In the case of the less reactive iodides **3**, **4** and **5** the progress of the reaction could be monitored, and the relative heights of the signals from the Me_3Si protons in the starting material and product at various times used to establish the extent of reaction. Good first-order kinetics were observed in all three cases for up to 80% completion of the reaction, and values of the rate constants, k, and the associated half-lives $t_{1/2}$, for the disappearance of the iodide are shown in table I. From iodides **1**, **2** and **5**, the products were exclusively the corresponding chlorides, though in the case of **2** and **5** there would probably have been some undetectable migration of the Ph or an Me group, respectively. (Reaction of the labelled iodide $(Me_3Si)_3CSi(CD_3)_2I$ with ICl in CCl_4 gives *ca* 15% of the rearranged chloride $(Me_3Si)_2[Me(CD_3)_2Si]CSiMe_2Cl$ [11]). Iodide **4** gave only the expected rearranged chloride $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Cl$, and **3** gave a mixture of the rearranged chloride $(Me_3Si)_2(PhMe_2Si)CSiMe_2Cl$ and the unrearranged $(Me_3Si)_3CSiMePhCl$ in a ratio of *ca* 75:25, in keeping with the proportion of rearrangement observed in the reaction of **3** with AgO_2CMe in $MeCO_2H$ [2a]. It will be seen that the γ-diphenyl iodide **1** is in the region of 150 times as reactive as **5**, and the monophenyl iodide **2** is *ca* 70 times as reactive as the latter, demonstrating once again that the two γ-Ph groups in **1** provide more anchimeric assistance than the single Ph group in **2**, but only by a fairly small factor. As in the reactions with AgOTs, compound **4** is a few times as reactive as **5** (the factor being *ca* 6 in the present case), confirming that the α-Ph groups can also assist ionization, presumably by some delocalization of the partial positive charge developed on the α-Si atom in the transition state.

Table. I Reaction of the iodides **1-5** with ICl in CCl_4 at 35°C.[a]

Iodide	$10^3k/s^{-1}$	$t_{1/2}/s$	Notes
1		*ca* 20	[b]
2		*ca* 60	[c]
3	0.37	1 870	[d]
4	1.4	460	[e]
5	0.24	2 900	

[a] The iodide (0.018 mmol) was dissolved in 0.5 cm^3 of 0.50 mol dm^{-3} ICl in CCl_4. [b] Reaction was *ca* 80% complete after *ca* 50 s and complete after 2.0 min. [c] Reaction was *ca* 70% complete after 2.0 min. [d] The products $(Me_3Si)_2(PhMe_2Si)CSiMe_2Cl$ and $(Me_3Si)_3CSiPhMeCl$ were formed in *ca* 75:25 ratio. [e] The product was $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Cl$.

Reaction of $(Me_3Si)_3CSiPh_2I$, 4, with $AgBF_4$

In previous studies of the reactions of **4** with silver or mercury salts or ICl only rearranged products of the form $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Y$ were isolated [2], but formation of small amounts of unrearranged product $(Me_3Si)_3CSiPh_2Y$ could have escaped detection. We thus decided to examine the reaction of **4** with $AgBF_4$, which has the advantage that formation of isomeric products can usually be detected by ^{19}F NMR spectroscopy. Initially we used CH_2Cl_2 as solvent and observed only the rearranged fluoride $(Me_3Si)_2(Ph_2MeSi)CSiMe_2F$, but when we carried out the reaction in Et_2O, we found that the product solution contained both the rearranged and unrearranged fluoride, showing ^{19}F NMR signals, at δ −134 and −157, respectively, in a height ratio of *ca* 85:15, confirming the view that the relative degree of steric hindrance at α- and γ-centres is not the only factor that determines the proportion of rearrangement.

Experimental section

The compounds **2** [13], **3-5** [10] and $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Cl$ [11] were made as previously described. Silver salts were dried before use.

Reactions were carried out under dry nitrogen. Unless otherwise indicated, $CDCl_3$ was used as solvent for recording of the NMR spectra (with residual $CHCl_3$ as internal reference for ^1H, $CFCl_3$ as internal reference for ^{19}F, and $SiMe_4$ as external reference for ^{13}C and ^{29}Si spectra). Mass spectra (EI) were determined at 70 eV.

