REACTION OF TRIS(TRIMETHYLSILYL)METHYLSILICON HALIDES WITH METHANOLIC SODIUM METHOXIDE. PROBABILITY OF SILA-OLEFIN INTERMEDIATES

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Summary

The compounds $TsiSiR_2X$ [Tsi = $Me_3Si)_3C$; R = Me, X = Cl, Br, I, or R = Ph, X = F, Cl, Br, I)] react with boiling 2 M MeONa-MeOH to give products of the type $(Me_3Si)_2CHSiR_2OMe$. It is suggested that the reaction proceeds through an elimination, analogous to $E2$ eliminations of alkyl halides, involving synchronous attack of MeO$^-$ at an Me_3Si group, liberation of X$^-$, and formation of $(Me_3Si)_2C=SiR_2$. The compounds TsiSiPhMeF and $TsiSiPhCl_2$ react analogously to give $(Me_3Si)_2CHSiPhMe(OMe)$ and $(Me_3Si)_2CHSiPh(OMe)_2$ [the latter presumably by solvolysis of the initially-formed $(Me_3Si)_2CHSiPhCl(OMe)$]. The compounds $TsiSiMe_2OMe$ and $TsiSiMe_3$ do not react, while $TsiSiMe_2H$ gives TsiH. The compound $TsiSiCl_3$ reacts with 0.1 M MeONa-MeOH to give the substitution and elimination products $TsiSiCl_2(OMe)$ and $(Me_3Si)_2CHSi(OMe)_3$ in ca. 1/2 ratio.

Introduction

We have previously shown that the presence of the tris(trimethylsilyl)methyl ("trisyl") group, $(Me_3Si)_3C$ (denoted by Tsi), in compounds of the type $TsiSiR_2X$ causes very large steric hindrance towards nucleophilic displacement of X [1,2]. Because the normal reaction path is forbidden, such compounds display unusual reactions [1,3], and this is the case in the reactions with sodium methoxide in methanol which we describe below.

Results and discussion

When the compounds $TsiSiR_2X$ (R = Me or Ph, X = OMe, Cl, Br, or I; R = Ph, X = F) were treated for several hours with refluxing 2 M sodium methoxide

in methanol, the products in cases in which reaction occurred were of the type $(Me_3Si)_2CHSiR_2OMe$. (eq. 1).

$$(Me_3Si)_3CSiR_2X + MeONa + MeOH \rightarrow (Me_3Si)_2CHSiR_2OMe + Me_3SiOMe$$
$$+ NaX \qquad (1)$$
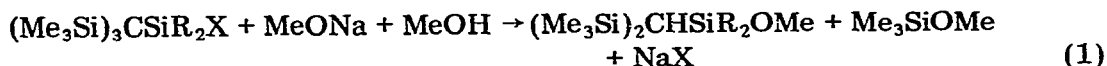
Details of the results are given in Table 1. For the reactions of $TsiSiPh_2X$ compounds with a large excess of base, rough first order rate constants were derived from the extents of reaction after various times (see Table 1), and the relative rates found to be (X =) F, 1; Cl, 2; Br, 3.5; I, 7. For the $TsiSiMe_2X$ compounds, pairs of compounds were treated with an excess of sodium methoxide, and the extents of reaction after a given time indicated approximate relative rates of (X =) Cl, 1; Br, 4; I, 20. No reaction was observed in the case of $TsiSiMe_3$ and $TsiSiMe_2OMe$, while $TsiSiMe_2H$ gave TsiH (see below).

