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THE REACTIONS OF CHLOROSILANES WITH (HYDROSILYL)ALKYL GRIGNARD REAGENTS

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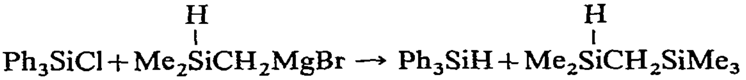
SUMMARY

Chlorosilanes are reduced by (hydrosilyl)methyl, -ethyl and -propyl Grignard reagents. Kinetic studies demonstrate that the reduction is first order in chlorosilane and second order in Grignard reagent, and it is concluded that for the (hydrosilyl)methyl compounds the lability of the hydrogen is due to electron donation from the adjacent methylene group, whereas for the (hydrosilyl)ethyl and -propyl compounds, neighbouring group participation by the methylene group probably plays some part in weakening the silicon–hydrogen bond.

Recently we reported that triphenylchlorosilane reacts with (dimethylsilyl)methylmagnesium bromide to give predominantly triphenylsilane and the Grignard dimer[1].



$$\mathrm{Ph_3SiCl + Me_2\overset{\overset{H}{|}}{Si}CH_2MgBr \rightarrow Ph_3SiH + Me_2\overset{\overset{H}{|}}{Si}CH_2SiMe_3}$$

Apart from the (diphenylsilyl)methyl Grignard which does not react this would appear to be a fairly general reaction of (hydrosilyl)methyl Grignard reagents with triphenylchlorosilane (Table 1).

Reduction also occurs with diphenylmethylchlorosilane but to a lesser extent; some normal coupling also takes place (see Table 1). The reaction of (dimethylsilyl)methylmagnesium bromide with trimethylchlorosilane has been investigated previously[2] and found to give good yields of the expected coupling product. In this case both the reduction and coupling reactions would produce the identical product.

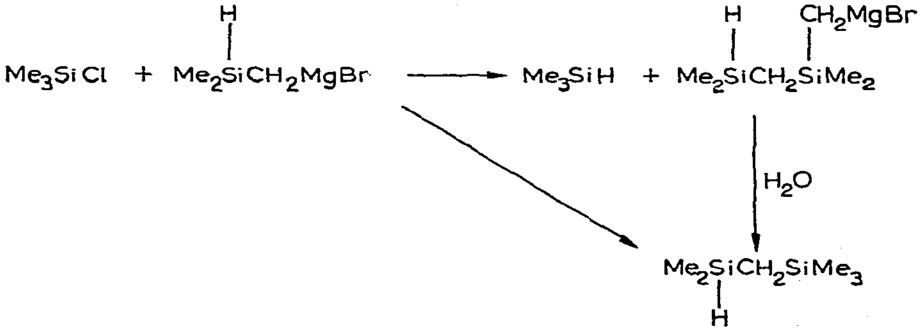


TABLE 1

PRODUCT YIELDS FROM THE REACTION OF HYDROSILYLALKYL GRIGNARD REAGENTS WITH TRIPHENYLCHLOROSILANE

Grignard (mole)[a]	*Products [yields (%)]*
Me_2SiHCH_2MgBr (0.06)	Ph_3SiH(90), Ph_3SiOH(5) $Me_2SiHCH_2SiMe_3$(80) $Me_2SiH(CH_2SiMe_2)_nCH_2SiMe_3$(20)
Me_2SiHCH_2MgBr[b](0.03)	Ph_3SiH(77), Ph_3SiOH(20) $Me_2SiHCH_2SiMe_2CH_2D$(60) $Me_2SiHCH_2(SiMe_2CH_2)_nSiMe_2CH_2D$(20)
Me_2SiDCH_2MgBr(0.03)	Ph_3SiD(67), Ph_3SiOH(29)
$MeSiH_2CH_2MgBr$ (0.04)	Ph_3SiH(75), $MeSiH_2CH_2SiMe_2H$(58) Ph_3SiOH(13), $Ph_3SiCH_2SiMeH_2$(12)
$PhMeSiHCH_2MgBr$ (0.05)	Ph_3SiH(80), Ph_3SiOH(15), $PhMe_2SiCH_2SiPhMeH$(75)
Ph_2SiHCH_2MgBr (0.04)	Ph_3SiH(O), Ph_2MeSiH(95)
$Ph_2SiH(CH_2)_2MgBr$ (0.06)	Ph_3SiH(50)
$MeSiH(CH_2)_3MgCl$ (0.05)	Ph_3SiH(80)
$MeSiHCH_2SiMe_2CH_2MgI$ (0.04)	Ph_3SiH(45)
Me_2SiHCH_2MgBr[c] (0.03)	Ph_2MeSiH(49), $Ph_2MeSiCH_2SiMe_2H$(44)
Me_2SiHCH_2MgBr[b,d] (0.02)	$Me_3SiCH_2SiMe_2H$(39) $Me_2SiHCH_2SiMe_2CH_2D$(34)