Preparation of $(Me_3Si)_2(Ph_2MeSi)CSiMe_2H$

Two methods were used for the preparation of this compound, as follows:

(a) A mixture of $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Cl$ (0.90 g, 1.96 mmol) and $LiAlH_4$ (0.90 g, 24 mmol) in THF (50 cm^3) was refluxed for 4 h then allowed to cool and added dropwise and cautiously to an excess of wet hexane. The mixture was added cautiously to cold saturated NH_4Cl, and the organic layer was separated, washed with water, dried ($MgSO_4$), and evaporated, to leave a solid, which was recrystallized from cold MeOH and then from pentane to give bis (trimethylsilyl)(methyldiphenylsilyl)(dimethylsilyl)methane (0.69 g, 83%).

Mp 121°C.

^1H NMR ($CDCl_3$) : δ 0.11 (6H, d, J(Si-H) 3.67 Hz, $SiMe_2$), 0.15 (18H, s, $SiMe_3$), 1.12 (3H, s, SiMe), 5.10 (1H, m, SiH), and 7.3-8.0 (10H, m, Ph); (acetone-d_6) δ 0.13 ($SiMe_2$), 0.17 ($SiMe_3$), 0.98 (SiMe), and 7.3-7.96.

^{13}C NMR: δ 1.8 (d, ^2J(C-H) 36 Hz, $SiMe_2$), 5.3 ($SiMe_3$), 5.9 (SiMe), 127-139 (Ph).

^{29}Si NMR: δ 0.13 (s, $SiMe_3$), −8.2 (d, J(Si-H) 196 Hz, $SiMe_2$), −15.1 (s, SiMe).

IR ν (SiH) 2 100 cm^{-1}.

MS: m/s 399 (50%, M−Me), 322 (100, M−Me−PhH), 248 (30), 247 (20), 175 (20), 135 (30), and 73 (25).

Anal calc for $C_{22}H_{38}Si_4$: C, 63.7; H, 9.2. Found: C, 65.3; H, 9.0.

(b) A 2.5 mol dm^{-3} solution of BuLi in hexane (15 cm^3, 0.037 mol of BuLi) cooled to −80°C was added dropwise to a stirred solution of $(Me_3Si)_2CCl_2$ (8.0 g, 0.035 mol) in a mixture of THF (40 cm^3), pentane (2 cm^3) and Et_2O (5 cm^3) maintained at −110°C. The mixture was stirred for a further 2 h then Ph_2MeSiF (8.46 g, 0.040 mol) cooled to −80°C was added with stirring. The mixture was kept at −110°C for 30 min, allowed to warm to room temperature overnight, then cautiously to saturated aqueous NH_4Cl. The organic layer was separated, washed with water, dried ($MgSO_4$), and filtered, and volatile materials were removed on a rotary evaporator. The residual oil was kept at 100°C/20 Torr to remove unchanged $(Me_3Si)_2Cl_2$ and then subjected to analysis by GLC-MS, which revealed the presence of the expected $(Me_3Si)_2(Ph_2MeSi)CH$ [m/z 341 (100%, M−Me), 263 (70), 197 (60), 135 (75) and 73 (85)] and another compound, apparently $Me_3Si)_2CBu_2$ [m/z 274 (10%, M^+), 197 (100), and 135 (20)], in *ca* 90:10 ratio. To a solution of some of this mixture (0.75 g) in THF (20 cm^3) was added a 1.25 mol dm^{-3} solution of MeLi in Et_2O (2.0 cm^3, 2.5 mmol of MeLi), and the mixture was refluxed for 4 h then allowed to cool. Neat Me_2SiHCl (3.0 mmol) was added and the mixture was refluxed for 1 h. After the usual hydrolytic work-up, recrystallization of the product from MeOH and then from pentane gave $(Me_3Si)_2(Ph_2MeSi)CSiMe_2H$, with properties identical to those noted under (a) above.

