Preparation and Reactions of Difunctional Sterically Hindered Organosilicon Compounds of the Type $(Me_3Si)_2C(SiMe_2X)(SiMe_2Y)$

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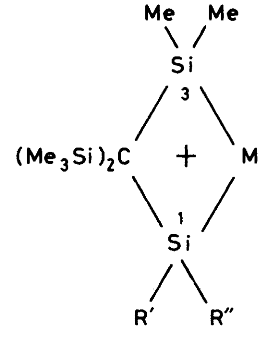
Reaction of TsiSiMeICl [Tsi = $(Me_3Si)_3C$] with AgY or $AgBF_4$ gave the rearranged species $R_2C(SiMe_2Cl)(SiMe_2Y)$ (Y = OSO_2CF_3, $OClO_3$, $OCOCF_3$, $OSO_2C_6H_4Me$-*p*, or F) (R = Me_3Si throughout). Correspondingly, TsiSiMeIF reacted with $AgSO_3CF_3$ to give $R_2C(SiMe_2F)(SiMe_2OSO_2CF_3)$ and with ICl to give $R_2C(SiMe_2F)(SiMe_2Cl)$; TsiSiMeIBr likewise gave $R_2C(SiMe_2Br)(SiMe_2OSO_2CF_3)$ on treatment with $AgSO_3CF_3$ but the di-iodide $TsiSiMeI_2$ reacted even with 1 molar equiv. of various silver salts to give $R_2C(SiMe_2Y)_2$ (Y = F, $OClO_3$, OSO_2CF_3, or $OSO_2C_2H_4Me$-*p*) along with unchanged $TsiSiMeI_2$. The iodo-hydride TsiSiMeHI gave only unrearranged TsiSiMeHF when treated with $AgBF_4$ in Et_2O, but a mixture of $R_2C(SiMe_2H)(SiMe_2F)$, TsiSiMeHF, and $R_2C(SiMe_2F)_2$ when CH_2Cl_2 was used as solvent. Other $R_2C(SiMe_2X)(SiMe_2Y)$ species were made as follows; (i) with X = H; Y = Cl, Br, or I, along with $R_2C(SiMe_2X)_2$, from $R_2C(SiMe_2H)_2$ with 1 molar equiv. of X_2; (ii) $R_2C(SiMe_2X)_2$ (X = Br or I) from $R_2C(SiMe_2H)_2$ and 2 molar equiv. of X_2; (iii) with X = F, Y = I, from $R_2C(SiMe_2F)(SiMe_2H)$ and I_2; (iv) with X = OMe, Y = Cl, from $R_2C(Cl)(SiMe_2OMe)$ [*via* $R_2C(Li)(SiMe_2OMe)$] and Me_2SiCl_2.

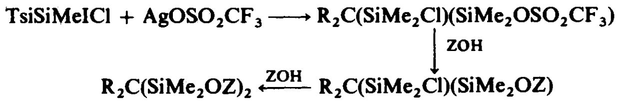
The methanolyses of several $R_2C(SiMe_2X)(SiMe_2Y)$ species were examined, and the results are discussed in terms of anchimeric assistance by the X or Y groups.

Much interesting chemistry has emerged from studies of compounds of the type TsiSiRR′X [Tsi = $(Me_3Si)_3C$].[1–8] This paper is concerned with the preparation and reactions of some related compounds, especially those of the type $(Me_3Si)_2C(SiMe_2X)(SiMe_2Y)$, where X and Y are identical or different functional groups.

The starting points for much of the work were the known compounds TsiSiMeHCl and TsiSiMeICl.[7] Treatment of TsiSiMeICl with $AgOSO_2CF_3$ in CH_2Cl_2 gave exclusively the rearranged species $R_2C(SiMe_2Cl)(SiMe_2OSO_2CF_3)$ (R = Me_3Si); this result is consistent with the previously reported formation of the rearranged dichloride $R_2C(SiMe_2Cl)_2$ on treatment of TsiSiMeICl with ICl,[3] and the reactions presumably proceed *via* Me-bridged cations of type (1) (R′ = Me, R″ = Cl). The $R_2C(SiMe_2Cl)(SiMe_2OSO_2CF_3)$ reacts very readily with MeOH to give the dimethoxide $R_2C(SiMe_2OMe)_2$, and with water in acetone to give the dihydroxide $R_2C(SiMe_2OH)_2$. Since $TsiSiMe_2Cl$ does not react with MeOH or aqueous acetone even on prolonged reflux, it seems that the $R_2C(SiMe_2Cl)(SiMe_2OSO_2CF_3)$ first forms $R_2C(SiMe_2Cl)(SiMe_2OZ)$ (Z = Me or H) (with assistance by the Cl to leaving of the OSO_2CF_3 group), and that the Si–Cl bond is then activated by the powerful anchimeric assistance from the γ-OZ group (see Scheme 1).[5,6]



(1)



$$\begin{tikzcd} TsiSiMeICl + AgOSO_2CF_3 \arrow[r] & R_2C(SiMe_2Cl)(SiMe_2OSO_2CF_3) \arrow[d, "ZOH"] \\ R_2C(SiMe_2OZ)_2 & R_2C(SiMe_2Cl)(SiMe_2OZ) \arrow[l, "ZOH"'] \end{tikzcd}$$

Scheme 1. Z = Me or H

Several other $R_2C(SiMe_2Cl)(SiMe_2X)$ compounds, namely those with X = F, $OClO_3$, $OCOCF_3$, or OSO_2Ph, were made analogously from the appropriate silver salt ($AgBF_4$ in the case of X = F).

The fluoro-iodide TsiSiMeIF (see later) reacted analogously with $AgOSO_2CF_3$ to give $R_2C(SiMe_2F)(SiMe_2OSO_2CF_3)$, with $AgBF_4$ to give $R_2C(SiMe_2F)_2$, and with ICl to give $R_2C(SiMe_2F)(SiMe_2Cl)$. The bromo-iodide TsiSiMeIBr (see later) likewise gave $R_2C(SiMe_2Br)(SiMe_2OSO_2CF_3)$ on treatment with $AgOSO_2CF_3$. The reactions of the di-iodide $TsiSiMeI_2$ are considered later.

When TsiSiMeHI was treated with $AgBF_4$ in Et_2O the unrearranged fluoride TsiSiMeHF was exclusively formed; this could be understood in terms of the much lower steric hindrance to nucleophilic attack at Si(1) in the intermediate (1) (R′ = Me, R″ = H). Surprisingly, however, the corresponding reaction in CH_2Cl_2 gave a mixture of rearranged and unrearranged fluorides, $R_2C(SiMe_2H)(SiMe_2F)$ (50%) and TsiSiMeHF (20%), along with the difluoride $R_2C(SiMe_2F)_2$ (30%). Since the difluoride can be assumed to have been formed from the rearranged species $R_2C(SiMe_2H)(SiMe_2F)$, with anchimeric assistance from the γ-F activating the Si–H bond towards reaction with the $AgBF_4$, roughly four times as much rearranged as unrearranged monofluoride must have been formed initially. It is possible that the differing behaviour in the two solvents is associated in some way with the fact that ether may (by giving $BF_3{\cdot}OEt_2$) assist the liberation of BF_3 which occurs on formation of the Si–F bond; *e.g.* with Et_2O present the BF_4^- may lose F^- to Si(1) before it can diffuse away from the neighbourhood of the initial reaction site.

The TsiSiMeHF, made as described above, gave TsiSiMeIF on treatment with ICl in CCl_4, and TsiSiMeHBr (made by reaction of $TsiSiMeH_2$ with one molar equiv. of Br_2) likewise gave TsiSiMeIBr.

Treatment of $TsiSiMeH_2$ with 2 molar equiv. of ICl gave the di-iodide $TsiSiMeI_2$; it seems that the TsiSiMeHI initially formed reacts preferentially at the Si–H bond (to give another Si–I bond) rather than at the Si–I bond to give an Si–Cl bond, even though the presence of one halogen on an SiH centre normally reduces markedly the ease of iodination.[8] It was hoped that treatment of $TsiSiMeI_2$ with 1 equiv. of a silver salt, AgY (actually $AgBF_4$ for introduction of F), would give compounds of the type $R_2C(SiMe_2I)(SiMe_2Y)$ (compare the reactions of TsiSiMeClI), but instead a mixture of $R_2C(SiMe_2Y)_2$ ($Y = F$, $OClO_3$, $OSO_2C_6H_4Me$-*p*, or OSO_2CF_3) and unchanged $TsiSiMeI_2$ was obtained. This indicates that when one Y group is introduced, to give $R_2C(SiMe_2I)(SiMe_2Y)$, the anchimeric assistance by the γ-Y group markedly activates the remaining Si–I bond towards reaction with the residual AgY. As expected, when an excess of AgY was used the $R_2C(SiMe_2Y)_2$ compounds with $Y = F$ (from $AgBF_4$), $OClO_3$, OSO_2Ph, or OSO_2CF_3 were obtained in good yields.

