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SOME REACTIONS OF GRIGNARD REAGENTS AND NONMETALLIC
HALIDES WITH BETA-FUNCTIONAL ORGANOSILANES.

BY

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SUMMARY

Previous studies of beta-functional organosilanes have been almost exclusively devoted to trialkylsilyl systems and their tendency to undergo extensive silicon-carbon bond cleavage. This dissertation describes some reactions of compounds of the type $\text{Ph}_n\text{Me}_{3-n}\text{SiCH}_2\text{CR}_2\text{X}$ (where $\text{X} = \text{OH}, \text{Br}$; $\text{R} = \text{H}, \text{Me}, \text{Ph}$; $n = 0-3$), especially the triphenylsilyl derivatives.

Reaction of (2-hydroxyalkyl)silanes with phosphorus tribromide and thionyl chloride was studied and migration of the silyl group from the alpha to the beta-carbon atom was observed. The accompanying fragmentation process not only increased with increasing alkyl substitution at silicon but also with increasing substitution at the beta position. An attempt was made to detect carbonium ions of the type $\text{R}_3\text{SiCH}_2\text{CH}_2^+$, proposed as intermediates in the rearrangement reaction.

Addition of Grignard reagents to (2-bromoethyl)-triphenylsilane gave not only the expected coupled products but also 1,4-bis(triphenylsilyl)butane and ethyltriphenylsilane ('exchange'). The relative yield of these products was found to be markedly dependent on the solvent and Grignard reagent employed. An investigation of the mechanism of reaction was carried out. Deuteration studies indicated that ethyltriphenylsilane was obtained not only from an organometallic intermediate ($\text{Ph}_3\text{SiCH}_2\text{CH}_2\text{MgBr}$) but also from other sources and the corresponding alkyl/aryl halide,

anticipated from a genuine halogen-metal exchange reaction, was not detected. Evidence is presented for the participation of radical intermediates and a mechanism involving single electron transfer is proposed. It is suggested that such processes may well be important in many reactions between alkyl halides and organometallic compounds.

A study of the secondary halide (2-bromopropyl)-triphenylsilane was also undertaken and both this compound and (2-bromoethyl)triphenylsilane were found to be resistant to silicon-carbon bond cleavage in protic solvents.

This work was carried out between 1968 and 1971 at the University of Aston in Birmingham. It has been done independently and has not been submitted for any other degree.

Alan J. Bourne.

Alan J. Bourne.

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I am also indebted to the Science Research Council for provision of a grant and to Dunlop Research Centre for 'leave of absence' during the period in which this work was performed.

Finally, I would like to thank my parents and those many people who in earlier years made this opportunity possible.

A.J.B.

To Christine.

'All philosophers, who find
Some favourite system to their mind
In every point to make it fit
Will force all nature to submit.'

- Thomas Love Peacock

'Headlong Hall'.

ERRATA

Page 4, line 13 - for '1-phenyl-2-chloro-2-methyl-butane' read '2-chloro-2-methyl-1-phenylbutane'.

Page 7, line 5 - for 'The latter is an example of a non-classical carbonium ion' read 'The latter is analogous to a non-classical carbonium ion'.

Page 32, line 17- for 'which not been included' read 'which have not been included'.

Page 71, line 23- for 'it is not possible to offer explanation' read 'it is not possible to offer an explanation'.

Page 107, line 3- for 'by the techniques IR, NMR and GLC' read 'by the techniques of IR, NMR and GLC'.

Page 125, line 19- for 'After drying the ethereal over' read 'After drying the ethereal solution over'.

Whenever the word 'ether' occurs unqualified in this text reference to diethyl ether is implied.

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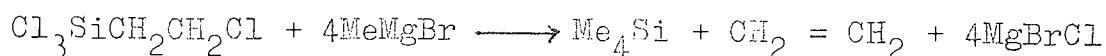
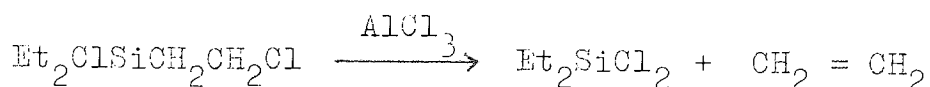
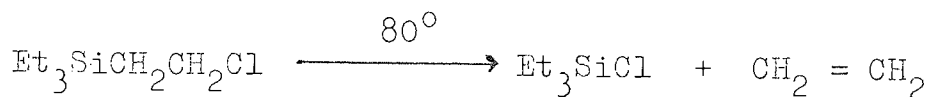
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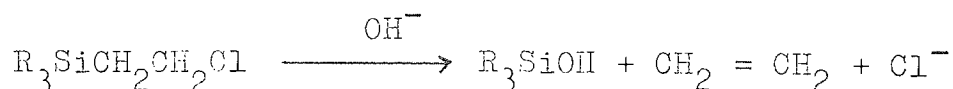
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GENERAL INTRODUCTION