Although no direct comparison was made, the reactions of $TsiSiPh_2X$ were evidently somewhat faster than those of the corresponding $TsiSiMe_2X$ compounds, the difference falling from a factor of ca. 5 for X = Cl to ca. 2—3 for X = Br, and 1.3 for X = I. The higher reactivity of $TsiSiPh_2Cl$ than of $TsiSiMe_2Cl$ is confirmed by the results of reactions with ethanolic potassium hydroxide described below.
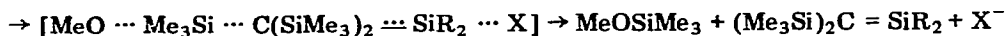
Three plausible routes to the products can be written (two of them having a common first step), and these are shown in Scheme 1. The first, Route 1, involves a rate-determining synchronous β-elimination to give the sila-olefin $(Me_3Si)_2C=SiR_2$, which then rapidly adds methanol to give the observed product. The other routes both involve an initial rate-determining cleavage of an Me_3Si—C bond to give the carbanion $(Me_3Si)_2(XR_2Si)C^-$; this could then either (i) acquire a proton to give $(Me_3Si)_2CHSiR_2X$, with the latter then undergoing solvolysis to give the product $(Me_3Si)_2CHSiR_2(OMe)$ (Route 2a), or (ii) lose X^- to give the sila-olefin, which would add methanol (Route 2b).

TABLE 1
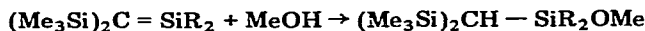
REACTIONS OF TsiSiYZW COMPOUNDS WITH BOILING MeONa—MeOH

YZW	[NaOMe] (M)	Time (h)	Products [a] and yields (%) [b]	Approx. k [c] (h^{-1})
Ph_2F	2.0	6	SM, 33; $(Me_3Si)_2CHSiPh_2OMe$, 67 [d]	0.17
Ph_2Cl	2.0	6	SM, 12; $(Me_3Si)_2CHSiPh_2OMe$, 88	0.35
Ph_2Br	2.0	1.0	SM, 54; $(Me_2Si)_2CHSiPh_2OMe$, 46	0.6
Ph_2I	2.0	0.5	SM, 55; $(Me_3Si)_2CHSiPh_2OMe$, 45	1.2
Me_2Cl	2.0	8	SM, 40; $(Me_3Si)_2CHSiMe_2OMe$, 60	0.07 [e]
Me_2Br	2.0	10	$(Me_3Si)_2CHSiMe_2OMe$, 95	0.2—0.3 [e]
Me_2I	2.0	8	$(Me_3Si)_2CHSiMe_2OMe$, 95	0.9 [e]
Me_3	2.0	24	SM, 100	
Me_2OMe	2.0	24	SM, 100	
Me_2H	2.0	4	$(Me_3Si)_3CH$, 100	
PhMeF	1.5	16	SM, 18 [f]; $(Me_3Si)_2CHSiPhMeOMe$, 26 [f]	
$PhCl_2$	2.0	4	$(Me_3Si)_2CHSiPh(OMe)_2$, 56 [f]	
Cl_3	0.10	1.5	$(Me_3Si)_3CSiCl_2(OMe)$, 33; $(Me_3Si)_2CHSi(OMe)_3$, 67	

[a] SM denotes starting material. [b] Yields as indicated by ^{1}H NMR spectrum of product mixture unless otherwise specified. [c] Very approximate value of apparent pseudo first order rate constant in 2.0 M MeONa—MeOH at b.p.. [d] Isolated in 62% yield. [e] Derived from data obtained in competition study, as described in Experimental section. [f] Isolated yield.
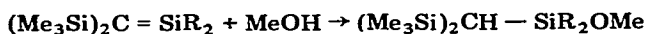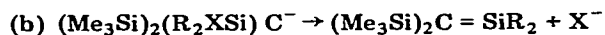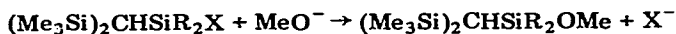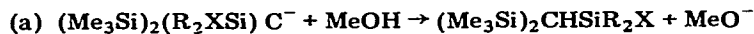
Route 1