The compound $R_2C(SiMe_2I)(SiMe_2F)$ was made, but by a different route, which involved use of the mixture of $R_2C(SiMe_2H)(SiMe_2I)$, $R_2C(SiMe_2I)_2$, and $R_2C(SiMe_2H)_2$ obtained by treatment of this last compound with iodine (see later). The mixture reacted with $AgBF_4$ to give a mixture of $R_2C(SiMe_2H)(SiMe_2F)$, $R_2C(SiMe_2F)_2$, and $R_2C(SiMe_2H)_2$, from which $R_2C(SiMe_2H)(SiMe_2F)$ was isolated by t.l.c. Treatment of this product with 1 molar equiv. of ICl gave $R_2C(SiMe_2I)(SiMe_2F)$.

A starting point for several $R_2C(SiMe_2X)(SiMe_2Y)$ species was the dihydride $R_2C(SiMe_2H)_2$, which was made by reduction of $R_2C(SiMe_2Cl)_2$[3] with $LiAlH_4$. Treatment of $R_2C(SiMe_2H)_2$ with 1 equiv. of I_2 in CCl_4 gave a mixture of $R_2C(SiMe_2H)(SiMe_2I)$, $R_2C(SiMe_2I)_2$, and unchanged $R_2C(SiMe_2H)_2$, and the monoiodide was isolated by t.l.c. Treatment of a similar product mixture with boiling MeOH for 1 h [after which no $R_2C(SiMe_2H)(SiMe_2I)$ remained] did not give any $R_2C(SiMe_2H)(SiMe_2OMe)$; the major product was $R_2C(SiMe_2OMe)_2$. The amount of the latter produced, and the rate at which it was formed, showed that it could not all have come from $R_2C(SiMe_2I)_2$, and it seems that a substantial amount of it must have come from the $R_2C(SiMe_2H)(SiMe_2OMe)$ initially formed from $R_2C(SiMe_2H)(SiMe_2I)$, the combination of anchimeric assistance by the γ-OMe group and catalysis by the HI present resulting in fairly ready methanolysis of the Si–H bond.

Treatment of $R_2C(SiMe_2H)_2$ with 2 molar equiv. of the appropriate halogen, X_2, gave the dihalides $R_2C(SiMe_2X)_2$ ($X = Cl$, Br, or I). An attempt to make the chloro-iodide by treatment of $R_2C(SiMe_2I)(SiMe_2H)$ with 1 molar equiv. of Cl_2 was unsuccessful, $R_2C(SiMe_2Cl)_2$ being formed along with unchanged $R_2C(SiMe_2I)(SiMe_2H)$. [Treatment of $R_2C(SiMe_2I)(SiMe_2H)$ with Br_2 gave analogous results.] It seems that once $R_2C(SiMe_2I)(SiMe_2Cl)$ is formed, attack of Cl_2 at the Si–I bond, anchimerically assisted by the γ-Cl ligand,[5] is faster than that at the Si–H bond in the starting material, the reaction being analogous to that of silicon iodides with ICl to give silicon chlorides.[8] The chloro-iodide $R_2C(SiMe_2I)(SiMe_2Cl)$ was, however, obtained by reaction of I_2 with the chloro-hydride $R_2C(SiMe_2H)(SiMe_2Cl)$ (see Scheme 2); the latter was formed in 55% yield along with 5% of $R_2C(SiMe_2Cl)_2$ and unchanged $R_2C(SiMe_2H)_2$ when this dihydride was treated with Cl_2 in CCl_4 under conditions aimed at maximizing mono- relative to di-chlorination (see Experimental section), and the product mixture was separated by t.l.c. The bromo-iodo-compound $R_2C(SiMe_2I)(SiMe_2Br)$ was made analogously (Scheme 2).

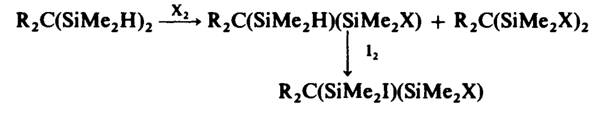
The iodo-fluoro-compound $R_2C(SiMe_2I)(SiMe_2F)$ was obtained by a different route (Scheme 3); the required compound was separated by t.l.c. from the difluoride $R_2C(SiMe_2F)_2$ and unchanged $R_2C(SiMe_2H)_2$.

The methoxy-chloride $R_2C(SiMe_2OMe)(SiMe_2Cl)$ was made *via* $R_2C(SiMe_2OMe)Cl$, and hence $R_2C(SiMe_2OMe)Li$ (*cf.* ref. 9), as shown in Scheme 4.

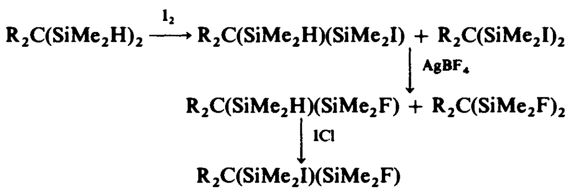
The compound $R_2C(SiMe_2OMe)(SiMe_2Cl)$ was also made on one occasion by metallation of $R_2CH(SiMe_2OMe)$ with MeLi in Et_2O–tetrahydrofuran followed by treatment with Me_2SiCl_2. This result could not be reproduced, however, the only product isolated in all subsequent attempts being $TsiSiMe_2Cl$, apparently formed by initial replacement of the OMe group of $R_2CH(SiMe_2OMe)$ by Me to give TsiH, which then underwent metallation in the usual way.

The bromide $R_2C(SiMe_2Br)Cl$ was also treated with (*a*) $AgBF_4$ to give the fluoride $R_2C(SiMe_2F)Cl$, and (*b*) Et_2NH and Bu^tOH (both dried by standard methods, but evidently containing some water) to give the hydroxide $R_2C(SiMe_2OH)Cl$. The dichloride $R_2C(SiMe_2Cl)Cl$ was obtained by treatment of $R_2C(SiMe_2H)Cl$ with Cl_2 in CCl_4.

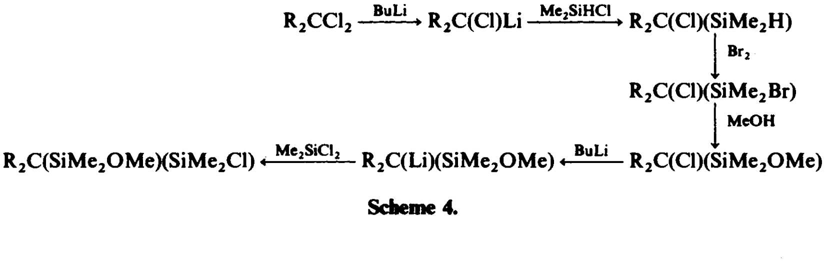
The compounds $R_2C(SiMe_2Y)_2$ with $Y = OClO_3$ or OSO_2CF_3 react with MeOH very readily, and those with $X = I$ or OSO_2Ph less readily to give the dimethoxide $R_2C(SiMe_2OMe)_2$.[5] The compounds $R_2C(SiMe_2Cl)(SiMe_2Y)$, with $Y = OClO_3$, ONO_2, $OCOCF_3$, or OSO_2CF_3, and also $R_2C(SiMe_2Br)(SiMe_2OSO_2CF_3)$, also react with MeOH, at various rates, to give $R_2C(SiMe_2OMe)_2$.[5] (Details of rate studies on these reactions will be presented in a later paper.) The dichloride $R_2C(SiMe_2Cl)_2$ did not react at a detectable rate with boiling MeOH [though it slowly gave $R_2C(SiMe_2OMe)_2$ on treatment with $AgNO_3$ in refluxing MeOH], but the chloro-fluoride $R_2C(SiMe_2Cl)(SiMe_2F)$ did react during 100 h under these



Scheme 2. $X = Cl$ or Br



Scheme 3.



