Some Reactions of Free Radicals and Grignard Reagents with Organosilicon Compounds

by

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Summary

Considerable confusion exists in the literature concerning the reactivity of allylsilanes in radical addition reactions. The reactions of allylsilanes with radical addition reagents have been reexamined and contrary to a previous report it has been found that both carbon tetrachloride and n-butyraldehyde add readily to allyltriethylsilane. Similar reactions of both trimethyl- and triphenylallylsilane with carbon tetrachloride and bromotrichloromethane also gave good yields of adducts. The relative reactivities of the double bond in three series of ω-alkenylsilanes, $R_3Si(CH_2)_nCH=CH_2$ (R = Me, Ph or Cl) toward addition by the trichloromethyl radical have been determined and the relative reactivities of vinyl- and allyltrimethylsilane toward free radical addition by n-dodecanethiol have been investigated. The factors affecting the reactivities of the various ω-alkenylsilanes toward radical addition reagents are discussed.

Unsuccessful attempts have been made to prepare compounds containing silacyclopropane rings via Grignard cyclisation reactions.

The reactions of hydrosilyl Grignard reagents with chlorosilanes have been investigated and silyl chloride reduction has been observed to predominate in many cases. A mechanism for the reduction process is suggested.

Silyl alkoxides were isolated in good yield from reaction of hydrosilylmethyl Grignard reagents with benzophenone together with smaller quantities of benzhydrol and 1,1-diphenylethylene. Possible mechanisms are discussed for the formation of the observed products. The products of reaction of benzoyl chloride and dimethylsilylmethylmagnesium bromide are those derived primarily from reduction processes. A mechanism is proposed involving the intermediacy of 2-silaisobutene.

The photolysis of hydrosilylmethyl Grignard reagents and their reaction with cuprous chloride have been examined with a view to the detection of silicon carbon π-bonded intermediates.

This work was carried out between 1969 and 1972 in the University of Aston in Birmingham. It has been done independently and has not been submitted for any other degree.

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I

RADICAL ADDITION REACTIONS OF ω-ALKENYLSILANES

1. Introduction

The anomalous reactivity of β-alkenylsilanes was first noted by Petrov and Mironov.[1] They observed that hydrogen bromide combined almost instantaneously with allyltrimethylsilane at -70° whereas vinyltrimethylsilane[2] and but-3-enyltrimethylsilane[3] react only slowly with hydrogen bromide at room temperature. Subsequently, in a study of the rates of electrophilic addition of thiocyanogen to ω-alkenyltrimethylsilanes, Petrov et al[4] found that allyltrimethylsilane was ten times more reactive than vinyltrimethylsilane. Their results are represented graphically in Fig. 1.

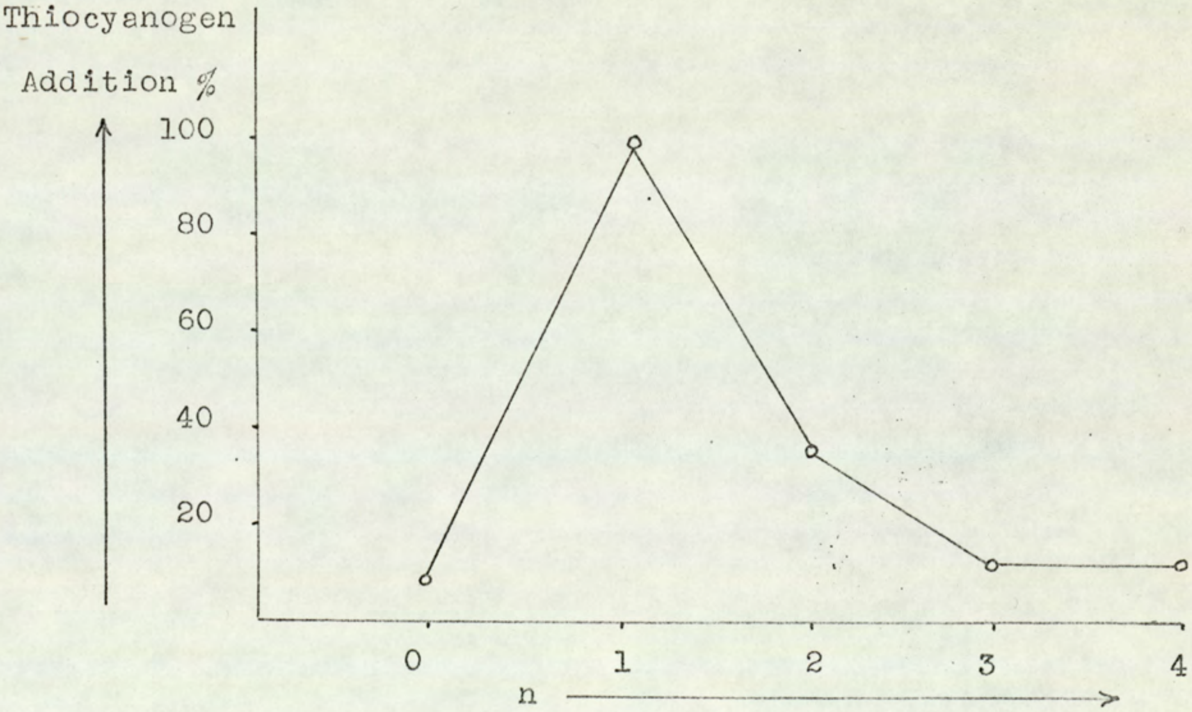
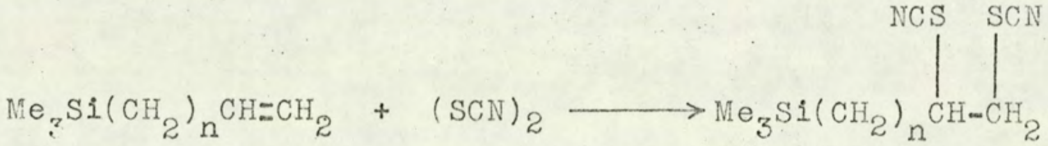


Fig. 1. Yields of addition products from reaction of thiocyanogen with compounds of the series $Me_3Si(CH_2)_nCH=CH_2$ after a period of 5 mins.



$$Me_3Si(CH_2)_nCH{=}CH_2 + (SCN)_2 \longrightarrow Me_3Si(CH_2)_n\overset{NCS}{CH}-\overset{SCN}{CH_2}$$

The anomalous reactivity and peculiar spectral properties of β-functional organosilicon compounds[5] has often been attributed to the well known phenomenon involving the conjugation of atoms in the 1,4-position (σ-σ or σ-π conjugation). For allyltrimethylsilane this can be represented as follows.

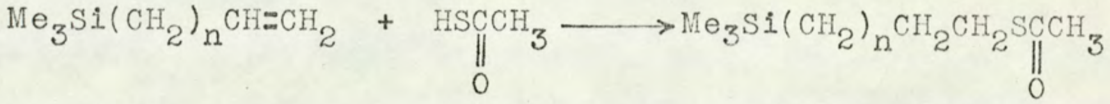
$$Me_3Si-CH_2-CH{=}CH_2 \longleftrightarrow Me_3Si^+ \; CH_2{=}CH-CH_2^-$$

According to Nesmeyanov[6] this phenomenon has the following distinct features; an increase in the reactivity of functional groups in the β-position relative to the silicon atom towards electrophilic reagents, a decrease in reactivity towards nucleophilic reagents, a decrease in reactivity in radical reactions if the radical intermediate has an unpaired electron in the β-position relative to the silicon atom and an increase in intensity for i.r. and Raman absorptions of groups in the β-position.

In accordance with this view σ-π conjugative stabilisation of β-silyl carbonium ion intermediates has been invoked to explain the high rates of solvolysis of β-haloalkylsilanes.[5,7]

Whilst the enhanced reactivity of allylsilanes in electrophilic addition reactions is well authenticated, the ease with which allylsilanes participate in radical addition reactions is much less clearly established and is the subject of considerable confusion in the literature.

The reactivity of ω-alkenylsilanes in radical addition reactions was first examined by Mironov and Pogonkina[8]. They demonstrated that thioacetic acid adds readily to ω-alkenylsilanes in the homologous series $Me_3Si(CH_2)_nCH{=}CH_2$. Allyl-



$$Me_3Si(CH_2)_nCH{=}CH_2 \;+\; HS\underset{\underset{O}{\|}}{C}CH_3 \longrightarrow Me_3Si(CH_2)_nCH_2CH_2S\underset{\underset{O}{\|}}{C}CH_3$$

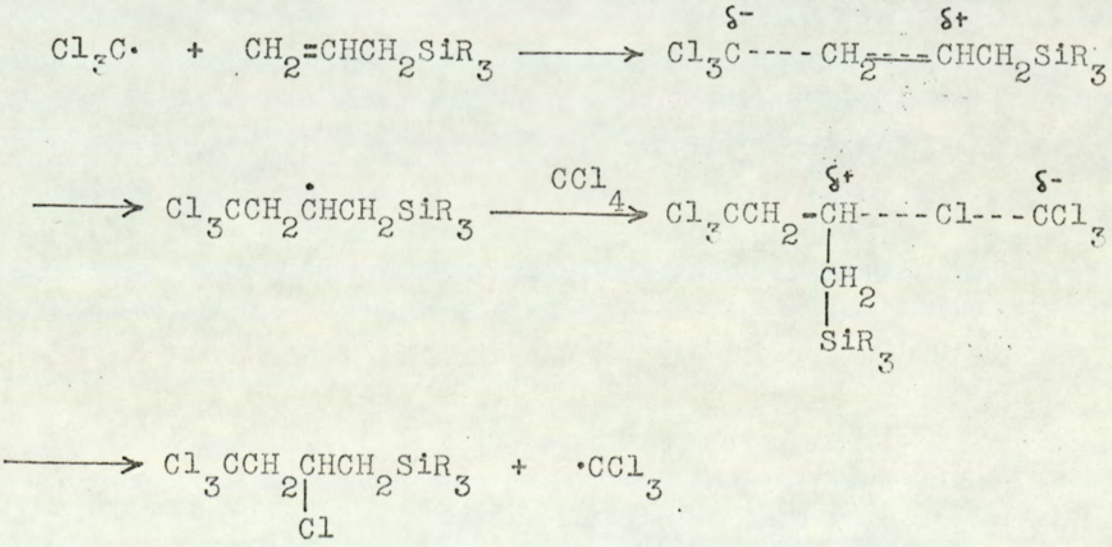
trimethylsilane was found to be most reactive although the latter was only slightly more reactive than but-3-enyltrimethylsilane, the complete order of reactivity being allyltrimethylsilane > but-3-enyltrimethylsilane > vinyltrimethylsilane. This is the order of reactivity found for electrophilic addition but is the reverse of the order predicted by Nesmeyanov[6] for radical addition.

Chernyshev[9] investigated the reaction of allyltriethylsilane with carbon tetrachloride, chloroform, n-butyraldehyde and methyl formate under radical conditions. In all reactions carried out both at atmospheric pressure at 70-100° and under pressure in an autoclave at 150°, no 1 : 1 adduct was isolated. As a rule the starting materials were recovered unchanged. Previous work[10] had shown that n-butyraldehyde, benzaldehyde, carbon tetrachloride and chloroform add readily to vinyltriethylsilane and but-3-enyltriethylsilane to give good yields of addition compounds. In keeping with the views of Nesmeyanov, the reluctance of allylsilanes to participate in radical addition reactions was attributed to stabilisation of the radical intermediate by σ-π conjugation thereby retarding the second stage of reaction and reducing the chain propagating power of the reaction.

$$Et_3SiCH_2\text{-}\dot{C}H\text{-}CH_2\text{-}X \longleftrightarrow Et_3Si\cdot \quad CH_2{=}CH\text{-}CH_2\text{-}X$$

It was concluded that the reactivities of ω-alkenyltrialkylsilanes $R_3Si(CH_2)_nCH{=}CH_2$ in radical addition reactions lie in the order allyl < but-3-enyl < vinyl. This is the reverse of the order found for the addition of electrophilic reagents.

The apparent high reactivity of thiyl radicals and low reactivity of trichloromethyl radicals with allylsilanes is surprising in view of the electrophilic nature of both these species. The positive inductive effect of the Me_3SiCH_2-group[11] ($\sigma^*_R = -0.26$) would be expected to favour reaction of allyltrialkylsilanes with an electrophilic radical, whereas reaction with donor acyl radicals generated from aldehydes should be a much less facile process. The stabilisation of any polar characteristics[12] (in the transition state for radical addition) by σ-π conjugation would also favour attack by an acceptor radical although the precise importance of these effects is difficult to predict.



$$Cl_3C\cdot + CH_2{=}CHCH_2SiR_3 \longrightarrow \overset{\delta-}{Cl_3C}\text{----}CH_2\text{----}\overset{\delta+}{C}HCH_2SiR_3$$

$$\longrightarrow Cl_3CCH_2\dot{C}HCH_2SiR_3 \xrightarrow{CCl_4} Cl_3CCH_2\text{-}\overset{\delta+}{C}H(CH_2SiR_3)\text{----}Cl\text{---}\overset{\delta-}{C}Cl_3$$

$$\longrightarrow Cl_3CCH_2CH(Cl)CH_2SiR_3 + \cdot CCl_3$$

In a recent review by Ruchardt[13] it was pointed out that polar effects will have a dominating influence on radical formation reactions in which the transition state occurs early along the reaction coordinate. Such reactions are exemplified by the addition of trichloromethyl or thiyl radicals to olefins where the chain carrying radical has a central hetero atom or electronegative substituents.

The manner in which polar effects bring about changes in the rates of radical addition reactions has received a good deal of discussion. The simplest picture, which was much used by Price[14] in his treatment of the problem, is that electron withdrawing and supplying groups set up permanent charge distributions in olefin and radical which may increase or decrease the energy required to bring the two species together in the transition state. Obviously, when one species possesses an excess and the other a deficiency of electrons at the site of reaction, the result will be a lowering of the required energy and an increase in the reaction rate.

Reliance on this treatment alone (which amounts to invoking the polarisation effects alone in the Ingold treatment of the theory of polar reactions) has been criticised[15] on the basis that it would predict a pronounced dependence of olefin reactivity ratios upon the dielectric constant of the medium, which is not observed. A way round this is to assume a mutual polarisation of radical and olefin as they approach the transition state (corresponding now to polarisability effects in the Ingold treatment) that becomes important only as the separation of the reactants becomes very small, so that few lines of force radiate into the surrounding medium. Finally, it has been suggested,[16] that at least in strongly alternating systems, the energy of the transition state may be lowered by the participation of resonance structures in which electron transfer has occured between radical and olefin.

Although polar effects in radical addition reactions might reasonably be expected to be of less importance than in electrophilic addition to alkenes, the reactivity order for the exothermic addition of acceptor radicals to ω-alkenyltrialkylsilanes should still parallel that for addition of thiocyanogen. This was the order observed by Mironov and Pogonkina[8] for the addition of thioacetic acid to ω-alkenyltrialkylsilanes. However, the possible effects of

$$\cdot CCl_3 + CH_2{=}CHR \longrightarrow Cl_3CCH_2\text{-}\dot{C}H\text{-}R \qquad (1)$$

$$Cl_3CCH_2\text{-}\dot{C}H\text{-}R + CCl_4 \longrightarrow Cl_3CCH_2\text{-}CHCl\text{-}R \qquad (2)$$

radical intermediate stability on the transfer step (2) cannot be overlooked, especially for the addition of relatively poor transfer reagents such as carbon tetrachloride and chloroform.

Recent observations concerning β-silyl radicals suggest that they probably do possess some additional stability relative to the corresponding carbon analogues although this is unlikely to be a very large effect. Krusic and Kochi[17] observed the radicals generated at low temperatures in the cavity of an e.s.r. spectrometer by photolysis of a mixture of tetraethylsilane and di-t-butyl peroxide. Together with the expected α-silyl radical they also identified a species consistent with β-hydrogen abstraction from the parent molecule.

$$Me_3COOCMe_3 \longrightarrow 2Me_3CO\cdot$$

$$(CH_3CH_2)_4Si + Me_3CO\cdot \longrightarrow (CH_3CH_2)_3Si\dot{C}HCH_3$$

$$(CH_3CH_2)_4Si + Me_3CO\cdot \longrightarrow (CH_3CH_2)_3CH_2\dot{C}H_2$$

Under similar conditions they were unable to detect primary alkyl radicals generated from alkanes by hydrogen abstraction. The more favourable polar effects in the transition state for exothermic β-hydrogen abstraction by

$$Et_3SiCH_2\text{-}\overset{\delta+}{C}H_2\text{------}H\text{-----}\overset{\delta-}{O}CMe_3$$

the electrophilic t-butoxy radicals makes the formation of a primary radical from tetraethylsilane seem more likely. However the β-silyl radicals definitely possess enhanced stability since the ^{29}Si splitting for the β-substituted radical ($a_{Si} = 37.4G$) is larger than that for the α-substituted radical ($a_{Si} = 15.2G$). The added stability of the β-substituted radical was attributed to a hyperconjugative effect similar to that proposed by Nesmeyanov.

$$Et_3SiCH_2\text{-}\dot{C}H_2 \longleftrightarrow Et_3Si\cdot \quad CH_2{=}CH_2$$

In a subsequent e.s.r. study of silyl radicals[18] it was pointed out that radicals with a β-silicon atom possess a hyperconjugative stabilisation energy of 1-2 kcal $mol.^{-1}$

The decomposition of the t-butyl ester of β-(trimethylsilyl)peroxypropionic acid has been studied by Vyazankin et al.[19] . Perester decomposition provides some insight into the stability of radicals[20] since concerted decomposition (simultaneous rupture of the oxygen-oxygen and carbon-carbon bonds) is generally associated with a high stability for the resulting radical R· . When decomposed this perester

$$RCO_3Bu^t \longrightarrow R\dot{C}O_2 \longrightarrow R\cdot + CO_2$$

was found to give fair to good yields of carbon dioxide and the disproportionation products ethyltrimethylsilane and vinyltrimethylsilane, together with a lower yield of the symmetrical dimer 1,4-bis(trimethylsilyl)butane. These results indicate a situation approaching concerted decomposition and are therefore consistent with higher stabilities for radicals containing β-silicon atoms, although they are clearly inconsistent with radicals of vastly enhanced stability.

The order of reactivity of ω-alkenyltrimethylsilanes towards free radical polymerisation has been investigated by a group of Russian workers.[21] They found that the allyl

$$Me_3Si(CH_2)_3CH{=}CH_2 > Me_3SiCH{=}CH_2 > Me_3Si(CH_2)_2CH{=}CH_2 > Me_3SiCH_2CH{=}CH_2$$

compound showed a marked reluctance to polymerise and in keeping with the views of Chernyshev[9] they suggeted that this was because the intermediate radical was highly stabilised by σ-π conjugation thus preventing the chain growing reaction. However the failure of allyltrimethylsilane to polymerise would seem to be equally consistent with the nucleophilic character of the generated radicals and the high double bond electron density of allyltrimethylsilane.

Cooper and Owen[22] observed that N-(silylmethyl) aromatic amines (e.g. Me_3SiCH_2NHPh) possess unexpectedly low oxidation potentials and this was said to be consistent with stabilisation of the intermediate cation radical by silyl-hyperconjugative electron release.

The most detailed study of the reactivity of ω-alkenylsilanes towards radical addition reagents was carried out by Sakurai et al.[23] They determined the relative rates of addition of bromotrichloromethane to compounds from the homologous series $Me_3Si(CH_2)_nCH{=}CH_2$ (n = 0-4). The data obtained are summarised in Table 1.

Table 1. Relative rates of addition of bromotrichloromethane to ω-alkenyltrimethylsilanes.[23]

Compound	Relative Rate
$Me_3SiCH{=}CH_2$ (a)	1.00
$Me_3SiCH_2CH{=}CH_2$	8.34 ±0.84
$Me_3Si(CH_2)_2CH{=}CH_2$	1.60 ±0.40
$Me_3Si(CH_2)_3CH{=}CH_2$	1.09 ±0.00
$Me_3Si(CH_2)_4CH{=}CH_2$	0.94

(a) reference standard

The most notable results from this work are (a) the exceptionally high rate of reaction of allyltrimethylsilane and (b) the reactivity order allyl > but-3-enyl > vinyl. The ability of allyltrimethylsilane to react with bromotrichloromethane is not altogether surprising since the latter is a much better transfer reagent than carbon tetrachloride; abstraction of the bromine atom from this polyhalomethane is a more facile process than abstraction of a chlorine atom from carbon tetrachloride.[24]

$$Cl_3CCH_2\text{-}\dot{C}H\text{-}CH_3 + BrCCl_3 \longrightarrow Cl_3CCH_2CHBrCH_3 + \cdot CCl_3$$

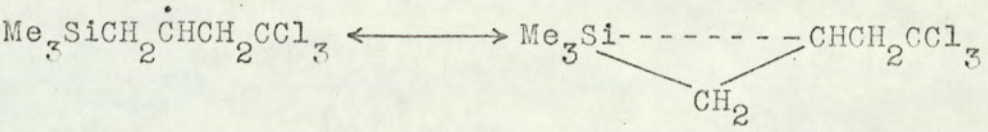
$$\Delta H = -14 \text{ kcal mol}^{-1}$$

$$Cl_3CCH_2\text{-}\dot{C}H\text{-}CH_3 + ClCCl_3 \longrightarrow Cl_3CCH_2CHClCH_3 + \cdot CCl_3$$

$$\Delta H = -8 \text{ kcal mol}^{-1}$$

However, the order of reactivity of the ω-alkenyltrimethylsilanes with bromotrichloromethane parallels that initially obtained by Mironov and Pogonkina for tha addition of thioacetic acid and is the reverse of the order reported by Chernyshev for the addition of carbon tetrachloride. Since the above transfer step is more favourable for bromotrichloromethane, any rate governing radical intermediate stabilisation should be of more importance for the carbon tetrachloride addition; but a complete reversal of the reactivity order with bromotrichloromethane would not be expected since both reactions involve exothermic addition of the electrophilic trichloromethyl radical.

To explain the high reactivity of allyltrimethylsilane in this reaction Sakurai proposed an extra resonance effect


$$\mathrm{Me_3SiCH_2\dot{C}HCH_2CCl_3} \longleftrightarrow \mathrm{Me_3Si}\underset{\mathrm{CH_2}}{\text{--------}}\mathrm{CHCH_2CCl_3}$$

in the radical intermediate. Homoconjugation was the favoured form of stabilisation in which the odd electron on the β-carbon atom was delocalised through the 3d orbitals of silicon. This is similar to an effect proposed by Nagy[25] as a result of quantum mechanical calculations carried out on allyltrimethylsilane. His observations were interpreted in terms of a long bond, with a π-bond order of 8%, between the 3d orbitals of silicon and the carbon atom in the β-position. This latter work has recently been criticised;[26] molecular orbital calculations suggest that the planar trans conformation, which is required for this type of interaction, is unlikely to be very highly populated. Furthermore, a study of the high resolution n.m.r. spectra of allyl-silanes[27] provided no evidence to support ground state dπ-pπ overlap in these compounds and the photoelectron spectrum of allyltrimethylsilane has been interpreted[28] in terms of σ-π conjugation between the ethylenic π-system and the π-type CH_2-Si σ molecular orbital. Sakurai favours stabilisation of the radical intermediate via homoconjugation rather than by σ-π conjugation since the e value for allyltrimethylsilane[29] (e = 0.01) is more positive than that of vinyltrimethylsilane (e = -0.14). This was regarded as evidence for homoconjugation since it was believed that the positive e value was consistent with the silyl group accepting electrons.

Clearly therefore, when the results concerning the relative rates of addition of radicals to ω-alkenyltrialkylsilanes are considered as a whole, there are inconsistencies between the data reported by different groups of workers. In an attempt to determine the factors governing reactivity of allylsilanes in radical addition reactions and to clarify the question of reactivity order of ω-alkenyltrialkylsilanes, the reaction of allylsilanes with aldehydes and polyhalogenomethanes was reinvestigated, and the rates of addition of bromotrichloromethane to compounds in the homologous series $Me_3Si(CH_2)_nCH=CH_2$ (n = 0-5) were redetermined. The relative reactivity of allyltrimethylsilane as determined by Sakurai, seemed too high for a reaction in which polar effects, although of importance, should predictably be of much less importance than for pure electrophilic addition. The result is also inconsistent with the not especially high reactivity of the β-hydrogens in Krusic and Kochi's work on abstraction from alkylsilanes.[30] The effect of electron withdrawing groups on silicon was also examined by determining the relative rates of addition of bromotrichloromethane to silanes in the series $Ph_3Si(CH_2)_nCH=CH_2$ and $Cl_3Si(CH_2)_nCH=CH_2$ (n = 0-3). It also seemed of interest to examine the reactivity of ω-alkenylsilanes with thiyl radicals. Addition of thiyl radicals has been shown by Walling[31] to parallel reactivity with trichloromethyl radicals; it is known that thiols add readily to allylsilanes[8,23,32] and problems from instability will be absent since the products contain no β-substituents.

2. The Reaction of Allylsilanes with Radical Reagents.

Using essentially the same reaction conditions as Chernyshev,[9] allyltrimethylsilane was reacted at reflux with a three fold excess of carbon tetrachloride in the presence of benzoyl peroxide as initiator. Under these conditions addition of carbon tetrachloride was a rapid process the reaction being complete within three hours. The change in the absorption positions of the terminal methylene and methine protons facilitated the monitoring of the reaction by n.m.r. spectroscopy. The addition compound could be isolated in good yield (Table 2.) by vacuum distillation of the products. However, once optimum yield had been attained, the 1 : 1 addition product readily decomposed at reflux temperatures (80°) by a β-elimination mechanism to give trimethylchlorosilane and 4,4,4-trichlorobut-1-ene. Decomposition was found to be complete within 24 h. The addition compounds of vinyltriethylsilane and but-3-enyltriethylsilane were previously prepared[10] using reaction times of 50 h. and the use of similar reaction times for allyltrimethylsilane would undoubtedly lead to complete decomposition of the addition product. It therefore seems likely that Chernyshev, not finding any high boiling materials amongst his products, assumed wrongly that no reaction had taken place.

To test this hypothesis, the products of reaction after 48 h. reflux were examined. As expected, the major products were those formed by β-elimination; trimethylchlorosilane and 4,4,4-trichlorobut-1-ene. By examination of the higher boiling residue two other products were identified. The first of these trimethylbenzoxysilane, was probably produced

Table 2. Addition products from reaction of allylsilanes with poyhalogenomethanes.

Compound	React. Time	React. Temp.	Yield	M.p./B.p.
$Me_3SiCH_2CHClCH_2CCl_3$	2.5 h.	80°	60%	$70-72^\circ$/1 mm.
$Me_3SiCH_2CHBrCH_2CCl_3$	6 h.	60°	80%	-
$Me_3Si(CH_2)_3CCl_3$	48 h.	63°	15%	$50-52^\circ$/1 mm.
$Ph_3SiCH_2CHClCH_2CCl_3$	1 h.	95°	80%	-
$Ph_3SiCH_2CHBrCH_2CCl_3$	6 h.	60°	100%	$45-49^\circ$
$Ph_3Si(CH_2)_3CCl_3$	24 h.	75°	65%	$81-88^\circ$
$Cl_3SiCH_2CHClCH_2CCl_3$	24 h.	80°	29%	$69-71^\circ$/0.7 mm.
$Cl_3SiCH_2CHBrCH_2CCl_3$	1.5 h.	104°	74%	$84-85^\circ$/0.35 mm.
$Et_3SiCH_2CHClCH_2CCl_3$	5.5 h.	80°	95%	-
$Et_3SiCH_2CHBrCH_2CCl_3$	4 h.	60°	100%	-

by subsequent reaction of trimethylchlorosilane with benzoic acid (a major decomposition product of the initiator). The 1 : 1 addition product of carbon tetrachloride and 4,4,4-trichlorobut-1-ene was also identified although it represented less than 1% of the reaction products. Since 4,4,4-trichlorobut-1-ene is known to be very unreactive with bromotrichloromethane,[33] the poor yield is not surprising. As final proof, the reaction of carbon tetrachloride with allyltriethylsilane (the silane used by Chernyshev) was followed by n.m.r. spectroscopy and an estimated yield of 95% of the 1 : 1 adduct was obtained after 5.5 h. The higher boiling point of this product relative to that of allyltrimethylsilane precluded its isolation by conventional vacuum distillation techniques.

Addition of carbon tetrachloride to allyltriphenylsilane was also a rapid process reaction being complete after 1 h. In this case, product decomposition by β-elimination was was much slower in keeping with the increased stability conferred on β-haloalkylsilanes when alkyl groups attached to silicon are replaced by phenyl groups.[34] In contrast reaction of carbon tetrachloride with allyltrichlorosilane afforded only a low yield of 1 : 1 adduct. This is not surprising since strong electron withdrawal by the trichlorosilyl group would make attack by the electrophilic trichloromethyl radical a much less favourable process.

Reaction of chloroform with the allylsilanes gave generally lower yields of addition compounds. This is as expected since chloroform is a much poorer transfer reagent than carbon tetrachloride.

$$Cl_3CCH_2\text{-}\dot{C}H\text{-}CH_3 \;+\; HCCl_3 \longrightarrow Cl_3CCH_2\text{-}CH_2\text{-}CH_3 \;+\; \cdot CCl_3$$

$$\Delta H \;=\; +1.2 \text{ kcal mol}^{-1}$$

In the previous examination of the addition of bromotrichloromethane to ω-alkenyltrimethylsilanes,[23] it was stated that the adduct with allyltrimethylsilane could not be isolated because of its rapid decomposition by β-elimination. However in the present study it was possible to isolate this product in high yield using a reaction temperature of 60°. Under similar conditions the bromotrichloromethane adducts of allyltriphenylsilane and allyltrichlorosilane together with that of allyltriethylsilane were also isolated in good yield.

In an examination of the reaction of allylsilanes with n-butyraldehyde under radical conditions, low yields of adducts were obtained for allyltrimethylsilane, allyltriphenylsilane and allyltriethylsilane. The isolation of any addition compound is surprising in view of the donor properties of both the silanes and the acyl radical. Presumably the enhanced stability of the β-silyl radical intermediates is sufficient to promote the acyl radical addition stage of the reaction.

3. The Relative Reactivities of ω-Alkenylsilanes towards Addition by Trichloromethyl Radicals.

The relative rates of addition of trichloromethyl radicals to the three series of ω-alkenylsilanes have been tabulated (Table 3.) and represented graphically (Fig. 2.).

By comparison of the relative rates of reactivity for the ω-alkenyltrimethylsilanes with those previously determined by Sakurai[23] it can be seen that excepting for allyltrimethylsilane the figures are of comparable magnitude. The high figure previously reported for allyltrimethylsilane is difficult to rationalise. A repeat of the exact conditions used by Sakurai gave a figure of 1.72 for the relative reactivity of this compound. Clearly this new figure is more in line with that predicted[23] from a consideration of inductive effects (1.57) and polar and resonance effects in the reaction.

Steric effects provided by chlorine substituents should be similar to those of methyl groups. Thus the lower general reactivity of the ω-alkenyltrichlorosilanes must be largely electronic in origin and is in keeping with strong electron

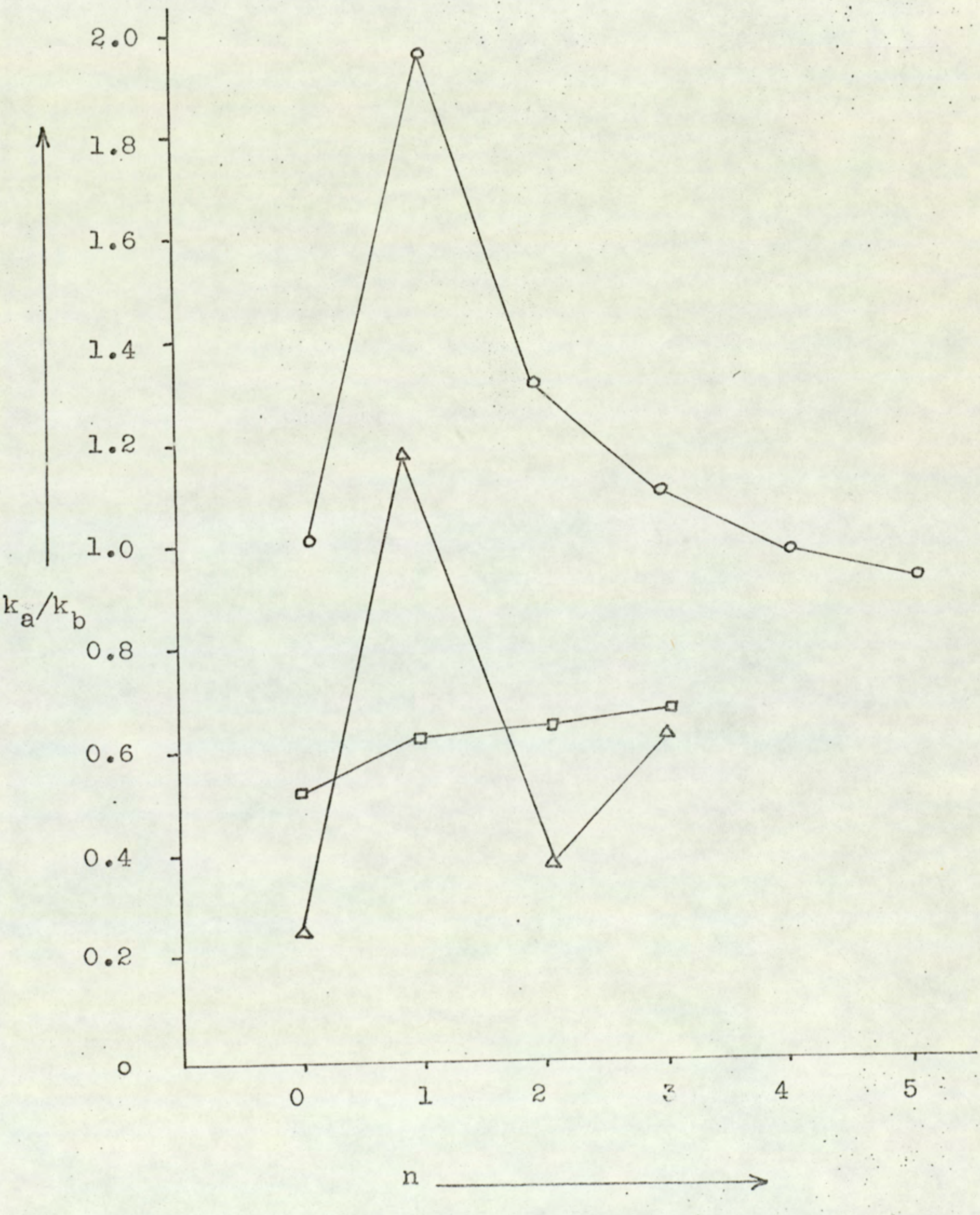
Table 3. Relative rates of addition of trichloromethyl radicals and n-dodecanethiyl radicals to ω-alkenylsilanes.

Compound	Relative Rate k_a/k_b	Av. Dev.	
$Me_3SiCH=CH_2$	1.00		(1.00)[a]
$Me_3SiCH_2CH=CH_2$	1.96	±0.21	(0.26)[a]
$Me_3Si(CH_2)_2CH=CH_2$	1.31	±0.04	
$Me_3Si(CH_2)_3CH=CH_2$	1.09	±0.04	
$Me_3Si(CH_2)_4CH=CH_2$	0.93	±0.06	
$Me_3Si(CH_2)_5CH=CH_2$	0.89	±0.06	
$Ph_3SiCH=CH_2$	0.223	±0.005	
$Ph_3SiCH_2CH=CH_2$	1.18	±0.09	
$Ph_3Si(CH_2)_2CH=CH_2$	0.373	±0.037	
$Ph_3Si(CH_2)_3CH=CH_2$	0.604	±0.043	
$Cl_3SiCH=CH_2$	0.518	±0.002	
$Cl_3SiCH_2CH=CH_2$	0.606	±0.024	
$Cl_3Si(CH_2)_2CH=CH_2$	0.628	±0.014	
$Cl_3Si(CH_2)_3CH=CH_2$	0.642	±0.055	

[a] relative rates of addition of n-dodecanethiyl radicals

Fig. 2. Relative rates of addition of trichloromethyl radicals to ω-alkenylsilanes at 60°

○ $Me_3Si(CH_2)_nCH=CH_2$; △ $Ph_3Si(CH_2)_nCH=CH_2$; □ $Cl_3Si(CH_2)_nCH=CH_2$.



