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The reduction of chlorosilanes with hydrosilylmethyl Grignard reagents

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It has been observed previously[1-3] that hydrosilylmethyl Grignard reagents react with trialkylchlorosilanes and -stannanes to give moderate to good yields of the normal coupling products. In contrast we have found that triphenylchlorosilane (I) reacts with dimethylsilylmethylmagnesium bromide (II) to give predominantly triphenylsilane (III) and (dimethylsilylmethyl)trimethylsilane (IV) together with smaller quantities of higher molecular weight products of the type $Me_3Si(CH_2SiMe_2)_nCH_2SiMe_2H$ where $n \geqslant 1$.

The yields of the main products from this reaction and some related reactions are given in Table 1.

TABLE 1

PRODUCT YIELDS FROM THE REACTIONS OF GRIGNARD REAGENTS WITH CHLOROSILANES

Grignard reagent	Concentration (*M*)	Chlorosilane[a]	Reduction (%)	Coupling (%)
Me_2SiHCH_2MgCl	0.06[b]	Ph_3SiCl	91	0
Me_2SiHCH_2MgBr	0.06[c]	Ph_3SiCl	90	0
Me_2SiHCH_2MgBr	0.03[b]	$Ph_2MeSiCl$	49	44
$MeSiH_2CH_2MgBr$	0.04[b]	Ph_3SiCl	75	12
Me_2CHCH_2MgBr	0.04[b]	Ph_3SiCl	3	92

[a]Chlorosilane concentration 0.02 *M*. [b]Solvent diethyl ether. [c]Solvent tetrahydrofuran.

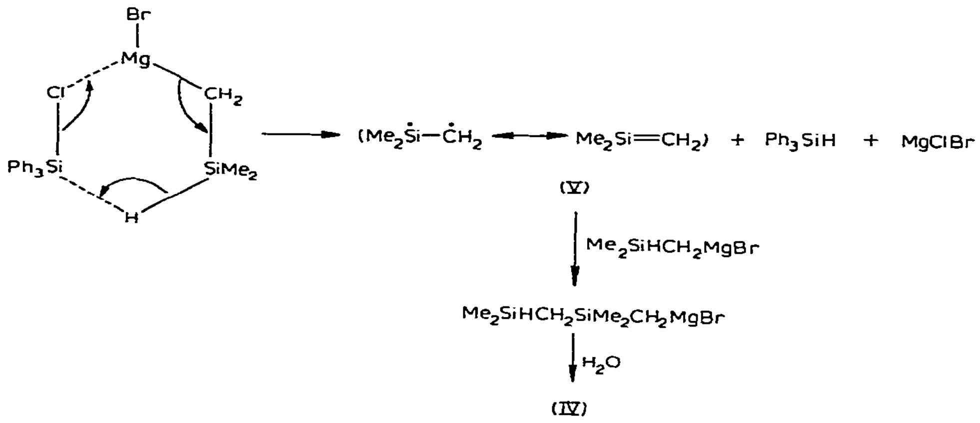
Reduction of I with dimethyldeuteriosilylmethylmagnesium bromide produced triphenyldeuteriosilane as the sole reduction product, and work-up of the reaction between I and II with deuterium oxide gave only III. These results indicate direct transfer of the silyl hydrogen from the Grignard reagent to the silyl halide and preclude the formation of triphenylsilylmagnesium bromide as a reaction intermediate.

It has been suggested that the formally analogous reductions[4] of alkoxy and chlorosilanes by alkyl Grignard reagents proceed by two parallel routes: (1) via the magnesium hydride formed from thermal decomposition of the Grignard reagent and (2) by direct reduction[4,5] through a six-centred transition state.

It is unlikely that the present reaction follows route (1), since the formation of III and IV are about 70% complete after 2 h at 60° at which temperature there is little or no self coupling with the Grignard reagent alone (eqn. 1).

$$\begin{tikzcd} 2Me_2SiCH_2MgBr \arrow[r] & Me_2SiHCH_2SiMe_2CH_2MgBr + MgBrH \arrow[d, "H_2O"] \\ & (IV) \end{tikzcd} \qquad (1)$$

If the reaction follows route (2) both the reduction and the Grignard self coupling reaction can be reasonably explained (eqn. 2).



(2)

Route (2) requires the formation of either a Si–C diradical or double bonded intermediate (V); such an intermediate would be expected to react almost instantaneously with excess Grignard reagent to give IV. This mechanism appears more attractive in the light of recent reports[6-8] which suggest there are a number of reactions which appear to involve such species as intermediates.

There is also the possibility that this reaction may proceed by a direct exchange process. We have established that mixtures of I and (bromomethyl)dimethylsilane do not undergo exchange alone or in the presence of phenylmagnesium bromide. However the adjacent MgBr group in II may be weakening the Si–H bond and promoting the exchange reaction.

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