Reactions at Silicon Centres bearing the Bulky Tris(phenyldimethylsilyl)methyl Ligand

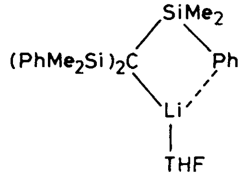
Colin Eaborn* and Abdulrahman I. Mansour
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, Sussex

Metallation of $(PhMe_2Si)_3CH$ with MeLi in tetrahydrofuran gives $(PhMe_2Si)_3CLi$, which reacts with MeI to give $(PhMe_2Si)_3CMe$, and also with Me_2SiHCl and $MeSiHCl_2$, to give $(PhMe_2Si)_3CSiMe_2H$ and $(PhMe_2Si)_3CSiMe(H)Cl$, respectively, but not with Me_3SiCl or a range of other organosilicon halides. The $(PhMe_2Si)_3CSiMe_2H$ gives the halides $(PhMe_2Si)_3CSiMe_2X$ (X = Cl, Br, and I) upon treatment with halogens, and the iodide is converted into various $(PhMe_2Si)_3CSiMe_2Y$ species (Y = F, OH, O_2CMe, O_2CCF_3, OSO_2CF_3, OCN, NCO, NCS) by treatment with appropriate silver salts. The iodide reacts with NaN_3 in $(MeOCH_2CH_2)_2O$ and with KSCN in MeCN to give $(PhMe_2Si)_3CSiMe_2N_3$ and $(PhMe_2Si)_3CSiMe_2NCS$, respectively, the reactions with KSCN in this solvent and in MeOH being fairly similar in rate to those of $(Me_3Si)_3CSiMe_2I$. In contrast, the latter is markedly less reactive than $(PhMe_2Si)_3CSiMe_2I$ in reactions with silver salts and in methanolysis, and this is tentatively attributed to greater anchimeric assistance (in 1,3 Si to Si bridging) by a Ph than by an Me group.

Much novel chemistry has emerged from studies of highly sterically hindered silicon compounds having a tris(trimethylsilyl)methyl ligand (the 'trisyl' ligand, frequently denoted by the symbol Tsi) attached to a functional silicon centre; *e.g.*, those of the type $(Me_3Si)_3CSiMe_2X$.[1–9] We thus decided to examine related compounds containing the tris(phenyldimethylsilyl)methyl ligand, $(PhMe_2Si)_3C$, which we frequently denote below by the symbol Tpsi. Our interest in such compounds was twofold: (*a*) we assumed that the introduction of a Ph group in place of one of the Me groups on each Si atom in the ligand would significantly increase the steric hindrance; (*b*) we thought that we might observe 1,3-migration of a Ph group from Si to Si, analogous to that of the Me group in some trisyl-silicon compounds,[1,3,6,9] and that such migration of a Ph group might occur more readily than that of an Me group. It later emerged that steric hindrance by the Tpsi ligand is not necessarily greater than that by the Tsi ligand, and the planned study of possible migration was frustrated by the failure to make suitable substrates. Many interesting results were obtained, however, and these are described below.

Results and Discussion

The starting point of the work was the compound $(PhMe_2Si)_3CH$ (TpsiH), which was made in 20% yield from $PhMe_2SiCl$, CCl_4, and Mg in tetrahydrofuran (THF).[10] The TpsiH was then metallated with MeLi under the conditions used for TsiH.[11] Initially it was thought that no metallation took place, since subsequent treatment with Me_3SiCl followed by hydrolytic work-up gave none of the expected $TpsiSiMe_3$, but only recovered TpsiH. However, treatment of the solution after metallation with MeI gave a 92% yield of TpsiMe, while treatment with D_2O gave TpsiD and TpsiH in 83:17 ratio, indicating that TpsiLi is, indeed, produced in good yield but has an abnormally low reactivity. It was subsequently found to react satisfactorily with Me_2SiHCl and $MeSiHCl_2$, to give $TpsiSiMe_2H$ and TpsiSiMeHCl, respectively, but not with Me_2SiCl_2, Me_3SiCl, Et_2SiCl_2, Et_2SiF_2, EtMeSiHCl, $PhMe_2SiCl$, $PhMe_2SiF$, PhMeSiHCl, or Ph_2SiF_2, all of which react satisfactorily with trisyl-lithium. It is noteworthy that when a solution of TpsiLi was refluxed with Me_3SiCl for 24 h there was no trace of a precipitate of LiCl, whereas such a precipitate appeared immediately upon subsequent addition of Me_2SiHCl.



(I)

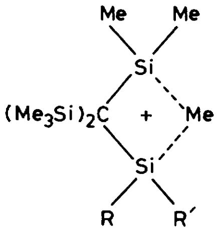
Initially we assumed that the much lower reactivity of TpsiLi than of trisyl-lithium towards the various silicon halides was to be attributed to markedly greater steric hindrance resulting from the presence of the Ph groups, but we abandoned this simple explanation, at least as the main factor, when it was shown that trisyl-lithium has a very different structure from that of TpsiLi, the former being an ionic lithiumate complex, $[Li(THF)_4][Li(Tsi)_2]$[12] and the latter a covalent monomeric species with a marked interaction between the Li atom and one of the Ph groups, as in (I).[13]

The lower reactivity of TpsiLi could be associated with the fact that the Li–C bond is shielded from attack by this Ph group and also possibly by the other Ph groups (see the detail of the structure[13]), but probably more important is that the negative charge on the $[Li(Tsi)_2]^-$ anion makes it more reactive towards electrophiles than the neutral TpsiLi. Furthermore, it was found that the SiCSi angles in $(PhMe_2Si)_3CH$ (as revealed for the solid by *X*-ray diffraction)[14] are actually smaller than those in $(Me_3Si)_3CH$ (as revealed for the vapour by electron diffraction),[15] suggesting that the Tpsi ligand may have a smaller effective bulk than the Tsi ligand, although the solid structure does not necessarily give an adequate guide to the effective bulk of the Tpsi ligand in solution, where the Ph groups can presumably rotate about the Si–Ph bonds.