$MeO^- + Me_3SiC(SiMe_3)_2SiR_2X$

$\rightarrow [MeO \cdots Me_3Si \cdots C(SiMe_3)_2 \cdots SiR_2 \cdots X] \rightarrow MeOSiMe_3 + (Me_3Si)_2C = SiR_2 + X^-$

transition state

$(Me_3Si)_2C = SiR_2 + MeOH \rightarrow (Me_3Si)_2CH - SiR_2OMe$

Route 2

$MeO^- + Me_3SiC(SiMe_3)_2SiR_2X \rightarrow MeOSiMe_3 + (Me_3Si)_2(R_2XSi) C^-$

(a) $(Me_3Si)_2(R_2XSi) C^- + MeOH \rightarrow (Me_3Si)_2CHSiR_2X + MeO^-$

$(Me_3Si)_2CHSiR_2X + MeO^- \rightarrow (Me_3Si)_2CHSiR_2OMe + X^-$

(b) $(Me_3Si)_2(R_2XSi) C^- \rightarrow (Me_3Si)_2C = SiR_2 + X^-$

$(Me_3Si)_2C = SiR_2 + MeOH \rightarrow (Me_3Si)_2CH - SiR_2OMe$
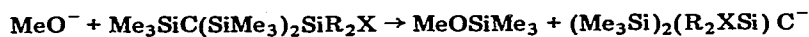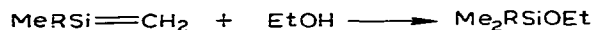
SCHEME 1

Of these possibilities we strongly favour Route 1, for the following reasons. (a) No detectable reaction occurs in the case of $(Me_3Si)_4C$ and $(Me_3Si)_3CSiMe_2$-OMe, and it is unlikely that the carbanions $(Me_3Si)_2(XMe_2Si)C^-$ with X = F, Cl, Br, I, would be much more rapidly formed than $(Me_3Si)_3C^-$ and, especially, $(Me_3Si)_2(MeOMe_2Si)C^-$; (b) the increase in the ease of reaction as X in $(Me_3Si)_3$-$CSiR_2X$ is varied in the sequences OMe, Cl, Br, I (R = Me) or F, Cl, Br, I (R = Ph) is as expected for a rate-determining step which involves breaking of the Si—X bond, whereas the stabilities of the anions $(Me_3Si)_2(XSiR_2)C^-$, and thus their ease of formation, would not be expected to vary significantly.

The faster reaction of $TsiSiPh_2X$ than of corresponding $TsiSiMe_2X$ compounds can, in terms of Route 1, be attributed in part to some stabilization of the forming sila-olefin by conjugation with the phenyl groups (although there is some indication that this may be a smaller effect than might have been expected [4]), and possibly in part to a greater release of steric strain which accompanies the elimination, since it is reasonable to assume that much of the driving force in these reactions comes from such relief of strain upon fragmentation. We should note, in this connection, that the rate sequence (X =) F < Cl < Br < I is also consistent with the sequence of increasing relief of strain, but if this were the dominant factor $(Me_3Si)_4C$ and $TsiSiMe_2OMe$ would also be expected to react; furthermore, the spread of rates for the various halides would be expected to be greater in the more crowded $TsiSiPh_2X$ than in the $TsiSiMe_2X$ systems, and while the relative rates reported are only rough estimates, the opposite is clearly the case.

The mechanism we favour, i.e. Route 1 in Scheme 1, is analogous to the familiar *E*2 elimination mechanism for alkyl halides. That such a process has not been previously observed with silicon halides can be attributed to the fact that direct substitution at the Si—X bond normally occurs very much readily. There is an even closer analogy to the mechanism, shown in Scheme 2, originally proposed by Kumada and his colleagues for the reaction of Me_2RSiSi-$MeR(CH_2X)$ (X = halogen) species with EtONa-EtOH [5].

EtO⁻ | Me₂RSi——SiMeR——CH₂——X ——→ EtOSiMe₂R + MeRSi══CH₂ + X⁻

MeRSi══CH₂ + EtOH ——→ Me₂RSiOEt

SCHEME 2

However, Tamao and Kumada later favoured the mechanism shown in Scheme 3 [6], in which rate-determining separation of an anion (as in our Route 2) is followed by loss of X⁻ from the latter with simultaneous addition of ethanol.