[a] The reaction was with triphenylchlorosilane except when stated otherwise.

[b] Reaction quenched with D_2O.

[c] With diphenylmethylchlorosilane.

[d] With trimethylchlorosilane.

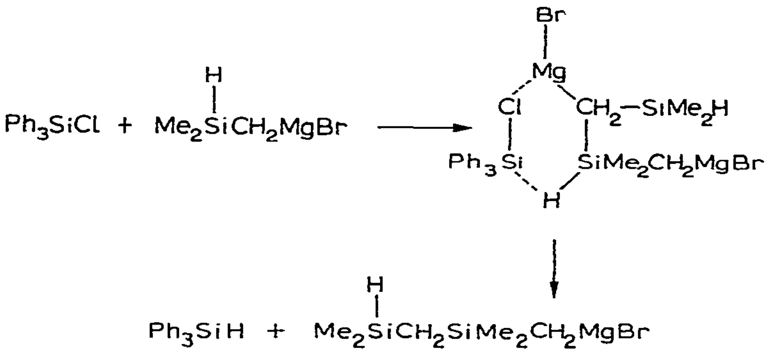
We found using deuterium oxide to terminate the reaction that approximately equal quantities of the product were formed by the two pathways.

These reductions by (hydrosilyl)methyl Grignard reagents are very similar to the reduction of alkoxy- and chlorosilanes by alkyl Grignards which have been shown[3] to proceed by two parallel routes: (1) via the magnesium hydride formed from thermal decomposition of the Grignard reagent and (2) by direct reduction through a six-centre transition state. We established that the reduction does not follow route (1) since the formation of triphenylsilane and the coupled product is complete under conditions in which there is little self-coupling of the Grignard. We have now carried out some kinetic investigations which indicate that neither does the reduction follow route (2).

The reaction of triphenylchlorosilane with (dimethylsilyl)methylmagnesium bromide was studied in tetrahydrofuran. Good third-order kinetics were observed over the first 30% of reaction ($k = 4.75 \times 10^{-4}\ l^2 \cdot mol^{-2} \cdot s^{-1}$ at 60°) and in the presence of a large excess of chlorosilane the reaction followed good second-order kinetics. This kinetic evidence is not in keeping with a mechanism which involves a six-centre transition state formed from one molecule of chlorosilane and one molecule of Grignard reagent.

We have established that this particular Grignard is not associated under the conditions of the reaction, therefore, it appears that the reduction of triphenylchlorosilane requires two molecules of Grignard reagent. It has been shown that in some cases the comparable reduction of ketones by Grignards can proceed by a radical mechanism[4], but such a mechanism seems unlikely in the present case since these reactions follow the same pathways in the presence of styrene, a known trap for radical intermediates in Grignard reactions.