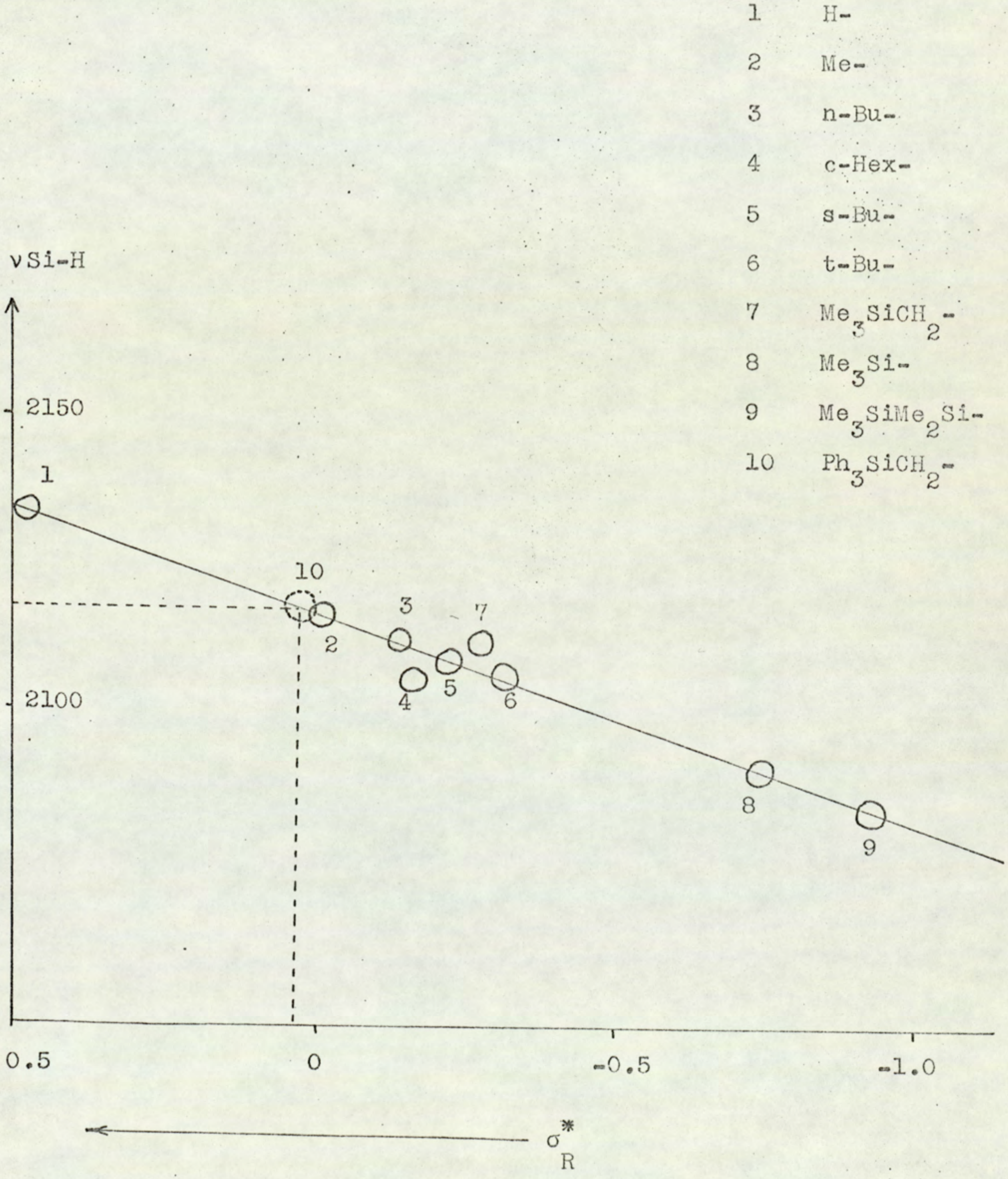
withdrawal by the trichlorosilyl group. A general increase in rate as the chain length increases is also expected as the effects of this group diminish. The absence in allyltrichlorosilane of any significant enhanced reactivity means that radical and transition state stabilising effects are of less importance than for allyltrimethylsilane. Clearly a homoconjugative effect of the type proposed previously[23] should be more important for the trichloro- compound where the silicon atom is more electropositive. Conversely σ-π conjugative effects stabilising either polar effects in the transition state or the radical intermediate will predictably be of much less importance. It therefore seems more likely that resonance interactions have a limited effect upon the reactivity of these compounds in radical addition reactions, but where effects are observable, these are more in keeping with the concept of σ-π conjugation.

The wide divergence of rates in the ω-alkenyltriphenylsilanes and more particularly, the high reactivity of allyltriphenylsilane, are at first sight unexpected. Although the σ^*_R value for the triphenylsilylmethyl group[35] +0.09, is in line with some electron donation, its electron releasing effect should be decidedly less than that of the trimethylsilylmethyl group[11] $\sigma^*_R = -0.26$. Thus on the grounds of inductive effects alone, a large increase in reactivity for allyltriphenylsilane relative to but-3-enyltriphenylsilane would not be expected, although the general increase in rates throughout the series is consistent with the diminishing effects of the sterically bulky phenyl substituents. Since there was only one previously reported determination of σ^*_R

for the triphenylsilylmethyl moiety it seemed worthwhile to clarify this point by a redetermination using another method. It has previously been observed that a good straight line correlation exists between the i.r. Si-H absorptions for compounds of the series $RSiMe_2H$ and the σ^*_R constants for the corresponding groups[36] R . This correlation is represented graphically in Fig. 3. Thus a knowledge of the i.r. Si-H absorption position for (triphenylsilylmethyl)dimethylsilane enables a new figure for σ^*_R of Ph_3SiCH_2- to be determined. Initial attempts to prepare (triphenylsilylmethyl)-dimethylsilane via the Grignard coupling of dimethylsilylmethylmagnesium chloride and triphenylchlorosilane were unsuccessful, high yields of triphenylsilane being isolated. The implications of this and other related reactions are discussed in another part of this thesis. Preparation was finally effected by coupling of triphenylsilylmethyllithium with dimethylchlorosilane. Accurate determination of the Si-H absorption position in the infra-red gave a figure of +0.04 for σ^*_R of Ph_3SiCH_2-, in close agreement with Brook's original figure.[35]

Thus the high reactivity of allyltriphenylsilane with bromotrichloromethane cannot be explained solely by a consideration of inductive effects. Work carried out previously on a series of phenylalkenes,[37] $Ph(CH_2)_nCH{=}CH_2$ provides some clues to the solution of this problem. The rates of addition of trichloromethyl radicals to this series of olefins was found to reach a maximum when n = 2. These results were interpreted in terms of an initial formation of a π-complex between the aromatic ring of the phenyl-alkene and the trichloromethyl

Fig. 3. Plot of νSi-H for RMe_2SiH against σ^*_R for R.



radical. Addition within the complex of the trichloromethyl radical to the double bond of the side chain then takes place (Fig. 4.). It was argued that if addition does occur within

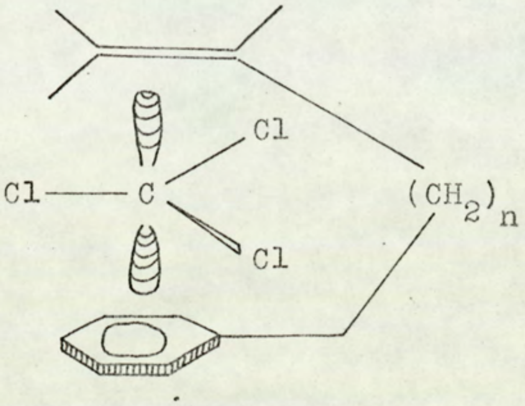


Fig. 4.

a complex, there should be a dependence of the rate of addition on the number of carbon atoms in the chain separating the double bond from the aromatic ring. If no complex is formed, or if addition is predominantly intermolecular, no such dependence should be noted and all members of the series should react at nearly the same rate. The variation in rates for this series of compounds is shown in Table 4.

Table 4. Relative rate constants for the addition of trichloromethyl radicals to $Ph(CH_2)_nCH{=}CH_2$ at 69.5°.

n	Relative Rate	n	Relative Rate
1	1.00	4	1.10 ±0.03
2	1.22 ±0.04	5	1.00 ±0.02
3	1.13 ±0.02	6	0.82 ±0.01

Similar arguments have recently been advanced[38] to explain large changes in the rates of benzilic hydrogen abstraction by trichloromethyl radicals for a series of α,ω-diphenylalkenes $Ph(CH_2)_nPh$ $n = 0-8$.

Such an effect , were it operating, should be of considerably more importance in a series of ω-alkenyltriphenylsilanes since these compounds contain three phenyl groups attached to the same site. On the basis of the previous investigation maximum reactivity would be expected for allyltriphenylsilane, i.e. where the double bond is four atoms away from the aromatic rings. Thus the high reactivity of allyltriphenylsilane in this reaction is best explained in terms of this complexing effect.

4. The Addition of Thiyl Radicals to ω-Alkenyltrimethylsilanes.

A more limited investigation of the addition of n-dodecanethiyl radicals to ω-alkenyltrimethylsilanes was also carried out. In the light of a previous study[31] it might be argued that the relative rates of addition of thiyl and trichloromethyl radicals to ω-alkenylsilanes should parallel one another. The rates of addition of thiyl radicals to vinyltrimethylsilane and allyltrimethylsilane are clearly at variance with this rationale. The results are more easily interpreted if the steric effects provided by the thiyl radical becomes important in the formation of the radical intermediate. Competitive reactions carried out previously[39] on a series of terminal olefins, show that the reactivities towards free radical addition by mercaptans are influenced by the extent of substitution on the 4-carbon of the olefin. It was found that the order of reactivity, 2-methylpent-1-ene >

2,4-dimethylpent-1-ene > 2,4,4-trimethylpent-1-ene towards addition by n-amyl mercaptan was parallel to that predicted by Newman's empirical "rule of six"[40] whereas reactivities of these olefins towards addition by bromotrichloromethane show no appreciable differences. The relative reactivities of these olefins towards various thiyl radicals and trichloromethyl radicals are tabulated (Table 5.).

Table 5. Relative reactivities of olefins towards addition by various adding reagents.[39]

Olefin	$n\text{-}C_5H_{11}SH$	CH_3SH	$n\text{-}C_{12}H_{25}SH$	$BrCCl_3$
$MeCH_2CH_2CMe{=}CH_2$	1.00	1.00	1.00	1.00
$Me_2CHCH_2CMe{=}CH_2$	0.26	-	-	1.05
$Me_3CCH_2CMe{=}CH_2$	0.08	0.16	0.08	0.99

These particular olefins were chosen because they could involve the type of steric effect suggested by Newman's "rule of six", namely that reaction at an unsaturated centre is sterically hindered by the atoms or groups positioned six atoms from the site at which reaction is taking place. Clearly, in the above series the number of hydrogens in the 6-position increases from three to nine. Examination of the results shows that increasing the number of methyl groups on the 4-carbon atom of the olefin, and hence increasing the number of hydrogens in the 6-position relative to the terminal carbon atom of the double bond, does markedly lower the reactivity of an olefin towards addition by mercaptans. These results are readily rationalised if the reversibility of the thiyl radical addition to olefins plays an important part in controlling the rate of reaction. The reversibility of thiyl radical addition to olefins[31] has been demonstrated by the rapid isomerisation of unchanged olefin in the addition of methyl mercaptan to cis- and to trans- but-2-ene. However it has been found that there is no isomerisation of the unchanged olefins in the addition of bromotrichloromethane to cis- and to trans- but-2-ene[41] and hence the relative rates of removal of the olefins from this reaction mixture is dependent only on the relative rates of addition of the trichloromethyl radical to the olefins. Thus the elimination of the thiyl radical is an important factor determining the reactivities of these olefins towards mercaptans. The small differences in reactivity towards addition by methyl mercaptan compared to the larger differences noted with n-amyl and n-dodecyl mercaptans is also consistent with this explanation. In the ω-alkenyltrimethylsilane series, the "rule of six" might logically be expected to be of most importance for allyltrimethylsilane, this compound having nine hydrogen atoms in the 6-position (Fig. 5.). Consequently, because of the

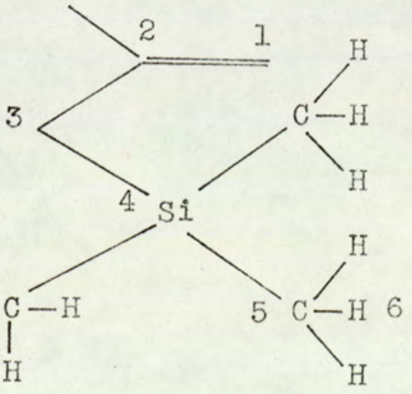


Fig. 5.

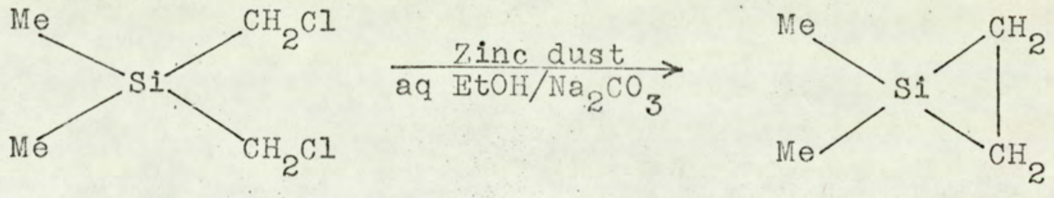
importance of steric effects, the relative rates of addition of thiyl radicals to ω-alkenylsilanes are of little use as a measure of olefin reactivity in radical addition reactions.

II

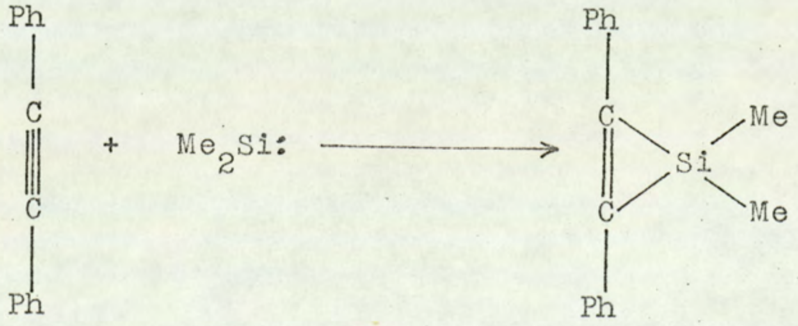
POSSIBLE SYNTHETIC ROUTES TO SILACYCLOPROPANES

1. Introduction

In recent years several unsuccessful attempts to prepare compounds containing silacyclopropane or silacyclopropene rings have been reported in the literature. In the first recorded attempts Roberts[42] treated bis(chloromethyl)-dimethylsilane with zinc dust in the hope of isolating 1,1-dimethylsilacyclopropane. Under conditions in which cyclopropanes are readily generated only (chloromethyl)trimethylsilane and a small amount of tetramethylsilane were detected.

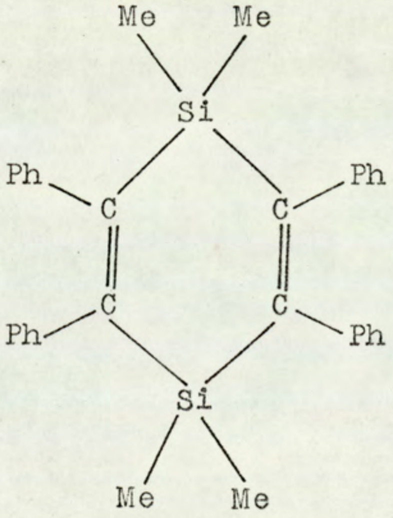


More recently, several reports appeared from a Russian group of workers in which they claimed to have prepared a series of silacyclopropenes and germacyclopropenes.[43] Syntheses were effected by insertion of a divalent intermediate of the respective Group IVB metal into the multiple bond of a disubstituted acetylene. Dimethylsilirene was



generated either by reaction of dimethyldichlorosilane with sodium in boiling xylene, or by thermal cleavage[44] of silicon-silicon bonds of the polymer $(Me_2Si)_{55}$. The products isolated were stable high melting materials which were unaffected by aerial oxidation or by bromine in carbon tetrachloride. Molecular weight determinations carried out in solution gave consistent results by extrapolation to infinite dilution and infra-red spectra further substantiated the structure of the products. However later work disproved the original structures assigned to these products[45-47] and they were shown by mass spectrometry to be cyclic dimers of the type shown, Fig. 6.

Fig. 6.

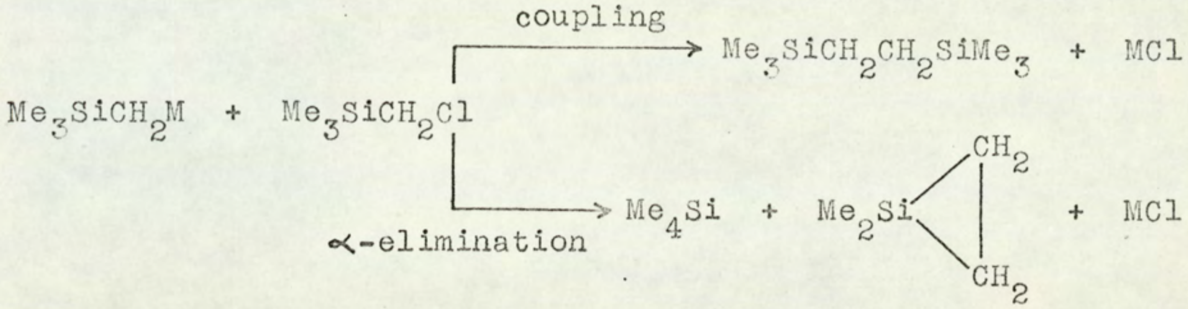


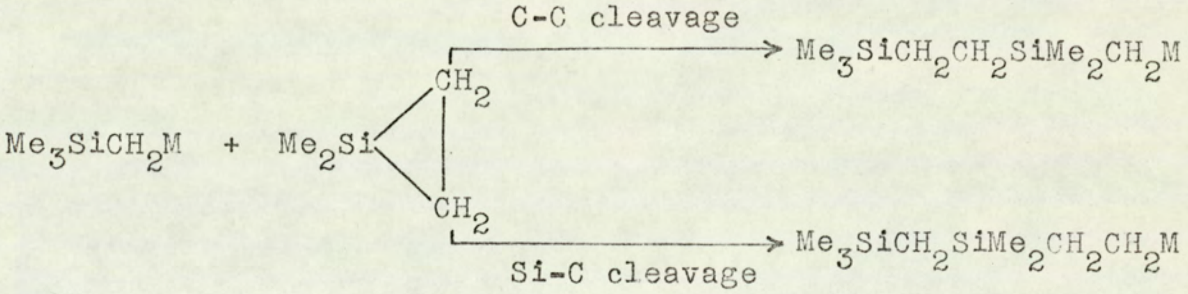
M^+ 472

Theory for silacyclopropene 236

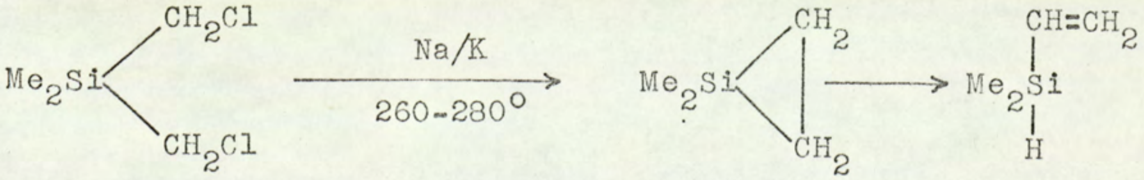
Conolly and Urry[48] studied the Wurtz reaction of (chloromethyl)trimethylsilane in a variety of solvents. To account for the formation of some of the products 1,1-dimethylsilacyclopropane was suggested as an intermediate although this was not isolated.

$$Me_3SiCH_2Cl \; + \; 2M \longrightarrow Me_3SiCH_2M \; + \; MCl$$





In a subsequent attempt to isolate a silacyclopropane Skell and Goldstein[49] studied the vapour phase reaction of bis(chloromethyl)-dimethylsilane with sodium/potassium in a helium atmosphere. None of the ring compound was isolated but the presence of vinyldimethylsilane amongst the products was suggested as evidence for its intermediacy. They attributed the large difference in thermal stability of cyclopropanes and silacyclopropanes ($\Delta E_{act} \sim 60$ kcal mol^{-1}) to the enhanced strain in the latter due to the presence of the silicon atom; C-Si-C bond angle 48°.



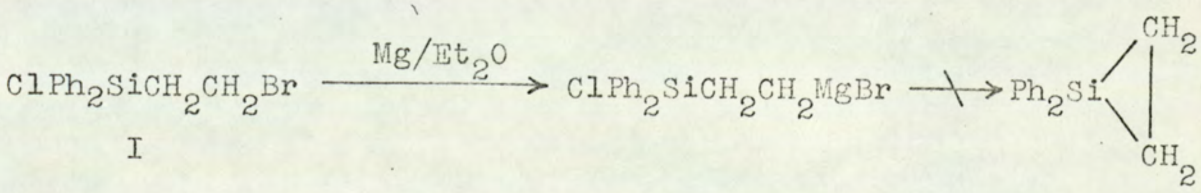
In the light of these results it seemed likely that a ring compound might be isolated when milder conditions were used for cyclisation; the attempted cyclisation of a Grignard reagent would provide such a route. The high reactivity of the silicon-chlorine bond towards coupling with Grignard reagents made the intramolecular reaction of a β-silyl-Grignard reagent a particularly attractive possibility although phenyl substituents on silicon would be necessary to stabilise the Grignard reagent relative to elimination of ethylene.[34]

2. Results and Discussion

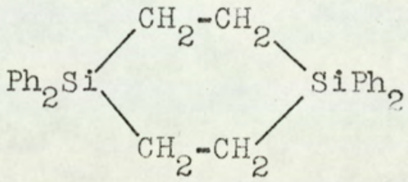
The desired starting material, β-bromoethyldiphenylchlorosilane (I) was prepared by addition of hydrogen bromide to vinyldiphenylchlorosilane.

$$CH_2{=}CHSiPh_2Cl \xrightarrow{HBr} \underset{I}{BrCH_2CH_2SiPh_2Cl}$$

However, no definitive proof of silacyclopropane formation was obtained when I was reacted with magnesium in diethyl ether. The major product, identified by n.m.r. appeared to be ethyldiphenylchlorosilane. This was presumably



formed by hydrogen abstraction by the Grignard reagent from the solvent. No n.m.r. signal was observed in the region up field from τ 9.4; the expected position for absorption of silacyclopropane ring protons. However, by chromatographing the products on silica gel a compound was isolated whose n.m.r. spectrum was consistent with the cyclic dimer.



An alternative route to a ring compound seemed to be via the analogous _gem_-dimethyl Grignard reagent (II); _gem_-dimethyl groups at the reactive centre are known to accelerate cyclisation.[40] Reaction of (2-bromo-2-methylpropyl)diphenylchlorosilane (III) with magnesium in diethyl ether led to a number of reaction products whose formation are represented in the scheme below (Fig. 7.).

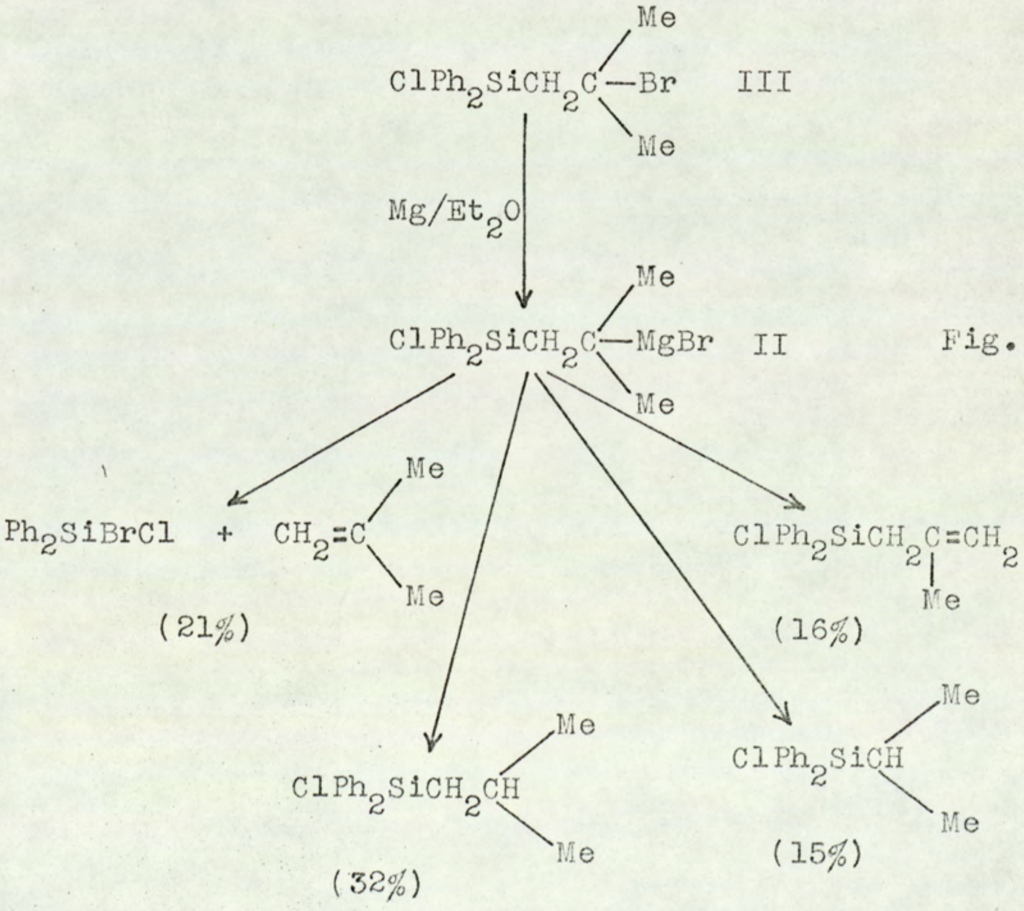
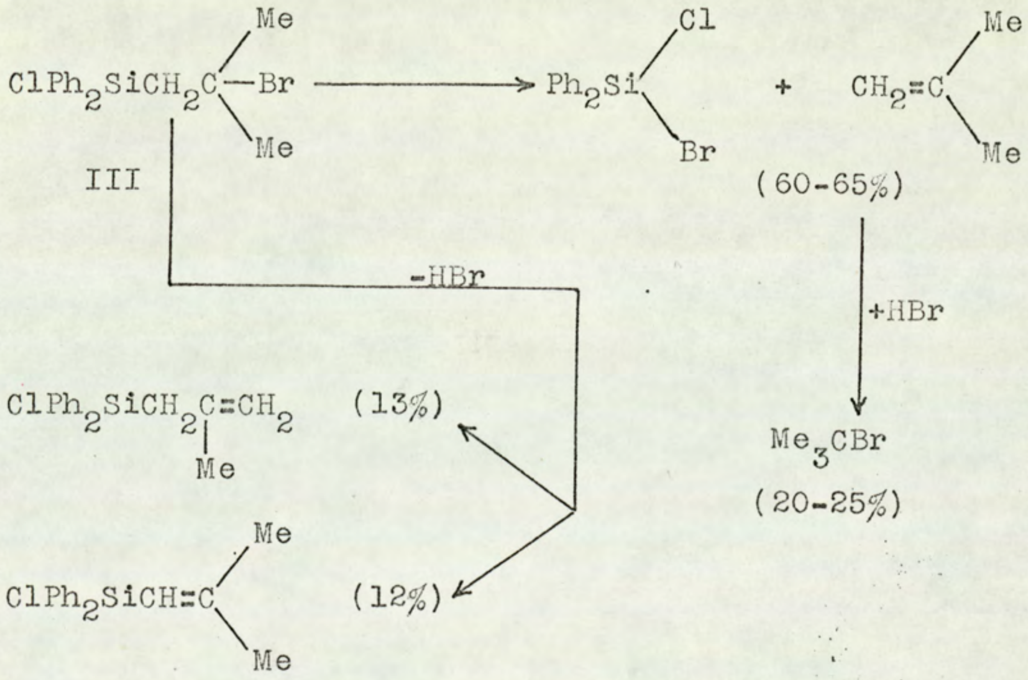


Fig. 7.

The products so obtained were easily identified by their characteristic n.m.r. spectra. I.r. analysis of the reaction products pointed to the presence of trace quantities of a hydrosilane. This could have arisen by breakdown of the intermediate silacyclopropane in a similar fashion to Skell's product although proof of this is not conclusive. The absence of an n.m.r. signal upfield from τ 9.4 in the reaction products was indicative of no three membered ring compound formation.

On contact with trace quantities of aluminium, III readily decomposed, breakdown being complete within 24 h.



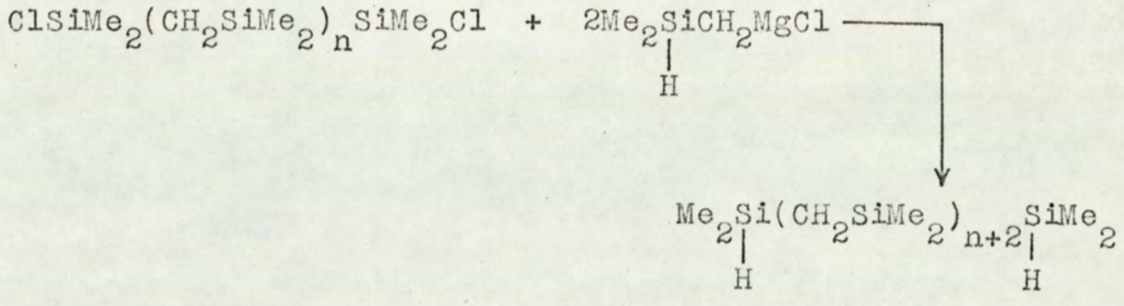
This type of decomposition is in sharp contrast to the stability normally conferred on β-haloalkyl silicon compounds with chlorine or phenyl substituents on silicon.[34] Thus β-bromoethyltriphenylsilane has no tendency towards β-elimination or loss of hydrogen bromide at room temperature.

III

THE REACTIONS OF HYDROSILYL GRIGNARD REAGENTS WITH CHLOROSILANES

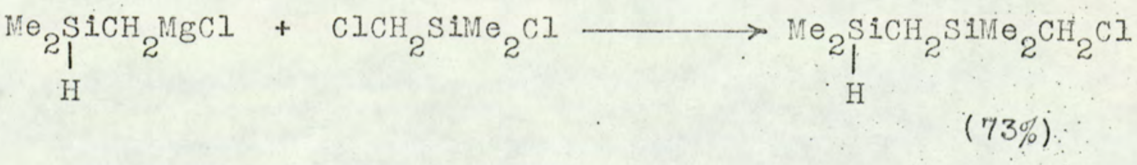
1. Introduction

Although the reaction of hydrosilyl Grignard reagents with chlorosilanes has previously received limited investigation, reports to date would suggest that reactions proceed in a normal fashion to give the expected coupling products. Greber and Degler[50] were the first to report the preparation of a hydrosilylmethyl Grignard reagent; they observed that (chloromethyl)dimethylsilane reacted with magnesium in anhydrous tetrahydrofuran to give the corresponding Grignard reagent in 95% yield. Subsequent reaction with dimethyldichlorosilane and with ωω'-dichloropolysilmethylenes afforded ωω'-dihydropolysilmethylenes in good yield. These



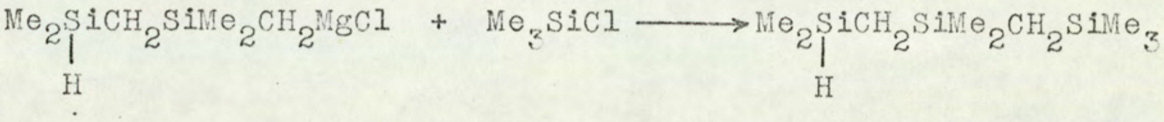
$$\mathrm{ClSiMe_2(CH_2SiMe_2)_nSiMe_2Cl + 2Me_2\underset{H}{Si}CH_2MgCl \longrightarrow Me_2\underset{H}{Si}(CH_2SiMe_2)_{n+2}\underset{H}{Si}Me_2}$$

workers also observed that this Grignard reagent coupled readily with trimethylchlorosilane to give (dimethylsilylmethyl)trimethylsilane (IV) (80%) and with (chloromethyl)dimethylchlorosilane to form (chloromethyl)(dimethylsilylmethyl)dimethylsilane. (Chloromethyl)(dimethylsilylmethyl)dimethyl-



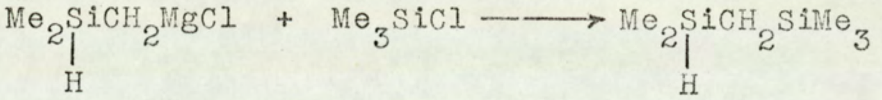
$$\mathrm{Me_2\underset{H}{Si}CH_2MgCl + ClCH_2SiMe_2Cl \longrightarrow Me_2\underset{H}{Si}CH_2SiMe_2CH_2Cl}\quad (73\%)$$

silane was found to react normally with magnesium in tetrahydrofuran to give the Grignard reagent (95%) and further reaction with trimethylchlorosilane afforded 1,1,1,3,3,5,5-heptamethyltrisilmethylene in good yield.



$$\underset{\substack{|\\ \mathrm{H}}}{\mathrm{Me_2Si}}\mathrm{CH_2SiMe_2CH_2MgCl} + \mathrm{Me_3SiCl} \longrightarrow \underset{\substack{|\\ \mathrm{H}}}{\mathrm{Me_2Si}}\mathrm{CH_2SiMe_2CH_2SiMe_3}$$

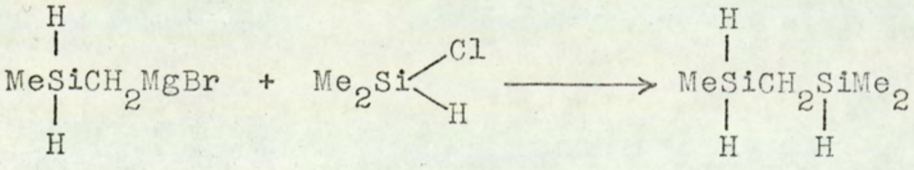
Subsequently, these results were partially confirmed by Schmidbaur and Waldmann[51] who observed that dimethylsilylmethylmagnesium chloride was produced in 93% yield by reaction of (chloromethyl)dimethylsilane with magnesium in dry diethyl ether and that this coupled normally with trimethylchlorosilane to give IV.