$(PhMe_2Si)_3CSiMe_2X$ **(1)**
$(Me_3Si)_3C$ = Tsi
$(PhMe_2Si)_3C$ = Tpsi

a; X = H
b; X = Cl
c; X = Br
d; X = I
e; X = OH
f; X = OMe

The compound $TpsiSiMe_2H$, (**1a**), was the starting point for a range of other derivatives. Thus it reacted readily with one molar proportion of ICl in CCl_4 to give exclusively the corresponding chloride (**1b**) [which was also obtained from (**1a**)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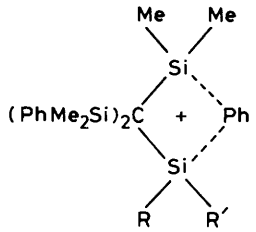
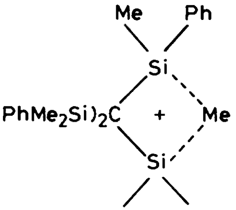

(III)


(IV)

and Cl_2 in CCl_4]. The formation of the chloride (**1b**) from ICl contrasts with that of the iodide $TsiSiMe_2I$ from $TsiSiMe_2H$ under similar conditions.[9] Although formation of the iodides from TsiSiRR′H and related species is usual, there are other examples of the formation of chloride, exclusively or along with the iodide, in the reaction with one molar proportion of ICl;[9,16] there must be only a small difference in the free energies of activation for chloride and iodide formation, so that relatively small influences can determine the outcome.

The bromide (**1c**) and iodide (**1d**) were made by treatment of (**1a**) with Br_2 and I_2, respectively, in CCl_4. The iodide was converted by an excess of ICl in CCl_4 into the chloride (**1b**).

We had initially hoped to study the reactions of suitable compounds of the type TpsiSiRR′I (*e.g.*, R = R′ = Et) with silver salts in order to investigate the possibility that there would be migration of a Ph group, to give products of the type $(PhMe_2Si)_2C(SiRR'Ph)(SiMe_2Y)$ *via* an intermediate of type (**III**), analogous to those of type (**II**) thought to be involved in the corresponding reactions of TsiSiRR′I species.[2,3,9] Since a Ph group is normally better than an Me group at bridging (*e.g.*, in Al_2R_6 species, or in 1,2-bridging in carbocations), species (**III**) might be expected to be more readily formed than those of type (**IV**). In practice, however, attempts to make suitable TpsiSiRR′I species failed, as noted above, and this aspect of the study has been postponed until such species are made or $TpsiSiMe_2I$ with isotopically labelled Me groups is available. The reactions with silver salts were still examined, however, in order to produce new functional silicon compounds and to see whether migration of Me groups consistent with the intermediacy of silicocations of type (**IV**) might occur.

Reactions with Silver Salts.—Treatment of (**1d**) with AgY ($Y = OSO_2CF_3$, O_2CMe, or O_2CCF_3) gave the simple substitution products $TpsiSiMe_2Y$. The unrearranged fluoride $TpsiSiMe_2F$ was likewise obtained from $AgBF_4$. If an Me-bridged cation of type (**IV**) were formed, then some attack of the incoming nucleophile would be expected to take place at the silicon atom bearing one Me and one Ph group, to give some rearranged product $(PhMe_2Si)_2C(SiMePhY)(SiMe_3)$, since corresponding reactions of the iodide TsiSiMePhI, which are thought go through an intermediate of type (**II**) (R = Me, R′ = Ph), do give a proportion of rearranged products of the type $(Me_3Si)_2C(SiMe_2Ph)(SiMe_2Y)$.[2] The simplest explanation of the absence of Me migration in reactions of (**1d**) is that a phenyl-bridged intermediate of type (**III**) (R = R′ = Me) is formed preferentially, the rearranged product in this case being indistinguishable from the unrearranged.

Significantly, the iodide (**1d**) reacts markedly more readily than $TsiSiMe_2I$ with silver salts. Thus when a mixture of (**1d**), $TsiSiMe_2I$, and AgO_2CMe (undissolved) in 1:1:2 mole ratio in CH_2Cl_2 was kept at room temperature for 1 h, 50% of (**1d**) was converted into the corresponding acetate, whereas no detectable amount (<3%) of acetate had been formed from $TsiSiMe_2I$. When a similar mixture, but involving AgSCN, was kept at room temperature, 75% of (**1d**) had disappeared after 1 h and all of it within 24 h, during which no reaction of $TsiSiMe_2I$ occurred. (We have never been able to bring the latter into reaction with AgSCN even under reflux in various solvents.) The product from (**1d**) was identical with that obtained by reaction with KSCN, and is believed to be the isothiocyanate, $TpsiSiMe_2NCS$. The large difference in reactivity between the two iodides possibly reflects greater assistance by a Ph than by an Me group to leaving of the iodide ion.

When the iodide (**1d**) was treated with AgOCN in CH_2Cl_2 at room temperature the i.r. spectrum of the solution after 30 min showed bands, at 2 245 and 2 275 cm^{-1}, respectively, characteristic[6] of SiOCN and SiNCO groupings; these bands had roughly the same intensity, and since the NCO band is normally stronger than that of OCN it is likely that the SiOCN species predominated. When the mixture was stirred for a further 30 min then worked up, with recrystallization of the solid product from hexane, only the isocyanate, $TpsiSiMe_2NCO$, was isolated, and it seems that isomerization of the normal cyanate to the isocyanate takes place somewhat more readily than that of $TsiSiMe_2OCN$.[6]

Treatment of the iodide (**1d**) with $AgOSO_2CF_3$ in moist ether gave the hydroxide (**1e**), the behaviour paralleling that of $TsiSiMe_2I$. Reaction with $AgNO_3$ in MeOH gave exclusively the methoxide, (**1f**); no nitrate was detected (though <5% of it would have escaped detection) whereas the corresponding reaction of $TsiSiMe_2I$ gave the methoxide and nitrate in 76:24 ratio.[2] It is possible that some of the nitrate $TpsiSiMe_2ONO_2$ was initially formed from (**1d**) but underwent solvolysis under the conditions used.

Solvolysis.—The reaction of the iodide (**1d**) with MeOH at 52 °C was monitored by ^1H n.m.r. spectroscopy and found to give a good first-order plot with a half-life of *ca.* 21 h. The presence of 0.05M-NaOMe increased the rate by about 23%, but there was no significant further increase in rate when the base concentration was raised to 0.10M, this behaviour being similar to that of the iodide $TsiSiMe_2I$[5] (and of the perchlorate $TsiSiMe_2OClO_3$[4] and triflate $TsiSiMe_2OSO_2CF_3$[17]). The absence of marked acceleration of the methanolysis of $TsiSiMe_2X$ species by base was initially taken to imply that the rate-determining step involved ionization in an S_N1 process to give a bridged cation of type (**II**) (R = R′ = Me),[4] but it was later shown that no rearrangement takes place in solvolysis of $TsiSiR_2I$ species (R = Et or Ph), indicating that the reactions are not simple S_N1 processes.[7] It is possible that they have a type of S_N2 (intermediate) mechanism,[18] in which there is nucleophilic assistance by the solvent but also much cationic character in the transition state, and results with $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2X)$ species, which contain the very effective methoxy bridging group,[19] suggest that there may be important anchimeric stabilization of the incipient cationic centre even though there is also nucleophilic involvement of solvent and no rearrangement.[19] The iodide (**1d**) is about 15 times as reactive in methanolysis as $TsiSiMe_2I$, which has a half-life of 13 days at 50 °C;[5] this is in keeping with the higher reactivity of (**1d**) towards silver salts, and we tentatively ascribe it to anchimeric assistance by a Ph group, though we cannot rule out the possibility that the Tpsi ligand gives rise to less steric hindrance than the Tsi ligand to solvation around the forming cationic centre.