The simplest schemes which would explain the third-order kinetics are a 'Swain' type mechanism[5] involving the formation of a Grignard complex which subsequently reacts with another molecule of Grignard, or a six-centre type reaction involving two molecules of Grignard. One would suspect whatever the mechanism of this reaction that one molecule of Grignard serves to labilise the halogen and the other to transfer a hydrogen, and that triphenylchlorosilane might be reduced by any mixture of Grignard and silane. This is not the case since triphenylchlorosilane was not reduced by mixtures of n-propylmagnesium bromide and dimethylphenylsilane, furthermore steric factors cannot be responsible for the lack of reduction since (phenylmethylsilyl)methylmagnesium halides readily reduce triphenylchlorosilane. It appears that electron donation from the methylene group is responsible for the strong reducing properties of the (hydrosilyl)methyl Grignard compounds. The methylene group need not be adjacent to the silicon–hydrogen to promote reduction since we have found that 2-(diphenylsilyl)ethylmagnesium bromide, 3-(dimethylsilyl)-ethylmagnesium bromide, 3-(dimethylsilyl)propylmagnesium chloride and {[(dimethylsilyl)methyl]dimethylsilyl}methylmagnesium iodide all reduce triphenylchlorosilane much more rapidly than alkyl Grignard compounds. The reduction of triphenylchlorosilane by 2-(diphenylsilyl)ethylmagnesium bromide gave good third-order kinetics ($k = 3.83 \times 10^{-6}\,l^2 \cdot mol^{-2} . s^{-1}$ at 60°). The decrease in the rate compared with the reaction of the (dimethylsilyl)methyl Grignard compound could be due to the larger substituents on silicon as well as the remoteness of the methylene group. Simple inductive effects would not be expected to exert much influence through two and three carbon atoms and neighbouring group participation by the methylene group is probably responsible for the lability of the hydrogens in the β- and γ-compounds. Other examples of this phenomenon have been observed previously in silicon systems[6].



EXPERIMENTAL

Materials

Literature procedures were followed in the preparation of triphenylchlorosilane[7], triphenylsilane[8], (3-chloropropyl)dimethylchlorosilane[9], (3-chloropropyl)-methyldichlorosilane[9], [(dimethylsilyl)methyl]trimethylsilane and ethyldiphenylsilane[10].

(Bromomethyl)dimethylsilane. This was prepared by reduction of 50 g (0.27 mol) of (bromomethyl)dimethylchlorosilane[11] with 3.1 g (0.082 mol) of lithium aluminium hydride in 150 ml of anhydrous diethyl ether. The product was isolated by fractionation; 29.4 g (71 %), b.p. 99–101°. NMR: τ 5.85 (m, 1 H,SiH), 7.50 (d, 2H,J 2 Hz, $SiCH_2$) and 9.78 (d, 6 H, J 4 Hz, Me_2Si).

(Bromomethyl)dimethyldeuteriosilane. Preparation was achieved by the above procedure using lithium aluminium deuteride as reducing agent, b.p. 99–101°. NMR: τ 7.50 (s, 2 H, $SiCH_2$) and 9.80 (s, 6 H, Me_2Si).

(Bromomethyl)methylsilane. Treatment of (bromomethyl)methyldichlorosilane[11] with lithium aluminium hydride in dry diethyl ether gave the product in 63% yield, b.p. 78–80° (lit.[12] b.p. 25°/80 mmHg). NMR: τ 5.87 (m, 2 H, SiH), 7.44 (quartet, 2 H, J 3 Hz, $SiCH_2$) and 9.68 (quartet, 3 H, J 4 Hz, Me_2Si).

(3-Chloropropyl)methylsilane. Reduction of (3-chloropropyl)methyldichlorosilane with lithium aluminium hydride in anhydrous diethyl ether gave the product in 60 % yield, b.p. 120–122°. NMR: τ 6.25 (m, 2 H, SiH), 6.49 (t, 2 H, J 7 Hz, CH_2Cl), 8.10 (m, 2H, CCH_2C), 9.15 (m, 2 H, CH_2Si) and 9.82 (t, 3 H, J 4 Hz, Me Si).

(3-Iodopropyl)methylsilane. A solution of 20 g (0.16 mol) of (3-chloropropyl)methylsilane in 150 ml of dry acetone was refluxed with 72.2 g (0.48 mol) of sodium iodide for 16 h. Sodium salts were removed by filtration, and fractionation gave 12.5 g (36 %) of product, b.p. 162–164°. NMR: τ 6.27 (m, 2 H, SiH), 6.82 (t, 2H, J 7 Hz, CH_2I), 8.06 (m, 2 H, CCH_2C), 9.18 (m, 2 H, CH_2Si) and 9.86 (t, 3 H, J 4 Hz, MeSi).

(3-Chloropropy)dimethylsilane. This was prepared in 66 % yield by reduction of (3-chloropropyl)dimethylchlorosilane with lithium aluminium hydride in dry diethyl ether, b.p. 134–136°. NMR: τ 6.13 (m, 1 H, SiH), 6.54 (t, 2 H, J 7 Hz, CH_2Cl), 8.19 (m, 2 H, CCH_2C), 9.26 (m, 2 H, CH_2Si) and 9.91 (d, 6 H, J 4.5 Hz, Me_2Si).