EtO⁻ + Me₂RSiSiMeRCH₂X → EtOSiMe₂R + [SiMeRCH₂X]⁻

[SiMeRCH₂X]⁻ + EtOH → EtOSiMe₂R + X⁻
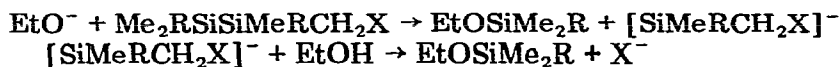
SCHEME 3

A mechanism, outlined in Scheme 4, analogous to our Route 1, was also proposed for the reaction of (Me₃SiOSiMe₂CH₂)₃B with NaOEt-EtOH [9].

EtO⁻ | B——CH₂——SiMe₂——OSiMe₃ ——→ EtO——B⟨ + CH₂══SiMe₂ + OSiMe₃⁻
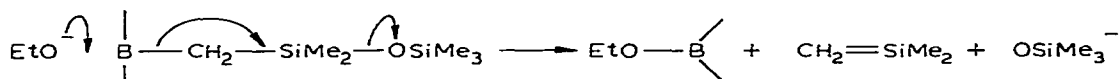
SCHEME 4

The compounds TsiSiPhMeF and TsiSiPhCl₂ undergo the fragmentation reactions to give (Me₃Si)₂CHSiPhMe(OMe) and (Me₃Si)₂CHSiPh(OMe)₂, respectively (Table 1). The compound TsiSiCl₃ reacts markedly more readily, and so 0.1 M rather than 2 M MeONa-MeOH was mainly used. The fragmentation product (Me₃Si)₂CHSi(OMe)₃ was again dominant, being formed in about 67% yield, but in this case the substitution product TsiSi(OMe)Cl₂ was also formed, in about 33% yield. When the progress of the reaction with boiling 0.1 M NaOH-MeOH was monitored by titration of the residual base in samples removed at appropriate intervals, it was found that ca. 33% of the total chlorine was displaced in about 12 min, ca. 60% in 45 min, ca. 66% in 90 min, and ca. 67% in 240 min. It is clear that the two products, TsiSi(OMe)Cl₂ and (Me₃Si)₂CHSi-(OMe)₃ are produced in concurrent processes in close to 1/2 ratio, and that TsiSi(OMe)Cl₂ does not react further under these conditions. When TsiSiCl₃ and TsiSi(OMe)Cl₂ were treated for 2 h with 2 M NaOMe-MeOH, effectively all (>95%) of the chloride ligands were displaced. The product mixture was complex, though it included substantial amounts of (Me₃Si)₂CHSi(OMe)₃, and was not investigated further.

The compound TsiSiMe₂H underwent complete decomposition during 4 h in refluxing 1 M NaOMe-MeOH, and the product after work-up was essentially pure (Me₃Si)₃CH. In this case it seems that because of the small size of the hydrogen atom the methoxide can fairly readily attack the SiMe₂H centre. (We have previously observed that the presence of a hydrogen atom at a silicon atom bearing a Tsi group markedly reduces the steric hindrance and permits direct nucleophilic attack [2]). It is of interest that the (Me₃Si)₃C group then leaves rather than the H; no doubt this is mainly because this gives the greater relief of steric strain, but we have noted above that the fairly high acidity of (Me₃Si)₃CH implies that (Me₃Si)₃C would leave fairly readily as the anion [7]. Conversion of the TsiSiMe₂H into TsiSiMe₂OMe before cleavage of the Tsi—Si bond is, of course, ruled out by the observation that TsiSiMe₂OMe is inert under these conditions.

In order to provide some comparison of the relative effects of the steric hindrance to substitution at $TsiSiMe_2$ and $t\text{-}Bu_3Si$ centres, $TsiSiMe_2Cl$ was treated with KOH-EtOH for 2 days under reflux, conditions under which $t\text{-}Bu_3SiCl$ undergoes effectively complete reaction [8]. Precipitation of the Cl^- produced from $TsiSiMe_2Cl$ showed that only about 70% of the latter had reacted. Thus $TsiSiMe_2Cl$ is at least 5 times less reactive, and since no simple substitution product was ever detected in the reactions with NaOMe-MeOH, it is likely that less (possibly much less) than 5% of substitution occurs with KOH-EtOH, and thus that in the latter medium nucleophilic displacement of chloride is more than 100 times as fast for $t\text{-}Bu_3SiCl$ as for $TsiSiMe_2Cl$. We have already seen that the compound $TsiSiPh_2Cl$ is more readily attacked by NaOMe-MeOH than is $TsiSiMe_2Cl$, and it loses all of its chlorine when treated with the KOH-EtOH for 2 days; but no doubt the greatly dominant reaction is fragmentation, with little if any, direct substitution.