The presence of 2 vol % of water in the MeOH increased the rate of solvolysis of (**1d**) by *ca.* 20%, and the product was a mixture of the methoxide (**1f**) and the hydroxide (**1e**) in 82:18 ratio, implying that the increase in rate is essentially due to an independent reaction with water, with little effect on the rate of the methanolysis itself.

Reactions with Alkali Metal Salts.—Samples of the azide TpsiSiMe$_2$N$_3$ and the isothiocyanate TpsiSiMe$_2$NCS, respectively, were made by reaction of the iodide (**1d**) with excess of (*a*) NaN$_3$ in bis(2-methoxyethyl) ether, and (*b*) KSCN in MeCN.* To obtain some measure of the reactivity of (**1d**) in the latter reaction a solution of the iodide (0.017M) and KSCN (0.10M) in MeCN was refluxed, and a sample was withdrawn after 15 min and found to contain (**1d**) and TpsiSiMe$_2$NCS in *ca.* 45:55 ratio, and after 30 min the ratio was *ca.* 25:75. When similar procedures were carried out but with 0.20 and 0.4M KSCN the corresponding ratios after 15 min were 30:70 and 10:90. These approximate figures are consistent with a first-order dependence on the concentration of the salt. A direct comparison showed that (**1d**) and TsiSiMe$_2$I have rather similar reactivities towards KSCN under these conditions; thus when a solution in MeCN of (**1d**), TsiSiMe$_2$I, and KSCN in a 1:1:7.5 molar ratio was refluxed for 10 min, 70% of (**1d**) and 62% of TsiSiMe$_2$I were converted into the corresponding isothiocyanates.

It is noteworthy that the iodide (**1d**) was found to undergo hydrolysis to give (**1e**) when refluxed with MeCN (the reaction was 80% complete in 6 h) even though the latter had been treated with CaH$_2$ to remove water; similar behaviour was observed with TsiSiMe$_2$I.[8]

The reactions of (**1d**) with various salts in MeOH were examined. When a mixture of (**1d**) (0.017M) and NaN$_3$ (0.4M) in MeOH was boiled under reflux, after 6 h (**1d**), the methoxide (**1f**) and the corresponding azide were present in *ca.* a 5:55:40 ratio. Under similar conditions TsiSiMe$_2$I gave exclusively the azide TsiSiMe$_2$N$_3$ (even with 0.1M-NaN$_3$),[8] and it is evident that azide ion competes with MeOH markedly less effectively in reaction with (**1d**) than with TsiSiMe$_2$I. Similarly, when a solution of (**1d**) (0.017M) and KSCN (0.40M) in MeOH was refluxed, after 6 h (**1d**), the methoxide (**1f**), and the isothiocyanate, TpsiSiMe$_2$NCS, were present in a 5:65:30 ratio. In the corresponding reaction of TsiSiMe$_2$I, but with only 0.10M-KSCN, the initial iodide, the methoxide, and the isothiocyanate were present in *ca.* a 38:12:50 ratio after 24 h.[8] This implies that a value of *ca.* 12:200 would be expected for the methoxide to isothiocyanate product ratio if 0.40M-KSCN were used, compared with the ratio of 65:30 observed for reaction of (**1d**), and thus that the thiocyanate ion competes with MeOH markedly less effectively (by roughly a factor of 36) in reaction with (**1d**) than in reaction with TsiSiMe$_2$I. When a solution of (**1d**), TsiSiMe$_2$I and KSCN in a 1:1:15 molar ratio in MeOH was refluxed for 4 h, n.m.r. spectroscopy showed that 90% of (**1d**) had reacted, to give the methoxide and isothiocyanate in a 74:16 ratio, and 30% of the TsiSiMe$_2$I had reacted to give a corresponding ratio of 6:24. If the reactions with KSCN are, for simplicity, regarded as of pseudo-first-order (the KSCN being in excess), the results imply that the overall reaction of (**1d**) is roughly 6 times as fast as that of TsiSiMe$_2$I, with (**1d**) very roughly 25 times the more reactive towards MeOH and the two iodides having roughly similar reactivities towards KSCN.

When a solution of (**1d**) and KOCN (0.40M) or CsF (0.40M) in MeOH was boiled under reflux, only the methoxide (**1f**) was present in each case after 18 h. The failure of fluoride ion to compete with MeOH is rather surprising, since the reaction of TsiSiMe$_2$I with only 0.10M-CsF gave the corresponding fluoride and methoxide in an 8:1 ratio,[8] and the implication is that (**1d**) is significantly less reactive than TsiSiMe$_2$I towards fluoride ion. [We should emphasize that none of the methoxide (**1f**) formed in these reactions with salts MX in MeOH come from reaction of the products TpsiSiMe$_2$Y with the solvent, since all relevant TpsiSiMe$_2$Y species (Y = NCS, NCO, F, or N$_3$) were recovered unchanged after 48 h in boiling MeOH.]

The fact that (**1d**) is markedly more reactive than TsiSiMe$_2$I towards MeOH and silver salts (reactions in which much silicocationic character is thought to be developed in the transition state) but not towards alkali metal salts (which are direct bimolecular processes) is consistent with the possibility that a Ph group of the Tpsi ligand provides greater anchimeric assistance than an Me group of the Tsi ligand.

Miscellaneous Reactions.—The hydroxide TpsiSiMe$_2$OH was converted into the acetate TpsiSiMe$_2$O$_2$CMe by boiling MeCOCl (the reaction was carried on for 24 h, but may well have been complete in a much shorter time). The corresponding reaction is known for TsiSiMe$_2$OH.[21]

Some reactions of TpsiSiMeHCl were briefly examined. This compound was recovered unchanged after refluxing for 24 h with a concentrated solution of I$_2$ in CCl$_4$. This contrasts with the ease of iodination of TpsiSiMe$_2$H by I$_2$ (which was complete in 3 h at room temperature), and illustrates the powerful effect of an α-halogen atom on the ease of halogenolysis of an Si–H bond (*cf.* reference 22).

Quantitative cleavage of the Tpsi–Si bond took place when a solution of TpsiSiMeHCl in 0.50M-NaOMe–MeOH was refluxed for 5 h; after work-up the solid product was found to be exclusively (PhMe$_2$Si)$_3$CH. We do not know whether this cleavage was the primary reaction, or, for example, followed replacement of the H or Cl ligand by OMe.