(3-Iodopropyl)dimethylsilane. Reaction of (3-chloropropyl)dimethylsilane with sodium iodide in anhydrous acetone gave the product in 64% yield, b.p. 179–181°. NMR: τ 6.10 (m, 1 H, SiH), 6.84 (t, 2 H, J 2 Hz, CH_2I), 8.11 (m, 2 H, CCH_2C), 9.29 (m, 2 H, CH_2Si) and 9.91 (d, 6 H, J 4.5 Hz, Me_2Si).

(2-Bromoethyl)diphenylchlorosilane. Dry hydrogen bromide was bubbled through a 20% solution of vinyldiphenylchlorosilane[13] in carbon tetrachloride. Evaporation of the solvent gave the product in quantitative yield. NMR: τ 2.70 (m, 10 H, Ph_2Si), 6.55 (m, 2 H, CH_2Br) and 8.06 (m, 2 H, CH_2Si).

(2-Bromoethyl)diphenylsilane. A solution of 8.56 g (0.027 mol) of (2-bromoethyl)diphenylchlorosilane in 20 ml of dry diethyl ether was added to a slurry of 0.27 g (0.007 mol) of lithium aluminium hydride in 10 ml of dry diethyl ether. The mixture was refluxed for 15 min and then hydrolysed and concentrated. The products were chromatographed on silica gel using benzene as eluant to give 4.5 g (58 %) of silane. NMR: τ 2.53 (m, 10 H, Ph_2Si), 5.07 (m, 1 H, SiH), 6.50 (m, 2 H, CH_2Br) and 8.12 (m, 2 H, CH_2Si).

(Bromomethyl)methylphenylsilane. A solution of 0.27 mol of phenylmagnesium bromide in 110 ml of dry diethyl ether was added dropwise to a solution of 50 g (0.27 mol) of (bromomethyl)methyldichlorosilane[11] in 20 ml of dry diethyl ether cooled to 0°. After addition the products were refluxed for 30 min, cooled and all magnesium salts were precipitated with an excess of light petroleum (b.p. 30–40°). Solvents were removed by distillation and the resulting concentrate was added dropwise to a slurry of 2.5 g (0.066 mol) of lithium aluminium hydride in 100 ml of dry diethyl ether.

Hydrolysis followed by vacuum fractionation gave 41.2 g (71%) of product, b.p. 64–66°/0.5 mmHg. NMR: τ 2.67 (m, 5 H, PhSi), 5.42 (septet, 1 H, J 4 Hz, SiH), 7.55 (d, 2 H, J 2.5 Hz, CH_2Br) and 9.63 (d, 3 H, J 4 Hz, MeSi).

(Bromomethyl)trichlorosilane. This was prepared in 3% yield by photobromination of methyltrichlorosilane using the method of Speier[11], b.p. 130–132°. NMR: τ 7.10 (s, 2 H, CH_2Br).

(Bromomethyl)diphenylsilane. A solution of 0.213 mol of phenylmagnesium bromide in 150 ml of dry diethyl ether was added dropwise to 24.5 g (0.107 mol) of (bromomethyl)trichlorosilane in 20 ml of dry diethyl ether. After reflux for 3 h the products were cooled, excess light petroleum (b.p. 30–40°) was added and the magnesium salts were removed by filtration. The concentrated filtrate was reduced with 1.41 g (0.037 mol) of lithium aluminium hydride in 70 ml of dry diethyl ether. After work up in the usual fashion vacuum distillation gave 14.34 g (49%) of product b.p. 139–140°/1 mmHg. NMR: τ 2.63 (m, 10 H, Ph_2Si), 4.81 (t, 1 H, 2.5 Hz, SiH) and 7.32 (d, 2 H, J 2.5 Hz, CH_2Br).

(Iodomethyl)[(dimethylsilyl)methyl]dimethylsilane. A solution of 0.42 mol of (dimethylsilyl)methylmagnesium bromide in 200 ml of dry tetrahydrofuran was refluxed with 50 g (0.17 mol) of triphenylchlorosilane for 4 h. The products were then cooled and a solution of 31.75 g (0.25 mol) of iodine in 50 ml of dry tetrahydrofuran was slowly added. Hydrolysis and fractionation gave 6.0 g (14%) of product b.p. 75–78°/10 mmHg. NMR: τ 5.96 (m, 1 H, SiH), 7.90 (s, 2 H, CH_2I), 9.85 (m, 12 H, Me_3Si, Me_2Si) and 10.27 (d, 2 H, J 4 Hz, $SiCH_2Si$).