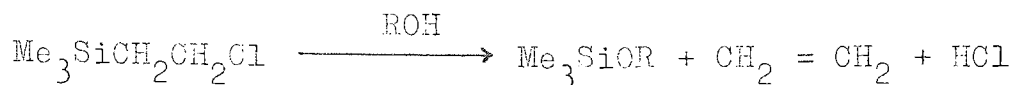
Interest in beta-functional organosilicon compounds arose because of their unusual chemical and physical behaviour. Ushakov and Itenberg¹ were the first to note the exceptional reactivity of the (2-halogenoalkyl)silanes $R_3SiCH_2CH_2X$ as compared with the R_3SiCH_2X and $R_3Si(CH_2)_3X$ compounds and with the carbon analogues $R_3CCH_2CH_2X$. The work of Sommer, Whitmore and their coworkers showed that the (2-halogenoalkyl)-trialkylsilanes were characterised by their instability and tendency to undergo fragmentation to silyl halide and olefin under the action of heat², aluminium chloride² and Grignard reagents³.



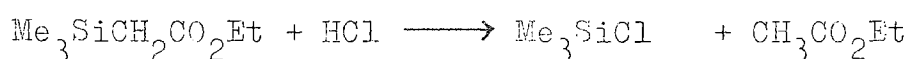
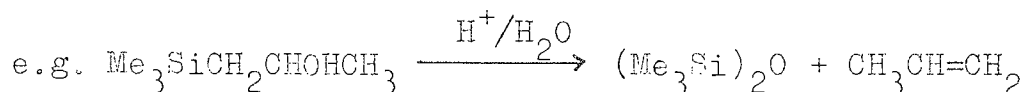
Such compounds react so rapidly with base that they may be titrated directly⁴



and are so susceptible to nucleophilic attack that they undergo fragmentation in protic solvents⁵.



Likewise, the (2-hydroxyalkyl)trialkylsilanes⁶, the corresponding esters⁷, acids⁶, ketones⁶ and cyanides⁸ (where a double or triple bond is located in a beta position to the silicon atom) readily decompose with a variety of chemical reagents.



The allylsilanes $\text{R}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ and benzylsilanes $\text{R}_3\text{SiCH}_2\text{C}_6\text{H}_5$ also show unusual spectral properties and high reactivity towards electrophilic reagents⁹.

Such anomalous behaviour is not restricted to organosilicon compounds. The corresponding compounds of lead¹⁰, germanium¹¹, tin¹⁰ and mercury¹² have similar properties. The term 'beta-effect' has been used to describe the behaviour of beta-functional organometallic compounds and Jarvie¹³ has reviewed this subject with respect to organosilicon systems. Reactions involving silicon-carbon bond cleavage have been summarised by Eaborn and Bott¹⁴.

The work described in this text is concerned with

two aspects of reactions of beta-functional organo-silanes and their mechanistic pathways.

- (1) The reaction of (2-hydroxyalkyl)silanes with thionyl chloride or phosphorus tribromide.
- (2) The reaction of (2-halogenoalkyl)silanes with Grignard reagents.

The extents of fragmentation which occur in these reactions were studied and the effect of substituting phenyl in place of alkyl groups at the silicon atom noted. During the work on reaction (2), it became apparent that the (2-bromoethyl)triphenylsilane - Grignard reagent system was particularly suitable for study of the more general reaction between Grignard compounds and alkyl halides. As a consequence, although this investigation was confined to the (2-halogenoalkyl)silanes, our sphere of interest moved from organosilicon chemistry to that of the mechanism of this more widely applicable reaction.

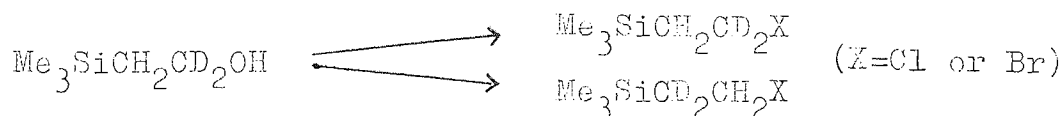
Chapter One.

REACTIONS OF (2-HYDROXYALKYL)SILANES WITH THIONYL
CHLORIDE OR PHOSPHORUS TRIBROMIDE AND A SEARCH FOR
THE 2-(TRIMETHYLSILYL)ETHYL CATION

1. Introduction

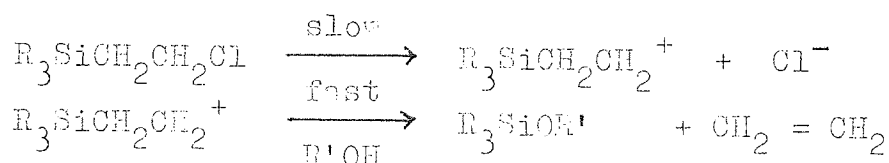
Reactions between alcohols and thionyl chloride or phosphorus tribromide are not usually considered to proceed via carbonium ion intermediates. However, in some cases rearrangements are observed which are characteristic of such ions (Wagner-Meerwein type rearrangements). Thus, thionyl chloride reacts with isopropylmethylcarbinol to give t-amyl chloride¹⁵ and with 2-methyl-2-phenylbutan-1-ol to give 1-phenyl-2-chloro-2-methylbutane¹⁶. Similar rearrangements were noted by Roberts and Mazur¹⁷ in reactions of cyclobutanol with thionyl chloride and cyclopropylcarbinol with thionyl chloride or phosphorus tribromide. Kivvila and Masterton¹⁸ in attempting to prepare cyclobutylcarbinyl bromide from cyclobutylcarbinol and phosphorus tribromide isolated some cyclopentyl bromide.