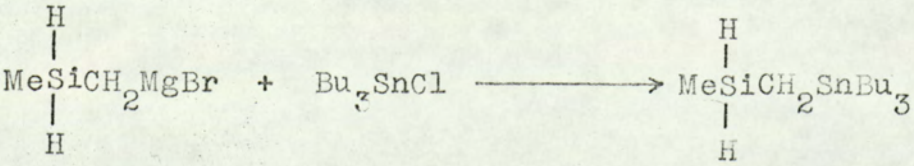
IV

$$\underset{\substack{|\\ \mathrm{H}}}{\mathrm{Me_2Si}}\mathrm{CH_2MgCl} + \mathrm{Me_3SiCl} \longrightarrow \underset{\substack{|\\ \mathrm{H}}}{\mathrm{Me_2Si}}\mathrm{CH_2SiMe_3} \qquad \mathrm{IV}$$

More recently, Owen and Cooke[52] investigated the reaction of a dilute solution of (bromomethyl)methylsilane with magnesium in diethyl ether and reported a Grignard analysis of 70%. Reaction with dimethylchlorosilane and tributyltin chloride gave good yields of coupling products.



$$\underset{\substack{|\\ \mathrm{H}}}{\overset{\substack{\mathrm{H}\\ |}}{\mathrm{MeSi}}}\mathrm{CH_2MgBr} + \mathrm{Me_2Si}\genfrac{}{}{0pt}{}{\diagup\mathrm{Cl}}{\diagdown\mathrm{H}} \longrightarrow \underset{\substack{|\\ \mathrm{H}}}{\overset{\substack{\mathrm{H}\\ |}}{\mathrm{MeSi}}}\mathrm{CH_2}\underset{\substack{|\\ \mathrm{H}}}{\mathrm{SiMe_2}}$$



$$\underset{\substack{|\\ \mathrm{H}}}{\overset{\substack{\mathrm{H}\\ |}}{\mathrm{MeSi}}}\mathrm{CH_2MgBr} + \mathrm{Bu_3SnCl} \longrightarrow \underset{\substack{|\\ \mathrm{H}}}{\overset{\substack{\mathrm{H}\\ |}}{\mathrm{MeSi}}}\mathrm{CH_2SnBu_3}$$

2. The Reaction of Triphenylchlorosilane with Hydrosilylmethyl Grignard Reagents

It has previously been pointed out (Chapter 1.) that a redetermination of σ_R^* for Ph_3SiCH_2- necessitated the preparation of (dimethylsilylmethyl)triphenylsilane. In an initial attempt to prepare this compound, the reaction of triphenylchlorosilane with dimethylsilylmethylmagnesium bromide was examined, since in the light of the previous reports it seemed probable that the coupling product would be formed in good yield. However this reaction was found to give predominantly triphenylsilane (91%) and (dimethylsilylmethyl)trimethylsilane IV (80%) together with smaller quantities of higher molecular weight products of the type $Me_2SiH(CH_2SiMe_2)_nCH_2SiMe_3$ where $n > 1$. The yields of the main products from this and some related reactions are given in Tables 6 and 7.

The reactions of methylsilylmethylmagnesium bromide and methylphenylsilylmethylmagnesium bromide with triphenylchlorosilane followed similar pathways, good yields of triphenylsilane being isolated together with little or none of the normal coupling products (Table 6.).

Triphenylsilane was shown to be absent from the products of reaction of triphenylchlorosilane and diphenylsilylmethylmagnesium bromide and presumably in this case, the steric constraints imposed upon the transition state are too great for reduction to take place.

Reaction of triphenylchlorosilane with dimethyldeuteriosilylmethylmagnesium bromide produced triphenyldeuteriosilane as the exclusive reduction product, whilst work up of the

Table 6. Product yields from the reactions of hydrosilyl Grignard reagents with triphenylchlorosilane.

Grignard (Conc. mol.)[a]	Products (%)
Me_2SiHCH_2MgCl (0.06)[b]	Ph_3SiH (91), Ph_3SiOH (5), $Me_2SiHCH_2SiMe_3$ (80), $Me_2SiH(CH_2SiMe_2)_nCH_2SiMe_3$ (20)
Me_2SiHCH_2MgBr (0.03)[b,c]	Ph_3SiH (77), Ph_3SiOH (20), $Me_2SiHCH_2SiMe_3$ (60), $Me_2SiHCH_2(SiMe_2CH_2)_nSiMe_3$ (20)
Me_2SiDCH_2MgBr (0.026)[b]	Ph_3SiD (67), Ph_3SiOH (29)
Me_2SiHCH_2MgBr (0.06)[d]	Ph_3SiH (91), Ph_3SiOH (5)
$MeSiH_2CH_2MgBr$ (0.04)[b]	Ph_3SiH (75), $MeSiH_2CH_2SiMe_2H$ (58) Ph_3SiOH (13), $Ph_3SiCH_2SiMeH_2$ (12)
$MeSiH_2CH_2MgBr$ (0.04)[b,e]	Ph_3SiH (58), Ph_3SiOH (24), $Ph_3SiCH_2SiMeH_2$ (18).
$PhMeSiHCH_2MgBr$ (0.049)[b]	Ph_3SiH (80), Ph_3SiOH (15), $PhMe_2SiCH_2SiPhMeH$ (75)
Ph_2SiHCH_2MgBr (0.04)[b]	Ph_3SiH (0), Ph_2MeSiH (190)
$Ph_2SiH(CH_2)_2MgBr$ (0.06)[b]	Ph_3SiH (50)
$Me_2SiH(CH_2)_3MgCl$ (0.045)[b]	Ph_3SiH (79)
$Me_2SiH(CH_2)_3MgI$ (0.02)[b]	Ph_3SiH (62), Me_2PrSiH (trace), $PrMe_2Si(CH_2)_3SiMe_2H$
$MeSiH_2(CH_2)_3MgI$ (0.016)[b]	Ph_3SiH (60)
$Me_2SiHCH_2SiMe_2CH_2MgI$ (0.04)[b]	Ph_3SiH (45)

[a] Triphenylchlorosilane concentration 0.02 mol. [b] Solvent diethyl ether. [c] Reaction terminated with deuterium oxide. [d] Solvent tetrahydrofuran. [e] Grignard reagent prepared from magnesium of improved purity.

Table 7. Miscellaneous reductions and attempted reductions with Grignard reagents in diethyl ether.

Grignard (Conc. mol.)	Reactant[a]	Products (%)
Me_2SiHCH_2MgBr (0.03)	$Ph_2MeSiCl$	Ph_2MeSiH (49), $Ph_2MeSiCH_2SiMe_2H$ (44)
Me_2SiHCH_2MgBr (0.02)	Me_3SiCl[b]	$Me_3SiCH_2SiMe_2H$ (39), $Me_2SiHCH_2SiMe_2CH_2D$ (34)
Me_2SiHCH_2MgBr (0.02)	Ph_3SiOMe	Ph_3SiH (0), $Me_2SiH(CH_2SiMe_2)CH_2SiMe_3$ (14)
Me_3SiCH_2MgBr (0.04)	Ph_3SiCl	Ph_3SiOH (100)
Me_2CHCH_2MgBr (0.04)	Ph_3SiCl	Ph_3SiH (4), $Ph_3SiCH_2CHMe_2$ (92)

[a] Concentration 0.02 mol. [b] Reaction terminated with deuterium oxide.

reaction between dimethylsilylmethylmagnesium bromide and triphenylchlorosilane with deuterium oxide gave only triphenylsilane. These results clearly 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.

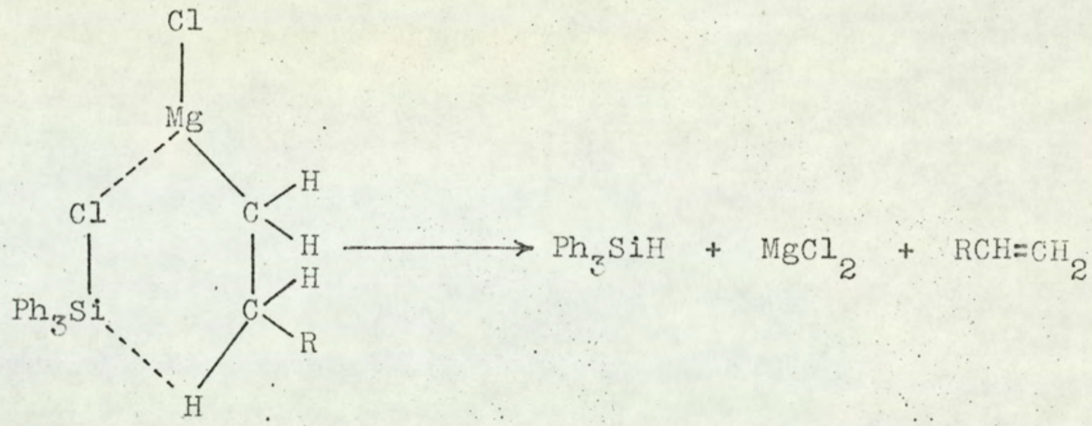
The easier transfer of the silyl hydrogen relative to hydrogen attached to carbon was demonstrated by the reaction of isobutylmagnesium bromide with triphenylchlorosilane (Table 7.). In this case coupling was the predominant route of the reaction, triphenylsilane being detected as only a minor product (4%).

3. The Mechanism of Reduction

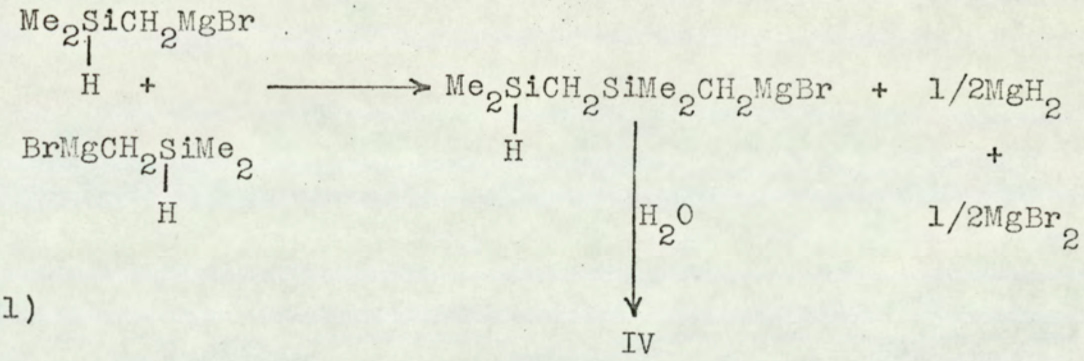
A number of possible mechanisms can be suggested to explain the formation of the observed products. It has recently been established[53] that the formally analogous reductions of alkoxy- and chlorosilanes by alkyl Grignard reagents proceed by two parallel routes. However it should be mentioned that these reductions only occur with sterically hindered chlorosilanes and then only at elevated temperatures ($\geqslant 100^{\circ}$). Route (a) is via the magnesium hydride formed from

$$\begin{tikzcd} 2RCH_2CH_2MgCl \arrow[r] & 2RCH{=}CH_2 & + & MgH_2 \arrow[rd, "2R_3SiCl"'] & + & MgCl_2 & \\ & & & & 2R_3SiH & + & MgCl_2 \end{tikzcd}$$

thermal decomposition of the Grignard reagent and route (b) by direct reduction[53,54] through a six centre transition state.

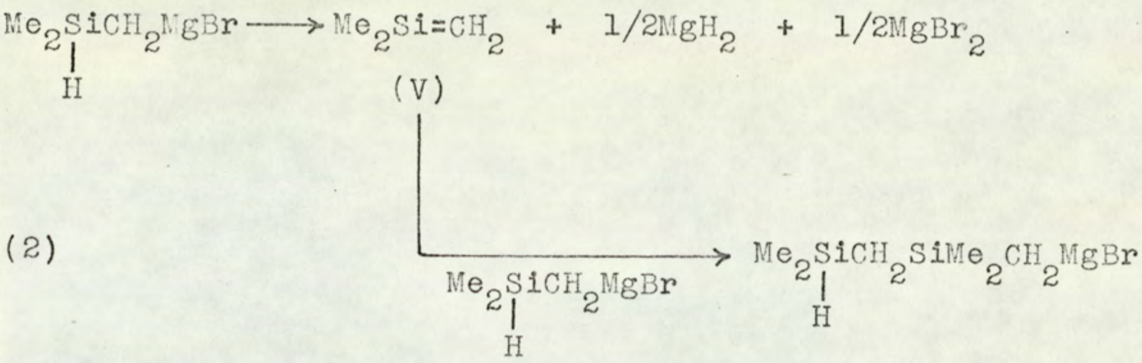


In the case of the hydrosilyl Grignard reagent the generation of magnesium hydride could occur via two routes. Firstly (1) by the coupling of one Grignard molecule with the silicon hydride bond of another molecule of Grignard reagent.



(1)

However previous reports suggest that whilst this type of coupling may be important in tetrahydrofuran[55] it does not normally occur at measurable rates in diethyl ether.[56] Magnesium hydride might also be generated by thermal elimination from the Grignard reagent (2) in a similar fashion to normal alkyl Grignard reagents. This route requires the formation of a silicon-carbon double bonded intermediate V; such an intermediate would be expected to react almost

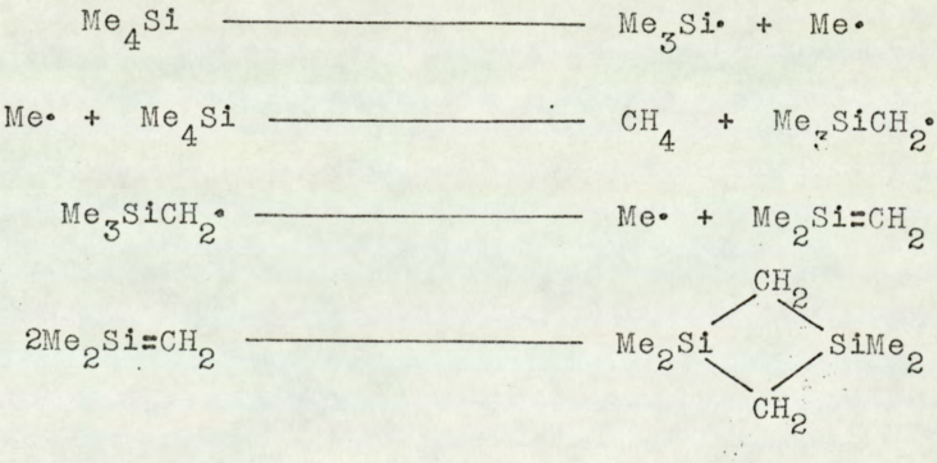


(2)

$$\underset{\mathrm{H}}{\mathrm{Me_2SiCH_2MgBr}} \longrightarrow \underset{(\mathrm{V})}{\mathrm{Me_2Si{=}CH_2}} + 1/2\mathrm{MgH_2} + 1/2\mathrm{MgBr_2}$$

$$\mathrm{(V)} \xrightarrow{\underset{\mathrm{H}}{\mathrm{Me_2SiCH_2MgBr}}} \underset{\mathrm{H}}{\mathrm{Me_2SiCH_2SiMe_2CH_2MgBr}}$$

instantaneously with excess Grignard reagent to give IV after hydrolysis. This mechanism appears more attractive in the light of recent observations[57-65] which suggest that there are a number of reactions which appear to involve such species as intermediates. Fritz and coworkers[57] have suggested the intermediacy of 2-silaisobutene V to explain the formation of some of the products from the pyrolysis of tetramethylsilane.



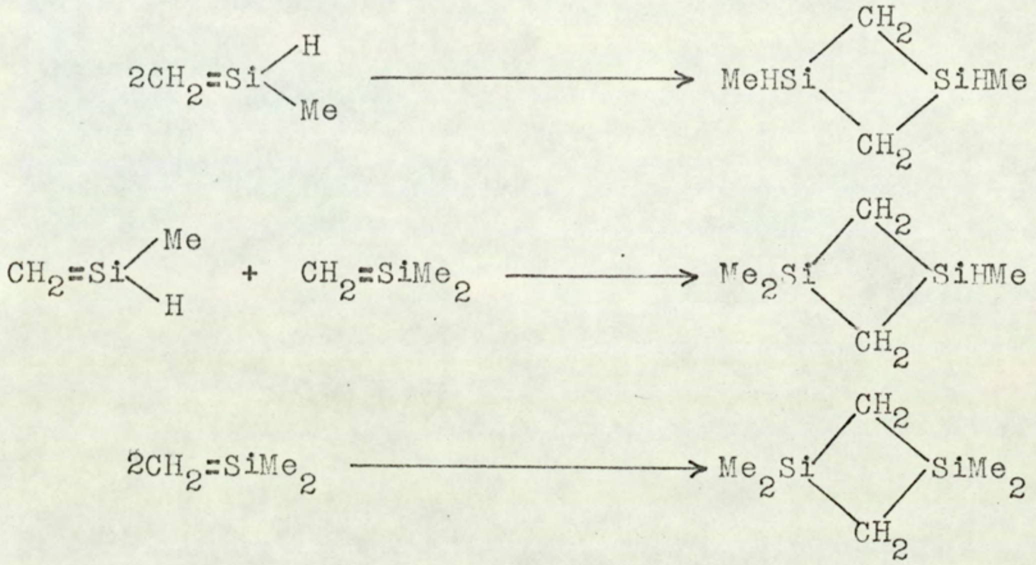
$$\mathrm{Me_4Si} \longrightarrow \mathrm{Me_3Si\cdot} + \mathrm{Me\cdot}$$

$$\mathrm{Me\cdot} + \mathrm{Me_4Si} \longrightarrow \mathrm{CH_4} + \mathrm{Me_3SiCH_2\cdot}$$

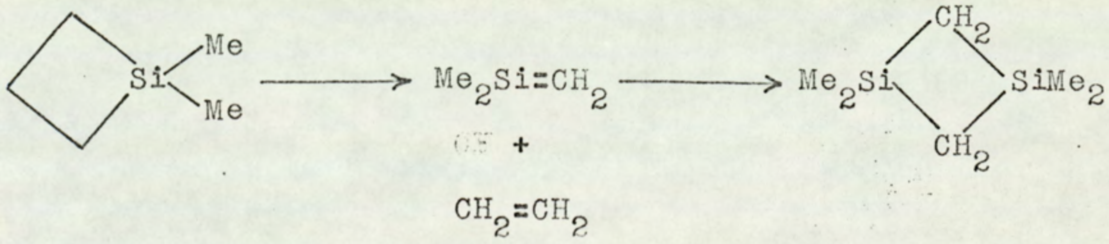
$$\mathrm{Me_3SiCH_2\cdot} \longrightarrow \mathrm{Me\cdot} + \mathrm{Me_2Si{=}CH_2}$$

The formation of V as a product precursor has also been suggested[58] in a more recent study of the pyrolysis of tetramethylsilane. The π-bond energy of V was estimated as lying between 30 and 42 kcal mol^{-1}; the π-bond energy in the analogous isobutene is about 60 kcal mol^{-1}.

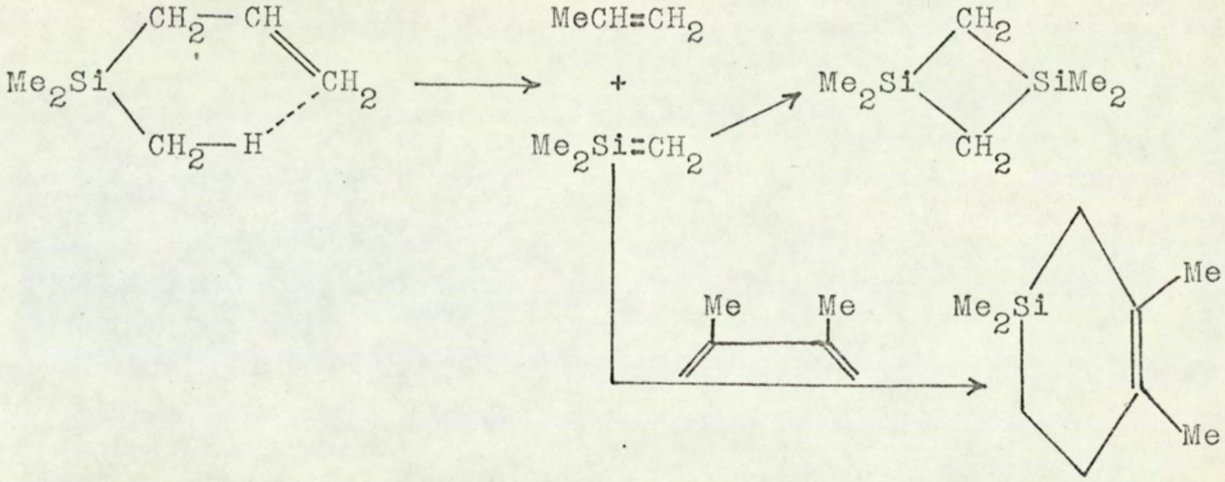
Similar intermediates have been proposed by Davidson[59] to account for the formation of 1,3-disilacyclobutanes in the pyrolysis of trimethylsilane.



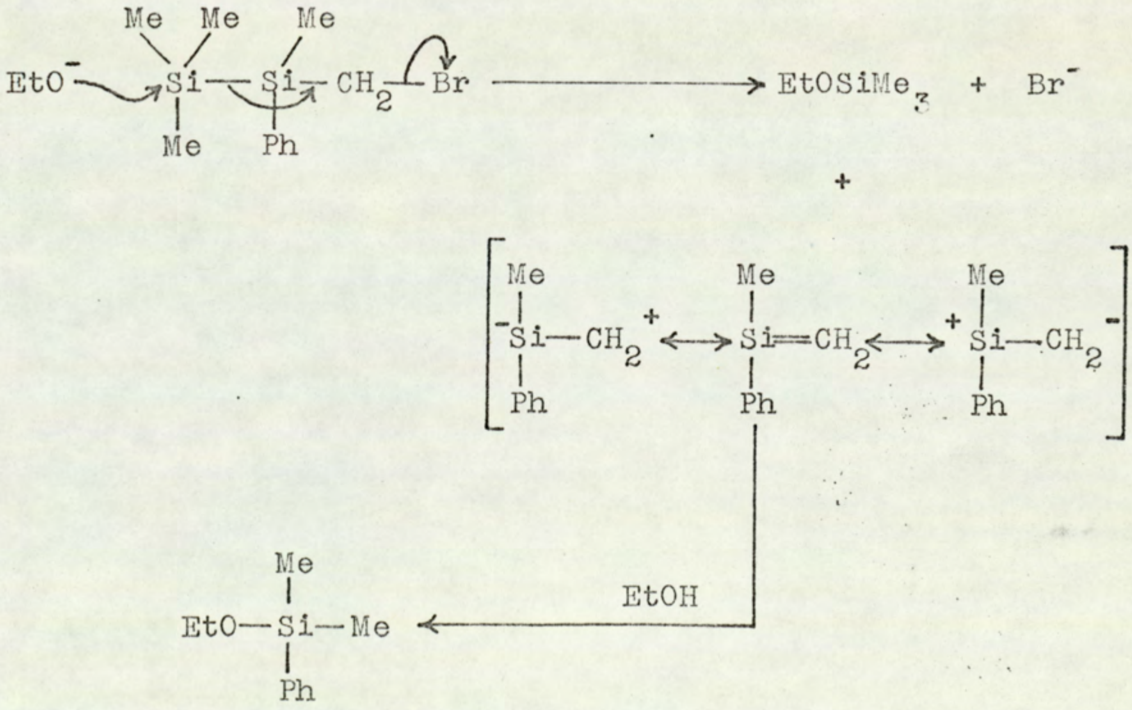
Gusel'nikov and Flowers[60] studied the pyrolysis of 1,1-dimethylsilacyclobutane and the formation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane was attributed to the dimerisation of intermediate V.



Strong evidence has been reported,[61] in favour of the intermediacy of 2-silaisobutene, in the pyrolysis of allyltrimethylsilane in which it was trapped by a Diels-Alder reaction with 2,3-dimethyl-1,3-butadiene.

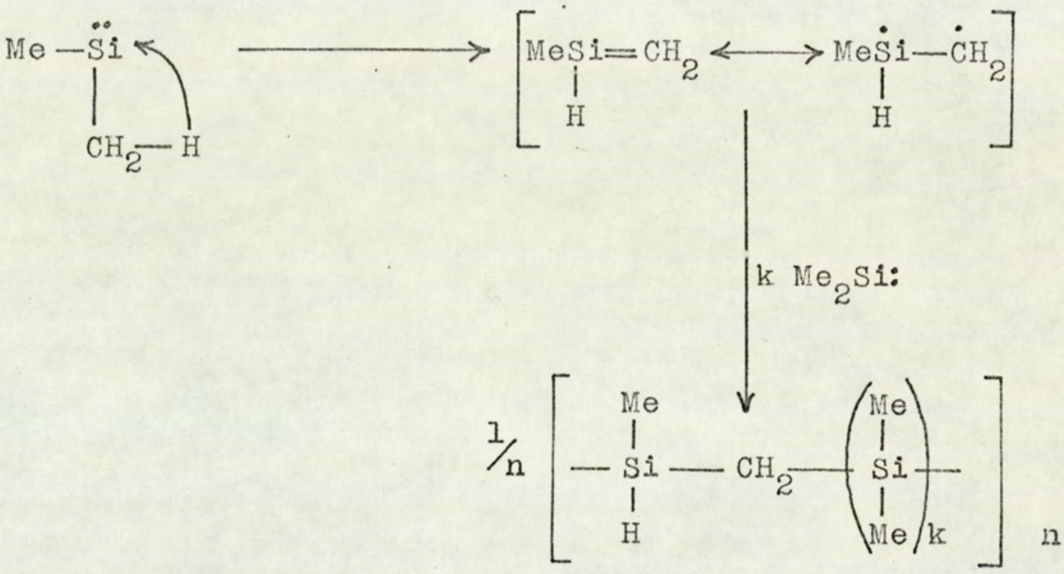


The involvement of silicon-carbon unsaturated species has also been proposed in a number of non pyrolytic reactions. Kumada et al[62] examined the reaction of (1-bromomethyl)tetramethyl-1-phenyldisilane with sodium ethoxide and suggested the formation of 2-phenyl-2-silapropene to explain the production of two of the observed products, namely trimethylethoxysilane and dimethylphenylethoxysilane.

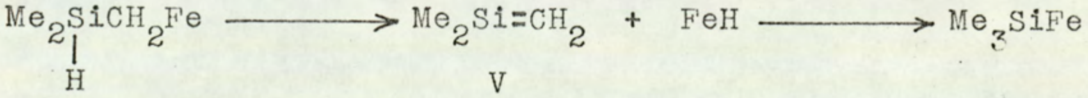


The reaction of dimethyldichlorosilane with lithium in tetrahydrofuran[63] yielded polymeric material containing the silicon-hydride moiety and the formation of an unsaturated precursor was again proposed to explain product formation

$$Me_2SiCl_2 \xrightarrow[THF]{Li} Me_2Si: \; + \; 2LiCl$$



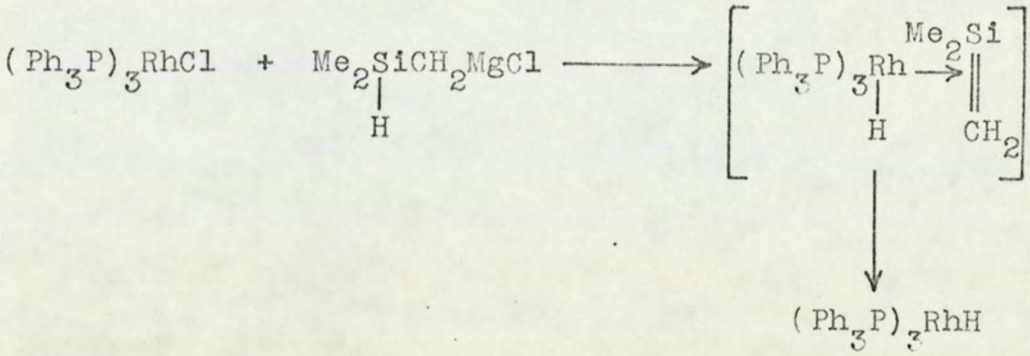
Pannell[64] interacted $Fe(CO)_2Cp^-$ and (chloromethyl)dimethylsilane and after treatment with triphenylphosphine he isolated $Me_3SiFeCOCpPPh_3$ in good yield. The suggested course of reaction was via an alkene elimination followed by an iron hydride addition to the unsaturated species. It was



$$\underset{\displaystyle H}{Me_2\overset{}{Si}}CH_2Fe \longrightarrow \underset{V}{Me_2Si{=}CH_2} \; + \; FeH \longrightarrow Me_3SiFe$$

pointed out that formation of V in no way vitiates the mechanism since the intermediate need never leave the coordination sphere of the iron atom and might thus be stabilised in a manner similar to cyclobutadiene in the complex $C_4H_4Fe(CO)_3$.

The most interesting report comes from the Lappert group[65] who examined the reaction of dimethylsilylmethylmagnesium chloride with $(Ph_3P)_3RhCl$. The formation of $(Ph_3P)_3RhH$ was

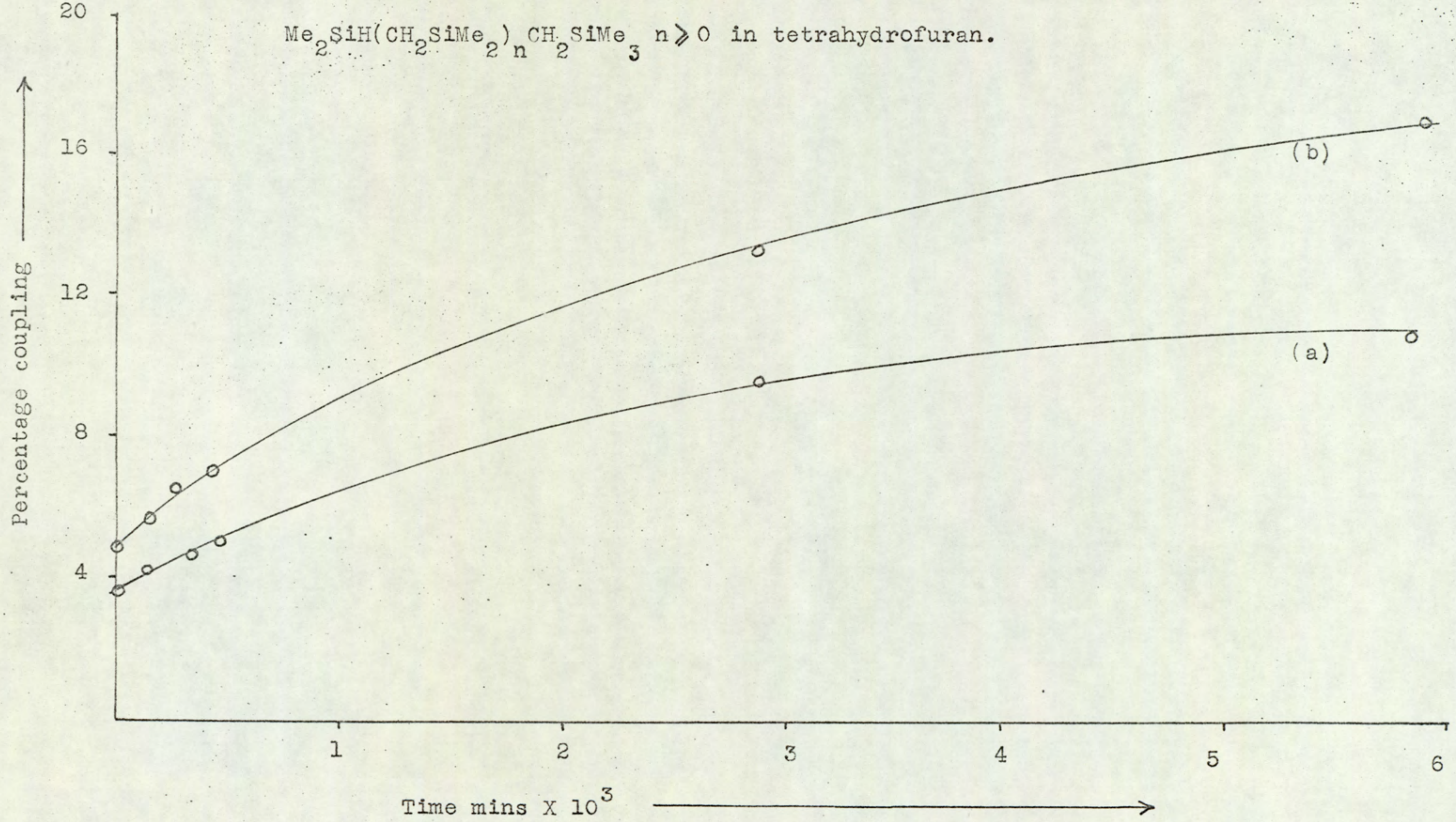


suggested to occur via the intermediacy of V.

Because of the intermediacy of silicon-carbon double bonded species in this wide range of reactions, it seemed possible that thermal elimination of magnesium hydride and formation of V might be important in the reduction of triphenylchlorosilane by dimethylsilylmethylmagnesium bromide. In order to assess the importance of self coupling in this reaction the decomposition of dimethylsilylmethylmagnesium bromide alone was examined in tetrahydrofuran. Whilst formation of $Me_2SiHCH_2SiMe_2CH_2MgBr$ and products of the type $Me_2SiH(CH_2SiMe_2)_nCH_2SiMe_2CH_2MgBr$ $n \geqslant 1$ occured at a measurable rate, this was very much slower than the rate of reaction of dimethylsilylmethylmagnesium bromide with triphenylchlorosilane (Figs. 8 and 9.). Consequently magnesium hydride formation, via coupling or thermal elimination, can be dismissed as major contributory pathways to product formation.

Self coupling of methylsilylmethylmagnesium bromide was found to be a much more rapid process. A 20% solution of (bromomethyl)methylsilane in anhydrous diethyl ether was

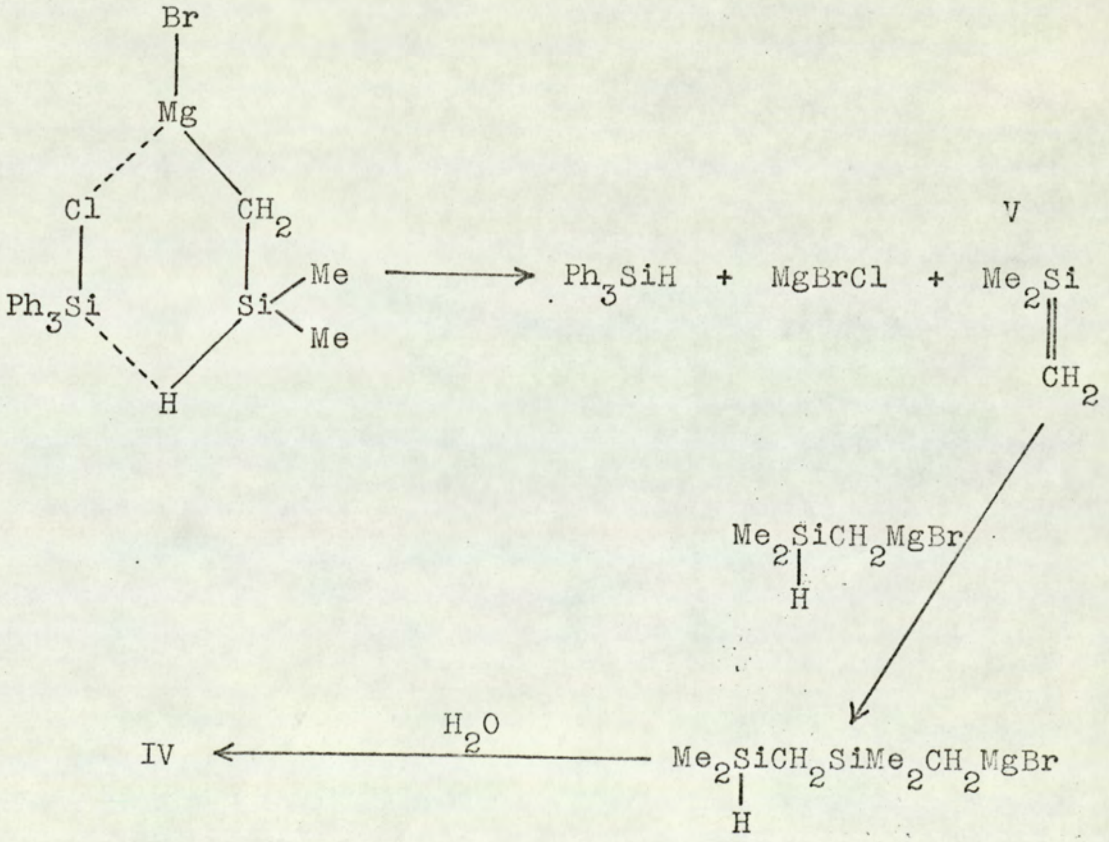
Fig. 8. Progress of self coupling reaction of Me_2SiHCH_2MgBr (a) formation of $Me_2SiHCH_2SiMe_3$ in tetrahydrofuran (b) formation of all products with the general formula $Me_2SiH(CH_2SiMe_2)_nCH_2SiMe_3$ $n \geqslant 0$ in tetrahydrofuran.



reacted with magnesium and the solution was refluxed for 0.5 h. After hydrolysis higher molecular weight products were detected in 44% yield. Clearly in this case reduction of triphenylchlorosilane via magnesium hydride could account for a large proportion of the triphenylsilane produced.