A surprising reaction occurred when (PhMe$_2$Si)$_4$C was treated with MeLi (made from MeCl) in Et$_2$O–THF in the hope of generating TpsiLi by a cleavage of the same general type as that just described. After 8 h under reflux, hydrolytic work-up followed by crystallization from MeOH gave a solid, which from its ^{1}H n.m.r. spectrum appeared to be a single product, showing peaks at δ(CH$_2$Cl$_2$) 0.23 (s), 1.58 (s), and 7.2—7.5 (m) with integration in a *ca.* 4:1:4 ratio. In CCl$_4$ the signal at δ 0.23 was split into two slightly separated peaks of equal height. The mass spectrum had the highest mass peaks at *m/z* 317 (35%) and 297 (85%) with the base peak at 135 ([PhMe$_2$Si]$^+$). These data are consistent with the formulation (PhMe$_2$Si)$_2$C(Me)(Cl); the peaks at *m/z* 317 and 297 correspond with [*M* − Me]$^+$ and [*M* − Cl]$^+$, respectively, and the splitting of the δ 0.23 peak (from the SiMe$_2$ protons) in CCl$_4$ can be ascribed to the prochirality of the central carbon atom. The chlorine presumably comes from the LiCl produced in the formation of MeLi from MeCl, but we cannot suggest any reasonable route to the final product. In an attempt to detect intermediates the reaction was repeated but with reflux for only 3 h, but the recovered solid was shown by ^{1}H n.m.r. spectroscopy to contain only the same product along with unchanged (PhMe$_2$Si)$_4$C, in an 85:15 ratio.

Experimental

Unless otherwise indicated ^{1}H n.m.r. spectra were recorded with solutions in CCl$_4$.

Preparation of (PhMe$_2$Si)$_n$CH$_{4-n}$ (n = 2—4)(cf. *reference* 10).—(*a*) A mixture of Me$_2$PhSiCl (82.4 g, 0.48 mol), in CCl$_4$ (19.2 g, 0.12 mol), Mg (11.2 g, 0.48 mol), and THF (300 cm^3) was stirred at room temperature for 8 h in a flask immersed in

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* The reaction of (**1d**) with NaN$_3$ in MeCN to give a tetrazole will be described elsewhere.[20]

an ultrasonic bath. Subsequently, 10% hydrochloric acid was cautiously added and the organic layer was separated and dried ($MgSO_4$). Removal of the solvent left an oil, and to this an excess of MeOH was added; the mixture was kept at −22 °C for 3 days, during which $(PhMe_2Si)_4C$ separated as needles (5.2 g, 20%), m.p. 207 °C (lit.,[10] 205—206 °C); $\delta_H(CCl_4)$ 0.24 (24 H, s, Me) and 7.0—8.0 (20 H, m, Ph).

(*b*) A mixture of $Me_2PhSiCl$ (72 g, 0.42 mol), CCl_4 (15.6 g, 0.10 mol), Mg (10 g, 0.41 mol), and THF (300 cm^3) was stirred at 50 °C for 8 h in a flask immersed in an ultrasonic bath. Work-up as above gave, after treatment with MeOH at −22 °C, $(PhMe_2Si)_3CH$ (12 g, 20%), m.p. 105 °C (lit.,[10] 105—106 °C); $\delta_H(CCl_4)$ 0.30 (18 H, s, Me), 0.51 (1 H, s, CH), and 7.0—8.0 (15 H, m, Ph); *m/z* 403 ($[M - Me]^+$) and 325 ($[M - PhH - Me]^+$). The mother liquor was filtered then evaporated, to leave an oil, which was distilled under vacuum to give bis[phenyl(dimethyl)silyl]methane (40 g), b.p. 132 °C at 1 mmHg (lit.,[23] 131 °C at 1 mmHg).

Metallation of $(PhMe_2Si)_3CH$.—(*a*) A solution of MeLi (2.8 mmol; prepared from MeBr) in Et_2O (1 cm^3) was added to a solution of $(PhMe_2Si)_3CH$ (1.0 g, 2.4 mmol) in THF (15 cm^3) under dry nitrogen. The Et_2O was distilled out and the remaining solution was refluxed for 6 h then cooled to room temperature. A solution of D_2O (0.056 g, 2.8 mmol) in THF (10 cm^3) was cautiously added dropwise with stirring and cooling. The mixture was subsequently stirred at room temperature for 1 h, then an excess of aqueous NH_4Cl was added. Ether extraction followed by washing, drying ($MgSO_4$), and evaporation of the extract gave a solid, which was shown by its mass spectrum to consist of $(PhMe_2Si)_3CD$ and $(PhMe_2Si)_3CH$ in an 83:17 ratio; the n.m.r. signal from the tertiary C–H proton was barely detectable.

(*b*) The solution obtained from $(PhMe_2Si)_3CH$ (1.0 g, 2.4 mmol) and MeLi (2.8 mmol) in THF (15 cm^3) as described under (*a*) was treated dropwise with a solution of MeI (0.45 g, 3.2 mmol) in THF, and the mixture was subsequently stirred at room temperature for 1 h. Work-up as in (*a*), above, left a solid, which was recrystallized from CCl_4 to give *methyl[tris(phenyldimethylsilyl)]methane* (0.95 g, 92%), m.p. 187 °C; δ_H 0.08 (18 H, s, $SiMe_2$), 1.60 (3 H, s, CMe), 7.2—7.8 (15 H, m, Ph); *m/z* 417 (11%, $[M - Me]^+$), 355 (2, $[M - Ph]^+$), 339 (12, $[M - PhH - Me]^+$), 282 (41, $[M - PhSiMe_3]^+$), and 135 (100) (Found: C, 72.4, H, 8.3. $C_{26}H_{36}Si_3$ requires C, 72.2; H, 8.3%).

Stability of $(PhMe_2Si)_3CLi$ (TpsiLi) *in THF*.—A solution of MeLi (8.0 mmol) (made from MeBr) in Et_2O (5 cm^3) was added to a solution of $(PhMe_2Si)_3CH$ (3.35 g, 8.0 mmol) in THF (40 cm^3). The Et_2O was slowly distilled out until the temperature of the refluxing liquid was 66—67 °C and the solution was boiled gently under nitrogen for 6 h. A sample was withdrawn and analysed for organolithium content by the double titration procedure involving use of 1,2-dibromoethane,[24] which showed it to be 0.162M (*ca.* 80%). The mixture was refluxed and samples were withdrawn from time to time and analysed; the molarities at various times after the first analysis were: 0.131, 24 h; 0.10, 48 h; 0.070, 72 h; 0.039, 96 h; and 0.011, 120 h.