Preparation of the $(Me_3Si)_2(Ph_2MeSi)CSiMe_2I$, **1**

A solution of $(Me_3Si)_2(Ph_2MeSi)CSiMe_2H$ (0.80 g, 1.93 mmol), $PhSiMe_3$ (0.60 g, 4.0 mmol) and I_2 (1.50 g, 5.9 mmol) in CCl_4 (25 cm^3) was stirred for 3 h at room temperature then shaken with aqueous $NaHSO_3$ and dried ($MgSO_4$). Removal of the solvent left a solid, which was recrystallized twice from pentane to give (iododimethylsilyl)bis(trimethylsilyl)(methyldiphenylsilyl)methane, **1** (1.0 g, 77%).

Mp 140°C

^{1}H NMR ($CDCl_3$): δ 0.38 (18H, s, $SiMe_3$), 1.06 (6H, s, $SiMe_2$), 1.08 (3H, s, SiMe), 7.27-7.80 (10H, m, Ph).

MS: m/z 525 (20%, M−Me), 447 (10, M−Me−PhH), 413 (15, M−I), 397 (20), 335 (100, M−I−PhH), 263 (20), 247 (35), 175 (25), 135 (50), and 73 (55).

Anal calc for $C_{22}H_{37}ISi_4$: C, 48.9; H 6.9. Found: C, 48.3; H, 6.7.

Reactions of **1** *with silver salts*

• *(a) With* $AgBF_4$

A solution of **1** (0.20 g, 0.37 mmol) in CH_2Cl_2 (10 cm^3) was stirred at room temperature with $AgBF_4$ (0.15 g, 0.51 mmol) for 15 min, after which the ^{1}H NMR spectrum of the solution indicated that no starting material remained and that only one product was present. The solution was filtered, then evaporated under reduced pressure to leave a solid, which was extracted several times with pentane. The extract was evaporated and the residue was recrystallized from MeOH to give $(Me_3Si)_2(Ph_2MeSi)CSiMe_2F$, with properties identical to those of an authentic sample.

• *(b) With* AgO_2CCF_3

The procedure described under (a) was repeated but with AgO_2CCF_3, 10 cm^3 of CH_2Cl_2, and a stirring time of 30 min, after which ^{1}H NMR spectroscopy indicated that only one compound was present. The solution was filtered and evaporated and the residual solid was recrystallized from pentane and shown to be $(Me_3Si)_2(Ph_2MeSi)CSiMe_2O_2CCF_3$ (0.16 g, 85%).

Mp 96°C (lit [14], 94°C).

IR: ν (C=O) 1 760 cm^{-1}.

^{1}H NMR (CCl_4): δ 0.30 ($SiMe_3$), 0.46 ($SiMe_2$), 1.02 (SiMe), 7.2-8.0 (Ph).

^{19}F NMR: δ −75.8.

Essentially identical results were obtained when Et_2O was used as the solvent.

• *(c) With* AgO_3SCF_3

The procedure was as described under (b) above with pentane as solvent, and starting from AgO_3SCF_3. Again only one compound appeared to be present after 30 min, and the solid isolated, mp 104°C, was shown to be $(Me_3Si)_2(Ph_2MeSi)CSiMe_2O_3SCF_3$, with properties identical to those of an authentic sample [15].

^{1}H NMR (CCl_4, 5% CH_2Cl_2): δ 0.31 ($SiMe_3$), 0.61 ($SiMe_2$) 1.01 (SiMe), and 7.2-8.0 (Ph).

^{19}F NMR: δ −76.5.

^{29}Si NMR ($CDCl_3$): −13.7 ($SiPh_2Me$), −1.07 ($SiMe_3$), 38.8 ($SiMe_2O$).

• *(d) With* AgO_2CMe

The procedure described under (b), with pentane as solvent, but with sublimation (155°C/0.2 Torr) of the initially isolated solid instead of recrystallization, gave $(Me_3Si)_2(Ph_2MeSi)CSiMe_2O_2CMe$ (0.16 g, 93%), with spectroscopic properties identical to those of an authentic sample [2a].

Mp 118°C.

^{1}H NMR (CCl_4): δ 0.25 ($SiMe_3$), 0.38 ($SiMe_2$), 0.95 (SiMe) and 7.0-8.0 (Ph).