It was shown previously¹⁹ that rearrangement occurs when (2-hydroxyethyl-2,2-d₂)trimethylsilane reacts with thionyl chloride or phosphorus tribromide and that a mixture of two isomeric halides is formed.



A similar rearrangement²⁰ is observed when solvolysis of the bromide $\text{Me}_3\text{SiCH}_2\text{CD}_2\text{Br}$ by aqueous methanol is allowed to proceed to about 50% completion. In this case the recovered bromide contains $\text{Me}_3\text{SiCH}_2\text{CD}_2\text{Br}$ and $\text{Me}_3\text{SiCD}_2\text{CH}_2\text{Br}$. The solvolytic reaction is the most thoroughly studied beta-elimination involving organo-silicon compounds and the following facts which provide evidence for the type of intermediate involved have been established:-

- (1) Ionization of the carbon-halogen bond is the rate determining step followed by subsequent breaking of the silicon-carbon bond¹⁹.



Such ionization implies considerable stabilization of the intermediate carbonium ion.

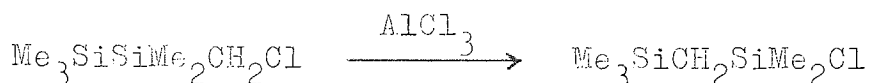
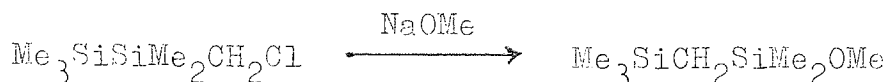
- (2) The Hammett rho factor for the solvolysis of the compounds $\text{XC}_6\text{H}_4\text{Me}_2\text{SiCH}_2\text{CH}_2\text{Cl}$ is -2.15 indicating a high positive charge at the silicon atom in the transition state²¹.
- (3) Although the kinetics of solvolysis are 1st order⁵, reaction of (erythro-1,2-dibromopropyl)trimethylsilane in aqueous ethanol results in highly stereospecific trans-elimination of bromotrimethylsilane¹⁹.

Other reactions where migration of the trimethylsilyl

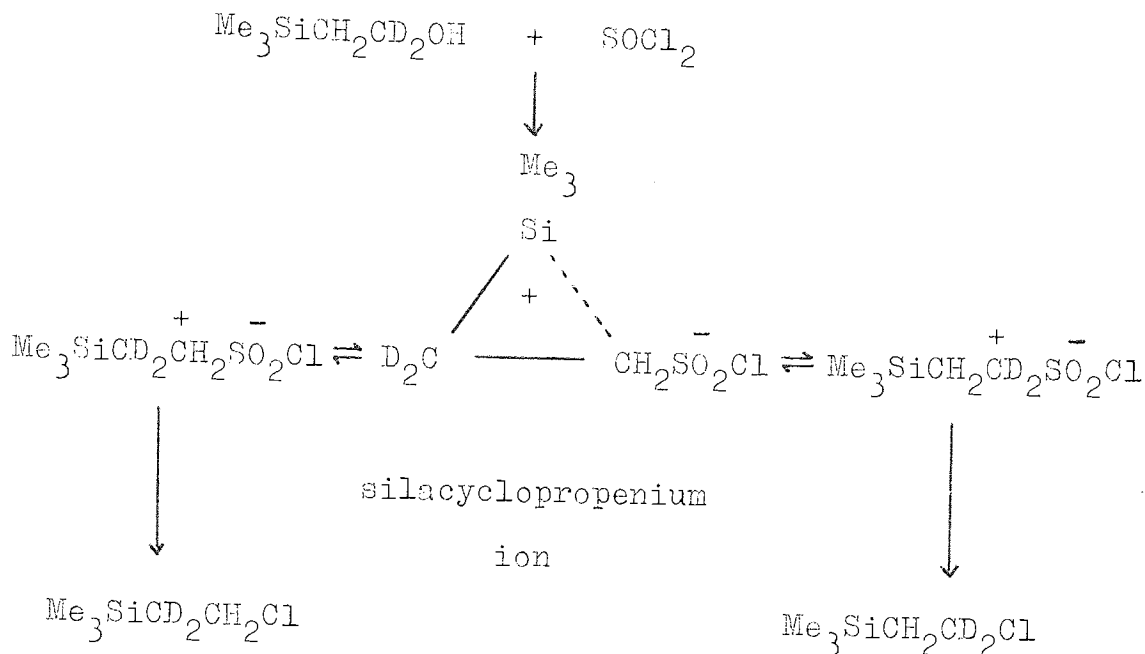
group to a beta-carbon atom occurs are known. Such a process is observed on heating acetoxymethyldisilanes²²