Attempted Reactions of TpsiLi *with Various Organosilicon Halides*.—A solution of Me_2SiCl_2 (0.60 g, 4.6 mmol) in THF (5 cm^3) was added to a solution of TpsiLi prepared from $(PhMe_2Si)_3CH$ (1.0 g, 2.4 mmol) and MeLi (2.8 mmol) in THF (15 cm^3). The mixture was refluxed for 24 h then worked up as described above to give a solid, which was shown by its ^1H n.m.r. spectrum to be exclusively $(PhMe_2Si)_3CH$.

The same result was obtained when the following halides were used: Me_3SiCl, Et_2SiCl_2, Et_2SiF_2, EtMeSiHCl, PhMeSiHCl, $PhMe_2SiCl$, $PhMe_2SiF$, and Ph_2SiF_2.

Preparation of $(PhMe_2Si)_3CSiMeHCl$.—A solution of $MeSiHCl_2$ (0.55 g, 4.5 mmol) in THF (5 cm^3) was added dropwise to a solution of TpsiLi made from $(PhMe_2Si)_3CH$ (1.0 g, 2.4 mmol) as described in (*a*) above. The mixture was refluxed for 2 h then worked up in the usual way to give a solid, which was recrystallized from EtOH to give *(chloro)(methyl)[tris(phenyldimethylsilyl)methyl]silane*, (0.98 g, 83%), m.p. 115 °C; δ_H 0.41 (3 H, d, Si*Me*HCl), 0.52 (18 H, d, Si*Me*$_2$Ph), 5.19 (1 H, m, SiH), and 6.7—7.0 (15 H, m, SiPh); ν(SiH) 2 160 cm^{-1}; *m/z* 481 (15%, $[M - Me]^+$), 417 (36, $[M - SiMeHCl]^+$), 403 (30, $[M - PhH - Me]^+$), and 135 (100) (Found: C, 62.9; H, 7.4. $C_{26}H_{37}ClSi_4$ requires C, 62.8; H, 7.5%).

Preparation of $(PhMe_2Si)_3CSiMe_2H$ ($TpsiSiMe_2H$).—The solution of TpsiLi obtained from $(PhMe_2Si)_3CH$ (1.0 g, 2.4 mmol) in THF (15 cm^3) as described in (*a*) above was treated dropwise with Me_2SiHCl (0.26 g, 2.8 mmol) in THF (5 cm^3). The mixture was stirred at room temperature for 1 h then worked up in the usual way to give a solid, which was recrystallized from EtOH to give *dimethyl[tris(phenyldimethylsilyl)methyl]silane* (0.85 g, 75%), m.p. 128 °C; δ_H 0.30 (6 H, d, *J* 2 Hz, Si*Me*$_2$H), 0.58 (18 H, s, Si*Me*$_2$Ph), 4.48 (1 H, m, SiH), 7.0—7.8 (15 H, m, Ph); *m/z* 461 (20%, $[M - Me]^+$), 417 (10, $[M - SiMe_2H]^+$), 397 (40), 381 (70), 340 (15, $[M - SiPhMe_2H]^+$), 325 (25), 309 (32), 247 (25), 197 (35), and 135 (100) (Found: C, 68.5; H, 8.3. $C_{27}H_{40}Si_4$ requires: C, 68.1; H, 8.4%).

Reactions of $TpsiSiMe_2H$, (**1a**), *with Halogens*.—(*a*) A solution of I_2 (1.06 g, 4.2 mmol) in CCl_4 (20 cm^3) was added to a solution of (**1a**) (1.0 g, 2.1 mmol) in CCl_4 (20 cm^3). The mixture was stirred at room temperature for 3 h, then shaken with aqueous $NaHSO_3$ to remove the residual I_2. The organic layer was separated, washed, dried ($MgSO_4$), and evaporated to leave a solid, which was recrystallized twice from hexane to give *(iodo)(dimethyl)[tris(phenyldimethylsilyl)methyl]silane*, (**1d**) (0.80 g, 63%), m.p. 154 °C; δ_H 0.81 (18 H, s, Si*Me*$_2$Ph), 1.26 (6 H, s, $SiMe_2I$), and 6.6—7.5 (15 H, m, Ph).

(*b*) A solution of ICl (0.39 g, 2.4 mmol) in CCl_4 (5 cm^3) was added dropwise with stirring to a solution of (**1a**) (1.0 g, 2.1 mmol) in CCl_4 (20 cm^3). The mixture was stirred at room temperature for 15 min then shaken with aqueous $NaHSO_3$. The organic layer was separated, washed, dried ($MgSO_4$), and evaporated to give a solid, which was recrystallized from MeOH to give *(chloro)(dimethyl)[tris(phenyldimethylsilyl)methyl]silane*, (**1b**) (0.70 g, 70%), m.p. 176 °C; δ_H 0.69 (6 H, s, $SiMe_2Cl$), 0.70 (18 H, s, Si*Me*$_2$Ph), and 6.7—7.4 (15 H, m, Ph); *m/z* 510 (3%, $[M]^+$), 495 (25, $[M - Me]^+$), 433 (25, $[M - Ph]^+$), 417 (30, $[M - SiMe_2Cl]^+$), 381 (70), 340 (70, $[M - SiPhMe_2Cl]^+$), 325 (60, $[M - SiPhMe_2Cl - Me]^+$), 309 (50), 197 (50), and 135 (100) (Found: C, 63.4; H, 7.8. $C_{27}H_{39}ClSi_4$ requires C, 63.4; H, 7.4%).

(*c*) A solution of Cl_2 (0.28 mmol) in CCl_4 (2.5 cm^3) was added with stirring to a solution of (**1a**) (0.10 g, 0.21 mmol) in CCl_4 (5 cm^3). The mixture was stirred at room temperature for 15 min then evaporated under reduced pressure to leave a solid, which from its ^1H n.m.r. spectrum was judged to be essentially pure (**1b**).

(*d*) A procedure similar to that described for reaction of ICl under (*b*), above, was used for reaction of Br_2 (2.4 mmol) in CCl_4 (10 cm^3) with (**1a**) (2.1 mmol) in CCl_4 (30 cm^3) and for work-up. The solid obtained was recrystallized twice from hexane and shown to be *(bromo)(dimethyl)[tris(phenyldimethylsilyl)methyl]silane*, m.p. 178 °C; δ_H 0.78 (18 H, s, Si*Me*$_2$Ph), 0.94 (6 H, s, $SiMe_2Br$), and 6.7—7.5 (15 H, m, Ph); *m/z* 539 (15%, $[M - Me]^+$), 477 (15, $[M - Ph]^+$), 397 (10), 381 (60), 340 (50, [*M* −

$SiPhMe_2Br]^+$), 325 (40), 309 (30), 197 (40), and 135 (100) (Found: C, 57.9; H, 7.2. $C_{27}H_{39}BrSi_4$ requires C, 58.4; H, 7.0%).