Scheme 4.

conditions, indicating that a γ-F provides more anchimeric assistance than a γ-Cl ligand. The products were shown to be $R_2C(SiMe_2OMe)_2$, $R_2C(SiMe_2OMe)(SiMe_2F)$, and $R_2C(SiMe_2F)_2$, in *ca.* 60:20:20 ratio. The formation of the difluoride was very surprising; we tentatively attribute it to attack of liberated fluoride ion on unchanged $R_2C(SiMe_2Cl)(SiMe_2F)$, but the fact that the concentration of F^- must be very low under the acidic conditions (caused by generation of HCl) argues against this. Reaction of the chloro-fluoride $R_2C(SiMe_2Cl)(SiMe_2F)$ with MeOH containing 0.5% of H_2O gave the hydroxy-fluoride $R_2C(SiMe_2OH)(SiMe_2F)$ (70%), the dimethoxide $R_2C(SiMe_2OMe)_2$ (10%), and the difluoride $R_2C(SiMe_2F)_2$ (20%); there was no detectable amount of $R_2C(SiMe_2OH)(SiMe_2OMe)$, $R_2C(SiMe_2OH)_2$, or $R_2C(SiMe_2OMe)(SiMe_2F)$. The predominant formation of the hydroxy-fluoride indicates that (*a*) the $R_2C(SiMe_2Cl)(SiMe_2F)$ reacts fairly selectively with the small amount of water present, and (*b*) the γ-OH group apparently provides less anchimeric assistance than the γ-OMe group, so that after the first step loss of the fluoride ligand is slower than it is for the reaction in anhydrous MeOH.

Experimental

Spectra.—The ^1H n.m.r. spectra were recorded at 60 or 90 MHz for solutions in CCl_4 containing $CHCl_3$ or CH_2Cl_2 as lock and reference. The ^{19}F n.m.r. spectra were recorded with a Perkin-Elmer R32 spectrometer operating at 84.6 MHz; the solutions were in CCl_4, containing $CFCl_3$ as internal standard, and chemical shifts are in p.p.m. relative to $CFCl_3$. The ^{29}Si n.m.r. spectra were recorded with a Bruker WP80 FT spectrometer at 15.92 MHz; solutions were in $CHCl_3$, with Me_4Si or $(Me_3Si)_2O$ as external reference, and chemical shifts are in p.p.m. relative to Me_4Si. For all spectra, positive shifts are to low field.

The i.r. spectra were recorded using liquid films (for liquids) or Nujol mulls (for solids) between NaCl plates, with a Perkin-Elmer 157G grating spectrometer.

Mass spectra was recorded at 70 eV. For analysis by linked g.l.c.–mass spectrometry a column of 3% OV-101 on Chromosorb G (100—120 mesh) was used. Kieselgel GF_{254} was used for t.l.c., with n-pentane as eluant.

Starting Materials.—The compounds $TsiSiMe_2I$, $TsiSiPh_2I$, TsiSiMeHCl, TsiSiMeICl, and $TsiSiH_3$ were prepared as described in ref. 7, $(Me_3Si)_2C(SiMe_2Cl)_2$ as in ref. 3, $R_2CH(SiMe_2OMe)$ as in ref. 10, and R_2CCl_2 (R denotes Me_3Si throughout) as in ref. 11.

Diethyl ether, n-pentane, and n-hexane were dried over Na wire; CCl_4 and CH_2Cl_2 were refluxed with $CaCl_2$ for 1 h then distilled off and stored over 4 A molecular sieve; tetrahydrofuran (THF) was refluxed with Na wire and benzophenone until a deep purple colour appeared, and was distilled from the mixture as required immediately before use; CH_3CN was refluxed over CaH_2 for 1 h then distilled off and stored over 4 A molecular sieve; MeOH was refluxed for some hours with $Mg(OMe)_2$, distilled off, and stored over 3 A molecular sieve.

Light petroleum refers to the fraction of b.p. 60—80 °C.

Reactions and Work-up.—Reactions were carried out at room temperature (*ca.* 21 °C) unless otherwise specified. Removal of solvent was performed under reduced pressure in all cases.

Preparations and Solvolysis of $R_2C(SiMe_2Cl)(SiMe_2X)$ ($X = OSO_2CF_3$, $OSO_2C_6H_4Me$-*p*, $OClO_3$, $OCOCF_3$, *or* F).—(*a*) (i) A mixture of TsiSiMeICl (1.00 g, 2.3 mmol) and $AgOSO_2CF_3$ (0.71 g, 2.7 mmol) in CH_2Cl_2 was stirred for 30 min under reflux. Filtration and evaporation left a solid, which was sublimed (90 °C at 0.2 Torr) to give *(chlorodimethylsilyl)[dimethyl(trifluoromethylsulphonyloxy)silyl]bis(trimethylsilyl)methane* (0.96 g, 91%), m.p. 202 °C (Found: C, 31.4; H, 6.7. $C_{12}H_{30}ClF_3O_3SSi_4$ requires C, 31.4; H, 6.6%); δ_H 0.35 (s, 18 H, $SiMe_3$), 0.69 (s, 6 H, $SiMe_2Cl$), and 0.79 (s, 6 H, $SiMe_2OSO_2CF_3$); δ_F −77.0 (s).

(ii) A solution of $R_2C(SiMe_2Cl)(SiMe_2OSO_4CF_3)$ (0.19 g, 0.41 mmol) in a mixture of CCl_4 (5 cm^3) and MeOH (5 cm^3) containing MeONa (0.41 mmol) was kept for 24 h. Removal of solvent and extraction of the residue with hexane, followed by evaporation of the extract, gave a solid, which was sublimed (75 °C at 0.1 Torr to give *bis(methoxydimethylsilyl)bis(trimethylsilyl)methane* (0.091 g, 65%), m.p. 295 °C (Found: C, 46.7; H, 10.5. $C_{13}H_{36}O_2Si_4$ requires C, 46.4; H, 10.8%); δ_H 0.19 (s, 18 H, $SiMe_3$), 0.26 (s, 12 H, $SiMe_2$), and 3.40 (s, 6 H, OMe); *m*/*z* 321 ($[M - Me]^+$), 305 ($[M - OMe]^+$), 217 ($[M - Me - Me_3SiOMe]^+$), 201 ($[M - OMe - Me_3SiOMe]^+$), 89 ($[MeOMe_2Si]^+$), and 73 ($[Me_3Si]^+$).

(iii) A solution of $R_2C(SiMe_2Cl)(SiMe_2OSO_2CF_3)$ (0.11 g, 0.24 mmol) in a mixture of acetone (8 cm^3) and H_2O (2 cm^3) was kept for 24 h, then evaporated. The residue was sublimed (80 °C at 0.2 Torr) to give *bis(hydroxydimethylsilyl)bis(trimethylsilyl)methane* (0.052 g, 71%), m.p. 197 °C (Found: C, 43.0; H, 10.4. $C_{11}H_{32}O_2Si_4$ requires C, 42.8; H, 10.5%); δ_H 0.28 (s, 18 H, $SiMe_3$), 0.34 (s, 12 H, $SiMe_2$), and 2.1 br (s, 2 H, OH); ν(OH) 3 500—3 200 cm^{-1}.

(*b*) (i) A mixture of TsiSiMeICl (1.00 g, 2.3 mmol) and $AgOSO_2C_6H_4Me$-*p* (0.70 g, 2.5 mmol) in CH_2Cl_2 (20 cm^3) was stirred for 90 h under reflux. Filtration and removal of solvent left an oil, which was taken up in boiling pentane. Cooling gave *(chlorodimethylsilyl)(dimethyl-*p*-tolylsulphonyloxysilyl)bis(trimethylsilyl)methane* (0.49 g, 45%), m.p. 136 °C (Found: C, 44.6; H, 7.5. $C_{18}H_{37}ClO_3SSi_4$ requires C, 44.9; H, 7.8%); δ_H 0.24 (s, 18 H, $SiMe_3$), 0.58 (s, 6 H, $SiMe_2Cl$), 0.72 (s, 6 H, $SiMe_2O$), 2.46 (s, 3 H, Ar*Me*), and 7.2—7.9 (m, 4 H, ArH)

(ii) A solution of $R_2C(SiMe_2Cl)(SiMe_2OSO_2C_6H_4Me$-*p*) (0.10 g) in MeOH (5 cm^3) was kept under reflux for 7 d. Removal of solvent left a solid, which was shown by ^1H n.m.r. spectroscopy to be exclusively $R_2C(SiMe_2OMe)_2$.

(*c*) (i) A mixture of TsiSiMeICl (1.03 g, 2.4 mmol) and $AgClO_4$ (1.00 g, 4.8 mmol) in CH_2Cl_2 (20 cm^3) was stirred under reflux for 1 h. Filtration followed by evaporation gave a solid, which was sublimed (120 °C at 0.2 Torr) to give *(chlorodimethylsilyl)(perchloryloxydimethylsilyl)bis(trimethylsilyl)methane* (0.66 g, 68%), m.p. 254 °C (decomp.) (Found: C, 32.7; H, 7.09. $C_{11}H_{30}Cl_2O_4Si_4$ requires C, 32.3; H, 7.4%); δ_H 0.41 (s, 18 H, $SiMe_3$), 0.75 (s, 6 H, $SiMe_2Cl$), and 0.85 (s, 6 H, $SiMe_2OClO_3$).