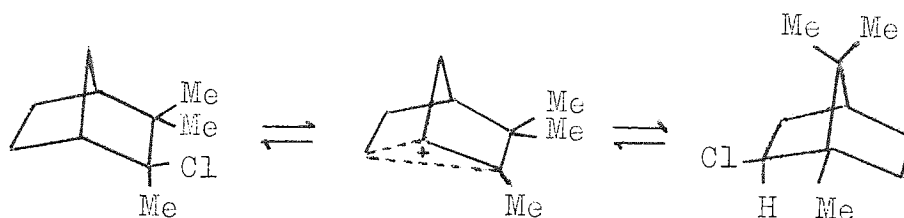
and similar rearrangements^{23,24} are induced by nucleophilic and electrophilic reagents.



It appears that all these rearrangements involving silicon are promoted by interaction between the silicon atom and the developing positive charge at the beta-carbon atom. A mechanism involving a cyclic intermediate has been proposed for the thermal rearrangement of acetoxymethyldisilanes²³ but by analogy with the $S_{\text{N}}1$ mechanism and consideration of the available evidence concerning the solvolytic reaction, Jarvie and her co-workers suggested that rearrangement of the alcohol with phosphorus tribromide and thionyl chloride might proceed by the following ion pair mechanism:-

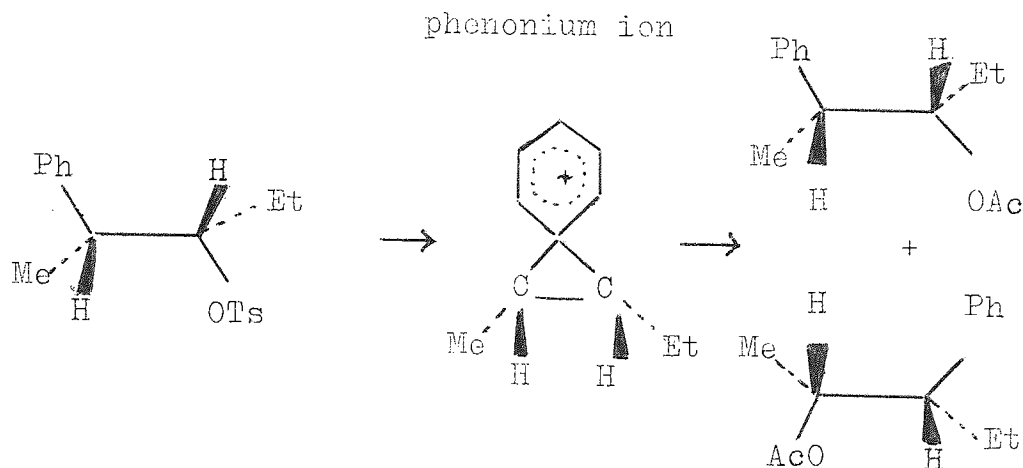


Kreevoy and Kowitz¹² have proposed a similar metal bridged ion as an intermediate in the deoxymercuration reaction and the possibility that rearrangement and solvolysis proceed via the silacyclopropenium ion intermediate seems reasonable. The latter is an example of a non-classical carbonium ion. The concept of such ions was first advanced by Nevell, de Salas and Wilson²⁵ to explain the Wagner-Meerwein type rearrangement of camphene hydrochloride to isobornyl chloride.



There has been much controversy over the existence of some bridged ions. Cram²⁶ suggested that phenonium ion intermediates might explain the enhanced rate of

acetyloysis of 2-phenylethyl tosylates and the formation of some rearranged product:-

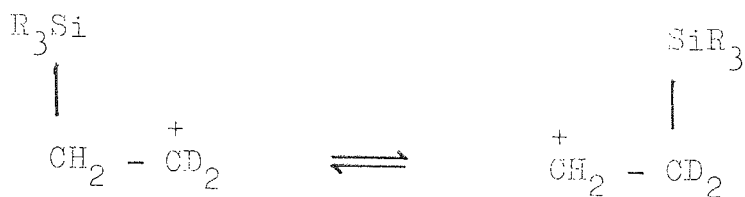


but Brown and his coworkers²⁷ have questioned the existence of such bridged ions and as an alternative have suggested rapidly equilibrating classical ions.