Reaction of (**1d**) *with* ICl.—A solution of ICl (0.027 g, 0.17 mmol) was added dropwise with stirring to a solution of (**1d**) (0.10 g, 0.17 mmol) in CCl_4 (9 cm^3). The mixture was stirred for 1 h at room temperature then evaporated under reduced pressure to leave a solid, which was shown by its ^1H n.m.r. spectrum to be the chloride (**1b**).

Reactions of $TpsiSiMe_2I$, (**1d**), *with Silver Salts.*—(*a*) A mixture of (**1d**) (0.80 g, 1.33 mmol) and $AgBF_4$ (0.30 g, 1.50 mmol) in CH_2Cl_2 (25 cm^3) was stirred at room temperature for 30 min. The solution was then filtered and evaporated, and the remanent solid was recrystallized from MeOH to give *(fluoro)(dimethyl)[tris(phenyldimethylsilyl)methyl]silane* (0.52 g, 79%), m.p. 125 °C; δ_H 0.28 (6 H, d, *J* 5 Hz, $SiMe_2F$), 0.59 (18 H, s, $Si\mathit{Me}_2Ph$), and 7.0—7.5 (15 H, m, Ph); δ_F (CCl_4 relative to external $CFCl_3$) −137 p.p.m. (s); *m/z* 494 (3%, $[M]^+$), 479 (25, $[M - Me]^+$), 416 (20, $[M - PhH]^+$), 401 (35, $[M - PhH - Me]^+$), 340 (50, $[M - SiPhMe_2F]^+$), 325 (55), 309 (24), 197 (30), and 135 (100) (Found: C, 65.4; H, 8.2. $C_{27}H_{39}FSi_4$ requires C, 65.6; H, 7.9%).

(*b*) A mixture of (**1d**) (1.66 mmol) and freshly prepared AgSCN (1.80 mmol) in CH_2Cl_2 (30 cm^3) was stirred at room temperature for 30 min, after which a sample was withdrawn and filtered through cotton-wool and its i.r. spectrum was determined; this showed the ν(SiNCS) band at 2 070 cm^{-1}. The mixture was stirred for a further 30 min then the solution was filtered, and evaporated under reduced pressure. The remanent solid was washed with MeOH and recrystallized twice from hexane to give *(isothiocyanato)(dimethyl)[tris(phenyldimethylsilyl)methyl]silane* (0.67 g, 75%), m.p. 136 °C; δ_H 0.41 (6 H, s, $SiMe_2NCS$), 0.64 (18 H, s, $Si\mathit{Me}_2Ph$), and 6.9—7.4 (15 H, m, Ph); ν(NCS) 2 070 cm^{-1}; *m/z* 533 (3%, $[M]^+$), 518 (3, $[M - Me]^+$), 440 (10), 397 (10), 381 (70), 340 (40), 325 (40), 309 (30), 197 (30), and 135 (100) (Found: C, 63.2; H, 7.6; N, 2.8. $C_{28}H_{39}NSSi_4$ requires C, 63.0; H, 7.3, N, 2.6%).

(*c*) A mixture of (**1d**) (0.017 mmol), $TsiSiMe_2I$ (0.017 mmol), AgSCN (0.035 mmol), and CH_2Cl_2 (0.5 cm^3) was placed in an n.m.r. tube, which was kept at room temperature with frequent shaking. After 1 h the n.m.r. spectrum showed that 75% of (**1d**) had been converted into the corresponding isothiocyanate, and that no $TsiSiMe_2NCS$ had been formed. The mixture was set aside for 24 h, after which the ^1H n.m.r. spectrum showed that only $TpsiSiMe_2NCS$ and $TsiSiMe_2I$ were present in solution.

(*d*) A similar procedure to that described under (*c*) above was carried out with AgO_2CMe in place of AgSCN. After 1 h the ^1H n.m.r. spectrum showed that 50% of (**1d**) but no detectable amount (<3%) of $TsiSiMe_2I$ had been converted into the corresponding acetates.

(*e*) A procedure similar to that described under (*b*) for reaction with AgSCN was used for reaction with AgOCN. The sample withdrawn after 30 min showed both ν(SiOCN) (2 245 cm^{-1}) and ν(SiNCO) (2 275 cm^{-1}) bands in the i.r.; the peaks were of roughly equal height. After a further 30 min filtration and evaporation gave a solid, which was recrystallized from hexane and shown to be *(isocyanato)(dimethyl)[tris(phenyldimethylsilyl)methyl]silane* (60%), m.p. 138 °C; δ_H 0.41 (6 H, s, $SiMe_2NCO$), 0.62 (18 H, s, $Si\mathit{Me}_2Ph$), and 7.0—7.5 (15 H, m, Ph); ν(SiNCO) 2 275 cm^{-1} (no band at 2 245 cm^{-1}); *m/z* 517 (90, $[M]^+$), 502 (45, $[M - Me]^+$), 424 (20), 381 (30), 340 (10), 325 (10), 197 (10), and 135 (100) (Found: C, 64.7; H, 7.8; N, 2.5. $C_{28}H_{39}NOSi_4$ requires C, 65.0; H, 7.7; N, 2.7%).

(*f*) A mixture of (**1d**) (0.50 mmol) and AgO_2CCF_3 (0.58 mmol) in CH_2Cl_2 (30 cm^3) was stirred at room temperature for 1 h, then filtered and evaporated. The solid obtained was washed with cold MeOH then recrystallized twice from hexane to give *(trifluoroacetoxy)(dimethyl)[tris(phenyldimethylsilyl)methyl]silane* (62%), m.p. 166 °C; δ_H 0.50 (6 H, s, $SiMe_2O$), 0.63 (18 H, s, $Si\mathit{Me}_2Ph$), and 6.9—7.6 (15 H, m, Ph) (Found: C, 59.5; H, 6.7. $C_{29}H_{39}F_3O_2Si_4$ requires C, 59.5; H, 6.7%).

(*g*) A mixture of (**1d**) (0.83 mmol), $AgOSO_2CF_3$ (0.85 mmol), and CH_2Cl_2 (50 cm^3) was stirred at room temperature for 30 min, then filtered and evaporated. The remanent solid was recrystallized from hexane to give *(trifluoromethanesulphonato)(dimethyl)[tris(phenyldimethylsilyl)methyl]silane* (68%), m.p. 158 °C; δ_H 0.70 (24 H, s, $Si\mathit{Me}_2Ph + SiMe_2O$) and 6.8—7.6 (15 H, m, Ph) (Found: C, 54.2; H, 6.1. $C_{28}H_{39}F_3O_3SSi_4$ requires C, 53.9; H, 6.3%).