(ii) A solution of $R_2C(SiMe_2Cl)(SiMe_2OClO_3)$ (0.10 g) in MeOH (5 cm^3) was kept for 2 h, then evaporated. The residue was shown (^1H n.m.r.) to be exclusively $R_2C(SiMe_2OMe)_2$.

(*d*) (i) A mixture of TsiSiMeICl (1.02 g, 2.3 mmol) and AgO_2CCF_3 (0.55 g, 2.5 mmol) in CH_2Cl_2 was stirred under reflux for 45 min. Filtration and evaporation, followed by sublimation (100 °C at 0.3 Torr) of the residue, gave *(chlorodimethylsilyl)(dimethyltrifluoroacetoxysilyl)bis(trimethylsilyl)methane* (0.81 g, 82%), m.p. 225 °C (Found: C, 37.1; H, 7.3. $C_{13}H_{30}ClF_3O_2Si_4$ requires C, 36.9; H, 7.2%); δ_H 0.32 (s, 18 H, $SiMe_3$), 0.64 (s, 6 H, $SiMe_2OCOCF_3$), and 0.68 (s, 6 H, $SiMe_2Cl$); δ_F −76.7 p.p.m. (s); ν(C=O) 1 775 cm^{-1}.

(ii) A solution of $R_2C(SiMe_2Cl)(SiMe_2OCOCF_3)$ (0.10 g) in MeOH (5 cm^3) was kept under reflux for 7 d. Removal of the solvent left exclusively $R_2C(SiMe_2OMe)_2$.

(*e*) A solution of $R_2C(SiMe_2Cl)(SiMe_2F)$ (0.14 g) in MeOH (10 cm^3) was kept under reflux for 100 h. Removal of the solvent left a solid, which was shown by ^1H n.m.r. spectroscopy to be a mixture. T.l.c. gave two fractions, *viz.* (in order of increasing R_F) (i) $R_2C(SiMe_2OMe)_2$ (as shown by its ^1H n.m.r. spectrum), and (ii) a mixture, shown by g.l.c.–mass spectrometry to consist of

$R_2C(SiMe_2F)_2$; *m/z* 297 ($[M - Me]^+$), and $R_2C(SiMe_2F)(SiMe_2OMe)$, *m/z* 309 ($[M - Me]^+$), 217 ($[M - Me - Me_3SiF]^+$), 205 ($[M - Me - Me_3SiOMe]^+$), and 201 ($[M - OMe - Me_3SiF]^+$). G.l.c. analysis (5% OV-101 at 200 °C) then showed the proportions of the three compounds in the initial product mixture to be (in the order of appearance above) 60:20:20.

(*f*) A solution of $R_2C(SiMe_2Cl)(SiMe_2F)$ (0.10 g, 0.03 mmol) in 0.5 vol% H_2O in MeOH was kept under reflux for 90 h. Removal of the solvent under vacuum left a solid. This was shown by g.l.c.–mass spectrometry to consist of three compounds: (i) $R_2C(SiMe_2F)_2$ (20%); (ii) $R_2C(SiMe_2OMe)_2$ (10%); and (iii) $R_2C(SiMe_2OH)(SiMe_2F)$ (70%), *m/z* 295 ($[M - Me]^+$), 279 ($[M - Me - MeH]^+$), 203 ($[M - Me - Me_3SiF]^+$), 187 ($[M - Me - MeH - Me_3SiF]^+$), 77 ($[FMe_2Si]^+$), 75 ($[HOMe_2Si]^+$), and 73 ($[Me_3Si]^+$). From the ^1H n.m.r. spectrum of the mixture, that of this last product could be seen to be δ_H 0.23 (s, 18 H, $SiMe_3$), 0.36 (s, 6 H, $Si\mathit{Me}_2OH$), 0.43 (d, 6 H, *J* 8 Hz, $SiMe_2F$), and 1.6 br (s, 1 H, OH).

Preparation and Reactions of TsiSiMeHF *and* TsiSiMeIF.—(*a*) A mixture of TsiSiMeHI (2.0 g, 5.0 mmol) and $AgBF_4$ (1.0 g, 5.1 mmol) in Et_2O (20 cm^3) was stirred for 30 min at room temperature. Filtration followed by evaporation left a solid, which was recrystallized from EtOH to give *[fluoro(methyl)silyl]tris(trimethylsilyl)methane* (1.1 g, 75%), m.p. >320 °C (Found: C, 44.7; H, 10.4. $C_{11}H_{31}FSi_4$ requires C, 44.8; H, 10.6%); δ_H 0.27 (s, 27 H, $SiMe_3$), 0.51 (dd, 3 H, *J* 8 Hz, SiMe), and 5.08 (dq, 1 H, SiH); δ_F −162 p.p.m. (dq, *J* 51 and 8 Hz, SiF); $\delta_{Si-\{^1H\}}$ −1.62 (d, *J* 4 Hz, $SiMe_3$) and 13.07 p.p.m. (d, *J* 290 Hz, SiMeHF); *m/z* 279 ($[M - Me]^+$), 205 ($[M - Me - Me_3SiH]^+$), 187 ($[M - Me - Me_3SiF]^+$), and 73 ($[Me_3Si]^+$); ν(SiH) 2 150 cm^{-1}.

(*b*) A mixture of TsiSiMeHI (1.83 g, 4.6 mmol) and $AgBF_4$ (1.95 g, 10 mmol) in CH_2Cl_2 was stirred at room temperature for 18 h. Filtration and removal of solvent left a solid, which was taken up in n-pentane. The solution was filtered and evaporated to leave a solid, shown by ^1H n.m.r. spectroscopy to be a mixture. Preparative g.l.c. (20% PEGA at 160 °C) gave, in order of elution, (i) TsiSiMeHF; (ii) $(Me_3Si)_2C(SiMe_2F)(SiMe_2H)$; and (iii) $(Me_3Si)_2C(SiMe_2F)_2$. The proportions of these components were shown by analytical g.l.c. to be 20:50:30.

(*c*) A 1M-solution of ICl in CCl_4 (3.0 cm^3; 3.0 mmol of ICl) was added dropwise at room temperature to a stirred solution of TsiSiMeHF (0.88 g, 3.0 mmol) in CCl_4 (10 cm^3). Removal of solvent left a solid, which was sublimed (100 °C at 0.1 Torr) to give a solid, m.p. >320 °C, judged from its n.m.r. spectra to be *[fluoro(iodo)(methyl)silyl]tris(trimethylsilyl)methane* (0.98 g, 78%); δ_H 0.33 (s, 27 H, $SiMe_3$) and 1.13 (d, 3 H, *J* 8 Hz, SiMe); δ_F 116.3 (q, *J* 8 Hz, SiF).

(*d*) A 1M-solution of ICl in CCl_4 (0.30 cm^3; 0.30 mmol of ICl) was added dropwise with stirring at room temperature to a solution of TsiSiMeFI (0.10 g, 0.24 mmol) in CCl_4 (5 cm^3). Removal of solvent and residual iodine left a solid, shown by its ^1H n.m.r. spectrum to be exclusively $R_2C(SiMe_2F)(SiMe_2Cl)$.

(*e*) A mixture of TsiSiMeFI (0.10 g, 0.24 mmol) and $AgBF_4$ (0.060 g, 0.31 mmol) in CH_2Cl_2 (5 cm^3) was stirred at room temperature for 30 min. Filtration followed by removal of solvent left a solid, shown by its ^1H n.m.r. spectrum to be $R_2C(SiMe_2F)_2$.

(*f*) A mixture of TsiSiMeFI (0.060 g; 0.14 mmol) and $AgOSO_2CF_3$ (0.040 g, 0.16 mmol) in CH_2Cl_2 was stirred at room temperature for 20 min. Filtration followed by removal of solvent left a solid, judged from its n.m.r. spectra to be exclusively (fluorodimethylsilyl)[dimethyl(trifluoromethylsulphonyloxy)silyl]bis(trimethylsilyl)methane; δ_H 0.32 (s, 18 H, $SiMe_3$), 0.49 (d, 6 H, *J* 8 Hz, $SiMe_2F$), and 0.75 (s, 6 H, $SiMe_2O$); δ_F −145.6 (m, SiF) and −77.6 (s, CF_3).