We finally note that if our suggested mechanism for the fragmentation of $TsiSiR_2X$ compounds in NaOMe-MeOH is correct, it may be practicable to generate sila-olfins by analogous processes (e.g. with F^- as nucleophiie) in inert media, and this possibility is being investigated.

Experimental

NMR spectra

The ^1H NMR spectra were recorded at 60 MHz with solutions in CCl_4 containing CH_2Cl_2 as reference.

Preparation of reagents

The methods of preparation of the trisyl-silicon compounds have been described [2].

Reactions of TsiSiPh$_2$X compounds

(a) A solution of $TsiSiPh_2F$ (0.20 g, 4.6 mmol) in 2 M NaOMe-MeOH (25 cm^3) was refluxed for 6 h and then added to water. Extraction with hexane, followed by washing, drying ($MgSO_4$), and evaporation of the extract left a liquid, the ^1H NMR spectrum of which showed the presence of only unchanged starting material (33%) and [bis(trimethylsilyl)methyl](methoxy)(diphenyl)-silane (67%). The latter was purified by preparative TLC (SiO_2; 4/1 hexane-chloroform) to give a liquid (0.10 g, 62%), n_D^{25} 1.542, the analysis and ^1H NMR spectrum of which are shown in Table 2.

(b) A solution of $TsiSiPh_2Cl$ (0.20 g, 4.4 mmol) in 2 M NaOMe-MeOH (25 cm^3) was refluxed for 6 h, then poured into a separatory funnel containing hexane (30 cm^3) and sufficient 2 M HNO$_3$ to neutralize the base present. After vigorous shaking the organic layer was separated, washed, dried ($MgSO_4$), and evaporated under reduced pressure, and the residue was shown by ^1H NMR spectroscopy to contain unchanged starting material (13%) and $(Me_3Si)_2CHSiPh_2OMe$ (87%). The chloride content of the combined aqueous layers was determined gravimetrically as AgCl, and the amount (56 mg) of the latter corresponded to 88% of reaction.

(c) The reactions of $TsiSiPh_2Br$ and $TsiSiPh_2I$ were similarly examined, but

with reaction times of 1 h and 0.5 h respectively. The results are shown in Table 1.

Reactions of TsiSiMe₂X compounds

(a) A solution of TsiSiMe$_2$Br (92.5 mg) in 2 M NaOMe-MeOH (10 cm^3) was refluxed for 6 h. The mixture was then worked up and analysed as described for the TsiSiPh$_2$Cl reaction above; the amount of AgBr corresponded to 95% reaction, and the liquid residue from the hexane extract was identified as (Me$_3$Si)$_2$CHSiMe$_2$OMe from its ^{1}H NMR spectrum (Table 2).

(b) The reaction of TsiSiMe$_2$I was carried out analogously for 3 h, with virtually identical results.

(c) A mixture of approximately 0.25 mmol each of TsiSiMe$_2$Cl and TsiSiMe$_2$Br was dissolved in CCl$_4$, and the peaks heights and intensities of the signals from the SiMe$_2$X protons indicated that the reagents were present in 42/58 ratio. The solvent was evaporated off and 2 M NaOMe-MeOH (100 cm^3) was added, and the mixture refluxed for 3 h. The mixture was worked up in the usual way, and ^{1}H NMR spectrum of the product mixture showed that it contained unchanged TsiSiMe$_2$Cl and TsiSiMe$_2$Br in 58/42 ratio. The ratio of the protons of (Me$_3$Si)$_3$C to those of (Me$_3$Si)$_2$CSiMe$_2$OMe was 59/41, indicating that about 41% of the possible (Me$_3$Si)$_2$CHSiMe$_2$OMe had formed. Thus ca. 57% of the TsiSiMe$_2$Br and ca. 19% of the TsiSiMe$_2$Cl had reacted. The rates are thus in the ratio log(1 − 0.57)/log(1 − 0.19), i.e. 4/1. The first order rate constants are very roughly 0.3 and 0.07 h^{-1}, respectively.