(*h*) A mixture of (**1d**) (0.85 mmol), $AgOSO_2CF_3$ (0.85 mmol), Et_2O (50 cm^3), and H_2O (5 cm^3) was stirred for 2 h at room temperature. The usual work-up gave a solid, which was recrystallized from hexane to give *(hydroxy)(dimethyl)[tris(phenyldimethylsilyl)methyl]silane* (87%), m.p. 122 °C; δ_H 0.26 (6 H, s, $SiMe_2O$), 0.62 (18 H, s, $Si\mathit{Me}_2Ph$), and 7.0—7.7 (15 H, m, Ph); ν(OH) 3 600 cm^{-1}; *m/z* 492 (3%, $[M]^+$), 477 (20, $[M - Me]^+$), 399 (75, $[M - PhH - Me]^+$), 397 (30, $[M - Ph - H_2O]^+$), 381 (40), 309 (30), 197 (40), and 135 (100) (Found: C, 65.4; H, 8.1. $C_{27}H_{40}OSi_4$ requires C, 65.8; H, 8.1%).

(*i*) A solution of (**1d**) (0.17 mmol) and $AgNO_3$ (0.17 mmol) in MeOH (10 cm^3) was stirred at room temperature for 1 h. Hexane was then added, followed by water. The organic layer was separated, washed, dried ($MgSO_4$), and evaporated under reduced pressure to leave a solid, which was identified from its ^1H n.m.r. spectrum as exclusively $TpsiSiMe_2OMe$, (**1f**).

Treatment of $TpsiSiMe_2Cl$, (**1b**), *with Silver Salts.*—A mixture of (**1b**) (1.1 mmol), $AgNO_3$ (1.5 mmol), and MeOH (50 cm^3) was stirred under reflux for 20 h. Addition of water and hexane, followed by the usual work-up, gave exclusively unchanged (**1b**).

The same result was obtained when AgOCN was used.

Reactions of $TpsiSiMe_2I$, (**1d**), *with Alkali Metal Salts.*—(*a*) A solution of (**1d**) (1.33 mmol) in bis-(2-methoxyethyl) ether (25 cm^3) was refluxed for 6 h in the presence of an excess of solid NaN_3. The solvent was then removed under reduced pressure and hexane was added followed by water. The hexane layer was separated, washed, dried ($MgSO_4$), and evaporated to leave *azido(dimethyl)[tris(phenyldimethylsilyl)methyl]silane* (70%), m.p. 127 °C; δ_H 0.39 (6 H, s, $SiMe_2N_3$), 0.63 (18 H, s, $Si\mathit{Me}_2Ph$), and 6.9—7.4 (15 H, m, Ph); ν(N_3) 2 130 cm^{-1}; *m/z* 517 (3%, $[M]^+$), 502 (3, $[M - Me]^+$), 489 (15, $[M - N_2]^+$), 381 (60), 340 (50), 325 (70), 309 (60), 197 (60), and 135 (100) (Found: C, 62.1; H, 7.9; N, 8.0. $C_{27}H_{39}N_3Si_4$ requires C, 62.6; H, 7.5; N, 8.1%).

(*b*) A solution of (**1d**) (0.17 mmol) and NaN_3 (4.0 mmol) in MeOH (10 cm^3) was refluxed for 6 h. Hexane was added followed by an excess of water, and the organic layer was separated, washed, dried ($MgSO_4$), and evaporated to leave a solid which was shown by ^1H n.m.r. spectroscopy and g.l.c. (5% OV101 on Chromosorb G) to consist of (**1d**), $TpsiSiMe_2N_3$, and the methoxide (**1f**) in a 5:40:55 ratio.

(*c*) A solution of (**1d**) (0.17 mmol) and 0.10M-KSCN (2.5 mmol) in MeCN (25 cm^3) was refluxed. Samples were withdrawn at various times, and quickly evaporated under reduced pressure; the solid obtained was extracted with CCl_4, and the ^1H n.m.r. spectrum of the solution was recorded. The heights of the signals from the $SiMe_2I$ and $SiMe_2NCS$ protons indicated that formation of the isothiocyanate was 55% complete after 0.25 h and 75% after 0.5 h.

When the procedure was repeated with 0.20 and 0.40M-KSCN the percentage conversions after 15 min were 70 and 90, respectively.

(*d*) A mixture of (**1d**) (0.17 mmol) and $TsiSiMe_2I$ (0.17 mmol) in 0.25M-KSCN (2.5 mmol) in MeCN (5 cm^3) was refluxed for 10 min. The solvent was then quickly removed under vacuum at room temperature to leave a solid, which was extracted with CCl_4. The ^1H n.m.r. spectrum of the solution showed that 70% of (**1d**) and 62% of $TsiSiMe_2I$ had been converted into the corresponding isothiocyanates.

(*e*) A solution of (**1d**) (0.17 mmol) and KSCN (4.0 mmol) in MeOH (10 cm^3) was refluxed for 6 h. The solvent was removed, and the remanent solid extracted with CCl_4. Washing, drying ($MgSO_4$), and evaporation of the extract left a solid, which was shown by ^1H n.m.r. spectroscopy and g.l.c. analysis (5.5% OV101 on Chromosorb G) to be a mixture of (**1d**), $TpsiSiMe_2NCS$, and $TpsiSiMe_2OMe$ in a 5 : 30 : 65 ratio.

(*f*) A solution of (**1d**) (0.17 mmol) and $TsiSiMe_2I$ (0.17 mmol) in 0.25M-KSCN (2.5 mmol) in MeOH (10 cm^3) was refluxed for 4 h, then the solvent was rapidly removed under reduced pressure at room temperature. The organic material was extracted into CCl_4, and the n.m.r. spectrum of the solution was recorded. This showed that *ca.* 90% of (**1d**) had reacted to give the methoxide and isothiocyanate in a 74:16 ratio, and 30% of $TsiSiMe_2I$ had reacted to give the methoxide and isothiocyanate in a 6:24 ratio.

(*g*) A solution of (**1d**) (0.17 mmol) and KOCN (4.0 mmol) in MeOH (10 cm^3) was refluxed. After 2 h a sample was removed, worked up, and analysed as in (*e*) above, and shown to contain (**1d**) and $TpsiSiMe_2OMe$, (**1f**), in a 40 : 60 ratio. The bulk of the solution was refluxed for a further 8 h, then evaporated, and the solid was extracted with CCl_4. The extract was filtered and evaporated to give exclusively (**1f**).

(*h*) The procedure described under (*g*) was used with CsF in place of KOCN. After 2 h reflux the mixture contained (**1d**) and (**1f**) in a 35:65 ratio, and after a further 6 h only the methoxide (**1e**) was present.