Preparation and Reactions of TsiSiMeIBr.—(*a*) A 1M-solution of Br_2 in CCl_4 (7.2 cm^3; 7.2 mmol) was added dropwise to a stirred solution of $TsiSiMeH_2$ (2.0 g, 7.2 mmol) in CCl_4 (10 cm^3). Removal of the solvent left a solid, judged from its ^1H n.m.r. spectrum [δ_H 0.28 (s, 27 H, $SiMe_3$), 0.85 (d, 3 H, *J* 3 Hz, SiMe), and 4.88 (q, 1 H, *J* 3 Hz, SiH)] to be TsiSiMeHBr. This was dissolved in CCl_4 (10 cm^3), and a 1M-solution of ICl in CCl_4 (7.2 cm^3; 7.2 mmol of ICl) was added. The solvent was removed to leave a solid, which was recrystallized from EtOH to give *[bromo(iodo)(methyl)silyl]tris(trimethylsilyl)methane* (3.20 g, 92%), m.p. >320 °C (Found: C, 27.2; H, 6.5. $C_{11}H_{30}BrISi_4$ requires C, 27.4; H, 6.3%); δ_H 0.44 (s, 27 H, $SiMe_3$) and 1.61 (s, 3 H, SiMe).

(*b*) A mixture of TsiSiMeBrI (0.72 g; 1.5 mmol), prepared as under (*a*), and $AgOSO_2CF_3$ (0.40 g, 1.6 mmol) in CH_2Cl_2 (10 cm^3) was stirred at room temperature for 15 min. Filtration and removal of solvent gave a solid, which was sublimed (120 °C at 0.5 Torr) to give *(bromodimethylsilyl)[dimethyl(trifluoromethylsulphonyloxy)silyl]bis(trimethylsilyl)methane* (0.62 g, 82%), m.p. 159 °C (Found: C, 29.2; H, 6.0. $C_{12}H_{30}BrF_3O_3SSi_4$ requires C, 28.6; H, 6.0%); δ_H 0.41 (s, 18 H, $SiMe_3$), 0.86 (s, 6 H, $SiMe_2OSO_2CF_3$), and 0.90 (s, 6 H, $SiMe_2Br$); δ_F −77.4 (s).

Solvolysis of $R_2C(SiMe_2Br)(SiMe_2OSO_2CF_3)$.—(*a*) A solution of $R_2C(SiMe_2Br)(SiMe_2OSO_2CF_3)$ (0.10 g, 0.20 mmol) in MeOH (5 cm^3) was kept at room temperature for 24 h then diluted with H_2O (5 cm^3). Extraction with light petroleum followed by washing, drying ($MgSO_4$), and evaporation of the extract left a solid, shown by its ^1H n.m.r. spectrum to be exclusively $R_2C(SiMe_2OMe)_2$.

(*b*) A solution of $R_2C(SiMe_2Br)(SiMe_2OSO_2CF_3)$ (0.10 g, 0.20 mmol) in 20 vol% H_2O in acetone (5 cm^3) was stirred at room temperauture for 24 h. Evaporation left a solid, shown by its ^1H n.m.r. spectrum to be exclusively $R_2C(SiMe_2OH)_2$.

Preparation and Reaction of $TsiSiMeI_2$.—(*a*) A solution of ICl (37 mmol) in CCl_4 (50 cm^3) was added dropwise to a stirred solution of $TsiSiMeH_2$ (5.0 g, 18 mmol) in CCl_4 (15 cm^3) at room temperature. Removal of the solvent left a solid, which was recrystallized from EtOH, then sublimed (140 °C at 0.1 Torr) to give a solid, (6.1 g, 64%), m.p. >320 °C, judged to be $TsiSiMeI_2$; δ_H 0.45 (s, 27 H, $SiMe_3$) and 1.90 (s, 3 H, SiMe).

(*b*) A mixture of $TsiSiMeI_2$ (0.10 g, 0.19 mmol) and $AgBF_4$ (0.040 g, 0.21 mol) in CH_2Cl_2 (5 cm^3) was stirred at room temperature for 30 min. Filtration and removal of solvent left a solid, shown from its ^1H n.m.r. structure to be a mixture of starting material (45%) and $R_2C(SiMe_2F)_2$ (55%).

(*c*) A mixture of $TsiSiMeI_2$ (0.50 g, 0.95 mmol) and $AgBF_4$ (0.40 g, 2.1 mmol) in CH_2Cl_2 (10 cm^3) was stirred at room temperature for 30 min. Filtration and removal of the solvent left a solid, which was sublimed (80 °C at 0.2 Torr) to give *bis(fluorodimethylsilyl)bis(trimethylsilyl)methane* (0.21 g, 71%) (Found: C, 42.3; H, 9.5. $C_{11}H_{30}F_2Si_4$ requires C, 42.2; H, 9.7%); δ_H 0.28 (s, 18 H, $SiMe_3$) and 0.43 (d, 12 H, *J* 8 Hz, $SiMe_2$); δ_F −146.0 (m, *J* 8 Hz, SiF).

(*d*) A mixture of $TsiSiMeI_2$ (0.090 g, 0.17 mmol) and $AgClO_4$ (0.035 g, 0.17 mmol) in CH_2Cl_2 was stirred at room temperature for 2 h. Filtration and evaporation left a solid, shown from its ^1H n.m.r. spectrum to be a 1:1 mixture of unchanged $TsiSiMeI_2$ with $R_2C(SiMe_2OClO_3)_2$.

(*e*) A mixture of $TsiSiMeI_2$ (0.45 g, 0.85 mmol) and $AgClO_4$ (0.36 g, 1.70 mmol) in CH_2Cl_2 (10 cm^3) was stirred at room temperature for 3 h. Filtration and evaporation under vacuum left a solid, which was recrystallized twice from n-pentane to give *bis[dimethyl(perchloryloxy)silyl]bis(trimethylsilyl)methane* (0.24 g, 60%) (Found: C, 28.1; H, 6.6. $C_{11}H_{30}Cl_2O_8Si_4$ requires C, 27.9; H, 6.4%); δ_H 0.36 (s, 18 H, $SiMe_3$) and 0.80 (s, 12 H, $SiMe_2$).

(*f*) A mixture of $TsiSiMeI_2$ (0.10 g, 0.19 mmol) and $AgOSO_2CF_3$ (0.050 g, 0.19 mmol) in CH_2Cl_2 (5 cm^3) was stirred at room temperature for 20 min. Filtration and evaporation left a solid, shown by its ^1H n.m.r. spectrum to be a 1:1 mixture of unchanged $TsiSiMeI_2$ with $R_2C(SiMe_2OSO_2CF_3)_2$.

(*g*) A mixture of $TsiSiMeI_2$ (0.62 g, 1.20 mmol) and $AgOSO_2C_6H_4Me$-*p* (0.70 g, 2.5 mmol) in CH_2Cl_2 (10 cm^3) was stirred under reflux for 65 h. Filtration and evaporation left a solid, which was recrystallized from MeOH to give *bis(dimethyl-p-tolylsulphonyloxysilyl)bis(trimethylsilyl)methane* (0.44 g, 60%), m.p. 175 °C (Found: C, 47.8; H, 6.9. $C_{25}H_{44}O_6S_2Si_4$ requires C, 48.7; H, 7.2%); δ_H 0.09 (s, 18 H, $SiMe_3$), 0.51 (s, 12 H, $SiMe_2$), 2.40 (s, 6 H, Ar*Me*), and 7.3—7.9 (m, 8 H, ArH).

(*h*) A procedure similar to that described under (*f*), but starting from $TsiSiMeI_2$ (0.19 mmol) and $AgOSO_2CF_3$ (0.19 mmol), gave a 1:1 mixture of $TsiSiMeI_2$ and $R_2C(SiMe_2OSO_2CF_3)_2$.

(*i*) A mixture of $TsiSiMeI_2$ (0.76 g, 1.40 mmol) and $AgOSO_2CF_3$ (0.80 g, 3.1 mmol) in CH_2Cl_2 was stirred at room temperature for 10 min. Filtration and evaporation left an oil, which was taken up in n-pentane. The solution was filtered and evaporated to leave an oil, which solidified. Sublimation (100 °C at 0.1 Torr) gave a solid, which was judged to be bis[dimethyl(trifluoromethylsulphonyloxy)silyl]bis(trimethylsilyl)methane (0.38 g, 46%); δ_H 0.35 (s, 18 H, $SiMe_3$) and 0.76 (s, 12 H, $SiMe_2$).