Reactions

The individual reactions of hydrosilyl Grignard reagents with chlorosilanes are summarised in Table 1. The general procedure is illustrated by the reaction of (dimethylsilyl)methylmagnesium bromide with triphenylchlorosilane. For other reactions brief notes are given when new products were isolated. Whenever possible the products were separated by distillation or column chromatography and identified by comparison with authentic samples.

Triphenylchlorosilane. (a) With (dimethylsilyl)methylmagnesium bromide. A solution of 5.89 g (0.02 mol) of triphenylchlorosilane in 30 ml of dry diethyl ether was added to a solution of 0.06 mol of (dimethylsilyl)methylmagnesium bromide in 20 ml of dry diethyl ether. Two thirds of the solvent was removed by distillation under nitrogen and the mixture was refluxed for 24 h, cooled and hydrolysed with 10% ammonium chloride solution. The organic phase was dried and fractionated to give 2.34 g (80%) of [(dimethylsilyl)methyl]trimethylsilane, b.p. 119–121° (lit.[2] b.p. 120°/751 mmHg) NMR: τ 5.89 (m, 1 H, SiH), 9.89 (d, 6 H, J 3 Hz, Me_2Si), 9.92 (s, 9 H, Me_3Si) and 10.22 (d, 2 H, J 4 Hz, CH_2Si). The mass spectrum showed a weak parent at m/e 146 with fragment peaks at 145 ($C_6H_{17}Si_2^+$), 131 ($C_5H_{15}Si_2^+$) and 73 ($C_3H_9Si^+$). The residue was chromatographed on silica gel and eluted first with light petroleum/benzene 5/1 to give 4.1 g (91%) of triphenylsilane, m.p. 32–34° (lit.[8] m.p. 36–37°). NMR: τ 2.53 (m, 15H, Ph_3Si) and 4.43 (s, 1 H, SiH). IR: ν_{max} (liq. film) 2120 (Si–H) and 1435 and 1110 (Si–Ph) cm^{-1}. Elution with benzene produced a fraction consisting of a mixture of products with the general formula $Me_2SiH(CH_2SiMe_2)_n$-CH_2SiMe_3 $n \geqslant 1$ in 20% yield. The mass spectrum showed characteristic $M-15$ ions at m/e 347 ($C_{14}H_{39}Si_5^+$), 275 ($C_{11}H_{31}Si_4^+$) and 203 ($C_8H_{23}Si_3^+$). Elution with diethyl ether afforded 0.28 g (5%) of triphenylsilanol m.p. 149–151° (lit.[11] m.p. 153–154°). NMR: τ 2.40 (m, 15 H, Ph_3Si) and 7.55 (s, 1 H, OH). IR: ν_{max} (KBr disc) 3360 (Si–OH) and 1435 and 1110 (Si–Ph) cm^{-1}.

(*b*). *With (dimethyldeuteriosilyl)methylmagnesium bromide.* Fractionation afforded 0.88 g (60%) of [dimethyldeuteriosilyl)methyl]trimethylsilane, b.p. 118–120°. NMR: τ 9.89 (s, 6 H, Me_2Si), 9.92 (s, 9 H, Me_3Si) and 10.22 (s, 2 H, $SiCH_2Si$). The mass spectrum showed a weak parent ion *m/e* 147 with fragment peaks at 145 ($C_6H_{16}DSi_2^+$) 132 ($C_5H_{14}DSi_2^+$) and 73 ($C_3H_9Si^+$). Chromatographing the residue on silica gel using light petroleum/benzene 5/1 as eluant afforded 1.49 g (66%) of triphenyldeuteriosilane, m.p. 33–35°, ν_{max} (liq. film) 1545 (Si–D) and 1435 and 1110 (Si–Ph) cm^{-1}; absorption at 2120 (Si–H) cm^{-1} was completely absent.