For the reaction of triphenylchlorosilane with dimethylsilylmethylmagnesium bromide several other possibilities exist for the mechanism of formation of the observed products. A feasible route would be by direct reduction through a six centre transition state in an analogous fashion to reduction by alkyl Grignard reagents.[53,54] Clearly this mechanism

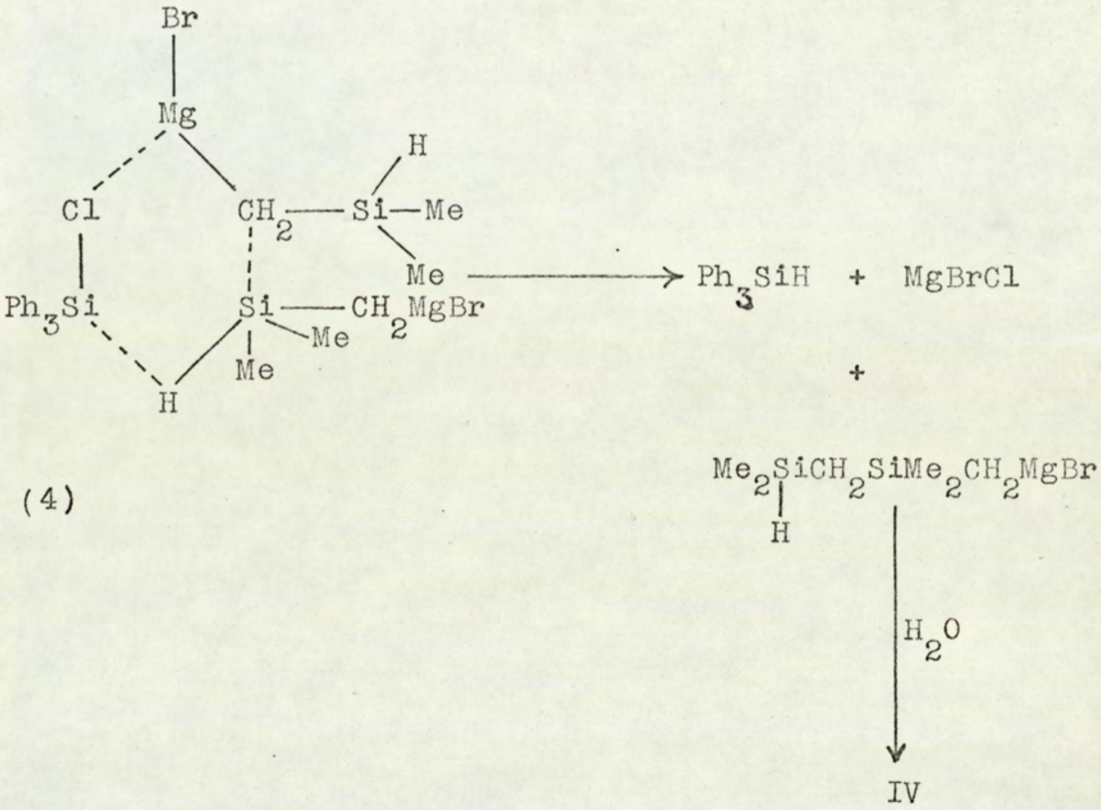
(3)



would again involve the formation of the intermediate V.

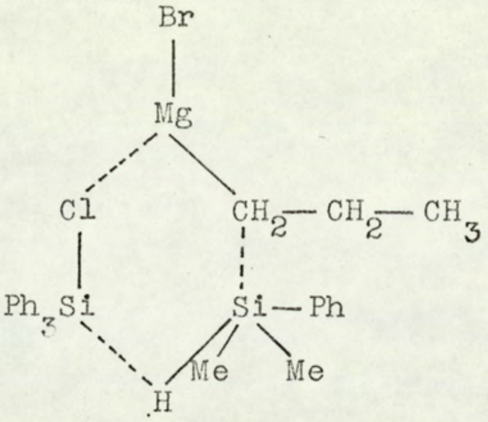
An alternative route (4) involves direct reduction through a transition state incorporating two molecules of

Grignard reagent, with simultaneous formation of the Grignard self coupling product. Although this mechanism involves


(4)

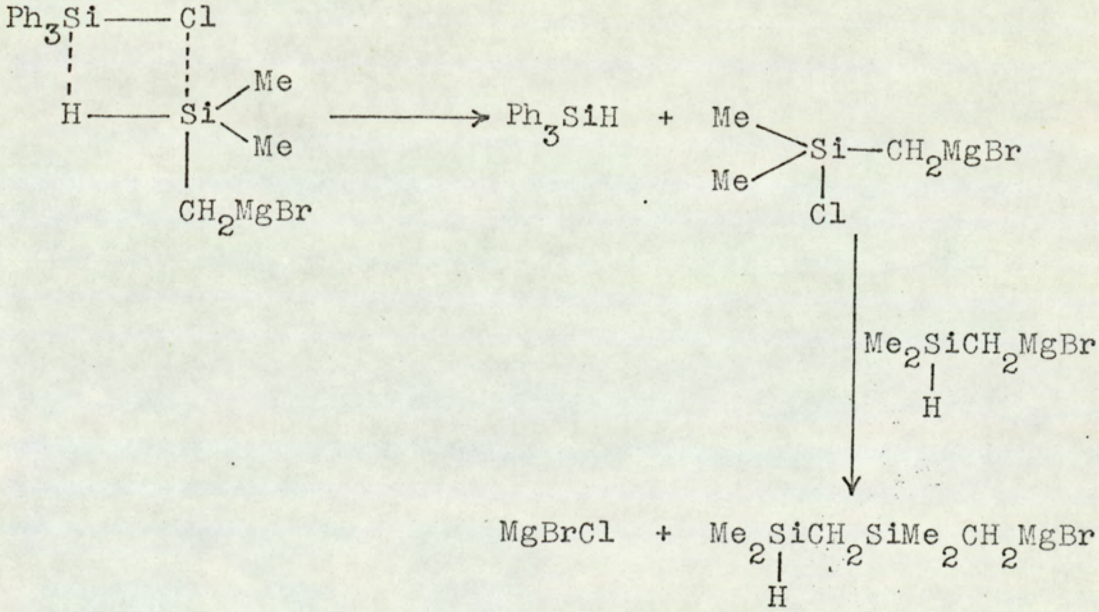
three reacting molecules it could be a pathway of lower energy than (3) since it does not require the formation of the high energy intermediate V.

Analysis of the products of reaction of triphenylchlorosilane, n-propylmagnesium bromide and dimethylphenylsilane showed triphenylsilane to be absent. If reduction occurs via (4) it might be expected that the above system would afford good yields of triphenylsilane. However in the former case, electron donation from the α methylene group probably labilises the silyl hydrogen thereby promoting the reaction. Since silicon interacts electronically with β and to a lesser extent γ substituents, it is not too surprising



that reduction also takes place when the magnesium halide moiety is displaced further from the silicon hydride.

There also exists the possibility that this reaction might proceed by a direct exchange process. However mixtures



of triphenylchlorosilane and (bromomethyl)dimethylsilane were shown not to exchange during long periods of reflux, although the adjacent magnesium bromide group could be weakening the silicon hydride bond and promoting exchange in the triphenylchlorosilane/dimethylsilylmethylmagnesium bromide reaction.

A free radical mechanism leading to product formation seems unlikely since reactions followed similar pathways in the presence of styrene; a known trap for radical intermediates in Grignard reactions.[66,67]

To help distinguish between the remaining possible mechanisms, the kinetics of the reaction of triphenylchlorosilane with dimethylsilylmethylmagnesium bromide was investigated in tetrahydrofuran at 60°. Good third order kinetics were observed over the first 30% of reaction (Figs. 9 and 10.) ($k = 4.75 \times 10^{-4}$ litres^{2} mole^{-2} sec^{-1} at 60.0°). Third order kinetics is clearly consistent with route (4) but not with the other two possibilities. Moreover the rate of disappearance of Grignard reagent in the presence of a large excess of chlorosilane followed second order kinetics (Fig. 11.); this is also in keeping with mechanism (4).

Thus (4) appears most consistent with the observed rate data providing the Grignard reagent is monomolecular in tetrahydrofuran over the concentration range used. Ashby and coworkers[68] have determined the degree of association of alkyl and aryl Grignard reagents in tetrahydrofuran; all were found to be essentially monomeric up to a concentration of 2.5 molar. However, there have been no reports concerning the degree of association of silyl Grignard reagents in solution and it seemed important to establish the non association of dimethylsilylmethylmagnesium bromide in tetrahydrofuran. Association studies were carried out under nitrogen using the ebullioscopic technique perfected by Ashby and Walker[69] and the monomeric nature of this Grignard

Fig. 9. Progress of reactions between triphenylchlorosilane and dimethylsilylmethylmagnesium bromide (initial concentrations equal) at 60° in tetrahydrofuran.

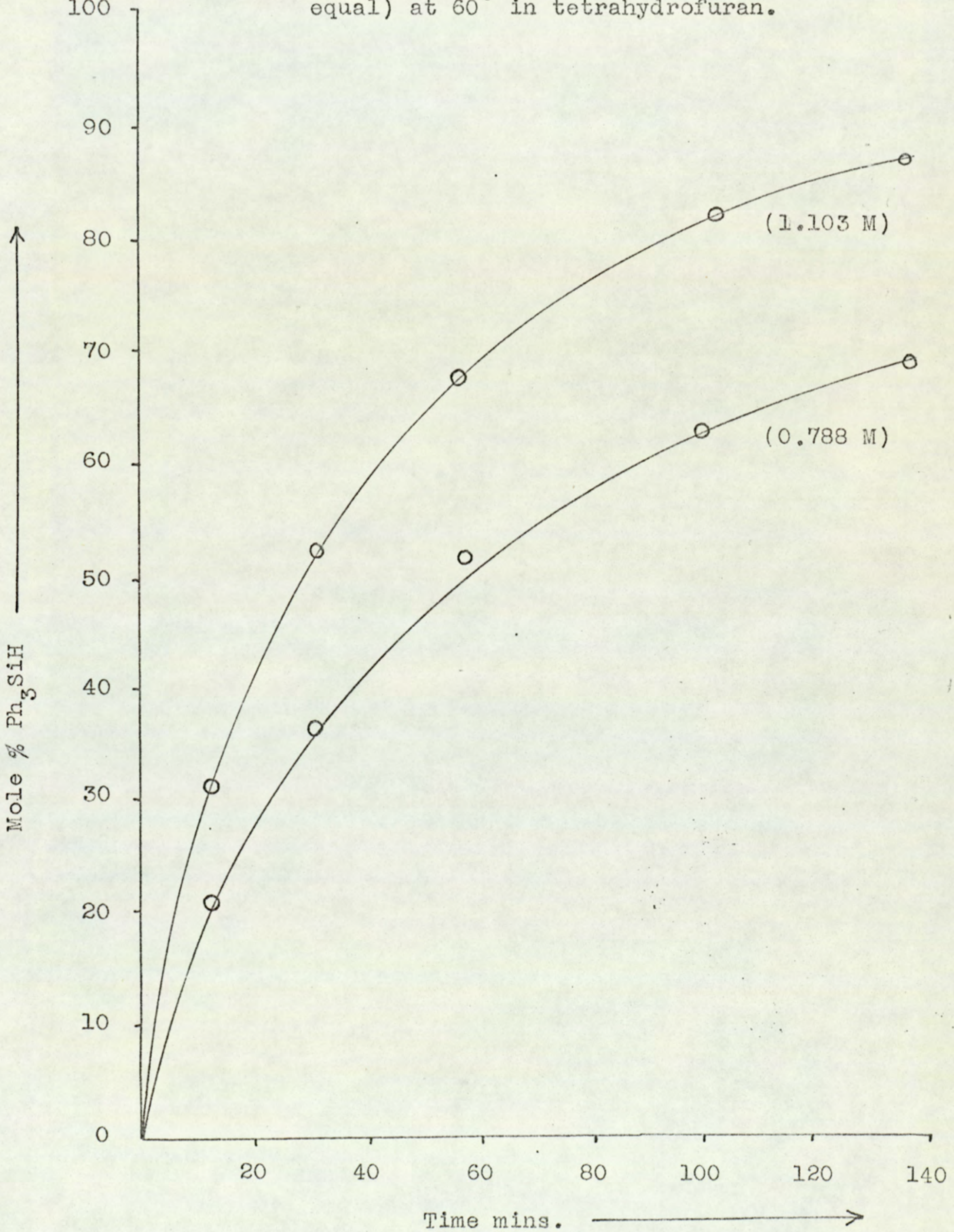


Fig. 10. Third order rate plot for triphenylchlorosilane/dimethylsilylmethylmagnesium bromide at 60° in tetrahydrofuran.

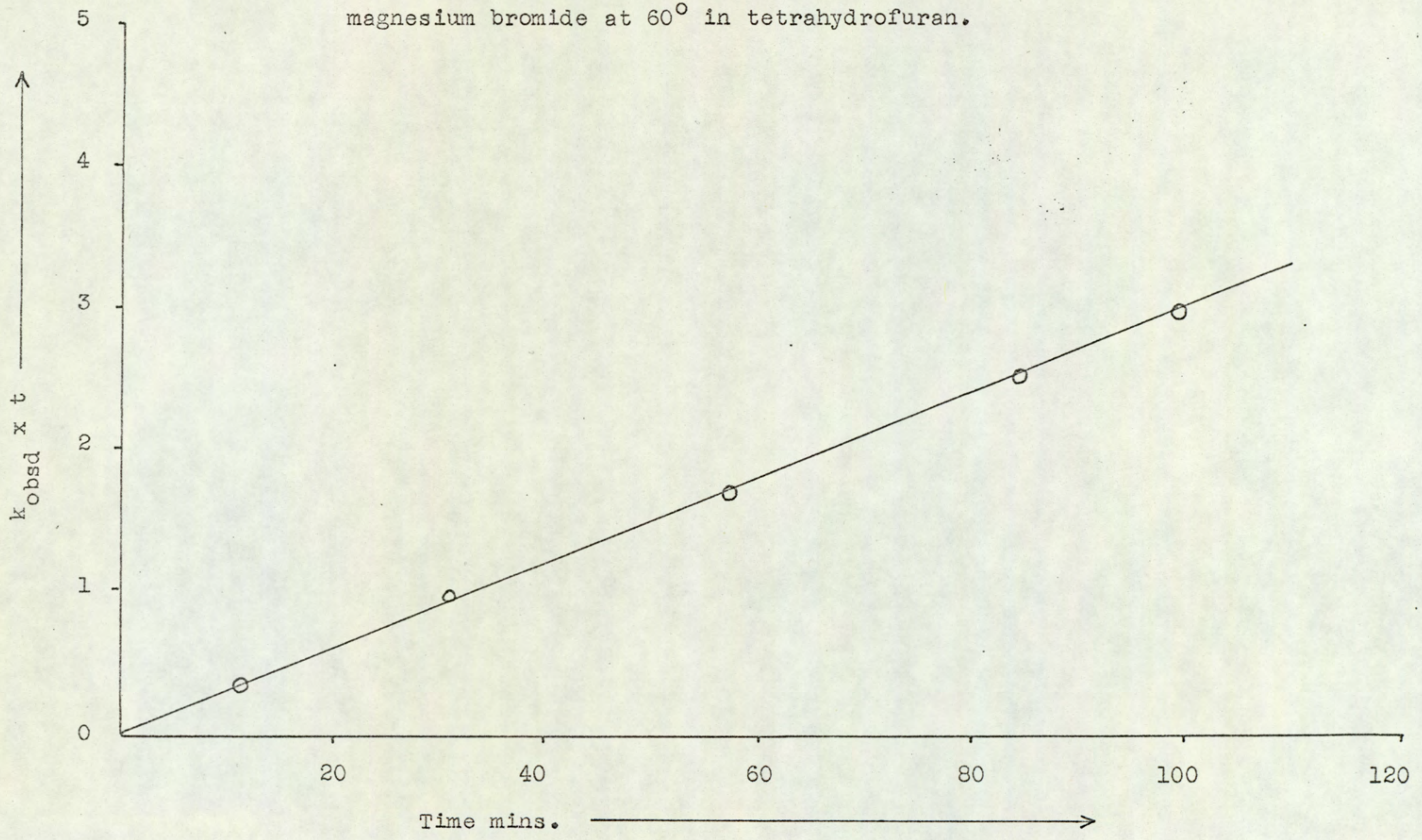


Fig. 11. Progress of reactions between dimethylsilylmethylmagnesium bromide and a large excess of triphenylchlorosilane at 60° in tetrahydrofuran.

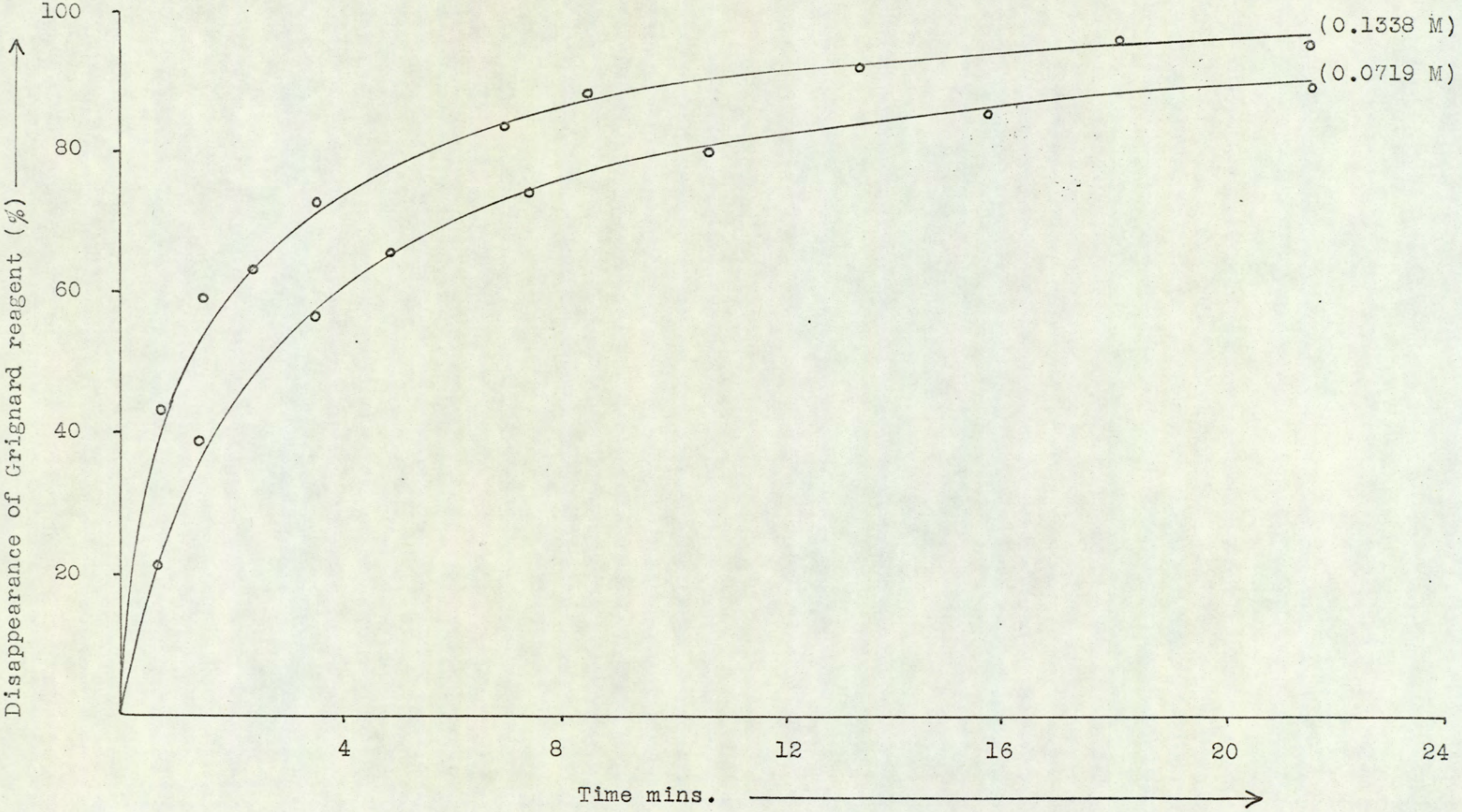
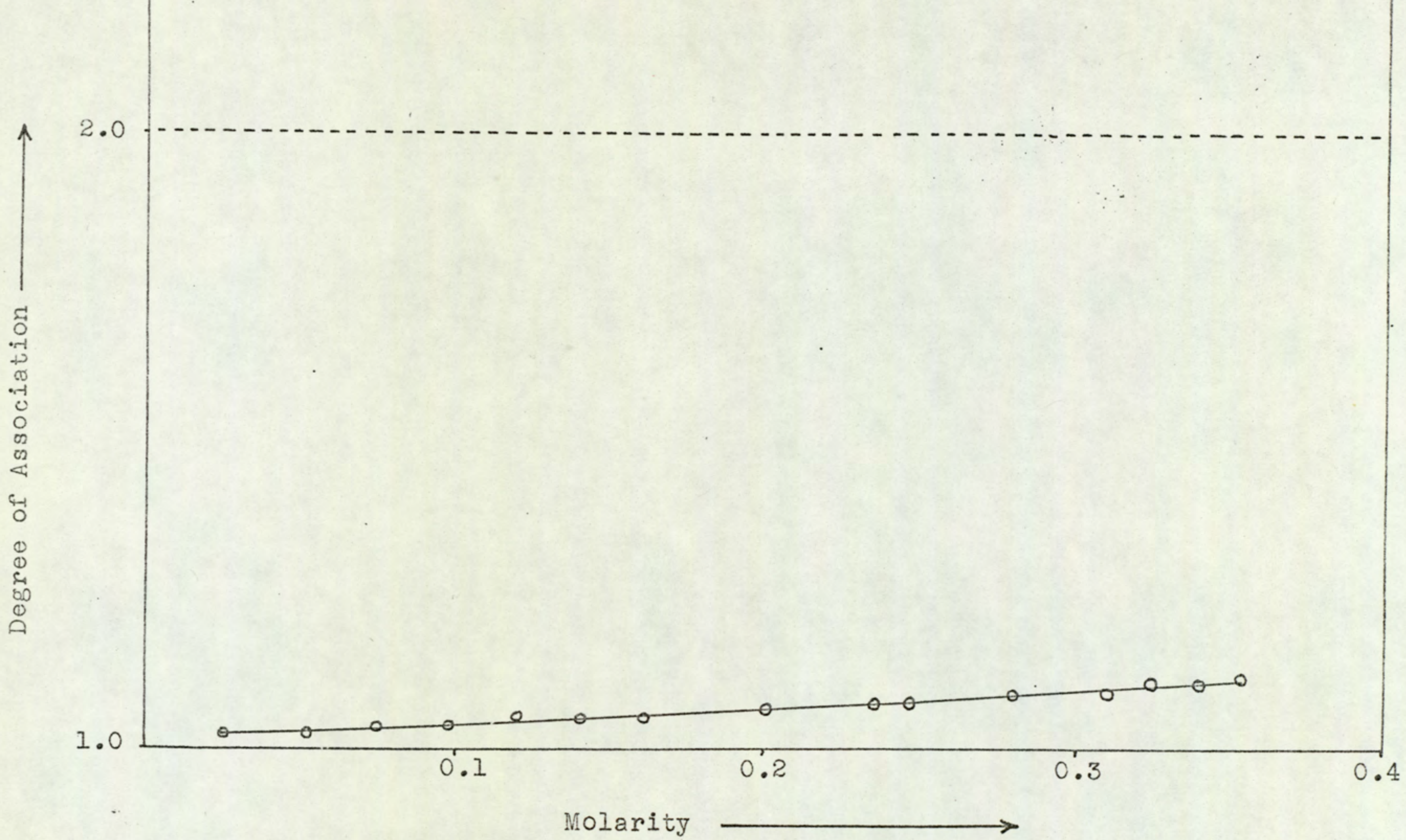


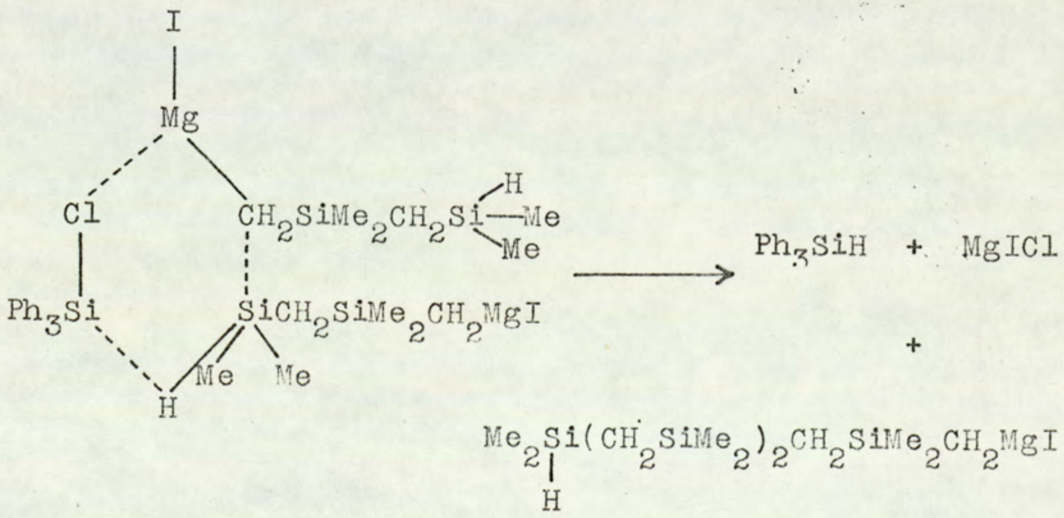
Fig. 12. Degree of association of dimethylsilylmethylmagnesium bromide in tetrahydrofuran



reagent was confirmed within the employed concentration range (Fig. 12.).

4. The Reduction of Triphenylchlorosilane by Grignard Reagents containing more remotely positioned Hydrosilyl Groups.

From consideration of the transition state (4), it is apparent that reduction should be equally likely when the hydrosilyl group is more remotely positioned from the magnesium bromide moiety. In keeping with this conclusion equi-molar mixtures of dimethylsilylmethylmagnesium bromide and triphenylchlorosilane gave > 50% yields of triphenylsilane (Fig. 9.). Clearly if the reduction species is confined to dimethylsilylmethylmagnesium bromide the maximum possible yield of triphenylsilane is 50%. To confirm that products of the type $Me_2SiH(CH_2SiMe_2)_nCH_2SiMe_2CH_2MgBr$ were responsible for the increased yield of triphenylsilane, (iodomethyl)(dimethylsilylmethyl)dimethylsilane was prepared and after conversion to the respective Grignard reagent was reacted with triphenylchlorosilane; triphenylsilane was produced in good yield (Table 6.), see page 34.



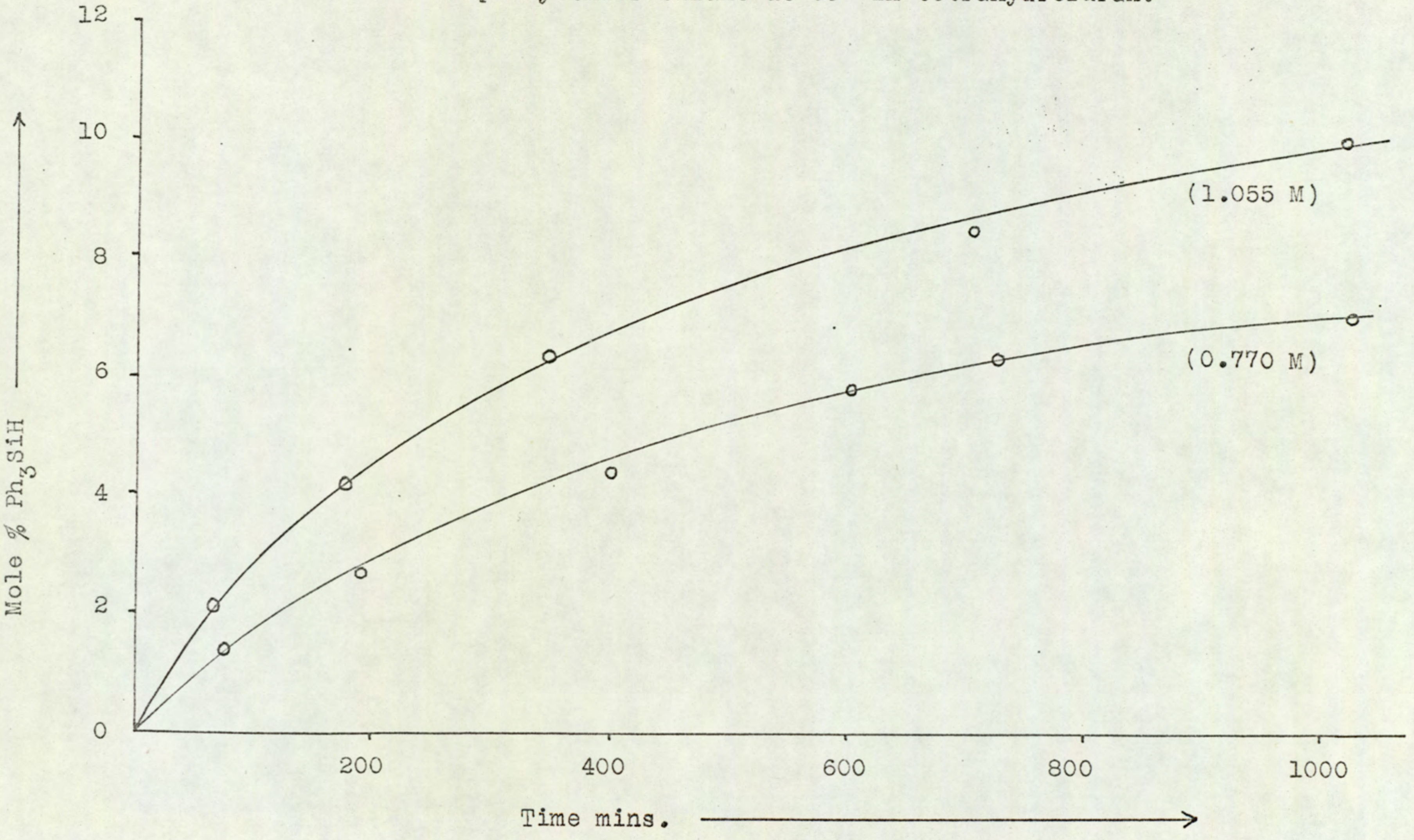
The reaction of (2-diphenylsilyl)ethylmagnesium bromide, (3-dimethylsilyl)propylmagnesium iodide and (3-methylsilyl)-propylmagnesium iodide with triphenylchlorosilane was also investigated. Each reaction led to good yields of triphenylsilane. The reduction of triphenylchlorosilane by (2-diphenylsilyl)ethylmagnesium bromide followed good third order kinetics. However, the unfavourable steric interactions in comparison to dimethylsilylmethylmagnesium bromide reduced the rate by a factor of 125 at 60° (Fig. 13.), ($k = 3.83 \times 10^{-6}$ litres^{2} mole^{-2} sec^{-1} at 60.0°).

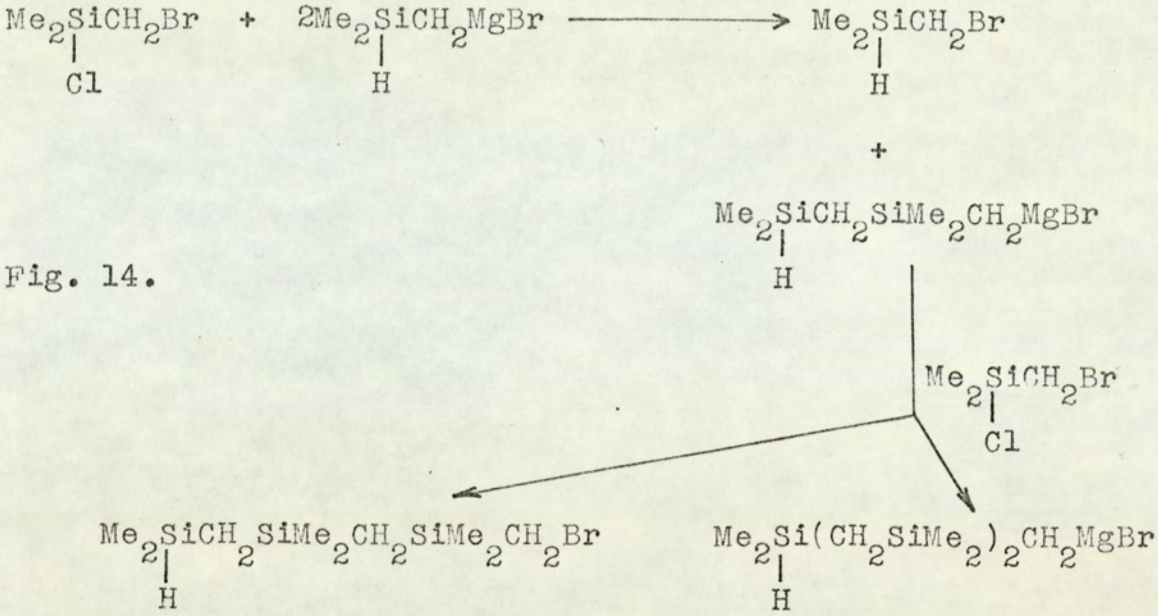
5. Reduction of Alkylchlorosilanes.

In order to show that (dimethylsilylmethyl)dimethylsilylmethylmagnesium halides were effective in the reduction of triphenylchlorosilane it was necessary to prepare the requisite halide (halomethyl)(dimethylsilylmethyl)dimethylsilane. However, initial attempts to prepare (bromomethyl)-(dimethylsilylmethyl)dimethylsilane were unsuccessful. It had previously been reported[50] that reaction of (chloromethyl)dimethylchlorosilane with dimethylsilylmethylmagnesium chloride led to good yields of (chloromethyl)(dimethylsilylmethyl)dimethylsilane. However, a repeat of this procedure using (bromomethyl)dimethylchlorosilane and dimethylsilylmethylmagnesium bromide afforded polymeric materials as the major products of reaction. These were presumably formed by the scheme represented in Fig. 14.

Preparation was finally achieved by addition of iodine to the products of reaction of dimethylsilylmethylmagnesium bromide and triphenylchlorosilane with isolation of (iodomethyl)(dimethylsilylmethyl)dimethylsilane from the reaction mixture.

Fig. 13. Progress of reactions between (2-diphenylsilyl)ethylmagnesium bromide and triphenylchlorosilane at 60° in tetrahydrofuran.