Preparation of TsiSiMeHX *Compounds* (X = H, I, *or* OMe).—(*a*) A refluxing mixture of TsiSiMeHCl (4.92 g, 0.016 mol) and $LiAlH_4$ (5.0 g, 0.13 mol) in THF (60 cm^3) was stirred under nitrogen for 1 h. Careful treatment with saturated aqueous NH_4Cl was followed by extraction with light petroleum. The extract was washed, dried ($MgSO_4$), and evaporated, to leave a solid, which was sublimed (80 °C at 0.2 Torr) to give *(methylsilyl)tris(trimethylsilyl)methane* (3.0 g, 69%), m.p. 255 °C (Found: C, 47.7; H, 11.6. $C_{11}H_{32}Si_4$ requires C, 47.7; H, 11.6%); δ_H 0.17 (s, 27 H, $SiMe_3$), 0.28 (t, 3 H, SiMe), and 3.90 (q, 2 H, SiH_2); δ_{Si} −4.41 (s, $SiMe_3$) and −36.5 (t, *J* 191 Hz, $SiMeH_2$); ν(SiH) 2 130 cm^{-1}.

(*b*) A solution of $TsiSiMeH_2$ (2.00 g, 7.2 mmol) and I_2 (3.00 g, 12 mmol) in n-heptane (5 cm^3) was boiled under reflux for 18 h under a stream of N_2. Removal of solvent and residual I_2 under vacuum gave a solid, which was sublimed (90 °C at 0.2 Torr) to give *[iodo(methyl)silyl]tris(trimethylsilyl)methane* (2.7 g, 92%), m.p. >320 °C (Found: C, 32.8; H, 7.8. $C_{11}H_{31}ISi_4$ requires C, 32.8; H, 7.8%); δ_H 0.31 (s, 27 H, $SiMe_3$), 1.14 (d, 3 H, SiMe), and 4.80 (q, 1 H, SiH); δ_{Si} 0.18 (s, $SiMe_3$) and −21.8 (d, *J* 232 Hz, SiMeHI); ν(SiH) 2 150 cm^{-1}.

(*c*) A solution of TsiSiMeHI (1.57 g) in a mixture of CCl_4 (10 cm^3) and MeOH (10 cm^3) was boiled under reflux for 30 min. Evaporation gave a solid, which was sublimed (100 °C at 0.2 Torr) to give *[methoxy(methyl)silyl]tris(trimethylsilyl)methane* (1.06 g, 89%) (Found: C, 46.2; H, 11.1. $C_{12}H_{34}OSi_4$ requires C, 47.0; H, 11.2%); δ_H 0.18 (s, 27 H, $SiMe_3$), 0.34 (d, 3 H, SiMe), 3.38 (s, 3 H, OMe), and 4.67 (q, 1 H, SiH); ν(SiH) 2 100 cm^{-1}.

Preparation of $R_2C(SiMe_2H)_2$ *and its Reactions with Halogens and Chlorinating Agents*.—(*a*) A mixture of $R_2C(SiMe_2Cl)_2$ (9.8 g, 0.028 mol) and $LiAlH_4$ (8.0 g, 0.21 mol) in refluxing THF (100 cm^3) was stirred under N_2 for 3 h, then carefully treated with saturated aqueous NH_4Cl (250 cm^3) and extracted with light petroleum (2 × 200 cm^3). The extract was washed, dried ($MgSO_4$), and evaporated to give a solid, which was recrystallized from EtOH to give *bis(dimethylsilyl)bis(trimethylsilyl)methane* (6.3 g, 80%), m.p. 286 °C (Found: C, 47.6; H, 11.9. $C_{11}H_{32}Si_4$ requires C, 47.7; H, 11.7%); δ_H 0.16 (s, 18 H, $SiMe_3$), 0.24 (d, 12 H, *J* 4 Hz, $SiMe_2$), and 4.11 (m, 2 H, *J* 4 Hz, SiH); δ_{Si} −0.46 (s, $SiMe_3$) and −16.4 (d, *J* 193 Hz, $SiMe_2H$); ν(SiH) 2 110 cm^{-1}.

(*b*) A solution of Cl_2 (2.50 mmol) in CCl_4 (3 cm^3) was added dropwise to a stirred solution of $R_2C(SiMe_2H)_2$ (0.30 g, 1.10 mmol) in CCl_4 (10 cm^3). Removal of the solvent left a solid, which was sublimed (100 °C at 0.1 Torr) to give $R_2C(SiMe_2Cl)_2$ (0.33 g, 88%), m.p. >320 °C (Found: C, 38.7; H, 8.3. Calc. for $C_{11}H_{30}Cl_2Si_4$: C, 38.2; H, 8.8%); δ_H 0.38 (s, 18 H, $SiMe_3$) and 0.70 (s, 12 H, $SiMe_2Cl$). The properties are consistent with those previously reported.[3]

(*c*) A similar procedure, but starting with $R_2C(SiMe_2H)_2$ (0.84 mmol) and 1.0M-Br_2 (1.8 mmol) in CCl_4 (10 cm^3) and culminating in sublimation (120 °C at 0.1 Torr), gave *bis(bromodimethylsilyl)bis(trimethylsilyl)methane* (0.31 g, 82%), m.p. >320 °C (Found: C, 30.8; H, 7.1. $C_{11}H_{30}Br_2Si_4$ requires C, 30.4; H, 7.0%); δ_H 0.42 (s, 18 H, $SiMe_3$) and 0.89 (s, 12 H, $SiMe_2$).

(*d*) A mixture of $R_2C(SiMe_2H)_2$ (0.50 g, 1.8 mmol) and I_2 (1.00 g, 3.9 mmol) in CCl_4 (20 cm^3) was stirred at room temperature for 18 h. Removal of solvent and residual I_2 under vacuum left a solid, which was subjected to t.l.c. The main fraction was evaporated, and the residual solid sublimed (100 °C at 0.2 Torr) to give *bis(iododimethylsilyl)bis(trimethylsilyl)methane*, (0.81 g, 83%), m.p. >320 °C (Found: C, 25.1; H, 5.6. $C_{11}H_{30}I_2Si_4$ requires C, 25.0; H, 5.7%); δ_H 0.48 (s, 18 H, $SiMe_3$) and 1.23 (s, 12 H, $SiMe_2$).

(*e*) A solution of Cl_2 (0.84 mmol) in CCl_4 (50 cm^3) was added dropwise at room temperature to a stirred solution of $R_2C(SiMe_2H)_2$ (0.30 g, 1.1 mmol) in CCl_4 (5 cm^3). Evaporation left a solid, shown by ^1H spectroscopy to be a mixture of $R_2C(SiMe_2H)_2$ (40%), $R_2C(SiMe_2Cl)(SiMe_2H)$ (55%), and $R_2C(SiMe_2Cl)_2$ (5%). T.l.c. gave *(chlorodimethylsilyl)(dimethylsilyl)bis(trimethylsilyl)methane* (0.12 g, 36%), m.p. 252 °C (Found: C, 42.1; H, 10.0. $C_{11}H_{31}ClSi_4$ requires C, 42.5; H, 10.1%); δ_H 0.28 (s, 18 H, $SiMe_3$), 0.36 (d, 6 H, *J* 4 Hz, Si*Me*$_2$H), 0.61 (s, 6 H, $SiMe_2Cl$), and 4.16 (m, 1 H, SiH); ν(SiH) 2 110 cm^{-1}.

(*f*) A mixture of $R_2C(SiMe_2H)_2$ (0.18 g, 0.65 mmol) and PCl_5 (0.13 g, 0.60 mmol) in CCl_4 (10 cm^3) was stirred at room temperature for 13 h. Evaporation left a solid, shown by ^1H n.m.r. spectroscopy to contain $R_2C(SiMe_2H)_2$, $R_2C(SiMe_2Cl)(SiMe_2H)$, and $R_2C(SiMe_2Cl)_2$ in 30:40:30 ratio.

(*g*) A mixture of $R_2C(SiMe_2H)_2$ (0.20 g, 0.71 mmol) and *N*-chlorosuccinimide (0.10 g, 0.73 mmol) in CCl_4 (10 cm^3) containing a catalytic amount of $(PhCOO)_2$ was refluxed with stirring for 5 h. Filtration and evaporation of the filtrate gave a solid, shown (^1H n.m.r.) to contain the same products as in (*f*) in 25:50:25 ratio.