(*c*). *With (dimethylsilyl)methylmagnesium bromide and termination with deuterium oxide.* Distillation gave 2.05 g (70%) of [(dimethylsilyl)methyl]dimethyl-(deuteriomethyl)silane, b.p. 118–120°. NMR: τ 5.89 (m, 1 H, SiH), 9.89 (d, 6 H, J 3 Hz, Me_2Si), 9.92 (s, 8 H, Me_2SiCH_2D) and 10.22 (d, 2 H, J 4 Hz, CH_2Si). The mass showed a weak parent ion *m/e* 147 with fragment peaks at 146 ($C_6H_{16}DSi_2^+$), 132 ($C_5H_{14}DSi_2^+$) and 74 ($C_3H_8DSi^+$). The IR spectrum of triphenylsilane isolated by chromatography showed the absence of Si–D absorption at 1545 cm^{-1}.

(*d*). *With (methylsilyl)methylmagnesium bromide.* Fractionation gave 2.85 g (58%) of [(methylsilyl)methyl]dimethylsilane, b.p. 70–72° (lit.[12] 62°/230 mmHg). NMR: τ 6.08 (m, 3 H, SiH), 9.94 (m, 9 H, MeSi, Me_2Si) and 10.25 (m, 2 H, $SiCH_2Si$). The remaining products were chromatographed on silica gel using light petroleum/benzene 5/1 as eluant to give a mixture of 3.9 g (75%) of triphenylsilane and 0.80 g (12%) of [(methylsilyl)methyl]triphenylsilane (yields estimated by NMR analysis).

(*e*). *With (methylphenylsilyl)methylmagnesium bromide.* The concentrated reaction products were chromatographed on silica gel and eluted with light petroleum/benzene 5/1 to give 4.4 g (80%) of [(methylphenylsilyl)methyl]dimethylphenylsilane. NMR: τ 2.64 (m, 10 H, Ph_2Si), 5.50 (m, 1 H, SiH) and 9.83 (m, 11 H, MeSi, Me_2Si). The mass spectrum showed a weak parent ion *m/e* 270 with fragment peaks at 255 ($C_{15}H_{19}Si_2^+$), 192 ($C_{10}H_{17}Si_2^+$) and 177 ($C_9H_{14}Si_2^+$). Further elution with the same solvent afforded 4.0 g (78%) of triphenylsilane.

(*f*). *With (diphenylsilyl)methylmagnesium bromide.* Chromatography afforded 8.1 g (90%) of methyldiphenylsilane. NMR: τ 2.54 (m, 10 H, Ph_2Si), 5.00 (quartet, 1 H, J 4 Hz, SiH) and 9.42 (d, 3 H, J 4 Hz, SiMe) and 5.42 g (98%) of triphenylsilanol.

(*g*). *With 2-(diphenylsilyl)ethylmagnesium bromide.* Elution of the concentrated products of silica gel with light petroleum/benzene 9/1 afforded a mixture of ethyldiphenylsilane (90%) and triphenylsilane (50%) (yields estimated by NMR analysis). Elution with benzene gave 7.6 g (90%) of [2-(diphenylsilyl)ethyl]ethyldiphenylsilane. NMR: τ 2.62 (m, 20 H, $2Ph_2Si$), 5.13 (m, 1 H, SiH) and 8.77 (m, 9 H, CH_2CH_2, CH_2CH_3).

(*h*). *With 3-(dimethylsilyl)propylmagnesium iodide.* The yield of triphenylsilane (62%) was estimated by NMR analysis.

(*i*). *With n-propylmagnesium bromide and dimethylphenylsilane.* A solution of 5.89 g (0.02 mol) of triphenylchlorosilane, 2.72 g (0.02 mol) of dimethylphenylsilane and 0.02 mol of n-propylmagnesium bromide in 5 ml of dry diethyl ether was refluxed for 24 h. The complete absence after work-up of triphenylsilane was demonstrated by NMR analysis.

(Dimethylsilyl)methylmagnesium bromide. (a). With methyldiphenylchlorosilane. Fractionation afforded 1.0 g (43 %) of [(dimethylsilyl)methyl]trimethylsilane, b.p. 116–119°. The residue was chromatographed on silica gel using light petroleum as eluant to give 1.94 g (41 %) of methyldiphenylsilane. NMR: τ 2.48 (m, 10 H, Ph_2Si), 4.93 (quartet, 1 H J 4 Hz, SiH) and 9.44 (d, 3 H, MeSi), Further elution with light petroleum gave 2.38 g (44 %) of [(dimethylsilyl)methyl]methyldiphenylsilane. NMR: τ 2.52 (m, 10 H, Ph_2Si), 5.97 (m, 1 H, SiH), 9.40 (s, 3 H, MeSi), 9.88 (m, 6 H, Me_2Si) and 10.17 (m, 2 H, $SiCH_2Si$).