(d) A mixture of TsiSiMe$_2$Br and TsiSiMe$_2$I was subjected to the procedure described under (c), but with reaction for only 1 h. The results indicated that approximately 58% of the iodide and 16% of the bromide had reacted. These figures correspond to relative rate constants of 5/1, and very approximate first order rate constants of 0.9 and 0.2 h^{-1}.

(e) A solution of TsiSiMe$_2$OMe (80 mg) in 2 M NaOMe-MeOH (35 cm^3) was refluxed for 24 h. The usual work-up showed that only unchanged starting

TABLE 2

^{1}H NMR SPECTRA AND ANALYSES OF PRODUCTS

Product	δ (ppm) ^{a}	Analysis Found (Calc.)(%)	
		C.	H.
(Me$_3$Si)$_2$CHSiMe$_2$OMe	—0.58(s, 1 H, CH); 0.09(s, 18 H, SiMe₃); 0.15(s, 6 H, SiMe₂); 3.33(s, 3 H, OMe)		
(Me$_3$Si)$_2$CHSiPh$_2$OMe	0.29(s, 1 H, CH); 0.03(s, 18 H, SiMe₃); 3.49(s, 3 H, OMe); 7.2—7.8(m, 10 H, Ph).	64.3(64.5)	8.5(8.6)
(Me$_3$Si)$_2$CHSiPhMeOMe	—0.23(s, 1 H, CH); 0.04(d, sepn. 7 Hz; 18 H, Me); 0.47(s, 3 H, SiMe); 3.28(s, 3 H, OMe); 7.1—7.7(m, 5 H, Ph)	58.5(58.1)	9.8(9.7)
(Me$_2$Si)$_2$CHSiPh(OMe)$_2$	—0.33(s, 1 H, CH); 0.13(s, 18 H, Me); 3.56(s, 6 H, OMe); 7.2—7.8(m, 5 H, Ph)	55.0(55.2)	9.1(9.2)
(Me$_3$Si)$_2$CHSi(OMe)$_3$	—0.73(S, 1 H, CH); 0.03(s, 18 H, SiMe₃); 3.52(s, 9 H, OMe)	42.7(42.8)	9.7(10.1)
(Me$_3$Si)$_3$CSiCl$_2$OMe	0.32(s, 27 H, SiMe₃); 3.60(s, 3 H, OMe)	36.5(36.5)	8.4(8.4)

^{a} In CCl₄, with CH$_2$Cl$_2$ as reference.

material was present. A similar result was obtained with TsiSiMe$_3$.

(f) A solution of TsiSiMe$_2$H (200 mg) in 2 M MeONa-MeOH (10 cm^3) was refluxed for 4 h then added to water. Extraction with hexane, followed by washing, drying (MgSO$_4$), and evaporation of the extract, left a liquid residue, which was identified as (Me$_3$Si)$_3$CH by comparison of its ^{1}H NMR and IR spectra with those of an authentic sample.

Reaction of TsiSiCl$_3$

(a) A sample of TsiSiCl$_3$ (0.37 g; 1.0 mmol) was dissolved in a boiling (ca. 0.12 M) MeONa-MeOH solution (50 cm^3), 5 cm^3 of which had been found to require 11.8 cm^3 of 0.050 M HCl for neutralization. Aliquots (5 cm^3) were withdrawn at suitable times and added to water, and the amounts of 0.050 M acid needed for neutralization found to be as follows; 0 min, 11.6 cm^3; 5 min, 10.9 cm^3; 15 min, 9.6 cm^3; 30 min, 8.6 cm^3; 45 min, 8.2 cm^3; 90 min, 7.8 cm^3; 240 min, 7.9 cm^3. Thus 65% of the chlorine atoms of the TsiSiCl$_3$ had been replaced.