(*h*) A solution of Br_2 (1.60 mmol) in CCl_4 (30 cm^3) was added dropwise with stirring to a solution of $R_2C(SiMe_2H)_2$ (0.50 g, 1.8 mmol) in CCl_4 (5 cm^3) at room temperature. Evaporation left a solid, shown (^1H n.m.r.) to be a mixture of $R_2C(SiMe_2H)_2$, $R_2(SiMe_2Br)(SiMe_2H)$, and $R_2C(SiMe_2Br)_2$ in 25:60:15 ratio. Preparative g.l.c. (20% OV-101 at 220 °C) gave *(bromodimethylsilyl)(dimethylsilyl)bis(trimethylsilyl)methane* (0.17 g, 26%) (Found: C, 37.3; H, 8.8. $C_{11}H_{31}BrSi_4$ requires C, 37.1; H, 8.8%); δ_H 0.28 (s, 18 H, $SiMe_3$), 0.37 (d, 6 H, Si*Me*$_2$H), 0.74 (s, 6 H, $SiMe_2Br$), and 4.16 (m, 1 H, SiH); ν(SiH) 2 110 cm^{-1}.

(*i*) A solution of I_2 (0.19 g, 0.75 mmol) and $R_2C(SiMe_2H)_2$ (0.26 g, 0.94 mmol) in CCl_4 (5 cm^3) was stirred at room temperature for 2 h. Evaporation under vacuum left a solid, shown (^1H n.m.r.) to be a mixture of $R_2C(SiMe_2H)_2$, $R_2C(SiMe_2I)(SiMe_2H)$, and $R_2C(SiMe_2I)_2$ in 30:40:30 ratio. The mixture was separated by t.l.c., and the second fraction yielded a solid, which was sublimed (80 °C at 0.1 Torr) to give *(iododimethylsilyl)(dimethylsilyl)bis(trimethylsilyl)methane* (0.08 g, 27%), m.p. >320 °C (Found: C, 33.5; H, 7.9. $C_{11}H_{31}ISi_4$ requires C, 32.8; H, 7.8%); δ_H 0.34 (s, 18 H, $SiMe_3$), 0.44 (d, 6 H, Si*Me*$_2$H), 1.05 (s, 6 H, $SiMe_2I$), and 4.16 (m, 1 H, SiH); ν(SiH) 2 110 cm^{-1}.

Methanolysis of $R_2C(SiMe_2H)(SiMe_2I)$.—A solution of $R_2C(SiMe_2H)_2$ (0.60 g, 2.2 mmol) and I_2 (0.56 g, 2.2 mmol) in CCl_4

(20 cm^3) was stirred for 2 h then diluted with light petroleum (30 cm^3). Washing with aqueous $NaHSO_3$ then with water, followed by separation, drying ($MgSO_4$), and evaporation of the organic layer left a solid (0.72 g), shown by ^1H n.m.r. spectroscopy to be a mixture of $R_2C(SiMe_2H)_2$ (50%), $R_2C(SiMe_2H)(SiMe_2I)$ (40%), and $R_2C(SiMe_2I)_2$ (10%). Half this mixture (0.36 g) was dissolved in MeOH, and the solution was kept under reflux for 1 h. Removal of solvent left a solid, which was separated by t.l.c. into two fractions. The first (0.11 g) was shown (^1H n.m.r.) to be unchanged $R_2C(SiMe_2H)_2$, and the second (0.10 g) to be a mixture of $R_2C(SiMe_2I)_2$ (20%) and $R_2C(SiMe_2OMe)_2$ (80%).

Preparation of $R_2C(SiMe_2X)(SiMe_2F)$ (X = H *or* I).—(*a*) The remaining half (0.36 g) of the mixture of $R_2C(SiMe_2H)_2$, $R_2C(SiMe_2H)(SiMe_2I)$, and $R_2(SiMe_2I)_2$ obtained in the preceding experiment was stirred for 30 min with $AgBF_4$ (0.40 g, 2.1 mmol) in CH_2Cl_2 (10 cm^3). Filtration and removal of solvent left a solid, which was separated by t.l.c. into three fractions. The middle fraction was collected and sublimed (80 °C at 0.2 Torr) to give *(fluorodimethylsilyl)(dimethylsilyl)bis(trimethylsilyl)methane* (0.07 g), m.p. >320 °C (Found: C, 44.8; H, 10.2. $C_{11}H_{31}FSi_4$ requires C, 44.8; H, 10.6%); δ_H 0.23 (s, 18 H, $SiMe_3$), 0.32 (d, 6 H, $SiMe_2H$), 0.38 (d, $SiMe_2F$), and 4.15 (m, 1 H, SiH); δ_F −146.0 (m).

(*b*) A (1M) solution of ICl (0.14 mmol) in CCl_4 (0.14 cm^3) was added to a stirred solution of $R_2C(SiMe_2H)(SiMe_2F)$ (0.040 g, 0.14 mmol) in CCl_4 (2.0 cm^3). Removal of solvent left a solid, which was sublimed (100 °C at 0.2 Torr) to give (fluorodimethylsilyl)(iododimethylsilyl)bis(trimethylsilyl)methane (0.030 g, 53%); δ_H 0.41 (s, 18 H, $SiMe_3$), 0.59 (d, 6 H, $SiMe_2F$), and 1.11 (s, 6 H, $SiMe_2I$); δ_F −145.7 (m).

Reactions of $R_2C(SiMe_2I)(SiMe_2H)$ *with Halogens.*—(*a*) A solution of Cl_2 (0.080 mmol) in CCl_4 (0.5 cm^3) was added to a stirred solution of $R_2C(SiMe_2I)(SiMe_2H)$ (0.034 g, 0.080 mmol) in CCl_4 (1 cm^3) at room temperature. Evaporation left a solid, shown (^1H n.m.r.) to be a 1:1 mixture of starting material and $R_2C(SiMe_2Cl)_2$.

(*b*) The procedure described under (*a*), but with Br_2 in place of Cl_2, gave a 1:1 mixture of starting material and $R_2C(SiMe_2Br)_2$.

Preparation of $R_2C(SiMe_2X)(SiMe_2I)$ (X = Cl *or* Br).—(*a*) A mixture of $R_2C(SiMe_2Cl)(SiMe_2H)$ (0.075 g, 0.24 mmol) in I_2 (0.065 g, 0.25 mmol) in CCl_4 (2 cm^3) was stirred at room temperature for 5 h. Evaporation under vacuum left a solid, which was sublimed (80 °C at 0.1 Torr) to give *(chlorodimethylsilyl)(iododimethylsilyl)bis(trimethylsilyl)methane* (0.080 g, 76%), m.p. >320 °C (Found: C, 30.5; H, 7.0. $C_{11}H_{30}ClISi_4$ requires C, 30.2; H, 6.9%); δ_H 0.41 (s, 18 H, $SiMe_3$), 0.74 (s, 6 H, $SiMe_2Cl$), and 1.13 (s, 6 H, $SiMe_2I$).

(*b*) A mixture of $R_2C(SiMe_2Br)(SiMe_2H)$ (0.13 g, 0.37 mmol) and I_2 (0.20 g, 0.79 mmol) in CCl_4 (5 cm^3) was boiled under reflux for 1.5 h. Evaporation left a solid, which was taken up in light petroleum (10 cm^3). The solution was washed with aqueous $NaHSO_3$, dried ($MgSO_4$), and evaporated to leave a solid, which was sublimed (140 °C at 0.1 Torr) to give *(bromodimethylsilyl)(iododimethylsilyl)bis(trimethylsilyl)methane* (0.094 g, 55%), m.p. >320 °C (Found: C, 28.6; H, 5.9. $C_{11}H_{30}BrISi_4$ requires C, 27.4; H, 6.3%); δ_H 0.45 (s, 18 H, $SiMe_3$), 0.93 (s, 6 H, $SiMe_2Br$), and 1.18 (s, 6 H, $SiMe_2I$).

Methanolysis of $R_2C(SiMe_2Cl)(SiMe_2X)$ (X = Cl *or* I).—(*a*) A solution of $R_2C(SiMe_2Cl)_2$ (0.10 g) in MeOH (5 cm^3) was boiled under reflux for 42 h. Evaporation left a solid, which was shown by its ^1H n.m.r. spectrum to be exclusively unchanged starting material.

(*b*) A mixture of $R_2C(SiMe_2Cl)_2$ (0.10 g, 0.29 mmol) and $AgNO_3$ (0.10 g, 0.59 mmol) in MeOH (5 cm^3) was stirred under reflux for 64 h. Filtration followed by evaporation gave a solid, shown by ^1H n.m.r. spectroscopy to be a 60:40 mixture of unchanged $R_2C(SiMe_2Cl)_2$ with $R_2(SiMe_2OMe)_2$.

(*c*) A solution of $R_2(SiMe_2Cl)(SiMe_2I)$ (0.030 g) in MeOH (2 cm^3) was boiled under reflux for 5 d. Evaporation gave exclusively $R_2C(SiMe_2OMe)_2$ (^1H n.m.r.).