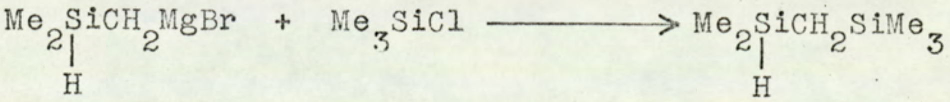
$$\mathrm{Me_2\underset{\underset{Cl}{|}}{Si}CH_2Br} + \mathrm{2Me_2\underset{\underset{H}{|}}{Si}CH_2MgBr} \longrightarrow \mathrm{Me_2\underset{\underset{H}{|}}{Si}CH_2Br} + \mathrm{Me_2\underset{\underset{H}{|}}{Si}CH_2SiMe_2CH_2MgBr}$$

$$\mathrm{Me_2\underset{\underset{H}{|}}{Si}CH_2SiMe_2CH_2MgBr} \xrightarrow{\mathrm{Me_2\underset{\underset{Cl}{|}}{Si}CH_2Br}} \mathrm{Me_2\underset{\underset{H}{|}}{Si}CH_2SiMe_2CH_2SiMe_2CH_2Br} + \mathrm{Me_2\underset{\underset{H}{|}}{Si}(CH_2SiMe_2)_2CH_2MgBr}$$

Fig. 14.

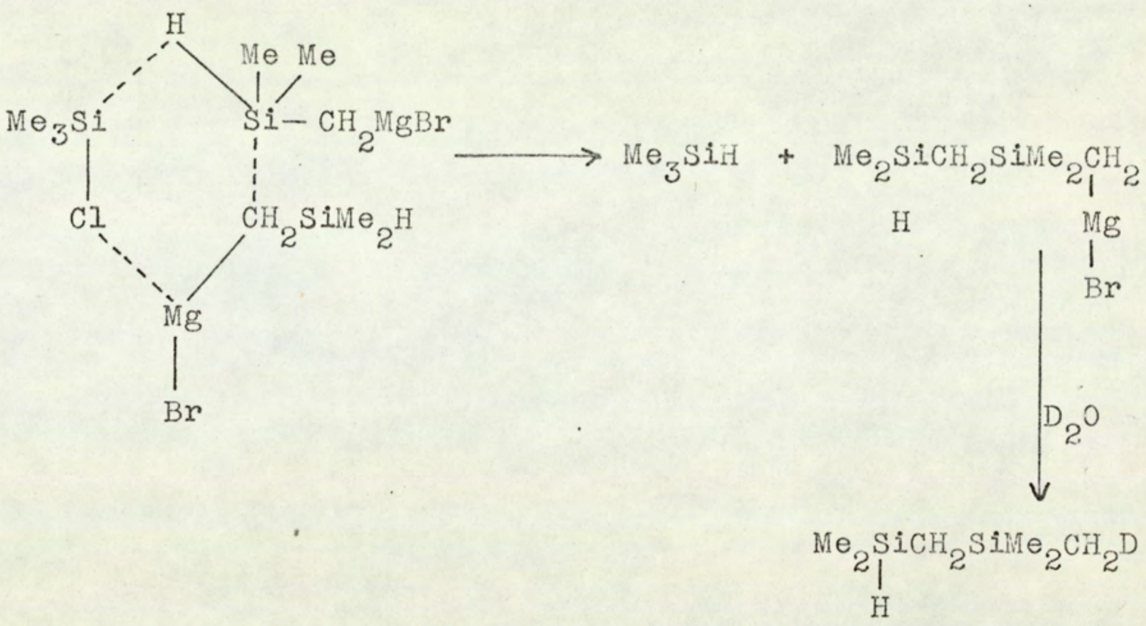
Since reduction was apparently a competing process in the interaction of (bromomethyl)dimethylchlorosilane and dimethylsilylmethylmagnesium bromide it seemed probable that this was generally true in reactions of this Grignard reagent with other trialkylchlorosilanes.

The coupling of trimethylchlorosilane with dimethylsilylmethylmagnesium bromide was reinvestigated but in this case the reaction was terminated with deuterium oxide. If IV is only formed by a normal coupling reaction there should be no incorporation of deuterium in the product. If however



$$\mathrm{Me_2\underset{\underset{H}{|}}{Si}CH_2MgBr} + \mathrm{Me_3SiCl} \longrightarrow \mathrm{Me_2\underset{\underset{H}{|}}{Si}CH_2SiMe_3}$$

IV is formed via a reductive process then one hydrogen atom of the terminal trimethylsilyl group should be replaced by deuterium. Mass spectral analysis indicated that the product



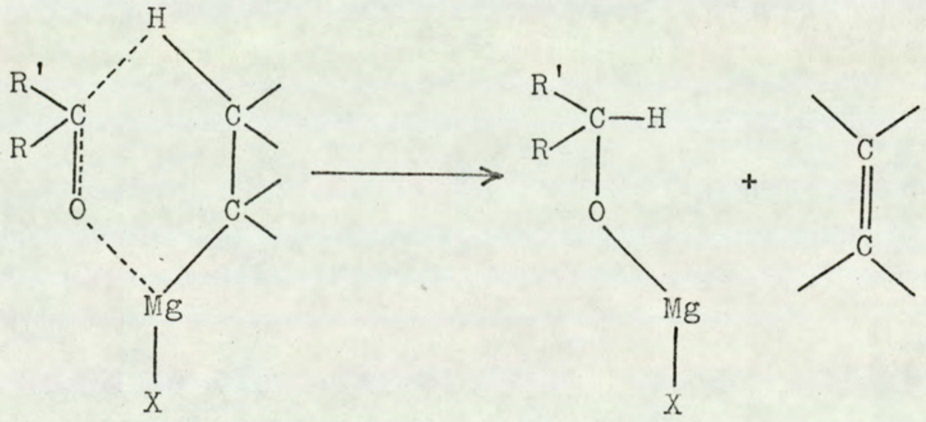
was formed by the two competing pathways, reduction accounting for 47% of IV produced in the reaction. The reaction of methyldiphenylchlorosilane and dimethylsilylmethylmagnesium bromide also proceeded via competitive coupling and reductive processes.

IV

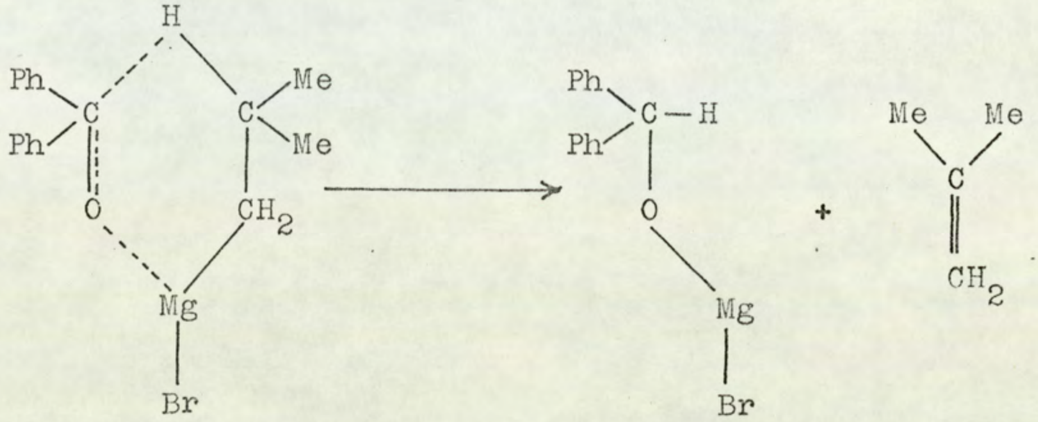
THE REACTIONS OF HYDROSILYL GRIGNARD REAGENTS WITH CARBONYL COMPOUNDS

1. Introduction

The facile reduction of chlorosilanes by hydrosilylmethyl Grignard reagents prompted an investigation of the reactions of these organometallic reagents with other species in which reduction might be observed together with concomitant elimination of a silicon carbon π-bonded product. The reduction of carbonyl compounds by Grignard reagents was first observed by Grignard[70] himself when he detected small quantities of benzyl alcohol amongst the products of reaction of isoamylmagnesium bromide and benzaldehyde. Since that time, the reduction of aldehydes and ketones by Grignard reagents has been repeatedly observed and the mechanism of reaction is now well established.[71] The reduction step involves transfer of a β-hydrogen atom from the Grignard reagent to the ketone or aldehyde with simultaneous elimination of olefin.



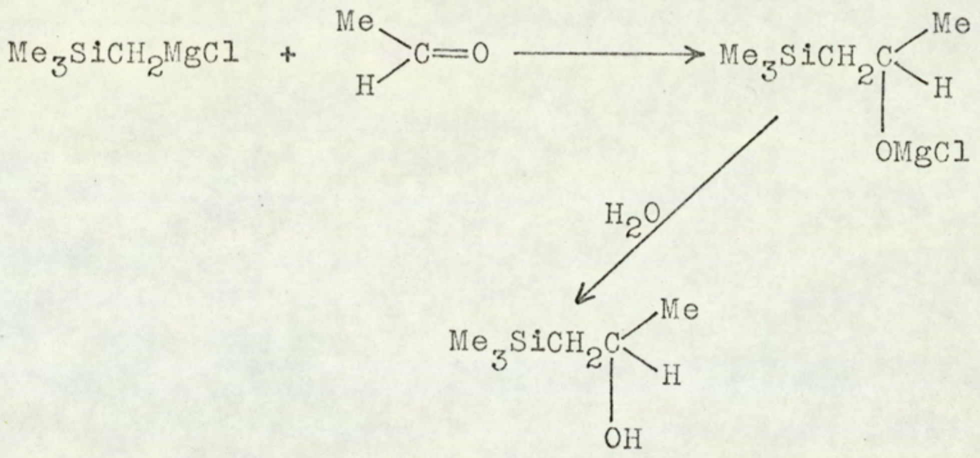
The reduction process often becomes competitive with normal addition for reaction of hindered ketones with bulky Grignard reagents and in some cases, it is the predominant pathway to reaction. Kharasch and Weinhouse[72] have observed that the reaction of benzophenone with isobutylmagnesium bromide affords benzhydrol in 94% yield.



Consequently, it seemed likely that the reaction of benzophenone with dimethylsilylmethylmagnesium bromide might follow a similar route providing an opportunity for the detection of V.

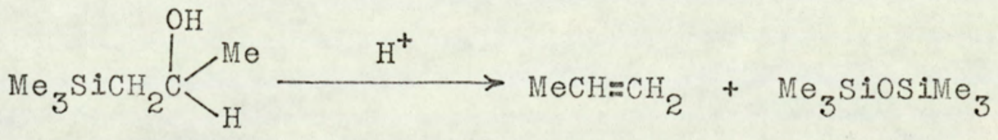
Whilst the reaction of hydrosilylmethyl Grignard reagents with chlorosilanes has previously received some investigation, there are no reports of the reaction of these Grignard reagents with carbonyl compounds. However, reaction of trimethylsilylmethylmagnesium halides with aldehydes and ketones have been studied and a consideration of these observations is of some relevance to the hydrosilyl systems.

Initially, the Sommer group[73] found that trimethylsilylmethylmagnesium chloride reacted normally with acetaldehyde to give the expected product, (trimethylsilylmethyl)methylcarbinol; unfortunately the yield was not reported.



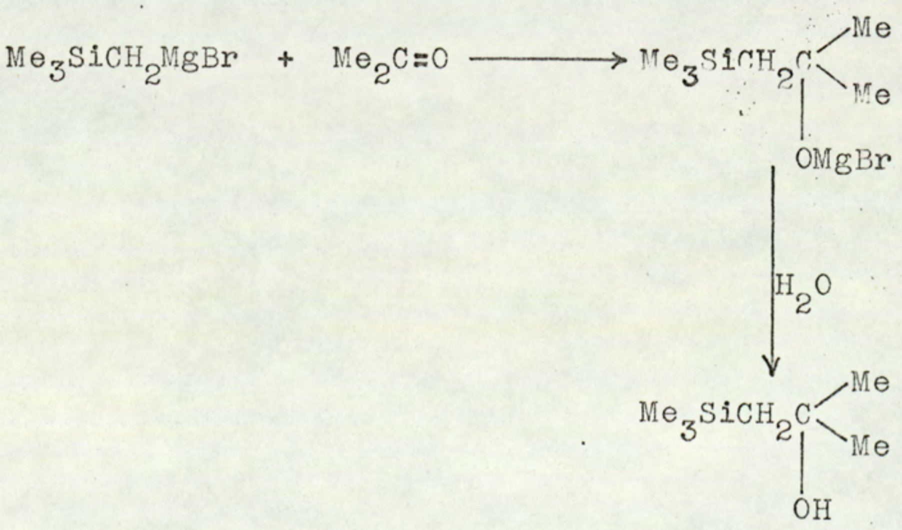
$$Me_3SiCH_2MgCl + MeCHO \longrightarrow Me_3SiCH_2CH(Me)OMgCl \xrightarrow{H_2O} Me_3SiCH_2CH(Me)OH$$

These workers also established that β-silyl alcohols are very sensitive to acid; (trimethylsilylmethyl)methylcarbinol readily eliminates propylene and most of the silicon appears as hexamethyldisiloxane.



$$Me_3SiCH_2CH(OH)Me \xrightarrow{H^+} MeCH{=}CH_2 + Me_3SiOSiMe_3$$

Hauser and Hance[74] reacted trimethylsilylmethylmagnesium bromide with acetone and isolated the expected tertiary alcohol, (trimethylsilylmethyl)dimethylcarbinol in 52% yield.

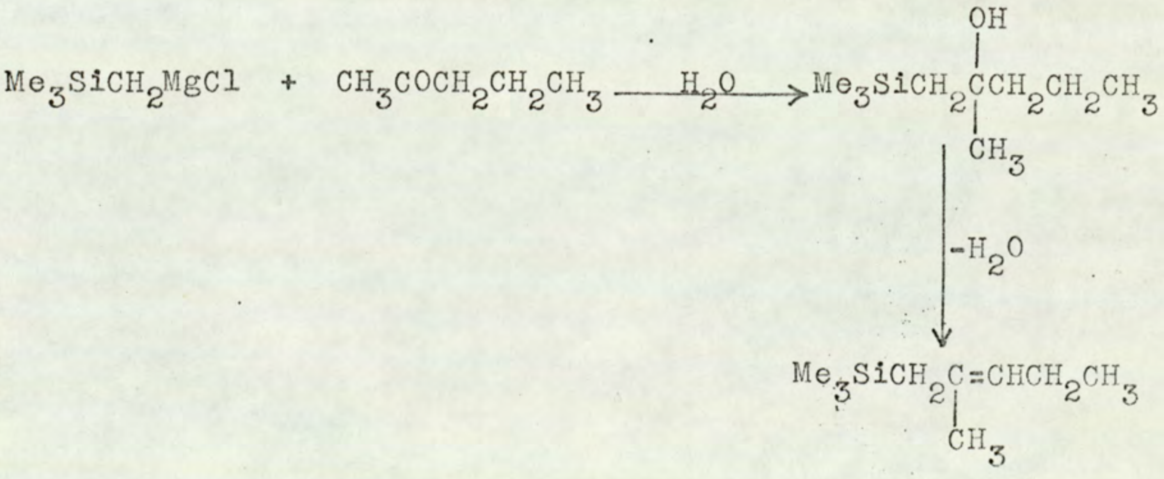


$$Me_3SiCH_2MgBr + Me_2C{=}O \longrightarrow Me_3SiCH_2C(Me)_2OMgBr \xrightarrow{H_2O} Me_3SiCH_2C(Me)_2OH$$

In contrast, an analogous reaction with benzaldehyde gave the expected product, (trimethylsilylmethyl)phenylcarbinol in much lower yield (14%). However, the remaining products of these two reactions were not identified.

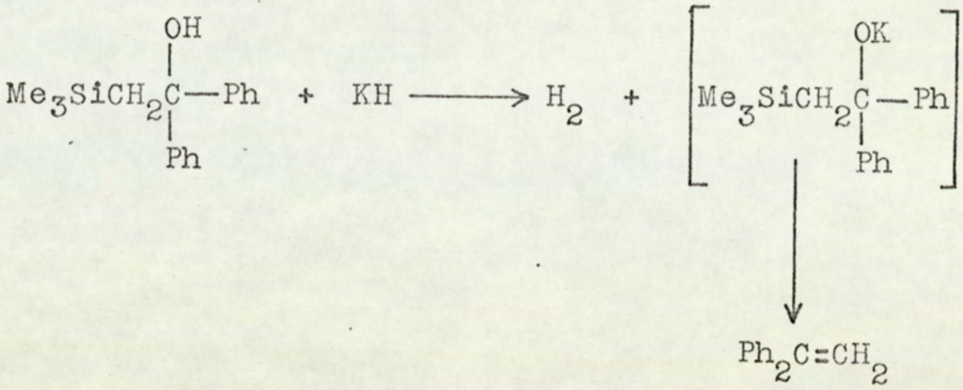
Subsequently, a group of Russian workers[75] investigated the reaction of methyl ethyl ketone with trimethylsilylmethylmagnesium chloride but isolated only a very low yield (1.9%) of (trimethylsilylmethyl)methylethylcarbinol. However, reaction with trichloroacetaldehyde gave 17% of (trimethylsilylmethyl)trichloromethylcarbinol and reaction with benzil afforded (trimethylsilylmethyl)phenylbenzoylcarbinol (69.5%).

In a similar study another Russian group[76] investigated the reaction of trimethylsilylmethylmagnesium chloride with methyl propyl ketone but isolated only (2-trimethylsilylmethyl)-pent-2-ene (32%) formed as a result of elimination.



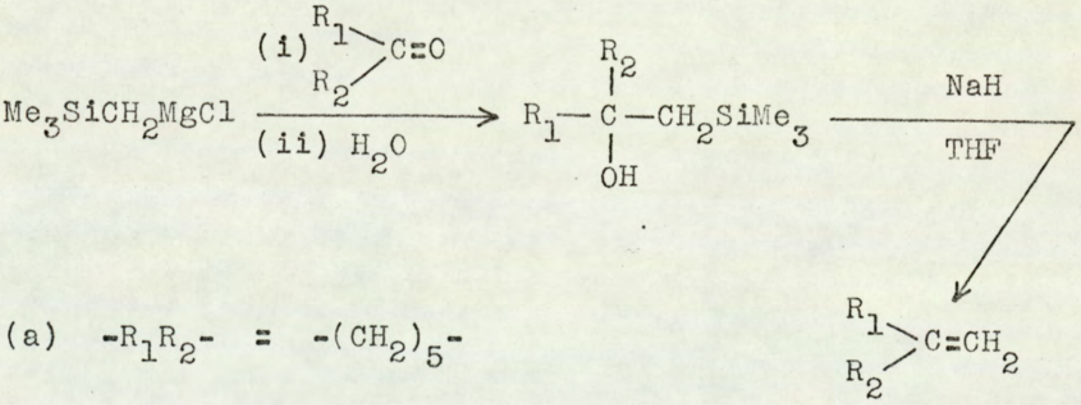
$$Me_3SiCH_2MgCl + CH_3COCH_2CH_2CH_3 \xrightarrow{H_2O} Me_3SiCH_2C(OH)(CH_3)CH_2CH_2CH_3 \xrightarrow{-H_2O} Me_3SiCH_2C(CH_3){=}CHCH_2CH_3$$

More recently, Peterson[77] has reported the preparation of a number of β-silyl alcohols by reaction of trimethylsilylmethylmagnesium chloride with acetone, benzaldehyde, benzophenone and n-octaldehyde. He found that these alcohols were readily cleaved by bases since good yields of the respective olefins were obtained on reaction with sodium or potassium hydride.



$$Me_3SiCH_2C(OH)(Ph)-Ph + KH \longrightarrow H_2 + [Me_3SiCH_2C(OK)(Ph)-Ph] \longrightarrow Ph_2C{=}CH_2$$

This observation has been confirmed[78] by reaction with other β-silyl alcohols. The ketone/Grignard reactions



$$Me_3SiCH_2MgCl \xrightarrow[\text{(ii) } H_2O]{\text{(i) } R_1R_2C{=}O} R_1-C(R_2)(OH)-CH_2SiMe_3 \xrightarrow[THF]{NaH} R_1R_2C{=}CH_2$$

(a) $-R_1R_2- = -(CH_2)_5-$

(b) $R_1 = CH_3$, $R_2 = -CH_2CH_2CH{=}CMe_2$

yielded the respective β-silyl alcohols in good yields and large quantities of olefins were isolated in their subsequent reaction with sodium hydride in tetrahydrofuran.

Consequently, it appears that β-silyl alcohols can be prepared by reaction of trimethylsilylmethylmagnesium halides with ketones and aldehydes but in the work up procedure, mild hydrolysis conditions must be employed to prevent product fragmentation. The use of dilute acid as the hydrolysing medium would undoubtedly lead to substantial amounts of cleavage products and whilst the Russian's failed to report their mode of hydrolysis this might explain their low alcohol yields

2. The Reaction of Ketones with Hydrosilylmethyl Grignard Reagents

The reaction of benzophenone with dimethylsilylmethylmagnesium bromide followed a rather unexpected course the major product being benzhydryloxytrimethylsilane (89%), together with smaller quantities of benzhydrol (8%), 1,1-diphenylethylene (3%) and (dimethylsilylmethyl)trimethylsilane (12%). None of the expected β-silyl alcohol was detected. The product yields from this and other related reactions are reproduced in Table 8. Reaction of benzophenone with dimethyldeuteriosilylmethylmagnesium bromide yielded deuteriobenzhydrol, whilst hydrolysis with deuterium oxide of the products from a reaction with unlabelled Grignard gave benzhydryloxydimethyldeuteriomethylsilane. These results indicate the transfer of the silyl hydrogen of the Grignard reagent to the tertiary carbon atom of the product and that benzhydryloxydimethylsilylmethylmagnesium bromide is the reaction product prior to hydrolysis.

Methylphenylsilylmethylmagnesium bromide and diphenylsilylmethylmagnesium bromide followed a similar pattern in their reaction with benzophenone and high yields of the respective silyl alkoxides were isolated.

Reaction of benzophenone with methylsilylmethylmagnesium bromide gave a much lower yield of the rearranged product benzhydryloxydimethylsilane and in this case benzhydrol was the major product. In a parallel reaction with labelled Grignard reagent, methyldideuteriosilylmethylmagnesium bromide, transfer of deuterium to the tertiary carbon atom of the rearranged product was again observed.

In contrast the reaction of dimethylsilylmethylmagnesium bromide with acetophenone afforded none of the respective silyl alkoxide and the only products derived from the ketone appeared to be 2-phenylpropene (41%) and 2-phenylethanol (59%). When acetone was the reacting ketone 1,1,3,3-tetramethyldisiloxane was the only identified product (Table 9.).

3. The Mechanism of Formation of the Products

The formation of benzhydrol undoubtedly arises via a reductive process and since deuteriobenzhydrol is produced in the benzophenone/dimethyldeuteriosilylmethylmagnesium bromide reaction it is clear that the silyl hydrogen is effecting reduction.

The most obvious mechanism of reduction involves the process which is formally similar to that for alkyl Grignard reagents. The silyl olefin V could then react with more

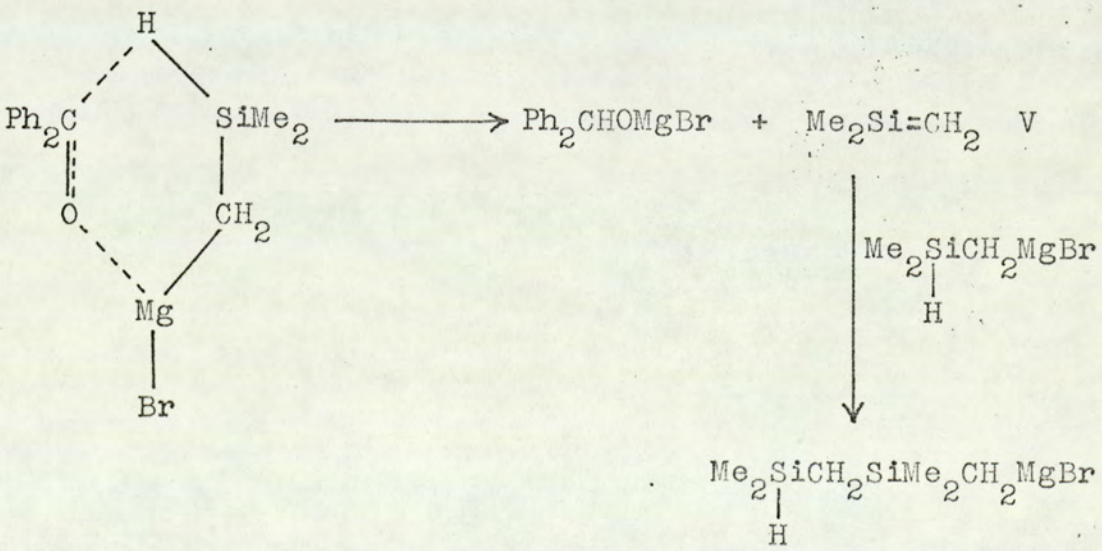


Table 8. Product yields from the reactions of hydrosilylmethyl Grignard reagents with benzophenone in diethyl ether.

Grignard (Conc. mol.)[a]	Products (%)
Me_2SiHCH_2MgBr (0.024)	$Ph_2CHOSiMe_3$ (89), $Ph_2C{=}CH_2$ (3), Ph_2CHOH (8), $Me_2SiHCH_2SiMe_3$ (12)
Me_2SiHCH_2MgBr (0.024)[b]	$Ph_2CHOSiMe_2CH_2D$ (87), $Ph_2C{=}CH_2$ (4), Ph_2CHOH (9)
Me_2SiHCH_2MgBr (0.024)[c]	$Ph_2CHOSiMe_3$ (54), $Ph_2C{=}CH_2$ (7), Ph_2CHOH (16), $Ph_2C{=}O$ (13), $Ph_2COHCOHPh_2$ (10)
Me_2SiDCH_2MgBr (0.024)	$Ph_2CDOSiMe_3$ (92), $Ph_2C{=}CH_2$ (3), Ph_2CDCH (5)
Me_2SiHCH_2MgBr (0.024)[d]	$Ph_2CHOSiMe_3$ (95), Ph_2CHOH (5)
Me_2SiHCH_2MgBr (0.024)[e]	$Ph_2CHOSiMe_3$ (76), Ph_2CHOH (21), $Ph_2C{=}CH_2$ (3)
$MeSiH_2CH_2MgBr$ (0.024)	$Ph_2CHOSiMe_2H$ (30), Ph_2CHOH (62), $Ph_2C{=}CH_2$ (8)
$MeSiD_2CH_2MgBr$ (0.024)	$Ph_2CDOSiMe_2D$ (28), Ph_2CDOH (65), $Ph_2C{=}CH_2$ (7)
$PhMeSiHCH_2MgBr$ (0.036)	$Ph_2CHOSiMe_2Ph$ (94), Ph_2CHOH (6), $PhMe_2SiH$ (170)[f]
Ph_2SiHCH_2MgBr (0.036)	$Ph_2CHOSiPh_2Me$ (84), Ph_2CHOH (16), Ph_2MeSiH (200)[f]

[a] Benzophenone concentration 0.012 mol. [b] Reaction terminated with deuterium oxide. [c] Reaction carried out at -50°. [d] Reaction carried out in the presence of styrene (0.04 mol.) [e] Reaction effected by addition of the Grignard reagent to a solution of benzophenone. [f] See experimental pages 116-117.

Table 9. Related reactions of Grignard reagents with ketones in diethyl ether.

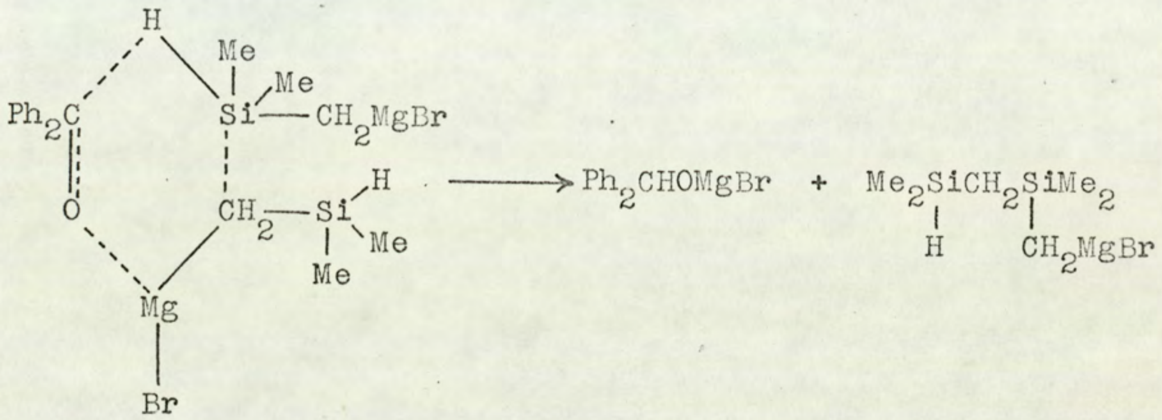
Grignard (Conc. mol.)	Reactant[a]	Products (%)
Me_2SiHCH_2MgBr (0.03)	$PhMeC=O$	$PhMeC=CH_2$ (41), $PhMeCHOH$ (59)
Me_2SiHCH_2MgBr (0.015)	$Me_2C=O$	$Me_2SiHOSiHMe_2$
Me_2SiHCH_2MgBr (0.02)	$Ph_2CHOMgBr$	Ph_2CHOH (97)
$Ph_2SiH(CH_2)_2MgBr$ (0.02)	$Ph_2C=O$	Ph_2CHOH (95), $Ph_2SiHCH=CH_2$ (95)
Me_3SiCH_2MgCl[b] (0.02)	$Ph_2C=O$	$Ph_2COHCOHPh_2$ (73), $Ph_2C=CH_2$ (18), $Ph_2COHCH_2SiMe_3$ (2.5), Ph_2CHOH (1) $Ph_2CH=CHSiMe_3$ (2.5), $Me_3SiCH_2CH_2SiMe_3$ (14)
Me_3SiCH_2MgCl[b, c]	$Ph_2C=O$	$Ph_2COHCH_2SiMe_3$ (major product), smaller quantities of $Ph_2C=O$, $Ph_2C=CH_2$ and $Ph_2C=CHSiMe_3$

[a] Concentration 0.01 mol. [b] Solvent tetrahydrofuran.

[c] Results taken from a personal communication from Dr. D. J. Peterson, reaction effected by addition of the Grignard reagent to a solution of the ketone.

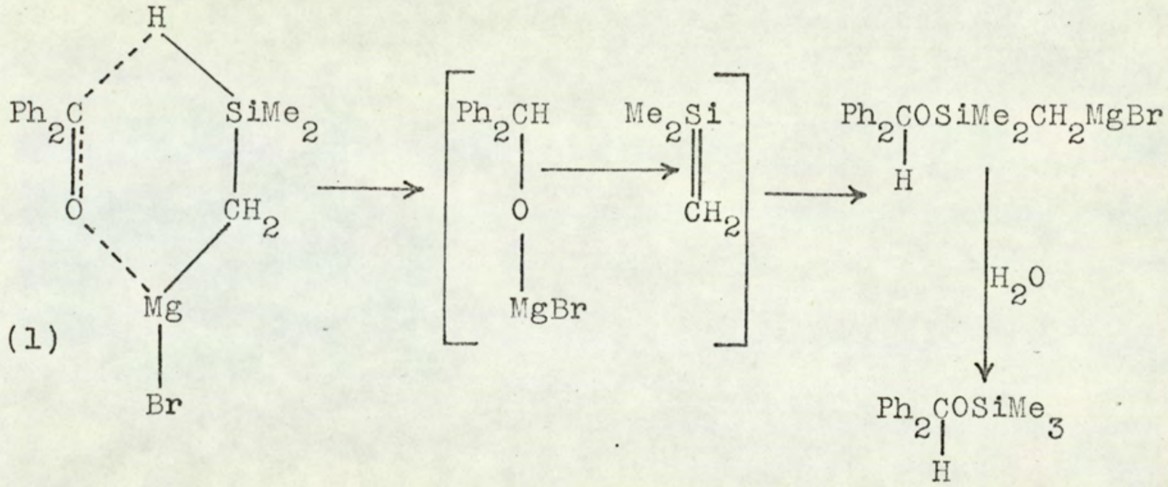
Grignard reagent to give IV after hydrolysis.

However, reduction via two molecules of the organometallic reagent would appear equally possible in the light of mechanistic studies on chlorosilane reduction (Chapter 3.).

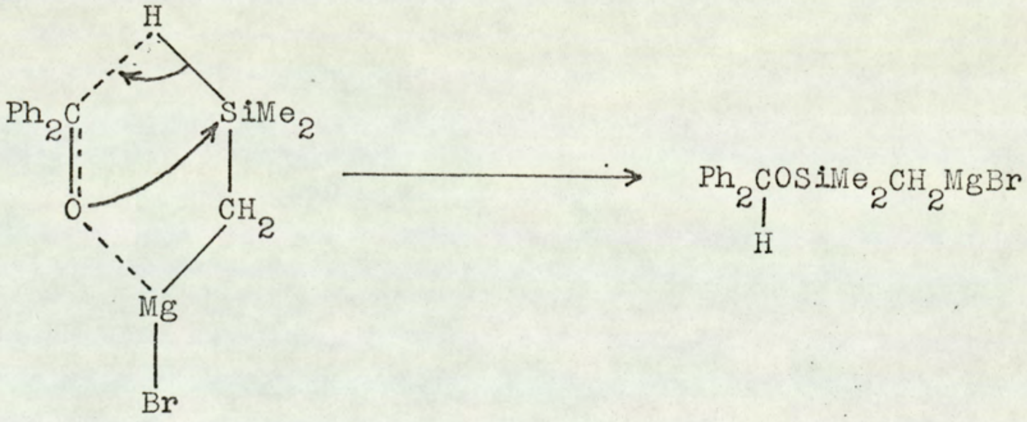


Alternatively, magnesium hydride formed in small quantities by the Grignard self coupling reaction, could account for all the benzhydrol produced. This latter possibility is also consistent with the much larger quantities of benzhydrol formed in the methylsilylmethylmagnesium bromide reaction since this Grignard reagent self couples extremely readily during preparation (Chapter 3.).

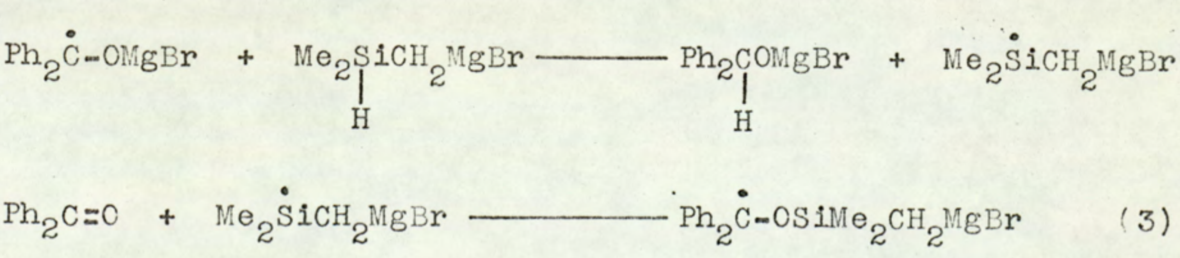
Several alternatives exist for the mechanism of formation of benzhydryloxytrimethylsilane from the dimethylsilylmethylmagnesium bromide/benzophenone reaction. By analogy with alkyl Grignard systems, reduction could first occur via a six centre transition state and the alkoxide so formed could then react with V to give the observed rearranged product.


(1)

Alternatively, reaction could be visualised through the same transition state but with attack of oxygen at silicon within the complex giving benzhydryloxydimethylsilylmethylmagnesium bromide in a direct process.