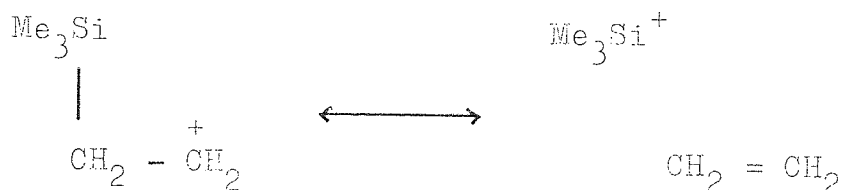


Nevertheless, non-classical carbonium ions have been suggested as intermediates in numerous reactions and the subject has been reviewed by Sargent²⁸ and by Bartlett²⁹.

In similar vein to Brown's criticism of phenonium ion participation, the silacyclopropenium ion mechanism might be rejected in favour of rearrangement proceeding through classical carbonium ions with migration succeeding ion formation.



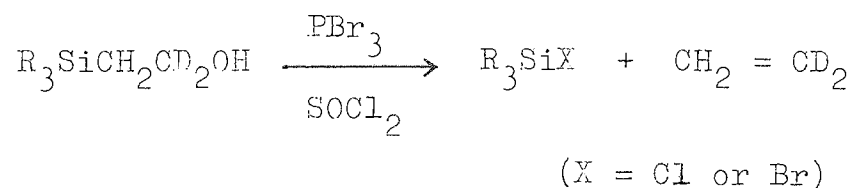
The stabilization of such ions might be partially explained by the strong electron releasing inductive effect of the Me_3SiCH_2 group (the Taft σ^* substituent = -0.26)³⁰. Stabilization might also be explained using the concept of $\sigma - \pi$ conjugation.



This type of resonance was first postulated by Nesmeyanov³¹ and has been widely used by Russian workers to explain reactivity, spectral properties and fragmentation of beta-substituted organometallic compounds. Eaborn and coworkers^{32,33} have suggested that the $\text{Me}_3\text{Si}-\text{C}$ bond is capable of considerable hyperconjugative electron release in order to explain the reactivity and the chemical shift data for compounds of the type $(\text{Me}_3\text{Si})_x \text{CH}_{3-x} \text{C}_6\text{H}_4\text{Z}$ (where $\text{Z} = \text{SiMe}_3, \text{CO}_2\text{H}, \text{CMe}_2\text{Cl}$ or ^{19}F and $x = 0 - 3$). In all cases the order of electron

release was $x = 2 > 1 > 3 > 0$ and was not solely consistent with inductive release by the trimethylsilyl group. The concept has also been discussed by Traylor and Ware³⁴. It would adequately provide an explanation for the high positive charge at silicon in the transition state of the solvolytic process but does not readily explain the stereospecific elimination which is observed. The question of the true carbonium ion intermediate remains unresolved.

Since the rearrangement reaction (irrespective of the nature of the carbonium ion intermediate) has been suggested to involve interaction of silicon with the developing positive charge at the beta-carbon atom, it was considered of interest to study whether such interaction was minimised or prevented by introduction of phenyl groups at the silicon atom. With this purpose in mind, a series of alcohols $\text{Ph}_x\text{Me}_{3-x}\text{SiCH}_2\text{CD}_2\text{OH}$ ($x = 0 - 3$) was prepared and their reactions with thionyl chloride or phosphorus tribromide studied both in terms of the rearrangement reaction and the accompanying fragmentation process



The effect of substituents at the beta-carbon atom was also investigated and in view of the apparent stability

of the carbonium ions $R_3SiCH_2CH_2^+$, an attempt was made to trap such an ion using the method of silane hydride transfer.