• *(e) With* $AgNO_3$

A solution of **1** (0.20 g, 0.37 mmol) in CH_2Cl_2 (15 cm^3) was stirred at room temperature with $AgNO_3$ (0.10 g, 0.59 mmol) for 15 min. Hexane was added and the solution decanted from the solid and added to water. The organic layer was separated, washed, dried ($MgSO_4$) and evaporated to leave a solid, which was recrystallized from pentane and shown to be $(Me_3Si)_2(Ph_2MeSi)CSiMe_2ONO_2$ (0.14 g, 80%).

Mp 160°C (lit [2a], 158°C).

IR: ν (NO_3) 1 590 and 1 285 cm^{-1}.

^{1}H NMR (CCl_4): δ 0.40 ($SiMe_3$), 0.47 ($SiMe_2$), 1.10 (SiMe) and 7.0-8.0 (Ph).

Competition studies

(a) A mixture of **5** (0.01 g, 0.24 mmol), **4** (0.13 g, 0.24 mmol) and $AgO_3SC_6H_4Me$-p (0.066 g, 0.24 mmol) in CH_2Cl_2 (20 cm^3) was stirred at room temperature and the progress of the reaction was monitored by ^{1}H NMR spectroscopy. After 1 h the solvent was removed under reduced pressure to leave a solid, which was extracted with pentane. The extract was filtered and evaporated to dryness. The residual solid was dissolved in CCl_4 containing 5% CH_2Cl_2 and the ^{1}H NMR spectrum recorded. This revealed that $(Me_3Si)_2(Ph_2MeSi)CSiMe_2O_3SC_6H_4Me$-p and $(Me_3Si)_3CSiMe_2O_3SC_6H_4Me$-p were present in *ca* 70:30 ratio, as indicated by the relative heights of the peaks from the $SiMe_3$ protons at δ 0.31 and 0.19, respectively.

(b) A mixture of **1** (0.13 g, 0.24 mmol), **5** (0.10 g, 0.24 mmol) and $AgO_3SC_6H_4Me$-p (0.66 g, 0.24 mmol) in CH_2Cl_2 (20 cm^3) was stirred at room temperature for 1 h. The ^{1}H NMR spectrum of the solution showed that all of the **1** had been converted into $(Me_3Si)_2(Ph_2MeSi)CSiMe_2O_3SC_6H_4Me$-p and that no detectable $(Me_3Si)_3CSiMe_2O_3SC_6H_4Me$-p had been formed.

(c) A mixture of the iodides **1** and **5** (each 0.24 mmol) was stirred with $AgNO_3$ (0.12 mmol) in anhydrous MeOH (20 cm^3) for 1 h. The solution was filtered then evaporated to leave a solid, which was taken up in $CDCl_3$. The ^{1}H NMR spectrum showed that the solution contained the unchanged iodides along with the methoxides $(Me_3Si)_2(Ph_2MeSi)CSiMe_2OMe$ and $(Me_3Si)_3CSiMe_2OMe$ in *ca* 85:15 ratio as indicated by the relative heights of the signals from the OMe protons at δ 3.55 and 3.35, respectively. Authentic samples of the methoxides were available.

(d) The procedure described under (c) was repeated but with **2** and **5**. The methoxides $(Me_3Si)_2(PhMe_2Si)CSiMe_2OMe$ and $(Me_3Si)_3CSiMe_2OMe$ were formed in a ratio of *ca* 64:36, as judged from the relative heights of the signals at δ 3.39 and 3.35, respectively. Authentic samples were available.

Reactions with ICl

The iodide (0.018 mmol) was dissolved in 0.50 cm^3 of 0.50 mol dm^{-3} ICl in CCl_4 (a 14-fold excess of ICl) in an NMR tube which was then firmly capped and placed in the probe of the spectrometer at 35°C. The spectrum was recorded within *ca* 1-2 min and then at appropriate intervals, and the extent of reaction at various times deduced from the relative heights of the ^{1}H NMR signals from the $SiMe_3$ protons in the starting material and product(s); in the case of **3** the combined heights of the relevant signals from both products was used. For iodides **3-5** a good first-order plot for disappearance of the iodide was obtained up to more than 80% completion of the reaction. The results are shown in table I.

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