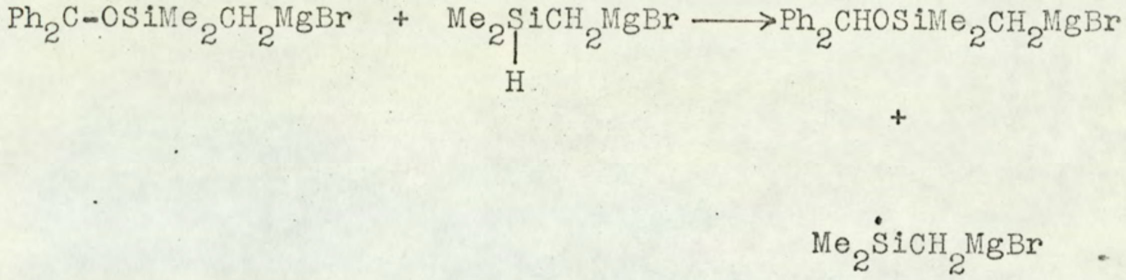

(2)

Finally an acceptable radical chain mechanism could be proposed to explain product formation.


(3)

$$\mathrm{Ph_2\dot{C}{-}OMgBr + Me_2\underset{\substack{|\\ H}}{Si}CH_2MgBr \longrightarrow Ph_2\underset{\substack{|\\ H}}{C}OMgBr + Me_2\dot{Si}CH_2MgBr}$$

$$\mathrm{Ph_2C{=}O + Me_2\dot{Si}CH_2MgBr \longrightarrow Ph_2\dot{C}{-}OSiMe_2CH_2MgBr} \qquad (3)$$



$$Ph_2\dot{C}\text{-}OSiMe_2CH_2MgBr + Me_2\underset{\displaystyle H}{\underset{|}{Si}}CH_2MgBr \longrightarrow Ph_2CHOSiMe_2CH_2MgBr + Me_2\dot{Si}CH_2MgBr$$

The plausibility of this mechanism is enhanced by previous reports[79,80] of addition of silanes to benzophenone to give silyl alkoxides. A radical chain mechanism[80] has been proposed for this reaction. However elevated temperatures (220-270°) are needed to induce reaction.

$$Ph_2C{=}O + Ph_3SiH \xrightarrow{h\nu \text{ or heat}} Ph_2\dot{C}OH + Ph_3Si\cdot$$

$$Ph_3Si\cdot + Ph_2C{=}O \longrightarrow Ph_2\dot{C}OSiPh_3$$

$$Ph_2\dot{C}OSiPh_3 + Ph_3SiH \longrightarrow Ph_3SiOCHPh_2 + Ph_3Si\cdot$$

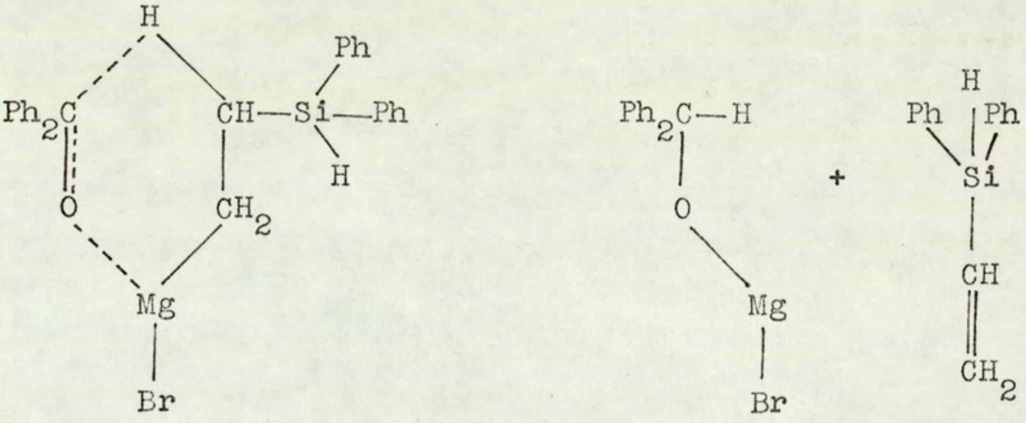
Similarly trimethylsilyl radicals generated by pyrolysis or photolysis of bis(trimethylsilyl)mercury add to acetone generating isopropoxytrimethylsilane.[81]

$$(Me_3Si)_2Hg \longrightarrow 2Me_3Si\cdot + Hg$$

$$Me_3Si\cdot + Me_2C{=}O \longrightarrow Me_3SiO\dot{C}Me_2$$

$$Me_3SiO\dot{C}Me_2 \xrightarrow{\text{Solvent}} Me_3SiOCHMe_2$$

However, reaction of benzophenone with dimethylsilylmethylmagnesium bromide in the presence of styrene also afforded benzhydryloxytrimethylsilane in high yield. Styrene has been used effectively as a free radical scavenger in Grignard reactions[66,67] and inhibition of a reaction involving free silyl radicals would certainly be expected. Consequently a radical chain mechanism would seem to be highly unlikely in this paricular case. Moreover, the reaction of (2-diphenylsilyl)ethylmagnesium bromide with benzophenone followed a normal reduction pattern and benzhydrol was produced in high yield together with vinyldiphenylsilane, the olefin produced by β-hydrogen abstraction.



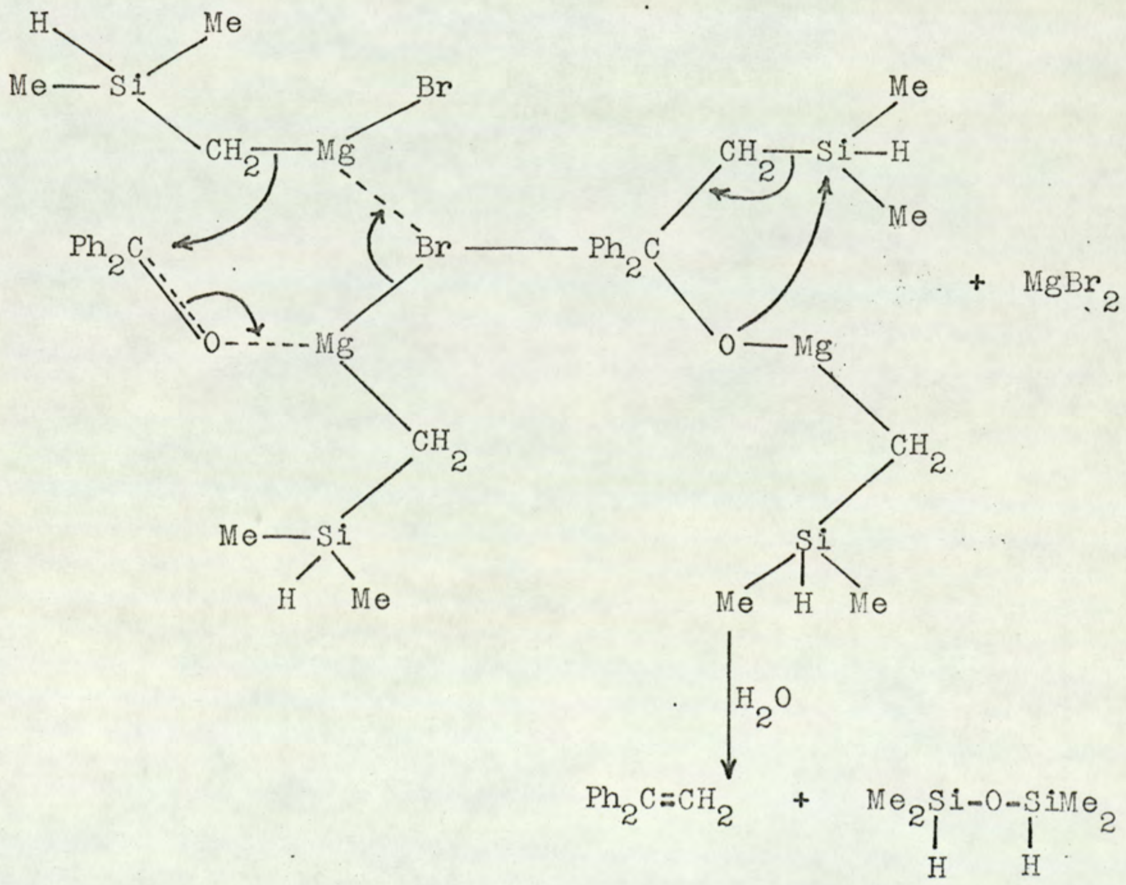
The non involvement of the silyl hydrogen in this reaction reflects the importance of the six membered transition state in controlling the reaction pathway.

Product formation via alkoxide reaction with the Grignard reagent is also ruled out since benzhydrol is the exclusive product from addition of dimethylsilylmethylmagnesium bromide to diphenylmethylalkoxymagnesium bromide.

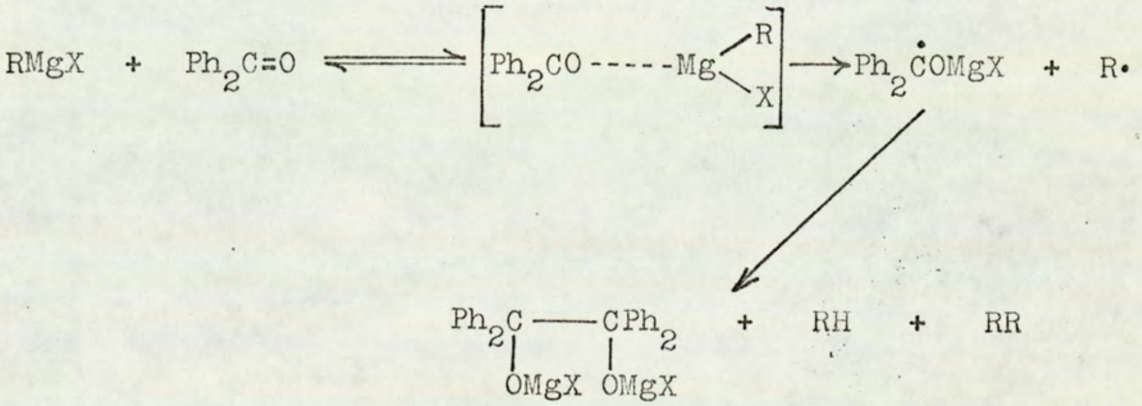
In an effort to establish the intermediacy of 2-silaisobutene in this reaction, mixtures of benzophenone and dimethylsilylmethylmagnesium bromide were studied at low temperature by n.m.r. spectroscopy. The spectrum produced on mixing the reactants at -28° is represented in Fig. 15. A fairly intense singlet absorption was observed at τ 9.51 which disappeared when the sample was allowed to warm to room temperature. This absorption is well displaced from those of any of the reactants or products containing the silicon-methyl moiety and is in the expected region for the methyl protons of V. The disappearance of this absorption on warming (Fig. 15.) is also consistent with this assignment.

Whilst the intermediacy of V in the reaction of benzophenone with dimethylsilylmethylmagnesium bromide seems probable, proof of its intermediacy in either or both of the rearrangement and reduction reactions is still lacking. Consequently, the mechanisms of formation of both benzhydrol and benzhydryloxytrimethylsilane are still uncertain.

It seems likely that 1,1-diphenylethylene arises via a normal addition reaction with subsequent cleavage of the β-silyl alkoxide.



It had previously been observed that small quantities of 1,1-diphenylethylene were produced on reaction of benzophenone with trimethylsilylmethylmagnesium chloride.[82] A reexamination of this reaction confirmed this observation (Table 9.) but the overall product distribution was markedly changed when the order of addition of the two reactants was reversed. This is a factor which had apparently gone unnoticed by previous workers. Thus, although addition of trimethylsilylmethylmagnesium chloride to a solution of benzophenone affords (trimethylsilylmethyl)diphenylcarbinol in good yield,[77,82] a reversal of this addition order gives benzopinacol as the major product (Table 9.) and in this case Wurtz Grignard coupling product, (2-trimethylsilylethyl)trimethylsilane, was also detected. The formation of benzopinacol and Wurtz coupling products have been ascribed previously to radical processes.[83]



$$RMgX + Ph_2C{=}O \rightleftharpoons \left[Ph_2CO\text{----}Mg\begin{matrix}R\\X\end{matrix}\right] \longrightarrow Ph_2\dot{C}OMgX + R\cdot$$

$$\longrightarrow \underset{OMgX}{Ph_2C}\text{—}\underset{OMgX}{CPh_2} + RH + RR$$

Clearly the formation of substantial quantities of ketyl radicals will be favoured by high Grignard and low ketone concentrations during addition.

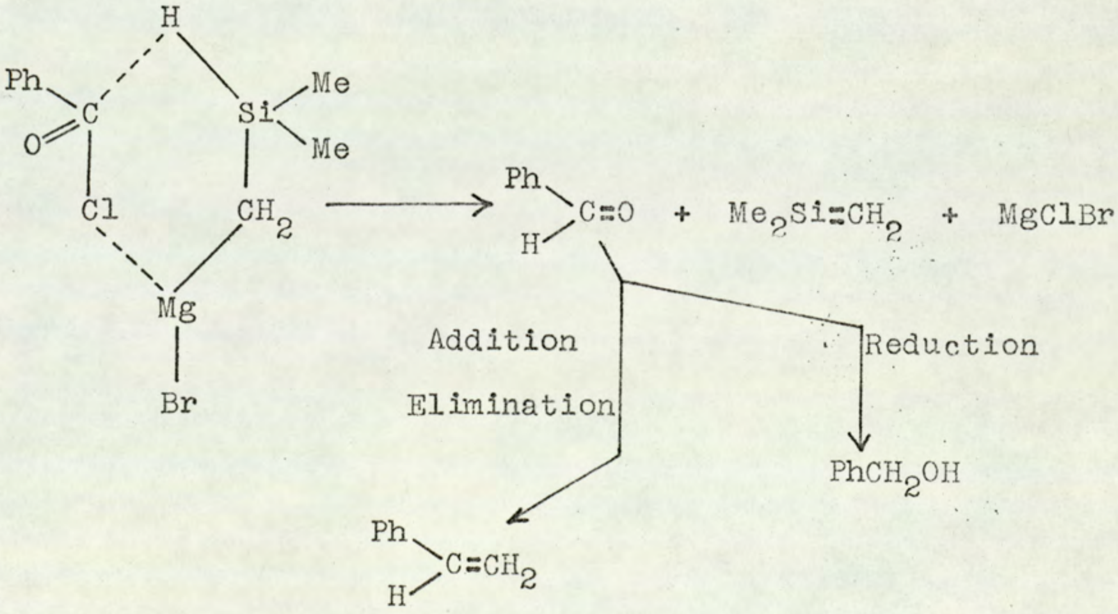
In contrast, the reversal of the order of addition was found to have little effect upon the hydrosilylmethyl

Grignard reagent/benzophenone reactions suggesting that ketyl radicals are not involved in major product forming steps.

The products of reaction of dimethylsilylmethylmagnesium bromide and acetophenone are those derived from addition elimination and reduction whilst the observed products from a reaction of this Grignard reagent with acetone are those formed exclusively by addition elimination. The reason for the lack of rearrangement in the acetophenone and acetone reactions is not immediately obvious.

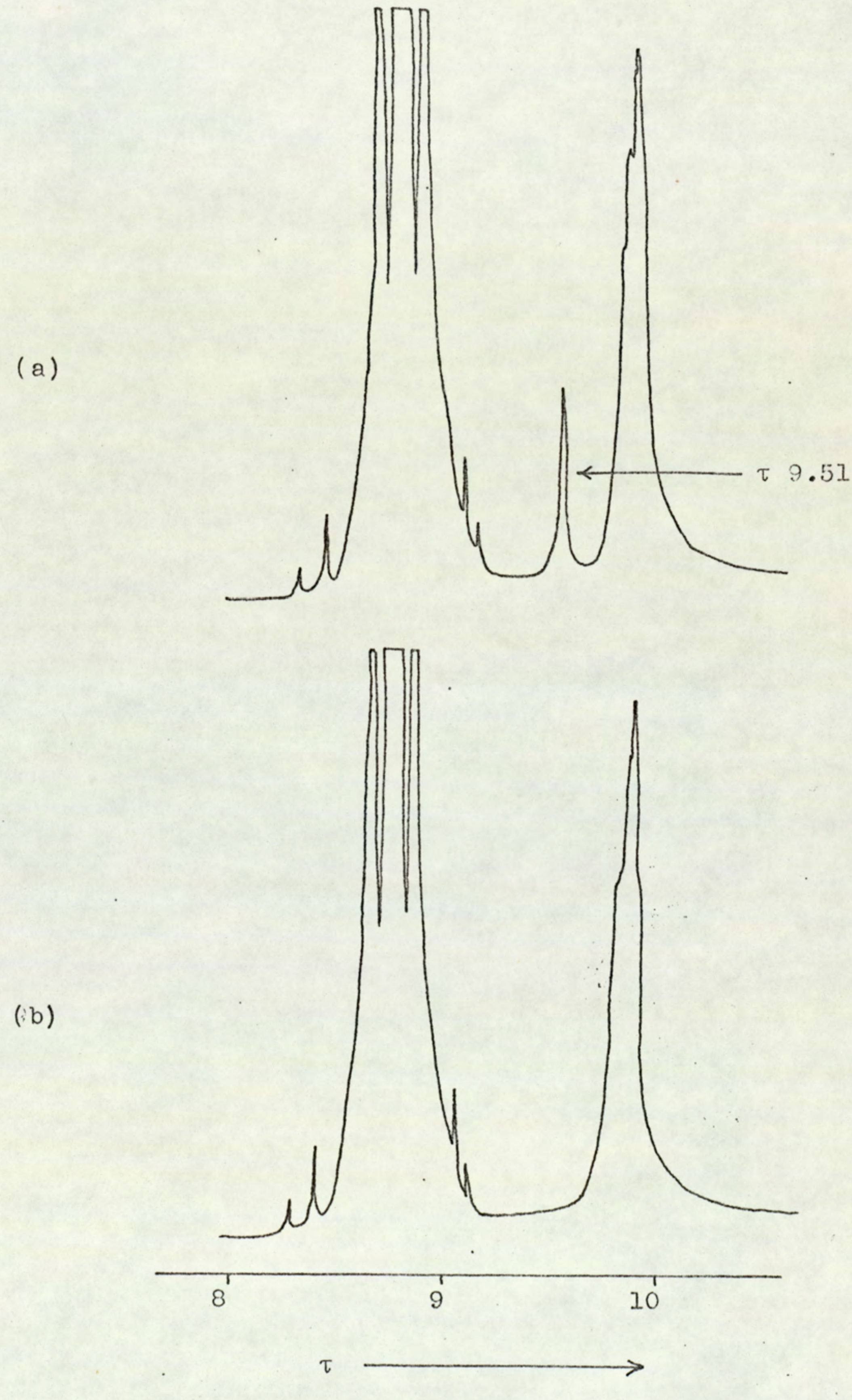
4. Reaction of Dimethylsilylmethylmagnesium Bromide with Benzoyl Chloride.

The addition of benzoyl chloride to dimethylsilylmethylmagnesium bromide in diethyl ether afforded styrene (54%), benzyl alcohol (46%) and (dimethylsilylmethyl)trimethylsilane (140%). The initial step in the reaction probably involves reduction of the carbon-halogen bond. Further reaction



either by reduction or addition elimination leads to the formation of the observed products. The probable intermediacy of V was again suggested by n.m.r. spectroscopy an intense singlet absorption being observed at τ 9.51 on mixing the reactants at -30°.

Fig. 15. 60 MHz N.m.r. spectra produced by reaction of benzophenone with dimethylsilylmethylmagnesium bromide in diethyl ether (a) at -28° (b) at 20°.



V

THE PHOTOLYSIS OF HYDROSILYLMETHYL GRIGNARD REAGENTS AND THEIR REACTION WITH CUPROUS CHLORIDE

1. Photolysis Reactions.

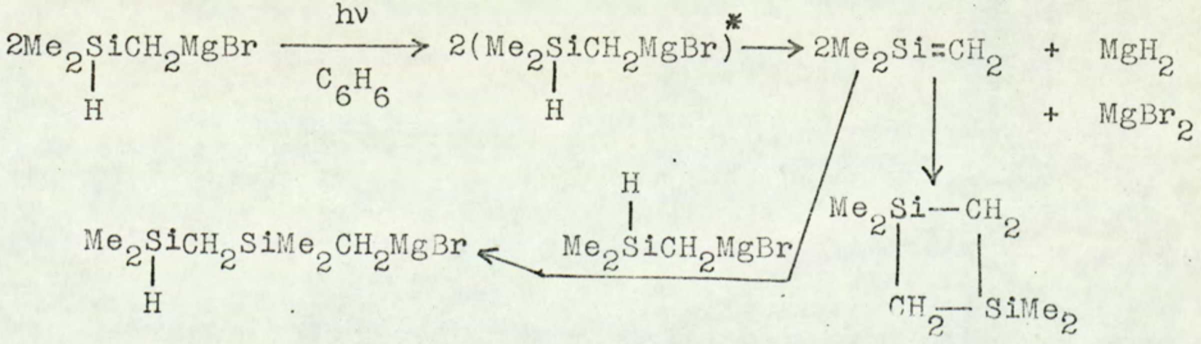
Literature reports concerning the photolysis of organometallics (covalent) are extremely sparse and in particular no information concerning the behaviour of alkyl Grignard reagents could be located. However Glaze and Brewer[84] have studied the photolysis of ethyllithium by mercury resonance radiation and two competing photolytic mechanisms were proposed; a LiH elimination reaction yielding ethylene (a)

$$(C_2H_5Li) \xrightarrow{h\nu} (C_2H_5Li)^{*} \longrightarrow LiH + C_2H_4 \qquad (a)$$

and a homolytic process which yields lithium metal, ethylene and ethane (b).

$$(C_2H_5Li)_n \xrightarrow{h\nu} (C_2H_5Li)_n^{*} \longrightarrow C_2H_6 + C_2H_4 + 2Li + (C_2H_5Li)_{n-2} \qquad (b)$$

In the light of these observations it seemed probable that dimethylsilylmethylmagnesium bromide might eliminate magnesium hydride in a similar fashion thus providing an opportunity for the detection of V.



Once formed, V would be expected to react by two routes; by addition of another molecule of Grignard reagent and by dimerisation in a cage type process to give 1,1,3,3-tetramethyl-1,3-disilacyclobutane. When photolysed a solution of dimethylsilylmethylmagnesium bromide in benzene was found to give reasonable yields of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (5%). However from previous reports relating to the photolysis of methylsilane[85] it became apparent that this ring dimer might also have been formed by two consecutive coupling reactions. In keeping with this proposal, irradiation of (dimethylsilylmethyl)dimethylsilylmethylmagnesium iodide afforded a similar yield of 1,1,3,3-tetramethyl-1,3-disilacyclobutane. Consequently, there is no firm evidence for the intermediacy of V in this reaction.

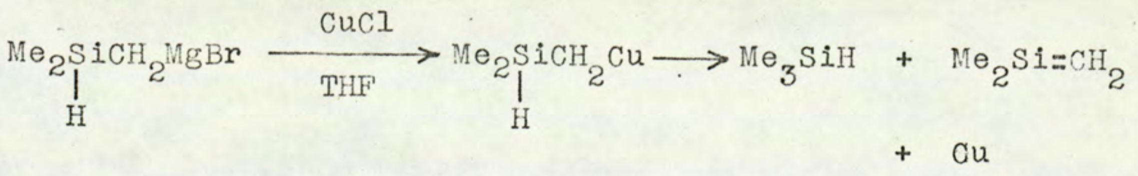
2. Cuprous Chloride Reactions.

The disproportionation of alkyl radicals derived from alkylcopper (I) species has recently been established.[86]

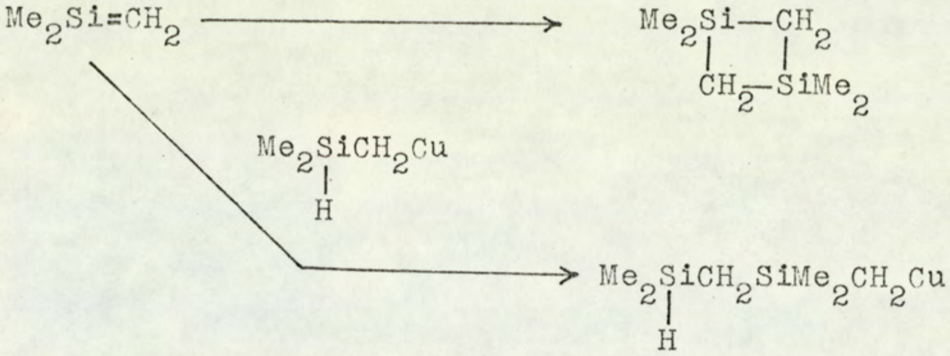
$$\mathrm{CH_3CH_2CH_2MgBr} + \mathrm{Cu^{I}Cl} \xrightarrow[\mathrm{THF}]{-78^{\circ}} \mathrm{CH_3CH_2CH_2Cu^{I}} + \mathrm{MgBrCl}$$

$$\mathrm{CH_3CH_2CH_2Cu^{I}} \xrightarrow{\mathrm{THF}} \underset{51\%}{\mathrm{CH_3CH{=}CH_2}} + \underset{49\%}{\mathrm{CH_3CH_2CH_3}} + \mathrm{Cu}$$

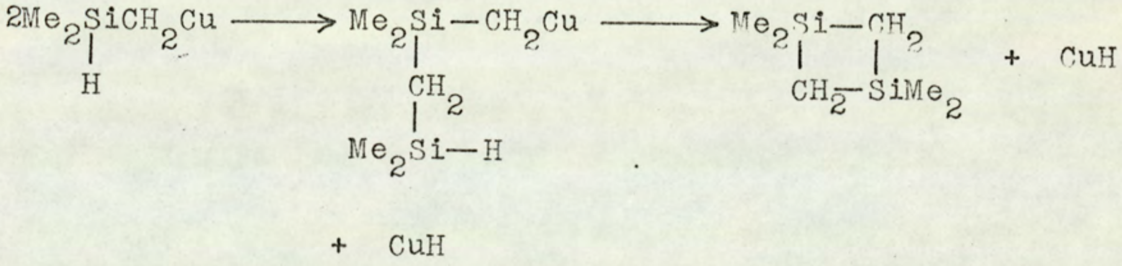
Accordingly, the reaction of dimethylsilylmethylmagnesium bromide with cuprous chloride was examined in the hope of effecting disproportionation to give V. Significant quantities



$$\mathrm{Me_2\underset{H}{\underset{|}{Si}}CH_2MgBr} \xrightarrow[\mathrm{THF}]{\mathrm{CuCl}} \mathrm{Me_2\underset{H}{\underset{|}{Si}}CH_2Cu} \longrightarrow \mathrm{Me_3SiH} + \mathrm{Me_2Si{=}CH_2} + \mathrm{Cu}$$



of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (4%) were detected amongst the products, however a dark brown precipitate of cuprous hydride was formed during reaction and it seemed likely that the ring dimer was formed once again via two consecutive coupling reactions rather than by dimerisation of V.



In harmony with this suggestion, (dimethylsilylmethyl)-dimethylsilylmethylmagnesium iodide also gave a similar yield of 1,1,3,3-tetramethyl-1,3-disilacyclobutane on reaction with cuprous chloride suggesting non participation of V in the dimethylsilylmethylmagnesium bromide reaction. Attempts to detect V by n.m.r. spectroscopy in the latter reaction also proved fruitless confirming the previous conclusions.

VI

EXPERIMENTAL

All melting points and boiling points are uncorrected.

N.m.r. spectra were usually determined using a Perkin-Elmer R14 100 MHz spectrometer employing a probe temperature of 33.5°. 60 MHz n.m.r. spectra, where recorded, were obtained with one of the following instruments; a Perkin-Elmer R10 60 MHz spectrometer using a probe temperature of 33.5° or a Varian Associates A60-A 60 MHz spectrometer employing a probe temperature of 40°. Unless otherwise stated, spectra were recorded from samples of neat liquids or 20% solutions in carbon tetrachloride or deuterochloroform. Absorption positions are quoted relative to tetramethylsilane (τ 10.00) as internal standard.

I.r. spectra were obtained using either a Perkin-Elmer Model 225 spectrometer, a Perkin-Elmer Model 237 spectrometer or a Perkin-Elmer Model 457 spectrometer.

Mass spectra were determined using an A.E.I. MS9 mass spectrometer. Normal operating conditions consisted of an ionising potential of 70 e.v. and an inlet temperature of 150°.

Routine g.l.c. analyses were carried out on a Pye-Unicam series 104 instrument using a silicone gum SE30 column (9ft. x 1/8in. o.d. or 5ft. x 1/8in. o.d.) with helium as carrier gas at a flow rate of 50 ml./min.

Interpretations of n.m.r. spectra were based on the texts of Mathieson,[87] Emsley, Feeny and Sutcliffe[88] and Jackman and Sternhell.[89] I.r. assignments were based on the texts of Bellamy[90] and Flett[91] and mass spectral interpretations were aided by the texts of Beynon, Saunders and Williams[92] and Budzikiewicz, Djerassi and Williams.[93]

Thin layer chromatography plates were spread, in accordance with the manufacturers instructions, with a 0.25 mm. thick layer of Silica-Gel G supplied by Mackerey, Nagel & Co. Silica Gel M.F.C. supplied by Messrs. Hopkins and Williams was used without further treatment for column chromatographic separations. Solvents used for chromatography were all "AnalaR" reagent grade materials.

Reagents.- Methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, tetramethylsilane, methyldichlorosilane, dimethylchlorosilane, silicon tetrachloride, trichlorosilane, vinyltrichlorosilane, diphenyldichlorosilane and diphenylmethylchlorosilane supplied by Midland Silicones and the "AnalaR" reagents benzene, chloroform, carbon tetrachloride, light petroleum (60-80°) and diethyl ether were used without further purification. Organometallic reagents were prepared in reagent grade diethyl ether or tetrahydrofuran previously redistilled from lithium aluminium hydride. Deuterochloroform was supplied by Koch Light and had an isotopic purity of 99.9%.

(i) Radical Addition Reactions of ω-Alkenylsilanes.

A Perkin-Elmer R14 100 MHz spectrometer was used for all kinetic determinations by n.m.r. G.l.c. analyses were carried out on a Pye-Unicam series 104 instrument using a silicone gum (SE30) column (9ft. x 1/8in. o.d.) with helium as carrier gas at a flow rate of 50 ml./min.

Reagents.- Chlorobenzene was shaken with small portions of concentrated sulphuric acid until the acid no longer became coloured. The chlorobenzene was washed with water, with 10% sodium bicarbonate solution and again with water, dried first over magnesium sulphate and then over phosphorus pentoxide and fractionally distilled through a 2ft. glass packed column. The fraction b.p. 130-130.5° was collected and used as standard in kinetic runs. Bromotrichloromethane was 99.4% pure as analysed by g.l.c. n-Dodecane thiol was redistilled before use and the fraction b.p. 93-93.5°/0.6 mm. was collected. 1,2-bis(1-Cyano-1-methylethyl)-diazene was used without further treatment. Benzoyl peroxide was recrystallised by dissolving in cold chloroform and precipitating with methanol.