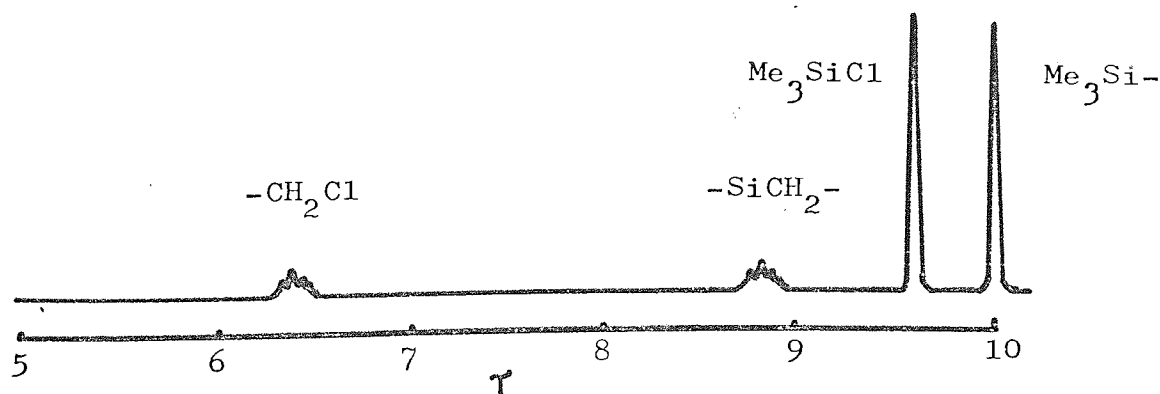
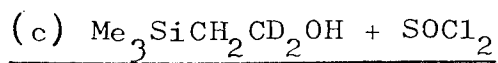
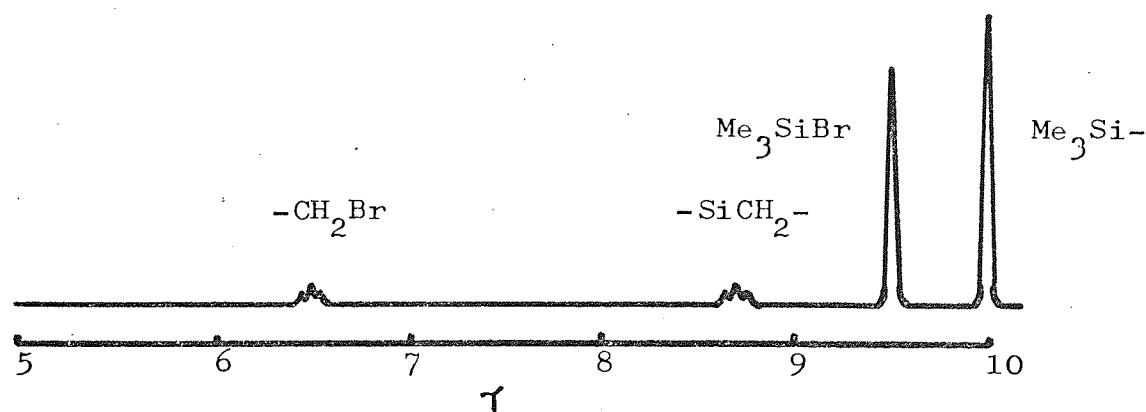
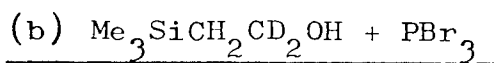
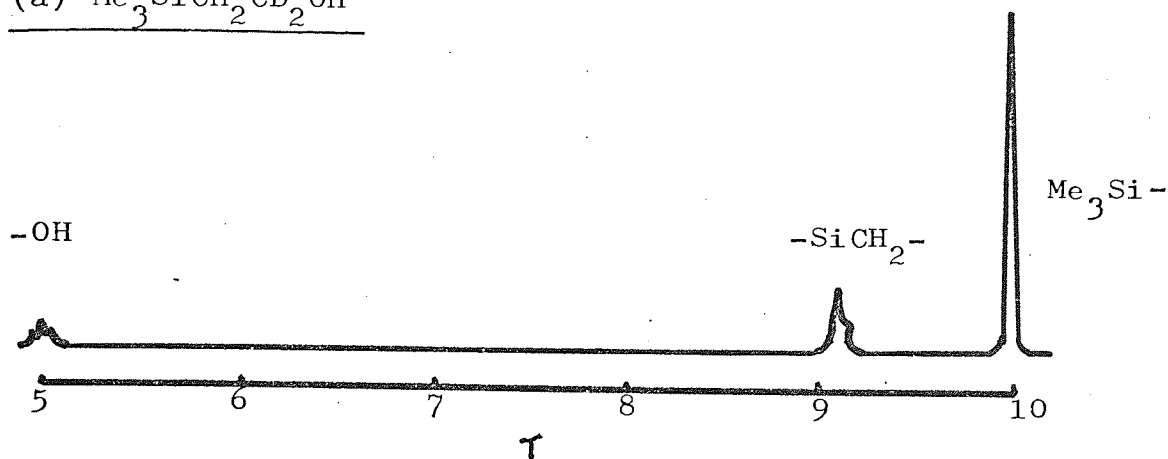
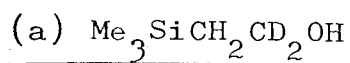
2. Rearrangement of (2-hydroxyethyl-2,2-d₂)silanes.

The reaction described by Jarvie et al¹⁹ was initially repeated and the formation of rearranged and unrearranged products ($Me_3SiCD_2CH_2X$ and $Me_3SiCH_2CD_2X$) was established by NMR spectroscopy. The alcohol $Me_3SiCH_2CD_2OH$ showed the expected methylene singlet at τ 9.1 whereas the product of reaction with thionyl chloride had two absorptions at τ 6.4 and 8.8 attributable to methylene protons adjacent to chlorine and silicon respectively. A similar reaction with phosphorus tribromide gave rise to absorptions at τ 6.5 ($-CH_2Br$) and 8.7 ($-SiCH_2-$). The peaks were broadened as is typical of deuteriated molecules but no proton spin coupling was observed. In addition to the peaks attributable to substitution products, those due to fragmentation (Me_3SiX) were also detected. The spectra of the products of these reactions are recorded in Figure 1.

Substitution of phenyl groups at the silicon atom had little effect upon the rearrangement and approximately the same relative proportions of rearranged and unrearranged products were obtained from reaction of all the primary compounds $Ph_xMe_{3-x}SiCH_2CD_2OH$ with both phosphorus tribromide and thionyl chloride. In all the

FIG.1.