Preparation of $R_2C(Cl)(SiMe_2X)$ (X = H, Br, Cl, F, OMe, *or* OH).—(*a*) A 1.6M-solution of Bu^nLi (0.096 mol) in hexane (60 cm^3), cooled to −80 °C, was added dropwise under N_2 during 1 h to a stirred solution of R_2CCl_2 (20.0 g, 0.087 mol) in a mixture of THF (80 cm^3), Et_2O (10 cm^3), and pentane (4 cm^3) maintained at −110 °C. The mixture was subsequently stirred for 2 h, then Me_2SiHCl (9.50 g, 0.10 mol), cooled to −80 °C, was added dropwise with stirring. The mixture was allowed to warm to room temperature then added to an excess of ice-cold saturated aqueous NH_4Cl. The organic layer was separated, washed, dried, and evaporated to leave a liquid, which was shown by g.l.c. (5% OV-101 at 180 °C) to consist of unchanged R_2CCl_2 (25%) and product (75%). The R_2CCl_2 was distilled off (96 °C at 30 Torr), and the residue, which solidified on cooling, was recrystallized from MeOH to give *chloro(dimethylsilyl)bis(trimethylsilyl)methane* (8.0 g, 36%), m.p. 110 °C (Found: C, 42.6; H, 10.0. $C_9H_{25}ClSi_3$ requires C, 42.7; H, 10.0%); δ_H 0.18 (s, 18 H, $SiMe_3$), 0.27 (d, 6 H, $SiMe_2$), and 4.11 (m, 1 H, SiH); ν(SiH) 2 130 cm^{-1}; *m/z* 254/252 ($[M]^+$), 239/237 ($[M - Me]^+$), and 73 ($[Me_3Si]^+$).

(*b*) A (1M) solution of Br_2 (5.0 mmol) in CCl_4 (5.0 cm^3) was added dropwise to a stirred solution of $R_2C(Cl)(SiMe_2H)$ (1.06 g, 4.2 mmol) in CH_2Cl_2 (5 cm^3). The solution was kept for a further 15 min then evaporated. The solid residue was sublimed (70 °C at 0.2 Torr) to give *(bromodimethylsilyl)(chloro)bis(trimethylsilyl)methane* (1.35 g, 97%), m.p. 197 °C (Found: C, 32.6; H, 7.4. $C_9H_{24}BrClSi_3$ requires C, 32.6; H, 7.4%); δ_H 0.30 (s, 18 H, $SiMe_3$) and 0.75 (s, 6 H, $SiMe_2$); *m/z* 334/332/330 ($[M]^+$), 319/317/315 ($[M - Me]^+$), and 73 ($SiMe_3$).

(*c*) The procedure described under (*b*), but with Cl_2 in place of Br_2, gave *chloro(chlorodimethylsilyl)bis(trimethylsilyl)methane* (0.12 g, 88%), m.p. 155 °C (Found: C, 37.7; H, 8.1. $C_9H_{24}Cl_2Si_3$ requires C, 37.6; H, 8.4%); δ_H 0.28 (s, 18 H, $SiMe_3$) and 0.60 (s, 6 H, $SiMe_2$).

(*d*) A mixture of $R_2C(Cl)(SiMe_2Br)$ (0.10 g, 0.30 mmol) and $AgBF_4$ (0.060 g, 0.31 mmol) in CH_2Cl_2 (5 cm^3) was stirred for 30 min then filtered. Evaporation of the solvent left a solid, which was sublimed (80 °C at 0.1 Torr) to give *chloro(fluorodimethylsilyl)bis(trimethylsilyl)methane* (0.070 g, 86%), m.p. 112 °C (Found: C, 39.7; H, 8.8. $C_9H_{24}ClFSi_3$ requires C, 39.9; H, 8.9%); δ_H 0.23 (s, 18 H, $SiMe_3$) and 0.41 (d, 6 H, $SiMe_2$); δ_F −153.5 (m).

(*e*) A solution of $R_2C(Cl)(SiMe_2Br)$ (0.25 g) in a mixture of CH_2Cl_2 (5 cm^3) and MeOH (5 cm^3) was kept for 24 h, then evaporated to give *chloro(methoxydimethylsilyl)bis(trimethylsilyl)methane* (0.18 g, 84%), m.p. 120 °C (Found: C, 42.4; H, 9.3. $C_{10}H_{27}ClOSi_3$ requires C, 42.4; H, 9.6%); δ_H 0.18 (s, 18 H, $SiMe_3$), 0.26 (s, 6 H, $SiMe_2$), and 3.44 (s, 3 H, OMe).

(*f*) (i) A solution of $R_2C(Cl)(SiMe_2Br)$ (0.22 g) in Et_2NH (4 cm^3) ('dried' over K_2CO_3 and stored over 4 Å molecular sieve) was kept for 10 min, then filtered and evaporated. The residue was sublimed (100 °C at 0.1 Torr) to give *chloro(hydroxydimethylsilyl)bis(trimethylsilyl)methane* (0.16 g, 90%), m.p. 113 °C (Found: C, 40.3; H, 9.0. $C_9H_{25}ClOSi_3$ requires C, 40.2; H, 9.4%); δ_H 0.25 (s, 18 H, $SiMe_3$), 0.34 (s, 6 H, $SiMe_2$), and 2.0 br (s, 1 H, OH); ν(OH) 3 690 and 3 600—3 300 cm^{-1}.

(ii) A mixture of $R_2C(Cl)(SiMe_2Br)$ (0.50 g, 1.5 mmol) and Bu^tOH (0.74 g, 10 mmol) (dried over CaH_2 and distilled from it before use) was kept under reflux for 30 min. Removal of volatile material left a solid, which was shown by its ^1H n.m.r. and i.r. spectra to be identical with the product obtained in (i).

Preparation and Methanolysis of $R_2C(SiMe_2OMe)(SiMe_2Cl)$.—(*a*) A 1.6M-solution of Bu^nLi in hexane (1.0 cm^3, 1.6 mmol) was added dropwise to a solution of $R_2C(Cl)(SiMe_2OMe)$ (0.40 g, 1.4 mmol) in a mixture of THF (10 cm^3), Et_2O (0.5 cm^3), and pentane (0.5 cm^3) at −100 °C. The mixture was kept at −100 °C for a further 1 h then allowed to warm to −78 °C, and Me_2SiCl_2 (0.25 cm^3, 2.1 mmol) was added with stirring. The mixture was allowed to warm to room temperature and the solvents and excess of Me_2SiCl_2 were removed under vacuum. The residual solid was extracted with pentane (10 cm^3) and the extract was filtered and evaporated to give a solid, which seemed from its ^1H n.m.r. spectrum to be a mixture of unchanged $R_2C(Cl)(SiMe_2OMe)$ (15%) and $R_2C(SiMe_2OMe)(SiMe_2Cl)$ (85%). Two recrystallizations from pentane followed by sublimation (100 °C at 0.2 Torr) gave *(chlorodimethylsilyl)(methoxydimethylsilyl)bis(trimethylsilyl)methane* (0.20 g, 41%), m.p. 297 °C (Found: C, 42.0; H, 9.4. $C_{12}H_{33}ClOSi_4$ requires C, 42.2; H, 9.8%); δ_H 0.28 (s, 18 H, $SiMe_3$), 0.36 (s, 6 H, $Si\mathit{Me}_2OMe$), 0.61 (s, 6 H, $SiMe_2Cl$), and 3.30 (s, 3 H, OMe); *m/z* 327/325 ($[M - Me]^+$), 311/309 ($[M - OMe]^+$), 305 ($[M - Cl]^+$), and 73 ($[Me_3Si]^+$).

(*b*) A solution of $R_2CH(SiMe_2OMe)$ (0.50 g, 2.0 mmol) in THF (10 cm^3) was added to a solution of MeLi (2.7 mmol) in Et_2O (3.0 cm^3) and the mixture was stirred for 20 h then treated with Me_2SiCl_2 (0.37 cm^3, 3.0 mmol). Addition of light petroleum (25 cm^3) then an excess of H_2O, followed by washing, drying ($MgSO_4$), and evaporation of the extract gave a solid, which was sublimed twice (70 °C at 0.2 Torr) to give $R_2C(SiMe_2OMe)(SiMe_2Cl)$ (0.31 g, 45%), with properties identical with those given under (*a*).

The foregoing experiment was carried out before that described under (*a*). Several subsequent attempts to repeat it gave only $TsiSiMe_2Cl$.

(*c*) A solution of $R_2C(SiMe_2OMe)(SiMe_2Cl)$ (0.050 g) in MeOH (2 cm^3) was kept for 1 h. Removal of the solvent under vacuum left a solid, shown by its ^1H n.m.r. spectrum to be exclusively $R_2C(SiMe_2OMe)_2$.

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