The following were prepared using standard procedures, vinyltrimethylsilane,[94] b.p. 54-54.5° (lit.,[94] b.p. 54.4°), ^1H n.m.r. τ 3.50-4.40 (3H, m) and 9.90 (9H, s), ν_{max} (liq. film) 1597 (C=C) and 950 (CH_2 wag) cm^{-1}; allyltrimethylsilane,[95] b.p. 84.5-85.5° (lit.,[95] b.p. 84.9°), ^1H n.m.r. τ 3.92-4.40 (1H, m), 4.98-5.23 (2H, m), 8.43 (2H, d, J 7.5 Hz) and 9.92 (9H, s), ν_{max} (liq. film) 1634 (C=C) and 894 (CH_2 wag) cm^{-1}; allyltrichlorosilane,[96] b.p. 117-118° (lit.,[96] b.p. 117-117.5°), ^1H n.m.r. τ 3.90-4.39 (1H, m), 4.60-4.89 (2H, m) and 7.68 (2H, d, J 8 Hz), ν_{max} (liq. film) 1645 (C=C) and 918 (CH_2 wag) cm^{-1}; pent-4-enyltrichlorosilane,[97] b.p. 163-165° (lit.,[97] b.p. 162-163°), ^1H n.m.r. τ 3.92-4.60 (1H, m), 4.74-5.12 (2H, m), 7.66-8.06 (2H, m), 8.12-8.48 (2H, m) and 8.48-8.75 (2H, m), ν_{max} (liq. film) 1645 (C=C) and 919 (CH_2 wag) cm^{-1}; vinyltriphenylsilane,[98] m.p. 67-69° (lit.,[98] m.p. 67-68°), ^1H n.m.r. τ 2.30-2.80 (15H, m) and 2.98-4.35 (3H, m), ν_{max} (KBr disc) 1590 (C=C) and 960 (CH_2 wag) cm^{-1} and allyltriethylsilane,[99] b.p. 170-172° (lit.,[99] 170-171.5°/748 mm.), ^{1}H n.m.r. τ 3.93-4.42 (1H, m), 4.99-5.29 (2H, m), 8.49 (2H, d, J 8.5 Hz) and 8.73-9.70 (15H, m), ν_{max} (liq. film) 1632 (C=C) and 893 (CH_2 wag) cm.$^{-1}$

But-3-enyltrimethylsilane.- But-3-ene-1-ol prepared by the reaction of dry gaseous formaldehyde with allylmagnesium bromide, was converted to 4-bromobut-1-ene by the method of Linstead and Rydon.[100] But-3-enylmagnesium bromide was prepared by reaction of 4-bromobut-1-ene (27 g., 0.2 mol.) with magnesium (4.86 g., 0.2 mol.) in anhydrous diethyl ether (135 ml.) and trimethylchlorosilane (27.1 g., 0.25 mol.) was run in. After reflux (48 h.), the mixture was hydrolysed with dilute ammonium chloride solution and the ether layer was separated, dried ($MgSO_4$) and fractionated. Yield 12 g., 41%, b.p. 111-113° (lit.,[101] b.p. 110.5°), ^{1}H n.m.r. τ 3.80-4.26 (1H, m), 4.75-5.12 (2H, m), 7.70-8.02 (2H, m), 9.18-9.43 (2H, m) and 9.94 (9H, s), ν_{max} (liq. film) 1640 (C=C) and 903 (CH_2 wag) cm.$^{-1}$

Pent-4-enyltrimethylsilane.- Methylmagnesium iodide prepared by reaction of iodomethane (95.2 g., 0.6 mol.) with magnesium (14.58 g., 0.6 mol.) in anhydrous diethyl ether (130 ml.) was added dropwise with stirring to a solution of pent-4-enyltrichlorosilane (29 g., 0.143 mol.) in dry diethyl ether (25 ml.) at a rate sufficient to maintain steady reflux. After continued reflux (24 h.) the products were worked up with ice cold ammonium chloride solution and the combined organic phase was dried ($MgSO_4$) and fractionated. Yield 17.9 g., 89%, b.p. 135-137° (lit.,[23] b.p. 31-32°/14 mm.), ^{1}H n.m.r. τ 3.90-4.41 (1H, m), 4.85-5.15 (2H, m), 7.75-8.06

(2H, m), 8.32-8.75 (2H, m), 9.30-9.56 (2H, m) and 10.00 (9H, s), ν_{max} liq. film) 1643 (C=C) and 911 (CH_2 wag) cm.$^{-1}$

Hex-5-enyltrimethylsilane.- (3-Chloropropyl)methyldichlorosilane[102] was converted to (3-chloropropyl)trimethylsilane[103] by reaction with methylmagnesium iodide. Subsequent reaction with sodium iodide in dry acetone gave (3-iodopropyl)trimethylsilane[103] in 82% yield. A solution of (3-iodopropyl)trimethylsilane (74.4 g., 0.3 mol.) in dry diethyl ether (50 ml.) was added to allylmagnesium bromide (0.5 mol.) in dry diethyl ether (400 ml.). After reflux (48 h.) and work up with ammonium chloride solution, the organic phase was dried ($MgSO_4$) and fractionated to give the product. Yield 21.4 g., 46%, b.p. 158-160° (lit.,[104] 158-159°/750 mm.), ^{1}H n.m.r. τ 3.94-4.38 (1H, m), 4.75-5.15 (2H, m), 7.77-8.08 (2H, m), 8.32-9.27 (4H, m), 9.33-9.63 (2H, m) and 10.00 (9H, s), ν_{max} (liq. film) 1644 (C=C) and 910 (CH_2 wag) cm.$^{-1}$

Hept-6-enyltrimethylsilane.- 4-Bromobutyltrimethylsilane was prepared by reaction of 4-hydroxybutyltrimethylsilane[105] with phosphorus tribromide using the method of Sommer et al.[106] Subsequently (4-trimethylsilyl)butylmagnesium bromide (0.177 mol.) was prepared in dry diethyl ether (150 ml.) and allyl bromide (64.3 g., 0.531 mol.) was slowly added. The resulting mixture was refluxed (10 h.), cooled, hydrolysed with ammonium chloride solution and the organic phase was dried ($MgSO_4$) and fractionated. Yield 21.8 g., 72%, b.p. 184-186°, ^{1}H n.m.r. τ 3.92-4.40 (1H, m), 4.84-5.13 (2H, m), 7.80-8.08 (2H, m), 8.30- 8.90 (6H, m), 9.31-9.60 (2H, m) and 10.00 (9H, s), ν_{max} (liq. film) 1643 (C=C) and 911 (CH_2 wag) cm.$^{-1}$

But-3-enyltrichlorosilane.- But-3-enylmagnesium bromide prepared by reaction of 4-bromobut-1-ene[100] (70 g., 0.52 mol.) with magnesium (12.62 g., 0.52 mol.) in dry diethyl ether (350 ml.) was added dropwise over a period of 1 h. to a solution of silicon tetrachloride (177 g., 1.04 mol.) in dry diethyl ether (100 ml.) cooled in ice. After addition the products were stirred at room temperature for 1 h. and then poured into light petroleum (b.p. 30-40°) and filtered. The filtrate was fractionated to give the product. Yield 40 g., 41%, b.p. 141-143°, ^{1}H n.m.r. τ 3.83-4.71 (1H, m), 4.72-5.12 (2H, m), 7.49-7.82 (2H, m) and 8.37-8.70 (2H, m), ν_{max} (liq. film) 1642 (C=C) and 911 (CH_2 wag) cm.$^{-1}$

Allyltriphenylsilane.- A solution of phenyllithium (0. 75 mol.) in dry diethyl ether (600 ml.) was added dropwise over a period of 2.5 h. to a solution of diphenyldichlorosilane (82.4 g., 0.325 mol.) in anhydrous diethyl ether (50 ml.). When addition was complete the products were refluxed for 1 h. Allylmagnesium bromide (0.5 mol.) in anhydrous diethyl ether (500 ml.) was then added slowly at a rate sufficient to maintain gentle reflux. Two thirds of the solvent was then removed by distillation and the remaining products were refluxed for 42 h. After work up with dilute ammonium chloride solution the organic phase was dried ($MgSO_4$) and concentrated. Yield 80.8 g., 83% m.p. 88-90° (from ligroin) (lit.,[107] m.p. 88.5-90°), ^{1}H n.m.r. τ 2.25-2.76 (15H, m), 3.90-4.40 (1H, m), 4.94-5.21 (2H, m) and 7.65 (2H, d, J 8 Hz), ν_{max} (KBr disc) 1630 (C=C) and 894 (CH_2 wag) cm.$^{-1}$

But-3-enyltriphenylsilane.- The Grignard reagent from 4-bromobut-1-ene[100] was prepared by reaction of the halide (27.0 g., 0.2 mol.) with magnesium (4.84 g., 0.2 mol.) in anhydrous tetrahydrofuran (110 ml.). A solution of triphenylchlorosilane (29.4 g., 0.1 mol.) in dry tetrahydrofuran (60 ml.) was run in over 0.5 h. and the mixture was refluxed for 120 h. After hydrolysis with cold ammonium chloride solution the ether phase was separated, dried ($MgSO_4$) and concentrated. Yield 24.1 g., 77%, m.p. 103-105^{o} (from ethanol-carbon tetrachloride 8 : 3), ^{1}H n.m.r. τ 2.25-2.90 (15H, m), 3.85-4.32 (1H, m), 4.80-5.22 (2H, m), 7.60-8.00 (2H, m) and 8.38-8.65 (2H, m), ν_{max} (KBr disc) 1642 (C=C) and 910 (CH_2 wag) cm.$^{-1}$

Pent-4-enyltriphenylsilane.- Allylmagnesium bromide (0.45 mol.) in anhydrous diethyl ether (400 ml.) was concentrated by distillation until most of the ether (80%) had been removed. Dry benzene (100 ml.) was run in and a solution of 2-bromoethyltriphenylsilane[34] (55.1 g., 0.15 mol.) in dry benzene (250 ml.) was slowly added. After addition the reactants were refluxed with stirring for 24 h. Work up with ammonium chloride solution followed by concentration yielded the product as a clear oil. N. m.r. analysis of the products indicated a 95% yield, with ethyltriphenylsilane as a minor impurity. The product was purified by chromatographing on silica gel using light petroleum- benzene (9 : 1) as eluant. Yield 44.3 g., 90%, m.p. 42-43^{o} (lit.,[109] m.p. 45-46^{o}), ^{1}H n.m.r. τ 2.20-2.98 (15H, m), 3.85-4.32 (1H, m), 4.80-5.22 (2H, m), 7.78-8.09 (2H, m) and 8.15-8.75 (4H, m), ν_{max} (KBr disc) 1641 (C=C) and 911 (CH_2 wag) cm.$^{-1}$

(Triphenylsilylmethyl)dimethylsilane.- Dimethylchlorosilane (8.0 g., 0.085 mol.) was added dropwise to a solution of triphenylsilylmethyllithium[110] (0.011 mol.) in anhydrous diethyl ether (100 ml.) cooled to -78°. The mixture was allowed to warm up to room temperature, hydrolysed with water and the ether phase was dried ($MgSO_4$) and concentrated to give an oil. The oil was chromatographed on silica gel and eluted with light petroleum-benzene (4 : 1) to give the product as a clear liquid. Yield 1.54 g., 41%, ^1H n.m.r. τ 2.34-2.94 (15H, m), 5.92 (1H, septet, J 4 Hz), ν_{max} (liq. film) 2118 (Si-H) cm^{-1}

2,4,4,4-Tetrachlorobutyltrimethylsilane.- Allyltrimethylsilane (5.7 g., 0.05 mol.), carbon tetrachloride (23.1 g., 0.15 mol.) and benzoyl peroxide (0.5 g., 2.09 mmol.) were refluxed for 2.5 h. Excess carbon tetrachloride was removed by rotary film evaporation. Yield 8.05 g., 60%, b.p. 70-72°/1 mm., ^1H n.m.r. τ 5.34-5.68 (1H, m), 6.47-7.01 (2H, m), 8.59 (2H, d, J 8 Hz) and 9.88 (9H, s). (Found : Si, 10.3; titratable Cl, 13.2. $C_7H_{14}Cl_4Si$ requires Si, 10.5; titratable Cl, 13.2%).

2,4,4,4-Tetrachlorobutyltriethylsilane.- This was prepared by the above procedure using a reflux period of 5.5 h. Yield 95%, ^1H n.m.r. τ 5.40-5.70 (1H, m), 6.49-7.05 (2H, m), 8.27-8.70 (2H, m) and 8.85-9.75 (15H, m). (Found : Si, 9.0; titratable Cl, 11.4. $C_{10}H_{20}Cl_4Si$ requires Si, 9.0; titratable Cl, 11.4%).

Extended reaction of allyltrimethylsilane with carbon tetrachloride.- Allyltrimethylsilane (11.4 g., 0.1 mol.), carbon tetrachloride (61.6 g., 0.4 mol.) and benzoyl peroxide

(3 g., 0.012 mol.) were refluxed for 48 h. Analysis of the final reaction mixture by n.m.r. showed that no 2,4,4,4-tetrachlorobutyltrimethylsilane was present. The major products were the two compounds formed by β-elimination; trimethylchlorosilane ^{1}H n.m.r. τ 9.64 (9H, s) and 4,4,4-trichlorobut-1-ene, ^{1}H n.m.r. τ 3.80-4.27 (1H, m), 4.58-4.83 (2H, m) and 6.64 (2H, d, J 7 Hz). Low boiling materials were removed by distillation at atmospheric pressure and the remaining products were vacuum distilled to give trimethylbenzoxysilane. Yield 3.5 g., 70% (based on peroxide), b.p. 56-60°/0.8 mm. (lit.,[111] b.p. 221°/760 mm.), ^{1}H n.m.r. τ 1.70-2.00 (2H, m), 2.45-2.85 (3H, m) and 9.60 (9H, s), ν_{max} (liq. film) 1695, 1600, 1584, 1449, 1311, 1280, 1171, 1095, 1067 and 844 ($SiOCOC_6H_5$)[112] and 1250 and 840 ($SiMe_3$) cm.$^{-1}$ (Found : Si, 14.4. $C_{10}H_{14}O_2Si$ requires Si, 14.5%). 1,1,1,-3,5,5,5-Heptachloropentane was also identified as a minor product (approx 2%) amongst the residue, ^{1}H n.m.r. τ 5.05-5.32 (1H, m) and 6.32-6.61 (4H, m).

<u>2-Bromo-4,4,4-trichlorobutyltrimethylsilane.</u>- Allyltrimethylsilane (1.14 g., 0.01 mol.), bromotrichloromethane (7.88 g., 0.04 mol.) and 1,2-bis(1-cyano-1-methylethyl)-diazene (50 mg., 0.3 mmol.) were heated at 60.0° in a constant temperature bath for 6 h. The products were then concentrated under vacuum keeping the temperature below 60°. N.m.r. analysis confirmed that the product was pure, apart from traces of initiator residues. Yield 2.49 g., 80%, ^{1}H n.m.r. τ 5.31-5.61 (1H, m), 6.30-6.90 (2H, m), 8.33 (2H, d, J 8 Hz) and 9.86 (9H, s). (Found : Br, 25.2; Si, 8.9. $C_7H_{14}BrCl_3Si$ requires Br, 25.6; Si, 9.0%).

2-Bromo-4,4,4-trichlorobutyltriethylsilane.- This was prepared analogously employing a reaction time of 4 h. at 60°. Yield quantitative, ^{1}H n.m.r. τ 5.36-5.64 (1H, m), 6.30-6.92 (2H, m), 7.99-8.51 (2H, m) and 8.90-9.62 (15H, m). (Found : Br, 22.5; Si, 7.9. $C_{10}H_{20}BrCl_3Si$ requires Br, 22.6; Si, 7.9%).

4,4,4-Trichlorobutyltrimethylsilane.- Allyltrimethylsilane (5.7 g., 0.05 mol.), chloroform (17.92 g., 0.2 mol.) and benzoyl peroxide (0.5 g., 2.09 mmol.) were refluxed for 48 h. Throughout the reaction benzoyl peroxide was added in 2.09 mmol. portions at periodic intervals so that at the end of the reaction a total of 10.44 mmol. of peroxide had been added. The reaction products were concentrated and distilled under vacuum to give the 1 : 1 adduct. Yield 1.72 g., 15%, b.p. 50-52°/1.5 mm. ^{1}H n.m.r. τ 7.22 (2H, t, J 8 Hz) and 10.00 (9H, s). (Found : Si, 11.9. $C_7H_{15}Cl_3Si$ requires Si, 12.0%).

2,4,4,4-Tetrachlorobutyltriphenylsilane.- Allyltriphenylsilane (7.5 g., 0.025 mol.), carbon tetrachloride (15.4 g., 0.1 mol.) and benzoyl peroxide (0.5 g., 2.09 mmol.) were refluxed for 1 h. Excess carbon tetrachloride was removed by rotary film evaporation and the product (clear oil) was purified by chromatographing on silica gel using light petroleum-benzene 9 : 1 as eluant. Yield 8.3 g., 79%, ^{1}H n.m.r. τ 2.07-2.80 (15H, m), 5.28-5.59 (1H, m), 6.75-6.91 (2H, m) and 7.71 (2H, d, J 8 Hz). (Found : Si, 6.2; titratable Cl, 7.78. $C_{22}H_{20}Cl_4Si$ requires Si, 6.2; titratable Cl, 7.8%).

2-Bromo-4,4,4-trichlorobutyltriphenylsilane.- Allyltriphenylsilane (3.0 g., 0.01 mol.), bromotrichloromethane (7.88 g., 0.04 mol.) and 1,2-bis(1-cyano-1-methylethyl)-diazene (50 mg., 0.3 mmol.) were heated in a constant temperature bath at 60^{o} for 6 h. Concentration under vacuum gave the product in quantitative yield (trace impurities of initiator residues), m.p. 45-49^{o}, ^{1}H n.m.r. τ 2.07-2.65 (15H, m), 5.13-5.47 (1H, m), 6.40-6.89 (2H, m) and 7.42 (2H, d, J 7.5 Hz). (Found : Br, 16.1; Si, 5.1. $C_{22}H_{20}BrCl_{3}Si$ requires Br, 16.0; Si, 5.6%).

4,4,4-Trichlorobutyltriphenylsilane.- Allyltriphenylsilane (7.5 g., 0.025 mol.), chloroform (11.95 g., 0.1 mol.) and benzoyl peroxide (0.5 g., 2.09 mmol.) were refluxed for 18 h. A further quantity of benzoyl peroxide (2.5 g., 10.44 mmol.) was added in portions at intervals throughout the reaction. After concentration under vacuum the product was purified by chromatographing on silica gel using light petroleum-benzene 9 : 1 as eluant. Yield 6.47 g., 65%, m.p. 81-88^{o}, ^{1}H n.m.r. τ 2.20-2.92 (15H, m) and 7.86-8.75 (6H, m). (Found : Si, 6.6. $C_{22}H_{21}Cl_{3}Si$ requires Si, 6.7%).

2,4,4,4-Tetrachlorobutyltrichlorosilane.- Allyltrichlorosilane (3.0 ml., 0.021 mol.), carbon tetrachloride (12.78 g., 0.083 mol.) and benzoyl peroxide (50 mg., 0.21 mol.) were refluxed for 25 h. Concentration followed by vacuum distillation gave the product. Yield 2.8 g., 29%, b.p. 69-71^{o}/0.7 mm. ^{1}H n.m.r. τ 5.20-5.51 (1H, m), 6.43-6.91 (2H, m) and 7.50-7.98 (2H, m). (Found : Si, 8.67; titratable Cl, 45.1. $C_{3}H_{5}Cl_{7}Si$ requires Si, 8.85; titratable Cl, 44.7%).

2-Bromo-4,4,4-trichlorobutyltrichlorosilane.- Allyltrichlorosilane (4.0 ml., 0.027 mol.), bromotrichloromethane (16.46 g., 0.082 mol.) and benzoyl peroxide (30 mg., 0.124 mmol.) were refluxed for 1.5 h. The mixture was then concentrated and distilled to give the product. Yield 7.53 g., 74%, b.p. 84-85^{0}/0.35 mm. ^{1}H n.m.r. τ 5.15-5.50 (1H, m), 6.22-6.78 (2H, m) and 7.18-7.90 (2H, m). (Found : Si, 7.2; titratable halogen 50.2. $C_4H_5BrCl_6Si$ requires Si, 7.5; titratable halogen, 49.8%).

Attempted preparation of 4,4,4-trichlorobutyltrichlorosilane.- Allyltrichlorosilane (3.0 ml., 0.021 mol.), chloroform (9.92 g., 0.083 mol.) and benzoyl peroxide (20 mg., 0.082 mmol.) were refuxed for 48 h. Further portions of benzoyl peroxide were added at intervals throughout the reaction until finally a total of 100 mg., 0.41 mmol. of peroxide had been added. The n.m.r. spectrum of the reaction mixture contained no absorption in the region τ 6.0-7.5 indicating no 1 : 1 adduct formation. The majority of the alkenylsilane was unreacted (85%) and the remaining absorptions were consistent with telomer formation.

1-Trimethylsilyl-4-heptanone.- Allyltrimethylsilane (1.5 g., 0.0132 mol.), n-butyraldehyde (3.2 g., 0.045 mol.) and benzoyl peroxide (20 mg., 0.082 mmol.) were refluxed for 48 h. Quantities of 1,2-bis(1-cyano-1-methylethyl)-diazene (10.0 mg., 0.06 mmol.) were added at periodic intervals throughout the reaction until at termination a total of 100 mg., 0.6 mmol. of initiator had been added. Vacuum distillation gave the product. Yield 0.48 g., 19.6%, b.p. 46-49^{0}/0.35 mm. ^{1}H n.m.r. τ 7.53-7.78 (4H, m), 8.12-8.72

(4H, m), 8.90-9.21 (3H, m), 9.37-9.65 (2H, m) and 10.00 (9H, s).

1-Triethylsilyl-4-heptanone.- This was prepared in an analogous fashion. Yield 10%, b.p. 101-105°/0.4 mm. ^{1}H n.m.r. τ 7.50-7.75 (4H, m), 8.15-8.73 (4H, m) and 8.90-9.63 (24H, m).

1-Triphenylsilyl-4-heptanone.- Allyltriphenylsilane (2.0 g., 6.6 mmol.), n-butyraldehyde (3.0 g., 0.042 mol.) and 1,2-bis(1-cyano-1-methylethyl)-diazene 20 mg., 0.12 mmol.) were refluxed for 48 h. Further portions of 1,2-bis(1-cyano-1-methylethyl)-diazene were added at intervals throughout the reaction until finally a total of 50 mg., 0.3 mmol. of initiator had been added. After concentration under vacuum the products were chromatographed on silica gel using light petroleum-benzene 1 : 1 as eluant. This gave unreacted allyltriphenylsilane. Yield 0.64 g., 32%, m.p. 84-86°. Elution with diethyl ether afforded essentially pure product. Yield 1.5 g., 61%. ^{1}H n.m.r. τ 2.25-2.80 (15H, m), 7.58-7.90 (4H, m) and 8.13-9.38 (9H, m).

Procedure for kinetic runs.- All kinetic runs were carried out in a constant temperature bath 60.00° ± 0.025°. At least three determinations were carried out on each olefin.

Rate of addition of bromotrichloromethane to (1) ω-alkenyltrimethylsilanes.- The reactants, bromotrichloromethane, olefin, standard olefin (usually vinyltrimethylsilane), chlorobenzene (g.l.c. standard) and 1,2-bis-(1-cyano-1-methylethyl)-diazene (initiator)were mixed accurately in the ratio 1.2 : 1 : 1 : 0.2 : 0.02 and immersed in a bath in sealed vessels. Reaction times of 1-4 h. were generally employed. Samples of initial and final reaction mixtures were analysed quantitatively by g.l.c. Average area ratios were determined from three measurements. The amount of chloroform detected was negligibly small in all cases indicating that hydrogen abstraction by the trichloromethyl radical was not a significant side reaction. The quantity of bromotrichloromethane consumed paralleled olefin disappearance showing that telomerisation was also insignificant. Rate constant ratios were calculated from the usual expression

$$k_a/k_b = \frac{\log(\text{initial moles a/final moles a})}{\log(\text{initial moles b/final moles b})}$$

As a check on this procedure the relative reactivity of the six silanes were determined together using a modification of the method of Walling and Helmreich.[31] Each alkenylsilane (5.0 mmol.), hexamethyldisiloxane (internal referance 5.0 mmol.) and 1,2-bis(1-cyano-1-methylethyl)-diazene (0.3 mmol.) were allowed to react as described previously. Initial and final reaction mixtures were analysed by g.l.c. ; the relative rates so obtained were in good agreement with those obtained by the previous method.

(2) <u>ω-Alkenyltrichlorosilanes.</u>- The procedure described for the ω-alkenyltrimethylsilanes was slightly modified. In order to obtain reproducible results by g.l.c. it was found necessary to pass several samples of a trichlorosilane (methyltrichlorosilane) through the column to remove all reactive hydrolysis sites.

(3) <u>ω-Alkenyltriphenylsilanes.</u>- G.l.c. analysis could not be used because of the thermal instability of the 1 : 1 adduct of allyltriphenylsilane and bromotrichloromethane,

and in this series the reaction mixtures were analysed by n.m.r. spectroscopy. Vinyltrimethylsilane or vinyltriphenylsilane was used as standard olefin in competitive reactions. In neither of these compounds does the n.m.r. absorption signal of the terminal methylene protons overlap with the absorption signal of the terminal methylene protons in other alkenylsilanes and accurate integration of the aromatic and olefinic regions of the spectrum gave a quantitative measure of olefin proportions. Relative signal areas produced by integration of the n.m.r. spectra of solutions of known composition were close to predicted values. The technique was shown to be accurate since relative reactivities for the ω-alkenyltrimethylsilanes as determined by n.m.r. were comparable with those obtained by the g.l.c. method.

To compare the relative rates of addition of bromotrichloromethane to a mixture of vinyltrimethylsilane and vinyltriphenylsilane the n.m.r. method was slightly modified. The n.m.r. spectra of mixtures containing known weights of the two silanes were integrated. Comparison of the signal areas for Me_3Si- and Ph_3Si- gave confirmation of the proportions of olefins present. To determine final concentrations of the two silanes present, samples of neat and evacuated reaction mixtures were analysed by n.m.r. Integration of the aromatic and olefinic regions of the spectrum after evacuation (unreacted vinyltrimethylsilane removed) gave the concentration of vinyltriphenylsilane remaining. The relative reactivities of the two olefins could then be determined.

(4) Addition of n-dodecanethiol to ω-alkenyltrimethylsilanes.- Vinyltrimethylsilane, allyltrimethylsilane, hexamethyldisiloxane, n-dodecanethiol and 1,2-bis(1-cyano-1-methylethyl)-diazene in the relative proportions 1 : 1 : 0.2 : 1 : 0.01 were placed in a sealed vessel and immersed in a constant temperature bath at 60.0° for 0.5 h. Samples of the initial and final reaction mixtures were analysed by g.l.c. However to obtain reproducible results it was necessary to clear the column by heating for a short period at high temperature after each injection.

(ii) Possible Synthetic Routes to Silacyclopropanes

Vinyldiphenylchlorosilane.- Phenylmagnesium bromide (0.66 mol.) in dry diethyl ether (250 ml.) was added dropwise to a stirred solution of vinyltrichlorosilane (54 g., 0.33 mol.) in dry diethyl ether (70 ml.) over a period of 6 h. After continued stirring at room temperature for 14 h. excess light petroleum (b.p. 40-60°) was added and all magnesium salts were removed by filtration. Distillation gave the product. Yield 49.6 g., 68%, b.p. 138-140°/3.5 mm. (lit.,[113] b.p. 133-136°/1.5 mm.), ^{1}H n.m.r. (60 MHz) τ 2.15-3.05 (10H, m) and 3.40-4.35 (3H, m).

(2-Bromoethyl)diphenylchlorosilane (I).- Vinyldiphenylchlorosilane (36.7 g., 0.15 mol.) and benzoyl peroxide (0.1 g., 0.4 mmol.) were dissolved in dry carbon tetrachloride (60 ml.). Dry hydrogen bromide was bubbled through the solution and after 12 h. when all vinylic absorption had disappeared (n.m.r. analysis), the products were concentrated firstly by rotary film evaporation and finally under high vacuum. Yield 49 g., quantitative (clear oil), ^{1}H n.m.r. (60 MHz) τ 2.30-3.10 (10H, m), 6.35-6.75 (2H, m) and 7.73-8.40 (2H, m). Patterns of absorptions centred at τ 6.55 and 8.07 were typical of an AA'XX' system.

Isocrotyldiphenylchlorosilane.- 1,2-Dibromoisobutane[114] was converted to isocrotyl bromide[114] by reaction with potassium hydroxide in ethylene glycol. Reaction of the halide (45 g., 0.33 mol.) with magnesium (8.1 g., 0.33 mol.) in dry tetrahydrofuran (150 ml.) using the Normant[115] method gave isocrotylmagnesium bromide. The Grignard reagent was decanted under nitrogen into a dropping funnel and added dropwise with stirring to a solution of diphenyldichlorosilane (84.3 g., 0.33 mol.) in dry tetrahydrofuran (50 ml.) over a period of 2 h. After cooling excess light petroleum (b.p. 30-40°) was added to precipitate all magnesium salts and distillation of the filtrate gave the product. Yield 66.2 g., 73%, b.p. 154-155°/1 mm. ^{1}H n.m.r. τ 2.10-2.90 (10H, m), 4.30 (1H, s) and 8.25 (6H, d, J 6.5 Hz).

(2-Bromo-2-methylpropyl)diphenylchlorosilane (III).- Dry hydrogen bromide was passed with stirring through isocrotyldiphenylchlorosilane (52.1 g., 0.2 mol.) until n.m.r. analysis indicated complete disappearance of olefinic unsaturation (4 h.). Excess hydrogen bromide was removed under vacuum to give the product as a pale yellow liquid which crystallised on cooling. Yield 68.3 g., quantitative, m.p. 15° ^{1}H n.m.r. τ 2.20-2.90 (10H, m), 7.37 (2H, d, J 8 Hz) and 8.23 (6H, d, J 6.5 Hz), ν_{max} (liq. film) 1430, 1115, (Si-Ph) and 1385, 1370 (gem dimethyl substituents) cm.$^{-1}$

Reaction of I with magnesium.- A solution of I (4.0 g., 0.012 mol.) in dry tetrahydrofuran (60 ml.) was added dropwise to a slurry of magnesium (2.0 g., 0.082 mol.) in dry tetrahydrofuran (10 ml.). After addition reflux was maintained for 24 h. The reaction mixture was then poured into excess light petroleum (b.p. 30-40^{o}), filtered and concentrated by rotary film evaporation. N.m.r. analysis showed the absence of absorptions up field from τ 9.4. T.l.c. using light petroleum-benzene 9 : 1 as eluant indicated the presence of at least two components R_f values 0.38 and 0.05. The faster moving component was separated by chromatographing 1 g. of the reaction product mixture on silica gel using light petroleum as eluant. This gave 0.13 g. of a white solid. The n.m.r. spectrum of this product was consistent with the cyclic dimer 1,1,4,4-tetraphenyl-1,4-disilacyclohexane τ 2.5-3.0 (20H, m) and 8.9 (8H, s).

Reaction of III with magnesium.- A solution of III (5 g., 0.014 mol.) in dry tetrahydrofuran (15 ml.) was added to a slurry of magnesium (1 g., 0.041 mol.) in dry tetrahydrofuran (5 ml.). The reaction was strongly exothermic and a dark colour, associated with Grignard formation, was soon developed. After 0.1 h., apparently because of reaction, this colour had disappeared and after a further 0.2 h. the reaction mixture was worked up as in the previous experiment. The n.m.r. spectrum of the reaction products contained no absorptions up field from τ 9.4. Integration of the total n.m.r. signal was consistent with 21% elimination of isobutylene. The reaction products appeared to contain three components, (2-methylallyl)-diphenylchlorosilane (16%), ^{1}H n.m.r. τ 2.20-2.90 (10H, m), 5.23-5.43 (2H, m), 7.68 (2H, d, J 12 Hz) and 8.40 (3H, d, J 12 Hz), isocrotyldiphenylchlorosilane (15%), ^{1}H n.m.r. τ 2.20-2.90 (10H, m), 4.30 (1H, s) and 8.25 (6H, d, J 6.5 Hz) and isobutyldiphenylchlorosilane (32%), ^{1}H n.m.r. τ 2.20-2.90 (10H, m), 7.80-8.09 (1H, m), 8.60 (2H, d, J 6 Hz) and 9.09 (6H, d, J 6 Hz).

Decomposition of III in the presence of aluminium.- III (5 g., 0.014 mol.) was left in contact with aluminium foil (0.02 g., 0.74 mmol.) for 24 h. N.m.r. analysis indicated total absence of all starting material (no methylene absorption at τ 7.37). Using known standards for comparison, t-butyl bromide (25%) was shown to be present by g.l.c. analysis. The formation of this product was also consistent with i.r. evidence ν_{max} (liq. film) 1385 and 1365 (Me_3C) cm^{-1} and n.m.r. data τ 8.30 singlet. Integration of the n.m.r. spectrum of the reaction products showed that isobutylene (40%) had been lost by elimination. The remaining products were identified by their characteristic n.m.r. absorptions, isocrotyldiphenylchlorosilane (15%) and (2-methylallyl)diphenylchlorosilane (12%).

Addition of hydrogen bromide to products from reaction of III with magnesium.- Dry hydrogen bromide was bubbled slowly through the reaction product mixture for a period of 1 h. N.m.r. analysis of the products showed the expected removal of absorptions associated with olefinic protons. These absorptions had been replaced by signals characteristic of III (30%). The remaining major products appeared to be diphenylbromochlorosilane (20%) and isobutyldiphenylchlorosilane (31%) (n.m.r. analysis).

(iii) The Reaction of Hydrosilyl Grignard Reagents with Chlorosilanes

Reagents.- Lithium aluminium deuteride was purchased from Ciba Chemicals and had an isotopic purity of 99.0%.

The following were prepared using previously documented procedures, triethylsilane,[116] b.p. 108-109° (lit.,[117] b.p. 108.7°), ^{1}H n.m.r. τ 6.22-6.42 (1H, m), 9.00 (9H, t, J 7 Hz) and 9.21-9.60 (6H, m); propyldimethylsilane,[118] b.p. 73-74° (lit.,[118] b.p. 74°/750 mm.), ^{1}H n.m.r. τ 5.85-6.17 (1H, m), 8.22-8.80 (4H, m), 9.02 (3H, t, J 8 Hz), 9.18-9.54 (2H, m) and 9.91 (6H, d, J 3.5 Hz); triphenylchlorosilane,[119] m.p. 103-105° (lit.,[119] m.p. 104-105°); triphenylsilane,[120] m.p. 32-34° (lit.,[121] m.p. 34-36°), ^{1}H n.m.r. τ 2.22-2.87 (15H, m) and 4.43 (1H, s); triphenylmethoxysilane,[122] m.p. 53-54° (lit.,[122] m.p. 54.5-55°), ^{1}H n.m.r. τ 2.08-2.93 (15H, m) and 6.41 (3H, s); (chloromethyl)dimethylsilane,[123] b.p. 81-82° (lit.,[123] b.p. 81.5°/732 mm.), ^{1}H n.m.r. τ 5.77-6.01 (1H, m), 7.18 (2H, d, J 2.5 Hz) and 9.79 (6H, d, J 4 Hz); (bromomethyl)trimethylsilane,[124] b.p. 115-116° (lit.,[124] b.p. 115.5°/742 mm.), ^{1}H n.m.r. τ 7.58 (2H, s) and 9.87 (9H, s); (3-chloropropyl)methyldichlorosilane,[102] b.p. 183-185° (lit.,[125] 184.5°/754 mm.), ^{1}H n.m.r. τ 6.46 (2H, t, J 6 Hz), 7.55-8.16 (2H, m), 8.60-8.99 (2H, m) and 9.10 (3H, s); (3-chloropropyl)-dimethylchlorosilane,[102] b.p. 178-180° (lit.,[102] b.p. 179°/750 mm.), ^{1}H n.m.r. τ 6.51 (2H, t, J 6 Hz), 7.93-8.33 (2H, m), 8.90-9.29 (2H, m) and 9.59 (6H, s).

(Bromomethyl)dimethylsilane.- This was prepared by reduction of (bromomethyl)dimethylchlorosilane^{124} (50 g., 0.27 mol.) with lithium aluminium hydride (3.1 g., 0.082 mol.) in anhydrous diethyl ether (150 ml.). Yield 29.4 g., 71%, b.p. 99-101°, ^{1}H n.m.r. τ 5.73-5.97 (1H, m), 7.50 (2H, d, J 2 Hz) and 9.78 (6H, d, J 4 Hz).

(Bromomethyl)dimethyldeuteriosilane.- Preparation was achieved by the above procedure using lithium aluminium deuteride as reducing agent, b.p. 99-101°, ^{1}H n.m.r. τ 7.50 (2H, s) and 9.80 (6H, s).

(Bromomethyl)methylsilane.- Lithium aluminium hydride (2 g., 0.053 mol.) was added to a solution of (bromomethyl)-methyldichlorosilane^{124} (20 g., 0.096 mol.) in anhydrous diethyl ether (60 ml.) and the mixture was refluxed for 0.5 h. Yield 7.62 g., 63%, b.p. 78-80° (lit.,^{52} b.p. 25°/80 mm.), ^{1}H n.m.r. τ 5.65-6.10 (2H, m), 7.44 (2H, quart., J 3 Hz) and 9.68 (3H, quart., J 4 Hz).

(3-Chloropropyl)methylsilane.- (3-Chloropropyl)methyldichlorosilane (57.45 g., 0.3 mol.) was reduced by dropwise addition to a slurry of lithium aluminium hydride (5.7 g., 0.15 mol.) in anhydrous diethyl ether (170 ml.). Yield 22.4 g., 60%, b.p. 120-122°, ^{1}H n.m.r. τ 6.18-6.32 (2H, m), 6.49 (2H, t, J 7 Hz), 7.90-8.31 (2H, m), 9.00-9.31 (2H, m) and 9.82 (3H, t, J 4 Hz).

(3-Iodopropyl)methylsilane.- (3-Chloropropyl)methylsilane (20 g., 0.16 mol.) was refluxed with sodium iodide (72.2 g., 0.48 mol.) in anhydrous acetone^{126} (150 ml.) for 16 h. Sodium salts were removed by filtration and the remaining solution was fractionated to remove most of the acetone. Water (50 ml.) was added and after extraction with diethyl ether the organic phase was dried ($MgSO_4$) and fractionated. Yield 12.5 g., 36%, b.p. 162-164°, ^1H n.m.r. τ 6.19-6.35 (2H, m), 6.82 (2H, t, J 7 Hz), 7.81-8.30 (2H, m), 9.00-9.36 (2H, m) and 9.86 (3H, t, J 4 Hz).

<u>(3-Chloropropyl)dimethylsilane.</u>- (3-Chloropropyl)-dimethylchlorosilane (17.1 g., 0.1 mol.) was reduced with lithium aluminium hydride (0.95 g., 0.025 mol.) in anhydrous diethyl ether (50 ml.). Yield 9.0 g., 66%, b.p. 134-136°, ^1H n.m.r. τ 5.92-6.34 (1H, m), 6.54 (2H, t, J 7 Hz), 7.98-8.40 (2H, m), 9.13-9.40 (2H, m) and 9.91 (6H, d, J 4.5 Hz).

<u>(3-Iodopropyl)dimethylsilane.</u>- A mixture of (3-chloropropyl)dimethylsilane (8.0 g., 0.058 mol.), sodium iodide (36 g., 0.24 mol.) and anhydrous acetone (150 ml.) were refluxed for 24 h. The products were filtered, concentrated, water was added and the lower layer was dried ($MgSO_4$) and distilled. Yield 8.4 g., 64%, b.p. 179-181°, ^1H n.m.r. τ 5.90-6.30 (1H, m), 6.84 (2H, t, J 7 Hz), 7.89-8.34 (2H, m), 9.14-9.44 (2H, m) and 9.91 (6H, d, J 4.5 Hz).