NMR spectra of reactions between (2-hydroxyethyl-2,2-d₂)-trimethylsilane and phosphorus tribromide or thionyl chloride.



reactions the proportion of beta-deuteriated product $R_3SiCH_2CD_2X$ formed was slightly greater than that of the alpha-deuteriated compound $R_3SiCD_2CH_2X$. It seems likely that this product ratio reflects the relative stabilities of the ion pair intermediates.

The effect of phenyl substitution was more marked in the fragmentation reaction. In this case, introduction of successive aromatic groups at silicon decreased the elimination process and little or no fragmentation was observed with the triphenyl compound. The results of these reactions are summarised in Table I. Electron deficiency at a beta-carbon atom generally promotes cleavage of the silicon-carbon bond¹⁴ and the effect of phenyl groups in stabilizing this bond may be due to the ability of the aromatic rings to delocalise the positive charge transferred to silicon in the transition state or the effect may be partially steric in origin³⁵ (this topic will be further discussed in Chapter 3). It is possible that the extent of elimination in the methyl-substituted systems might be somewhat decreased by the initial purification of the phosphorus tribromide or thionyl chloride used. Nevertheless, since the same reagents were used throughout the series of reactions, the results obtained must reflect the relative stabilities of the systems involved. The fragmentation process may be a reaction of the (2-halogenoalkyl)silane, the (2-hydroxyalkyl)silane or the carbonium ion intermediate. However,

TABLE 1

Rearrangement and fragmentation in reaction of (2-hydroxyethyl-2,2-d₂)silanes
with phosphorus tribromide or thionyl chloride.

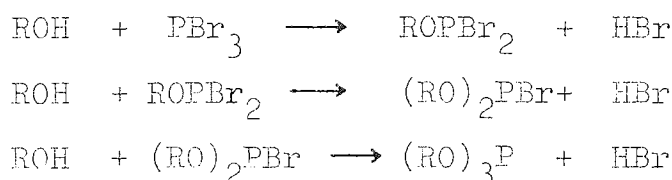
alcohol	% composition			
	SiCH ₂	CH ₂ X	fragmentation	SiCH ₂ /CH ₂ X
Reaction with thionyl chloride (X=Cl)				
Me ₃ SiCH ₂ CD ₂ OH	29	27	44	1.07
Me ₂ PhSiCH ₂ CD ₂ OH	33	29	38	1.14
MePh ₂ SiCH ₂ CD ₂ OH	38	36	26	1.06
Ph ₃ SiCH ₂ CD ₂ OH	49	47	4 ^a	1.05
Reaction with phosphorus tribromide (X=Br)				
Me ₃ SiCH ₂ CD ₂ OH	30	27	43	1.11
Me ₂ PhSiCH ₂ CD ₂ OH	31	28	41	1.11
MePh ₂ SiCH ₂ CD ₂ OH	40	36	24	1.11
Ph ₃ SiCH ₂ CD ₂ OH	33	27 ^b	0 ^a	1.22

a Determined as the difference between observed and theoretical aromatic intensities.

b Overlap of integrals at τ 8.0 permitted only approximate calculation, a third peak at τ 8.1 accounted for 40% of the total methylene absorption.

the former possibility seems unlikely since approximately the same yields of elimination products are obtained from reaction of any one of the alcohols with both thionyl chloride or phosphorus tribromide and it is known³⁶ that bromo-compounds undergo desilicohalogenation more readily than the corresponding chloro-compounds.

The reaction of the alcohol $\text{Ph}_3\text{SiCH}_2\text{CD}_2\text{OH}$ with phosphorus tribromide is worthy of comment. In addition to absorptions due to methylene protons adjacent to silicon and bromine, an additional peak at τ 8.1 was observed. This was the main absorption detected immediately after addition of the reagents and it then decreased with time whilst the other methylene absorptions increased. After about 60 min the peaks assumed a constant ratio and remained unchanged even after 7 days. The reaction between alcohols and phosphorus tribromide has been suggested by Gerrard³⁷ to proceed via the following stages:-



and it seems possible that this additional absorption may be due to one of these phosphate esters. The presence of phenyl groups on the silicon atom might tend to make such compounds more stable than the methyl-

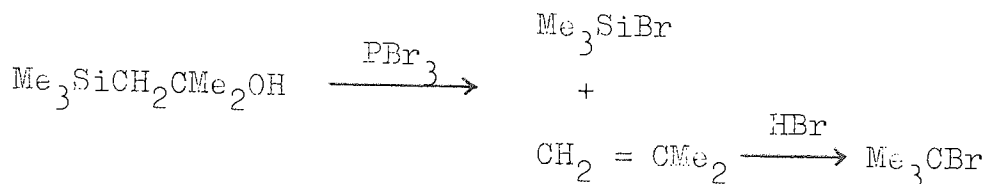
substituted analogues which probably undergo decomposition relatively quickly.