(b) A solution of TsiSiCl$_3$ (200 mg, 0.55 mmol) in 0.10 M NaOMe-MeOH was refluxed for 2 h. Hexane was added, and inorganic material extracted with water. The chloride ion was determined as AgCl; 0.170 g of the latter was obtained, corresponding to liberation of 2.2 of the 3 Cl atoms of the TsiSiCl$_3$.

(c) A solution of TsiSiCl$_3$ (1.0 g) in 0.10 M MeONa-MeOH (150 cm^3) was refluxed for 1.5 h. The methanol was evaporated off, hexane was added, and the hexane solution washed, dried (MgSO$_4$), and evaporated. The ^{1}H NMR spectrum of the product mixture was recorded, and the mixture was then treated with MeOH-EtOH to give a white solid, which was purified by sublimation and identified as TsiSiCl$_2$(OMe) (see Table 2). The MeOH-EtOH solution was evaporated to leave a liquid which was identified from its ^{1}H NMR spectrum as (Me$_3$Si)$_2$CHSi(OMe)$_3$ (see Table 2). With the separate spectra of the two products available, it could be seen that the original product mixture contained TsiSiCl$_2$(OMe) and (Me$_3$Si)$_2$CHSi(OMe)$_3$ in ca. 1/2 ratio.

Reaction of TsiSiPhMeF

A solution of TsiSiPhMeF (1.0 g, 2.7 mmol) in 1.5 M MeONa-MeOH (40 cm^3) was refluxed for 16 h. Hexane was added, and the organic layer washed several times with water, then dried (MgSO$_4$) and evaporated. The liquid residue was subjected to preparative TLC (SiO$_2$, hexane) to give: (i) unchanged TsiSiPhMeF (0.18 g, 18%), m.p. 98°C (authentic ^{1}H NMR spectrum); (ii) a liquid, identified as (Me$_3$Si)$_2$CHSiPhMeOMe (0.22 g, 26%) (see Table 2); (iii) a small amount of solid (0.017 g), m.p. 148°C, which was however, shown by GLC (2 m, 5% OV$_1$ on 100—120 mesh Chromosorb G) to contain two components; presumably by coincidence, the analysis corresponded with TsiSiPhMe-(OMe) (Found: C, 56.7; H, 10.0. C$_{18}$H$_{38}$OSi$_4$ calcd.: C, 56.5; H, 9.9%), as did the ^{1}H NMR spectrum except for the splitting of the signal in the Me$_3$Si region: δ 0.13 and 0.16 (total 27H, SiMe$_3$); 0.48 (s, 3H, SiMe); 3.36 (s, 3H, OMe); 7.0—8.0 ppm (m, 5H, Ph).

Reaction of TsiSiPhCl$_2$

A solution of TsiSiPhCl$_2$ (2.0 g, 4.9 mmol) in 2 M MeONa-MeOH (70 cm^3)

was refluxed for 4 h then added to hexane (50 cm^3). The organic layer was washed several times with water, then dried (MgSO$_4$) and evaporated to give a liquid residue. The latter was subjected to preparative TLC (SiO$_2$, 4/1 hexane-CHCl$_3$) to give (i) a liquid, (Me$_3$Si)$_2$CHSiPh(OMe)$_2$ (0.90 g, 56%) (see Table 2); (ii) a liquid (0.20 g, ca. 13%) which may be (Me$_3$Si)$_2$CHSiPh(OH)(OMe), produced by hydrolysis of the initial product (Found: C, 54.1; H, 8.9. C$_{14}$H$_{28}$O$_2$Si$_3$ calcd.; C, 53.9; H, 9.0%); δ: —0.28 (s, 1H, CH); 0.10(s) and 0.13(s), in 40/50 ratio (combined intensity 18H, SiMe$_3$); 2.47 (br. s, 1H, OH); 3.46 (s, 3H, OMe); 7.1—7.8 ppm (m, 5H, Ph); IR; ν(SiOH), 3420 cm^{-1} (br).

Acknowledgments

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