<u>(Dimethylsilylmethyl)trimethylsilane.</u>- The Grignard reagent from (bromomethyl)dimethylsilane was prepared by reaction of the halide (5 g., 0.027 mol.) with magnesium (1.5 g., 0.062 mol.) in dry diethyl ether (20 ml.). Trimethylchlorosilane (1.45 g., 0.013 mol.) was added and the mixture refluxed for 14 h. Work up in the usual fashion gave the product. Yield 1.8 g., 90%, b.p. 120° (lit.,[127] b.p. 120°/751 mm.), ^1H n.m.r. τ 5.79-6.00 (1H, m), 9.89 (6H, d, J 3 Hz), 9.92 (9H, s) and 10.22 (2H, d, J 4 Hz).

(3-Dimethylsilylpropyl)propyldimethylsilane.- Preparation was effected by reaction of (3-dimethylsilyl)propylmagnesium iodide (0.02 mol.) with propyldimethylchlorosilane[128] (0.02 mol.) in anhydrous diethyl ether (50 ml.). Yield 0.4 g., 10%, b.p. 194-196°, ^{1}H n.m.r. τ 5.88-6.13 (1H, m), 8.30-9.60 (13H, m), 9.91 (6H, d, J 2.5 Hz) and 9.92 (6H, s).

Ethyldiphenylsilane.- This was prepared by reduction of ethyldiphenylchlorosilane (24.7 g., 0.1 mol.) with lithium aluminium hydride (1.9 g., 0.05 mol.) in dry diethyl ether (50 ml.). Yield 19.1 g., 90%, b.p. 120°/1 mm. (lit.,[129] b.p. 119.8°/1 mm.), ^{1}H n.m.r. τ 2.25-2.70 (10H, m), 5.03-5.18 (1H, m) and 8.91 (5H, s).

(2-Bromoethyl)diphenylsilane.- (2-Bromoethyl)diphenylchlorosilane (8.56 g., 0.027 mol.) in dry diethyl ether (20 ml.) was slowly added to a slurry of lithium aluminium hydride (0.27 g., 0.007 mol.) in dry diethyl ether (10 ml.). After reflux (0.25 h.), hydrolysis and concentration under vacuum, the products were chromatographed on silica gel using benzene as eluant to give the silane as a clear oil. Yield 4.5 g., 58%, ^{1}H n.m.r. τ 2.22-2.84 (10H, m), 5.00-5.14 (1H, m), 6.35-6.65 (2H, m) and 7.95-8.30 (2H, m).

(Bromomethyl)methylphenylsilane.- Phenylmagnesium bromide (0.27 mol.) in dry diethyl ether (110 ml.) was added dropwise to a solution of (bromomethyl)methyldichlorosilane[124] (50 g., 0.27 mol.) in dry diethyl ether (20 ml.) cooled to 0°. After addition the products were refluxed (0.5 h.), 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 lithium aluminium hydride (2.5 g., 0.066 mol.) in dry diethyl ether (100 ml.). Hydrolysis followed by vacuum fractionation afforded the product. Yield 41.2 g., 71%, b.p. 64-66°/0.5 mm., ^{1}H n.m.r. τ 2.30-3.03 (5H, m), 5.42 (1H, sept., J 4 Hz), 7.55 (2H, d, J 2.5 Hz) and 9.63 (3H, d, J 4 Hz).

<u>(Bromomethyl)trichlorosilane.</u>- Methyltrichlorosilane (500 g., 3.35 mol.) was placed in a 1L photochemical reactor equipped with a Hanovia u.v. lamp, dropping funnel, condenser and gas inlet. Bromine (133.8 g., 1.67 mol.) was allowed to drop into the irradiated liquid as chlorine was allowed to bubble through at a brisk rate. Irradiation was maintained until the deep red colour of bromine had been completely discharged. Fractionation gave the product. Yield 25 g., 3.3%, b.p. 130-132°, ^{1}H n.m.r. τ 7.10 (2H, s).

<u>(Bromomethyl)diphenylsilane.</u>- Phenylmagnesium bromide (0.213 mol.) in diethyl ether (150 ml.) was added dropwise to (bromomethyl)trichlorosilane (24.5 g., 0.107 mol.) in diethyl ether (20 ml.). 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 lithium aluminium hydride (1.41 g., 0.037 mol.) in dry diethyl ether (70 ml.) and after work up in the usual fashion the product was isolated by vacuum distillation. Yield 14.34 g., 49%, b.p. 139-140°/1 mm., ^{1}H n.m.r. τ 2.23-3.03 (10H, m), 4.81 (1H, t, J 2.5 Hz) and 7.32 (2H, d, J 2.5 Hz).

(Iodomethyl)(dimethylsilylmethyl)dimethylsilane.- Dimethylsilylmethylmagnesium bromide (0.42 mol.) in tetrahydrofuran (200 ml.) was refluxed with triphenylchlorosilane (50 g., 0.17 mol.) for 4 h. The products were then cooled and a solution of iodine (31.75 g., 0.25 mol.) in dry tetrahydrofuran (50 ml.) was slowly added. Hydrolysis and fractionation gave the product. Yield 6.0 g., 14%, b.p. 75-78^{o}/10 mm., ^{1}H n.m.r. τ 5.77-6.14 (1H, m), 7.90 (2H, s), 9.70-10.00 (12H, m) and 10.27 (2H, d, J 4 Hz).

Reaction of hydrosilyl Grignard reagents with chlorosilanes.- The individual reactions and products are summarised in Tables 6 and 7. The general procedure is illustrated by the reaction of dimethylsilylmethylmagnesium chloride 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 dimethylsilylmethylmagnesium chloride.- A solution of dimethylsilylmethylmagnesium chloride in dry diethyl ether (20 ml.) was prepared from magnesium (1.46 g., 0.06 mol.) and (chloromethyl)dimethylsilane (6.52 g., 0.06 mol.). A solution of triphenylchlorosilane (5.89 g., 0.02 mol.) in dry diethyl ether (30 ml.) was run in and two thirds of the solvent was removed by distillation under nitrogen. The mixture was then refluxed for 24 h., cooled and hydrolysed with 10% ammonium chloride solution (15 ml.). Diethyl ether (20 ml.) was added and the aqueous phase was separated. This layer was extracted with ether (3 x 15 ml.) and the combined ether layers were dried ($MgSO_4$) and fractionated. This afforded (dimethylsilylmethyl)trimethylsilane 2.74 g., 80%, b.p. 119-121° (lit.,[127] b.p. 120°/751 mm.); the ^1H n.m.r. spectrum was identical with that of the previously prepared sample; ν_{max} (liq. film) 2109 (Si-H), 1251 and 850 ($SiMe_3$) cm.$^{-1}$; the mass spectrum showed a weak parent ion m/e 146 (1%), m/e (main peaks) 145 ($C_6H_{17}Si_2^+$, 9%), 131 ($C_5H_{15}Si_2^+$, 100%) and 73 ($C_3H_9Si^+$, 71%). The residue was chromatographed on silica gel and eluted first with light petroleum-benzene 5 : 1 to give triphenylsilane 4.1 g., 91%, m.p. 32-34° (lit.,[120] m.p. 36-37°), ^1H n.m.r. τ 2.22-2.87 (15H, m) and 4.43 (1H, s), 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 $Me_2SiH(CH_2SiMe_2)_nCH_2SiMe_3$ $n \geqslant 1$. Yield 0.58 g., 20%; the mass spectrum showed characteristic (M-15) ions at m/e 347 ($C_{14}H_{39}Si_5^+$, 1%), 275 ($C_{11}H_{31}Si_4^+$, 29%) and 203 ($C_8H_{23}Si_3^+$, 100%). Elution with diethyl ether afforded triphenylsilanol. Yield 0.28 g., 5%, m.p. 149-151° (lit.,[130] m.p. 153-154°), ^1H n.m.r. τ 2.10-2.71 (15H, m) and 7.55 (1H, s), ν_{max} (KBr disc) 3360 (Si-OH) and 1435 and 1110 (Si-Ph) cm.$^{-1}$

(b) With dimethyldeuteriosilylmethylmagnesium bromide.- (Dimethyldeuteriosilylmethyl)trimethylsilane was isolated by fractionation. Yield 0.88 g., 60%, b.p. 118-120°, ^1H n.m.r. τ 9.89 (6H, s), 9.92 (9H, s) and 10.22 (2H, s); the mass spectrum showed a weak parent ion m/e 147 (1%), m/e (main peaks) 145 ($C_6H_{16}DSi_2^+$, 4%), 132 ($C_5H_{14}DSi_2^+$, 100%)

and 73 ($C_3H_9Si^+$, 43%). Chromatographing the residue on silica gel using light petroleum-benzene 5 : 1 as eluant afforded triphenyldeuteriosilane. Yield 1.49 g., 66%, 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.

<u>(c) With dimethylsilylmethylmagnesium bromide and termination with deuterium oxide.</u>- Distillation gave (dimethylsilylmethyl)dimethyldeuteriomethylsilane. Yield 2.05 g., 70%, b.p. 118-120°, ^{1}H n.m.r. τ 5.79-6.00 (1H, m), 9.89 (6H, d, J 3 Hz), 9.92 (8H, s) and 10.22 (2H, d, J 4 Hz); the mass spectrum showed a weak parent ion m/e 147 (1%), m/e (main peaks) 146 ($C_6H_{16}DSi_2^+$, 7%), 132 ($C_5H_{14}DSi_2^+$, 100%) and 74 ($C_3H_8DSi^+$, 50%). The residue was chromatographed on silica gel using light petroleum-benzene 5 : 1 as eluant to give triphenylsilane. Yield 3.44 g., 76%, m.p. 32-34°, ν_{max} (liq. film) 2120 (Si-H) and 1435 and 1110 (Si-Ph) cm^{-1}; absorption at 1545 (Si-D) cm^{-1} was completely absent.

<u>(d) With methylsilylmethylmagnesium bromide prepared from magnesium turnings.</u>- (Methylsilylmethyl)dimethylsilane was isolated by fractionation. Yield 2.85 g., 58%, b.p. 70-72° (lit.,[52] 62°/230 mm.), ^{1}H n.m.r. τ 5.83-6.32 (3H, m), 9.83-10.05 (9H, m) and 10.25 (2H, m). The remaining products were chromatographed on silica gel using light petroleum-benzene 5 : 1 as eluant to give a mixture of triphenylsilane. Yield 3.9 g., 75% and (dimethylsilylmethyl) triphenylsilane. Yield 0.80 g., 12% (yields estimated by n.m.r. analysis), ^{1}H n.m.r. τ 2.20-2.85 (15H, m), 5.96-6.23

(1H, m), 9.30-9.48 (2H, m) and 10.02-10.22 (6H, m).

<u>(e) With methylphenylsilylmethylmagnesium bromide.</u>- The concentrated reaction products were chromatographed on silica gel and eluted with light petroleum-benzene 5 : 1 to give (methylphenylsilylmethyl)dimethylphenylsilane. Yield 4.4 g., 80% (clear oil), ^{1}H n.m.r. τ 2.27-3.00 (10H, m), 5.37-5.64 (1H, m) and 9.68-9.97 (11H, m); the mass spectrum showed a weak parent ion m/e 270 (3%), m/e (main peaks) 255 ($C_{15}H_{19}Si_2^+$, 30%), 192 ($C_{10}H_{17}Si_2^+$, 53%) and 177 ($C_9H_{14}Si_2^+$, 100%). Further elution with the same solvent mixture afforded triphenylsilane. Yield 4.0 g., 78%.

<u>(f) With diphenylsilylmethylmagnesium bromide.</u>- The products were chromatographed on silica gel using light petroleum-benzene 9 : 1 as eluant to give methyldiphenylsilane. Yield 8.1 g., 190% (based on chlorosilane), ^{1}H n.m.r. τ 2.24-2.85 (10H, m), 5.00 (1H, quart., J 4 Hz) and 9.42 (3H, d, J 4 Hz). Elution with diethyl ether gave triphenylsilanol. Yield 5.42 g., 98%.

<u>(g) With (2-diphenylsilyl)ethylmagnesium bromide.</u>- Elution of the concentrated products on silica gel with light petroleum-benzene 9 : 1 afforded a mixture of ethyldiphenylsilane (90%) and triphenylsilane (50%) (yields estimated by n.m.r. analysis). Elution with benzene afforded (2-diphenylsilylethyl)ethyldiphenylsilane. Yield 7.6 g., 90%, ^{1}H n.m.r. τ 2.35-2.90 (20H, m), 5.02-5.24 (1H, m) and 8.27-9.30 (9H, m).

<u>(h) With (3-dimethylsilyl)propylmagnesium iodide.</u>- The products were concentrated by fractionation and propyldimethylsilane (trace) and (3-dimethylsilylpropyl)propyl-

dimethylsilane (35%) were identified by g.l.c. The yield of triphenylsilane (62%) was estimated by n.m.r. analysis.

(i) With isobutylmagnesium bromide.- Column chromatography of the products on silica gel using light petroleum-benzene 4 : 1 gave isobutyltriphenylsilane. Yield 5.81 g., 92%, m.p. 71-72° (lit.,[131] m.p. 74.5-75°), ^{1}H n.m.r. τ 2.32-2.82 (15H, m), 8.03 (1H, septet, J 7 Hz), 8.61 (2H, d, J 7 Hz) and 9.10 (6H, d, J 7 Hz). The presence of trace quantities of triphenylsilane (4%) were detected by n.m.r. analysis (singlet absorption τ 4.55) and by g.l.c.

(j) With n-propylmagnesium bromide and dimethylphenylsilane.- Triphenylchlorosilane (5.89 g., 0.02 mol.), dimethylphenylsilane (2.72 g., 0.02 mol.) and n-propylmagnesium bromide (0.02 mol.) in dry diethyl ether (5 ml.) were refluxed for 24 h. The complete absence after work up of triphenylsilane was demonstrated by n.m.r. analysis. n-Propyltriphenylsilane and triphenylsilanol were the only products derived from the triphenylchlorosilane.

(k) With n-propylmagnesium bromide and triethylsilane.- Using essentially the above procedure the reactants were refluxed for 24 h. The absence of triphenylsilane was established by n.m.r. analysis.

Dimethylsilylmethylmagnesium bromide (a) with methyldiphenylchlorosilane.- (Dimethylsilylmethyl)trimethylsilane was isolated by fractionation. Yield 1.0 g., 43%, b.p. 116-119°. The residue was chromatographed on silica gel using light petroleum as eluant to give methyldiphenylsilane. Yield 1.94 g., 49%, ^{1}H n.m.r. τ 2.21-2.77 (10H, m), 4.93 (1H, quart., J 4 Hz) and 9.44 (3H, d, J 4 Hz). Further elution with light petroleum afforded (dimethylsilylmethyl)-methyldiphenylsilane. Yield 2.38 g., 44%, ^{1}H n.m.r. τ 2.17-2.85 (10H, m), 5.70-6.05 (1H, m), 9.40 (3H, s), 9.72-10.05 (6H, m) and 10.07-10.27 (2H, m).

(b) With trimethylchlorosilane and termination with deuterium oxide.- Fractionation afforded a mixture of (dimethylsilylmethyl)trimethylsilane and (dimethylsilylmethyl)-dimethyldeuteriomethylsilane. Yield 2.13 g., 73%, b.p. 119-121°. The relative yields of the two products were estimated from mass spectral peak intensities at m/e values of 131 and 132 due to (M-15) ions. Intensities were corrected for ^{29}Si natural abundance and for loss of (M-16) from (dimethylsilylmethyl)dimethyldeuteriomethylsilane.

(c) With triphenylmethoxysilane.- Work up after the normal 24 h. reaction period afforded only unreacted triphenylmethoxysilane and Grignard self coupling products $Me_2SiH(CH_2SiMe_2)_nCH_2SiMe_3$ $n \geqslant 0$ (yield 14% estimated by n.m.r. analysis).

Reaction of (bromomethyl)methylsilane with magnesium in diethyl ether.- A solution of (bromomethyl)methylsilane (4.0 g., 0.029 mol.) in anhydrous diethyl ether (15 ml.) was added to a stirred slurry of magnesium (0.97 g., 0.04 mol.) and anhydrous diethyl ether (5 ml.). After addition the products were refluxed with stirring for 0.5 h., hydrolysed, dried ($MgSO_4$) and concentrated by fractionation. Acetone (0.5 g., internal standard) was added and a yield of 44% of self coupling Grignard products was estimated by accurate integration of the n.m.r. spectrum of the reaction products.

Kinetic procedure.-

Dimethylsilylmethylmagnesium bromide with triphenylchlorosilane (initial concentrations equal).- The rate of reaction of triphenylchlorosilane with dimethylsilylmethylmagnesium bromide was monitored by observing the change in intensity of the i.r. absorption band of triphenylsilane at 2120 cm.$^{-1}$ Dimethylsilylmethylmagnesium bromide was prepared by the reaction of (bromomethyl)dimethylsilane (9.79 g., 0.064 mol.) with magnesium (1.71 g., 0.07 mol.) in anhydrous tetrahydrofuran (35 ml.). The precise concentration of the Grignard reagent was determined using a previously described method.[132] Kinetic runs were carried out in a constant temperature bath controlled to 60.00° ± 0.025°. The reactants, dimethylsilylmethylmagnesium bromide (0.017 mol.) and triphenylchlorosilane (4.96 g., 0.017 mol.) in dry tetrahydrofuran (10 ml.) 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 i.r. spectroscopy using cells of constant thickness. The percentage transmission at 2120 (Si-H) and 3080 (C-H) cm^{-1} were 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 tetrahydrofuran (15 ml.) as diluting solvent and rate plots for the formation of triphenylsilane were constructed.

Dimethylsilylmethylmagnesium 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 by a gas evolution method devised by Gilman.[133] A solution of triphenylchlorosilane (9.6 g., 0.032 mol.) in anhydrous tetrahydrofuran (50 ml.) was mixed with a solution of dimethylsilylmethylmagnesium bromide (0.0039 mol.) in dry tetrahydrofuran (4 ml.) in a magnetically stirred reaction vessel immersed in a constant temperature bath controlled to 35° ± 0.025°. Samples were removed at intervals and hydrolysed with dilute hydrochloric acid and the volume of trimethylsilane evolved was measured. The procedure was repeated using tetrahydrofuran (27 ml.) as diluting solvent and rate plots were constructed.

(2-Diphenylsilyl)ethylmagnesium bromide and triphenylchlorosilane (initial concentrations equal).- (2-Diphenylsilyl)ethylmagnesium bromide (0.017 mol.), triphenylchlorosilane (4.97 g., 0.017 mol.) and anhydrous tetrahydrofuran (16 ml.) were mixed 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 n.m.r. spectroscopy. The relative intensities of absorptions at τ 4.55 (Si-H of Ph_3SiH) and τ 5.00-5.25 (Si-H of other products) were measured accurately and the degree of reduction to give triphenylsilane was determined. The process was repeated using tetrahydrofuran (27 ml.) as diluent and rate plots were constructed in the normal fashion.

Self coupling of dimethylsilylmethylmagnesium bromide.- Di-n-butyl ether (2.0 ml., 0.012 mol.), diphenyl ether (2.0 ml., 0.014 mol.) and dimethylsilylmethylmagnesium bromide (0.028 mol.) in tetrahydrofuran (20 ml.) were mixed under nitrogen and immersed in a constant temperature bath controlled to $60.00^{\circ} \pm 0.025^{\circ}$. Samples were withdrawn at appropriate time intervals and analysed quantitatively by g.l.c. for (dimethylsilylmethyl)trimethylsilane using di-n-butyl ether as internal standard. Samples were then concentrated under vacuum and analysed for $Me_2SiH(CH_2SiMe_2)_nCH_2SiMe_3$ $n \geqslant 1$ by n.m.r. using diphenyl ether as internal standard.

Grignard association studies.- The degree of association of dimethylsilylmethylmagnesium bromide at various concentrations in tetrahydrofuran was determined using the modified Cottrell's apparatus designed by Ashby and Walker.[69] The apparatus was purged with nitrogen and dry tetrahydrofuran (50 ml.) was added via a syringe. The temperature reading on the Beckman thermometer was noted at the boiling point of the pure solvent. Suitable volumes of a 1.33 molar solution of dimethylsilylmethylmagnesium bromide in tetrahydrofuran were added via a syringe and boiling point changes were noted. The degree of association was calculated using the expression.

$$i = \frac{W_2M_1}{W_1M_2}\left[\frac{1}{e^{\Delta T_B M_1/1000K_B} - 1}\right]$$

Where W_1 is the weight of solvent, W_2 is the weight of solute, M_1 is the molecular weight of the solvent, M_2 is the formula weight of the solute, $\triangle T_B$ the boiling point elevation and K_B the molal boiling point elevation constant. The latter was determined at the operating pressure using a number of solutes of known molecular weight.

(iv) The Reaction of Hydrosilyl Grignard Reagents with Carbonyl Compounds

Reagents.- Magnesium was supplied by New Metals and Chemicals Ltd. and had a purity of 99.975%. Reagent grade benzophenone was recrystallised twice from 95% ethanol and distilled under vacuum, b.p. 88°/0.05 mm.; g.l.c. analysis indicated a purity of at least 99.95%.

The following were prepared using previously outlined methods, (chloromethyl)trimethylsilane,[123] b.p. 81-82° (lit.,[123] b.p. 81.5°/732 mm.), ^{1}H n.m.r. τ 7.28 (2H, s) and 9.87 (9H, s); benzhydryloxytrimethylsilane,[134] b.p. 124-125°/2 mm. (lit.,[134] b.p. 124-124.5°/2 mm.), ^{1}H n.m.r. τ 2.50-2.95 (10H, m), 4.20 (1H, s) and 9.95 (9H, s); (2-trimethylsilylethyl)trimethylsilane,[135] b.p. 150-152° (lit.,[136] b.p. 151-152°/761 mm.), ^{1}H n.m.r. τ 9.63 (4H, s) and 10.03 (18H, s); hexamethyldisiloxane,[137] b.p. 98-99° (lit.,[138] b.p. 98.5°/760 mm.).

(Bromomethyl)methyldideuteriosilane.- Lithium aluminium deuteride (2 g., 0.048 mol.) was added to a solution of (bromomethyl)methyldichlorosilane[124] (20 g., 0.096 mol.) in anhydrous diethyl ether (70 ml.) and the mixture was refluxed for 0.5 h. Yield 6.58 g., 55%, b.p. 78-80°, ^{1}H n.m.r. τ 7.44 (2H, s) and 9.67 (3H, s).

Reaction of hydrosilyl Grignard reagents with ketones.- The procedure for reaction of ketones with hydrosilyl

Grignard reagents is illustrated by the addition of benzophenone to dimethylsilylmethylmagnesium bromide. For subsequent reactions brief notes are given when new products were isolated. Whenever possible involatile products were separated by column chromatography and identified by comparison of their physical properties and n.m.r. spectra with those of authentic samples. Volatile components were characterised by comparison of g.l.c. retention times with thos of authentic samples.

Benzophenone (a) with dimethylsilylmethylmagnesium bromide.- Dimethylsilylmethylmagnesium bromide was prepared by reaction of (bromomethyl)dimethylsilane (3.67 g., 0.024 mol.) with magnesium (0.73 g., 0.03 mol.) in anhydrous diethyl ether (12 ml.). A solution of benzophenone (2.19 g., 0.012 mol.) in dry diethyl ether (5 ml.) was added and reflux was maintained for 0.5 h. The products were then cooled and hydrolysed with 10% ammonium chloride solution (15 ml.); diethyl ether (10 ml.) was added and the organic phase was separated. The aqueous phase was extracted with ether (3 x 15 ml.) and the combined organic layers were dried ($MgSO_4$) and fractionated to remove most of the ether. G.l.c. analysis of the remaining products showed the presence of (dimethylsilylmethyl)trimethylsilane (12%). The vacuum concentrated reaction products were chromatographed on silica gel using light petroleum-benzene 2 : 1 as eluant. The first fraction consisted of a mixture of benzhydryloxytrimethylsilane and 1,1-diphenylethylene (the latter was characterised by g.l.c. and characteristic n.m.r. singlet absorption at τ 4.61). Further elution gave pure benzhydryloxytrimethylsilane (clear oil), ^{1}H n.m.r. τ 2.50-2.95 (10H, m), 4.20 (1H, s) and 9.95 (9H, s); the mass spectrum showed a parent ion m/e 256 (34%), m/e (main peaks) 241 ($C_{15}H_{17}OSi^+$, 17%), 179 ($C_{10}H_{15}OSi^+$, 37%), 167 ($C_{13}H_{11}^+$, 100%), 165 ($C_{13}H_9^+$, 29%) and 73 ($C_3H_9Si^+$, 49%). The product yields, 1,1-diphenylethylene (3%) and benzhydryloxytrimethylsilane (92%) were estimated by accurate integration of the n.m.r. spectrum of the reaction product mixture. Elution with diethyl ether afforded benzhydrol. Yield 0.11 g., 5%, m.p. 65-67° (from ethanol) (lit.,[139] m.p. 69°), ^{1}H n.m.r. τ 2.68 (10H, s), 4.25 (1H, s) and 6.31 (1H, s); mass spectrum M^+ 184.

(b) With dimethyldeuteriomethylmagnesium bromide.- Column chromatography afforded 1,1-diphenylethylene (3%) and deuteriobenzhydryloxytrimethylsilane (89%), ^{1}H n.m.r. τ 2.50-2.95 (10H, m) and 9.95 (9H, s); the mass spectrum showed a parent ion m/e 257 (28%), m/e (main peaks) 242 ($C_{15}H_{16}DOSi^+$, 16%), 180 ($C_{10}H_{14}DOSi^+$, 33%), 168 ($C_{13}H_{10}D^+$, 100%), 166 ($C_{13}H_8D^+$, 28%) and 73 ($C_3H_9Si^+$, 43%). Relative yields were estimated by accurate integration of the n.m.r. spectrum of the reaction product mixture. Elution with diethyl ether gave deuteriobenzhydrol (7%), m.p. 66-67°, ^{1}H n.m.r. τ 2.68 (10H, s) and 6.31 (1H, s); mass spectrum M^+ 185.

(c) With dimethylsilylmethylmagnesium bromide and termination with deuterium oxide.- The following were isolated by chromatographing on silica gel; 1,1-diphenylethylene (4%) and benzhydryloxydeuteriotrimethylsilane (87%), ^{1}H n.m.r. τ 2.50-2.94 (10H, m), 4.21 (1H, s) and 9.96 (8H, s);

the mass spectrum showed a parent ion m/e 257 (27%), m/e (main peaks) 242 ($C_{15}H_{16}DSi^+$, 12%), 180 ($C_{10}H_{14}DOSi^+$, 36%), 167 ($C_{13}H_{11}^+$, 100%), 165 ($C_{13}H_9^+$, 32%) and 74 ($C_3H_8D^+$, 53%). Benzhydrol was also isolated. Yield 0.20 g., 9%, mass spectrum M^+ 184 (the absence of deuterium in the alcohol was presumably due to exchange during work up).

(d) With methylsilylmethylmagnesium bromide.- The vacuum concentrated reaction products were chromatographed on silica gel using light petroleum-benzene 9 : 1 as eluant. This yielded a mixture of 1,1-diphenylethylene (8%), benzhydryloxydimethylsilane (30%), ^1H n.m.r. τ 2.34-2.90 (10H, m), 4.08 (1H, s), 4.80-5.10 (1H, m) and 9.80 (6H, d, J 4 Hz) and a mixture of polymeric products formed from self coupling of the Grignard reagent. Elution with diethyl ether afforded benzhydrol (62%), m.p. 64-66°.

(e) With methyldideuteriosilylmethylmagnesium bromide.- Column chromatography afforded 1,1-diphenylethylene (7%), deuteriobenzhydryloxydimethyldeuteriosilane (33%), ^1H n.m.r. τ 2.34-2.90 (10H, m) and 9.80 (6H, s) and deuteriobenzhydrol (60%).

(f) With methylphenylsilylmethylmagnesium bromide.- Chromatographing the concentrated reaction products on silica gel and eluting with light petroleum-benzene 9 : 1 gave dimethylphenylsilane. Yield 2.77 g., 170% (based on benzophenone), ^1H n.m.r. τ 2.40-2.85 (5H, m), 5.46 (1H, septet, J 4 Hz) and 9.73 (2H, d, J 4 Hz). Elution with benzene afforded benzhydryloxydimethylphenylsilane (clear oil). Yield 3.58 g., 94%, ^1H n.m.r. τ 2.31-3.13 (15H, m), 4.25 (1H, s) and 9.73 (6H, s).

(g) With diphenylsilylmethylmagnesium bromide.- Reaction was effected by refluxing the Grignard reagent/ketone mixture for 12 h. The vacuum concentrated reaction products were chromatographed on silica gel using light petroleum-benzene 9 : 1 as eluant to give methyldiphenylsilane. Yield 5.13 g., 200% (based on ketone). Elution with benzene gave benzhydryloxymethyldiphenylsilane (clear oil). Yield 3.83 g., 84%, ^{1}H n.m.r. τ 2.27-3.16 (20H, m), 4.18 (1H, s) and 9.57 (3H, s).

(h) With (2-diphenylsilyl)ethylmagnesium bromide.- Elution of the concentrate with light petroleum-benzene 9 : 1 through a silica gel column afforded a mixture of ethyldiphenylsilane (67%) and vinyldiphenylsilane (95%), ^{1}H n.m.r. τ 2.30-2.90 (10H, m), 3.25-4.30 (3H, m) and 4.75-4.86 (1H, m); the relative yields were estimated by n.m.r. Elution with diethyl ether produced benzhydrol. Yield 3.49 g., 95%, m.p. 65-66° (from ethanol).

(i) With trimethylsilylmethylmagnesium chloride.- A solution of trimethylsilylmethylmagnesium chloride (0.02 mol.) was prepared in anhydrous tetrahydrofuran (12 ml.). Benzophenone (2.19 g., 0.01 mol.) in anhydrous tetrahydrofuran (5 ml.) was added and reflux was maintained for 0.5 h. A mauve colour was produced upon addition, characteristic of the presence of ketyl radicals and this persisted throughout the reaction. G.l.c. analysis of the fractionated concentrate showed tha presence of (2-trimethylsilylethyl)trimethylsilane (14%) and hexamethyldisiloxane (5%). After concentration under vacuum the residue was chromatographed on silica gel using light petroleum-benzene 1 : 1 as eluant to give a mixture of 1,1-diphenylethylene (18%), ^{1}H n.m.r. τ 2.58 (10H, s) and 4.58 (2H, s) and 2-trimethylsilyl-1,1-diphenylethylene (2.5%), ^{1}H n.m.r. τ 2.65 (10H, s), 3.80 (1H, s) and 10.08 (9H, s). The mass spectrum showed m/e (main peaks) 252 ($C_{17}H_{20}Si^+$), 237 ($C_{16}H_{17}Si^+$) and 180 ($C_{14}H_{12}^+$) consistent with a mixture of these two products. Elution with benzene gave benzopinacol. Yield 1.34 g., 73%, m.p. 189-191° (lit.,[139] m.p. 185-186°), ^{1}H n.m.r. τ 2.52-2.88 (10H, m) and 6.88 (1H, s). Elution with diethyl ether afforded a mixture of benzhydrol (1%) and (trimethylsilylethyl)diphenylcarbinol (2.5%), ^{1}H n.m.r. τ 2.45-3.03 (10H, m), 7.99 (1H, s), 8.20 (2H, s) and 9.95 (9H, s).

Reaction of dimethylsilylmethylmagnesium bromide with (a) acetophenone.- (Dimethylsilylmethyl)trimethylsilane (30%) and 1-methyl-1-phenylethylene (41%) were detected in the product mixture by g.l.c. Chromatographing the vacuum concentrated reaction products on silica gel using diethyl ether as eluant afforded 1-phenylethanol. Yield 0.72 g., 59%, ^{1}H n.m.r. τ 2.76 (5H, s), 5.31 (1H, quart., J 7 Hz), 6.40 (1H, s) and 8.65 (3H, d, J 7 Hz).

(b) With acetone.- 1,1,3,3-Tetramethyldisiloxane was isolated by fractionation.

(c) With benzoyl chloride.- Benzoyl chloride (0.70 g., 0.005 mol.) was added to dimethylsilylmethylmagnesium bromide (0.05 mol.) in dry diethyl ether (20 ml.). After reflux (0.5 h.) the products were worked up as usual and g.l.c. analysis of the concentrate showed the presence of (dimethylsilylmethyl)trimethylsilane (140% based on benzoyl chloride). Column chromatography of the vacuum concentrate on silica gel using light petroleum-benzene 4 : 1 as eluant afforded styrene 0.28 g., 54%, ^{1}H n.m.r. τ 2.54-2.90 (5H, m), 3.46-3.56 (1H, m), 4.27-4.41 (1H, m) and 4.79-4.89 (1H, m). Elution with diethyl ether gave benzyl alcohol. Yield 0.25 g., 46% (the n.m.r. spectrum and g.l.c. retention time were identicalwith those of an authentic specimen).

(d) With diphenylmethoxymagnesium bromide.- Phenylmagnesium bromide (0.01 mol.) in dry diethyl ether (6 ml.) was added dropwise to a solution of benzaldehyde (1.06 g., 0.01 mol.) in dry diethyl ether (5 ml.). After addition the products were refluxed for 0.5 h. and then a solution of dimethylsilylmethylmagnesium bromide (0.01 mol.) in dry diethyl ether (5 ml.) was run in and reflux was maintained for a further 1 h. Work up in the usual fashion gave benzhydrol. Yield 1.78 g., 97%, m.p. 65-66°.

(v) The Photolysis of Hydrosilylmethyl Grignard Reagents and their Reaction with Cuprous Chloride

Reagents.- "AnalaR" cuprous chloride was stored under vacuum over phosphorus pentoxide prior to use. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane was prepared by the method of Gilman et al,[140] b.p. 117-119° (lit.,[140] b.p. 117-119°), ^{1}H n.m.r. τ 9.78 (12H, s) and 9.97 (4H, s).

Photolysis of (a) dimethylsilylmethylmagnesium bromide.- Dimethylsilylmethylmagnesium bromide (0.02 mol.) was prepared in dry diethyl ether (12 ml.) and a large portion of the ether was removed by distillation. Dry benzene (13 ml.) was added and distillation was continued until a head temperature of 80° had been established. The Grignard solution was then cooled, made up to 15 ml. with more dry benzene, transferred to a sealed quartz tube, placed in the irradiation chamber of a Geigy weatherometer and photolysed for 48 h. After hydrolysis the products were analysed by g.l.c. and the following were shown to be present, 1,1,3,3-tetramethyl-1,3-disilacyclobutane (5%) and (dimethylsilylmethyl)-trimethylsilane (14%).

(b) (Dimethylsilylmethyl)dimethylsilylmethylmagnesium iodide.- Using essentially the above procedure 1,1,3,3-tetramethyl-1,3-disilacyclobutane (7%) was identified by g.l.c.

Reaction of cuprous chloride (a) with dimethylsilylmethylmagnesium bromide.- Dimethylsilylmethylmagnesium bromide (0.052 mol.) in anhydrous tetrahydrofuran (30 ml.) was added dropwise to a stirred slurry of cuprous chloride (5.4 g., 0.055 mol.) in dry tetrahydrofuran (20 ml.) cooled to -78°. The mixture was allowed to warm up to room temperature and reaction was observed at -25° with the deposition of a dark brown precipitate of cuprous hydride. After stirring at room temperature for 24 h. the products were hydrolysed with water and the organic phase was dried ($MgSO_4$) and fractionated. G.l.c. analysis of the concentrate showed the presence of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (4%) and (dimethylsilylmethyl)trimethylsilane (9%). N.m.r. analysis indicated that the products of the type $Me_2SiH(CH_2SiMe_2)_nCH_2SiMe_3$ $n \geqslant 1$ were present to the extent of 16%.

(b) With (dimethylsilylmethyl)dimethylsilylmethylmagnesium iodide.- Using an analogous procedure 1,1,3,3-tetramethyl-1,3-disilacyclobutane was identified by g.l.c. (5%).

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