(b). With trimethylchlorosilane and termination with deuterium oxide. Fractionation afforded a mixture of [(dimethylsilyl)methyl]trimethylsilane and [(dimethylsilyl)methyl]dimethyl(deuteriomethyl)silane. The relative yields of the two products were estimated from mass spectral peak intensities of m/e values of 131 and 132 due to $M-15$ ions.

Kinetic procedures

(Dimethylsilyl)methylmagnesium bromide with triphenylchlorosilane (initial concentrations equal). The rate of reaction of triphenylchlorosilane with (dimethylsilyl)methylmagnesium bromide was monitored by observing the change in intensity of the IR absorption band of triphenylsilane at 2120 cm^{-1}. Kinetic runs were carried out in a constant temperature bath controlled to 60.00 ±0.025°. The reactants, (dimethylsilyl)methylmagnesium bromide (0.017 mol) and triphenylchlorosilane (4.96 g, 0.017 mol) in 10 ml of dry tetrahydrofuran were mixed under nitrogen in a magnetically stirred reaction vessel and immersed in the bath. At suitable intervals of time samples were removed, run into excess light petroleum to precipitate magnesium salts, filtered, concentrated under vacuum and analysed as 20% solutions in carbon tetrachloride by IR spectroscopy using cells of constant thickness. The percentage transmission at 2120 and 3080 (C–H) cm^{-1} was measured and the concentration of triphenylsilane was determined with the help of a calibration curve prepared from mixtures of triphenylsilane and triphenylchlorosilane of known composition. The process was repeated using 15 ml of tetrahydrofuran as diluting solvent and rate plots for the formation of triphenylsilane were constructed.

(Dimethylsilyl)methylmagnesium bromide with a large excess of triphenylchlorosilane. The rate of disappearance of Grignard reagent in the presence of a large excess of triphenylchlorosilane was followed employing the gas evolution method devised by Gilman *et al.*[12]. Samples were removed at intervals and hydrolysed with dilute hydrochloric acid and the volume of trimethylsilane evolved was measured.

2-(Diphenylsilylethyl)ethylmagnesium bromide and triphenylchlorosilane (initial concentrations equal). 2-(Diphenylsilyl)ethylmagnesium bromide (0.017 mol) and triphenylchlorosilane (0.017 mol) were dissolved in 16 ml of tetrahydrofuran and immersed in a constant temperature bath controlled to 60.00° ±0.025°. At suitable time intervals samples were removed, hydrolysed, concentrated under vacuum and analysed by NMR spectroscopy. The relative intensities of absorptions at τ 4.45 (SiH of Ph_3SiH) and 5.00–5.25 (SiH of other products) were measured accurately and the degree of reduction to give triphenylsilane was determined. The process was repeated using 27 ml of tetrahydrofuran as diluent.

Self coupling of dimethylsilylmethylmagnesium bromide. A mixture of 2.0 ml (0.012 mol) of di-n-butyl ether, 2.0 ml (0.014 mol) of diphenyl ether, 0.028 mol of

·(dimethylsilyl)methylmagnesium bromide and 20 ml of tetrahydrofuran were immersed, under nitrogen, in a constant temperature bath at 60.00°. Samples were withdrawn at appropriate time intervals and analysed quantitatively by GLC for [(dimethylsilyl)methyl]trimethylsilane using di-n-butyl ether as internal standard (analyses were carried out on a Pye-Unicam series 104 instrument using a silicone gum SE30 5ft. × 1/8in. o.d. column). Samples were then concentrated under vacuum and analysed for $Me_2SiH(CH_2SiMe_2)_nCH_2SiMe_3$ $n \geqslant 1$ by NMR using diphenyl ether as internal standard.

Grignard association studies. The degree of association of (dimethylsilyl)-methylmagnesium bromide at various concentrations in tetrahydrofuran was determined using the ebullioscopic method of Ashby and Walker[16].

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