Solvolysis of $TpsiSiMe_2I$, (**1d**).—(*a*) A solution of (**1d**) (1.0 g, 1.66 mmol) in MeOH (50 cm^3) was boiled under reflux. After 48 h a sample was removed and shown by ^1H n.m.r. spectroscopy to contain (**1d**) and $TsiSiMe_2OMe$ (**1f**) in 6:94 ratio. Refluxing was continued for a further 48 h, and then the solution was kept at −22 °C. The solid that separated was filtered off and dried, and shown to be *(methoxy)(dimethyl)[tris(phenyldimethylsilyl)methyl]silane*, (**1f**), (0.66 g, 78%), m.p. 138 °C; δ_H 0.21 (6 H, s, $SiMe_2O$), 0.62 (18 H, s, $Si\mathit{Me}_2Ph$), 3.41 (3 H, s, OMe), and 7.0—7.5 (15 H, m, Ph); *m/z* 506 (3%, $[M]^+$), 491 (65, $[M - Me]^+$), 429 (50, $[M - Ph]^+$), 413 (70), 397 (25), 381 (75), 341 (75), 340 (55, $[M - SiPhMe_2OMe]^+$), 325 (65), 309 (60), 279 (40), 197 (50), and 135 (100) (Found: C, 66.4; H, 8.1. $C_{28}H_{42}OSi_4$ requires C, 66.4; H, 8.3%).

(*b*) A sample of (**1d**) (0.10 g, 0.166 mmol) was dissolved in a small (*ca.* 0.01 cm^3) drop of CCl_4, then MeOH (0.5 cm^3) was added and the mixture was briefly shaken then filtered through cotton-wool into an n.m.r. tube. The tube was stoppered, placed in a thermostatted bath at 52 °C, and removed at appropriate intervals for recording of the ^1H n.m.r. spectrum. The reaction was monitored up to *ca.* 93% completion (72 h), and the data gave a good first-order plot with rate constant of 0.93×10^{-6} s^{-1}, corresponding to a half-life of 21 h.

Similar procedures but using MeOH containing 0.05 or 0.10M-NaOMe gave good first-order plots with rate constants of 1.13×10^{-6} ($t_{\frac{1}{2}}$ 17 h) and 1.16×10^{-6} s^{-1}.

(*c*) A similar procedure to that described under (*b*) but with 2 vol % H_2O in MeOH gave a first-order plot with $k = 1.11 \times 10^{-6}$ ($t_{\frac{1}{2}}$ 17 h) for disappearance of (**1d**) (as judged by the heights of the $SiMe_2I$ peaks at δ 1.26 relative to the combined heights of the $Si\mathit{Me}_2OH$ and $Si\mathit{Me}_2OMe$ peaks at δ 0.25 and 0.21, respectively). The ratio of the methoxide to the hydroxide product was 4.5 ± 0.3 throughout.

Attempted Methanolysis of Various $TpsiSiMe_2X$ *Compounds*.—The compounds $TpsiSiMe_2X$ (X = Cl, Br, NCO, and NCS) were recovered unchanged after 48 h reflux in MeOH.

Reaction of $TpsiSiMe_2OH$ (**1e**) *with* MeCOCl.—A mixture of (**1e**) (0.2 g) and MeCOCl (10 cm^3) was refluxed for 24 h. The volatile species were then evaporated off under vacuum to leave a solid, which was recrystallized from hexane to give *(acetoxy)(dimethyl)[tris(phenyldimethylsilyl)methyl]silane*, (0.18 g, 85%), m.p. 148 °C; δ_H 0.45 (6 H, s, $SiMe_2O$), 0.62 (18 H, s, $Si\mathit{Me}_2Ph$), 2.00 (3 H, s, OMe), and 6.9—7.5 (15 H, m, Ph); *m/z* 519 (20%, $[M - Me]^+$), 457 (10, $[M - Ph]^+$), 399 (40, $[M - SiPhMe_2]^+$), 383 (20), 340 (30), 325 (35), 309 (15), 249 (30), 197 (25), and 135 (100) (Found: C, 64.8; H, 8.2 $C_{29}H_{42}O_2Si_4$ requires C, 65.2; H, 7.9%).

Miscellaneous Reactions.—(*a*) *Reaction of* $(PhMe_2Si)_4C$ *with* MeLi. A 1.80M solution of MeLi (0.92 mmol) in Et_2O (0.51 cm^3) (prepared from MeCl) was added to a solution of $(PhMe_2Si)_4C$ (0.50 g, 0.91 mmol) in THF (20 cm^3). The mixture was refluxed for 8 h then cooled, and an excess of water was added followed by hexane. The organic layer was separated, washed, dried ($MgSO_4$), and evaporated, and the residual oil was treated with cold MeOH to give a solid; $\delta_H(CH_2Cl_2)$ 0.23 (s), 1.58 (s), and 7.2—7.8 (m) (integration ratio *ca.* 4 : 1 : 4) (in CCl_4, signal at δ 0.23 was a doublet); *m/z* 317 (35%, $[M - Me]^+$), 297 (85, $[M - Cl]^+$), 197 (30, $[M - SiPhMe_2]^+$), 162 (45), 147 (50), and 135 (100, $[SiPhMe_2]^+$). [The value of *M* is based on assumed formulation as $(PhMe_2Si)_2C(Me)(Cl)$, see Discussion section.]

The experiment was repeated but with only 3 h reflux. The solid isolated was shown by its ^1H n.m.r. spectrum to consist of $(PhMe_2Si)_4C$ and the product described above in *ca.* a 15:85 ratio.

(*b*) *Reaction of* TpsiSiMeHCl *with* NaOMe–MeOH. A solution of TpsiSiMeHCl (0.30 g) in 0.5M-NaOMe in MeOH (10 cm^3) was refluxed for 5 h. Addition of Et_2O followed by water, then separation, washing, drying ($MgSO_4$), and evaporation of the ethereal layer gave a solid which was shown (^1H n.m.r. spectroscopy and g.l.c.) to be $(PhMe_2Si)_3CH$ by comparison with an authentic sample.

(*c*) *Reaction of* TpsiSiMeHCl *with* I_2. A solution of I_2 (0.51 g, 2.0 mmol) and TpsiSiMeHCl (0.20 g, 0.40 mmol) in CCl_4 (15 cm^3) was refluxed for 24 h, then cooled and shaken with aqueous $NaHSO_3$. The organic layer was separated, washed, dried ($MgSO_4$), and evaporated to give only unchanged TpsiSiMeHCl (^1H n.m.r. spectrum).

Acknowledgements

We thank the S.E.R.C. for support, the Dow Corning Co., Ltd., for gifts of organosilicon chemicals, the Ministry of Higher Education of the Kingdom of Saudi Arabia for the award of a Postgraduate Research Scholarship to A. I. M., and Mr R. W. Bott for valuable comments.

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Received 21*st August* 1984; *Paper* 4/1457