3. The effect of substituents at the beta-carbon atom.

Reaction between thionyl chloride and the secondary alcohol $\text{Ph}_3\text{SiCH}_2\text{CHMeOH}$ gave rise to the halide $\text{Ph}_3\text{SiCH}_2\text{CHMeCl}$ as principal product. The ratio of aromatic to methylene protons was slightly greater than 15/2 and this excess of aromatic absorption was assumed to be due to fragmentation and formation of chlorotriphenylsilane. The proportion of this product did not exceed 6%. Similarly, reaction with phosphorus tribromide gave $\text{Ph}_3\text{SiCH}_2\text{CHMeBr}$ with less than 7% of the breakdown product. Thus, as in the case of the primary alcohol $\text{Ph}_3\text{SiCH}_2\text{CH}_2\text{OH}$, little or no fragmentation is observed in these reactions. In contrast, the secondary compound does not give rise to the additional methylene absorption, attributed to phosphate ester, when reacted with phosphorus tribromide. The lack of rearrangement observed with the secondary alcohol would seem to be consistent with relative carbonium ion stabilities. One would expect that the ion $\text{Ph}_3\text{SiCH}_2\overset{+}{\text{C}}\text{HMe}$ is more stable than its primary isomer $\text{Ph}_3\text{SiCH}\overset{+}{\text{C}}\text{MeCH}_2$ and that rearrangement is for this reason unfavourable.

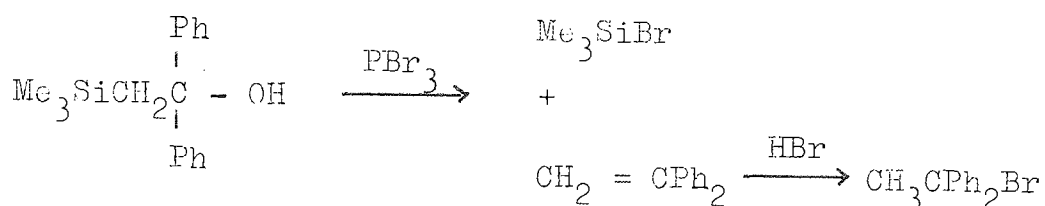
Reactions of the tertiary compounds $\text{Me}_3\text{SiCH}_2\text{CMe}_2\text{OH}$ and $\text{Me}_3\text{SiCH}_2\text{CPh}_2\text{OH}$ were also studied and in contrast to the previously described alcohols underwent complete elimination. The NMR spectrum from a reaction between

the former compound and phosphorus tribromide indicated that bromotrimethylsilane and t-butyl bromide were the only products remaining.



Reaction with thionyl chloride occurred in a similar manner and chlorotrimethylsilane and t-butyl chloride were detected. The spectra of the products of the two reactions are recorded in Figure 2.

Addition of phosphorus tribromide to the alcohol $\text{Me}_3\text{SiCH}_2\text{CPh}_2\text{OH}$ produced 1-bromo-1,1-diphenylethane and bromotrimethylsilane.

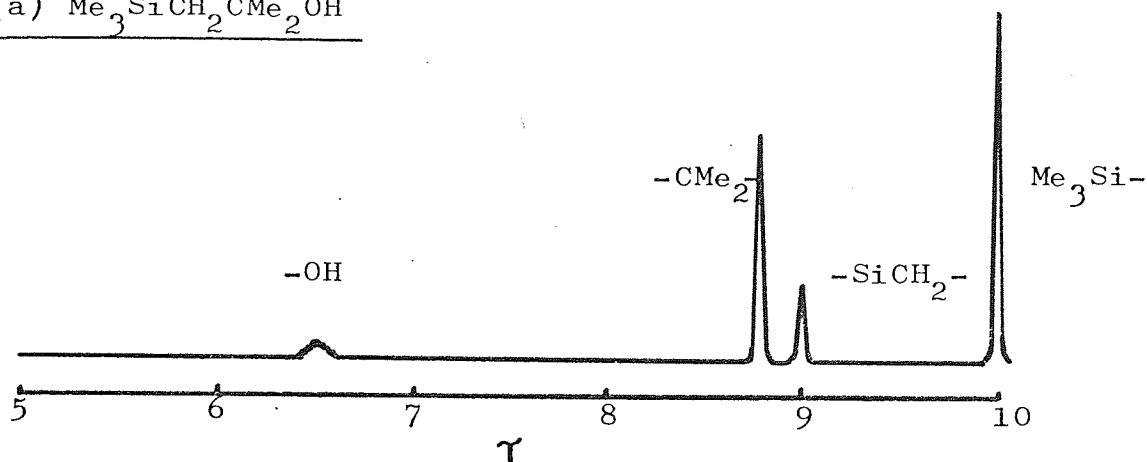


However, reaction with thionyl chloride at first appeared irregular. Further investigation indicated that initial fragmentation to 1,1-diphenylethylene had once again occurred but that instead of hydrogen chloride addition to the double bond, substitution with thionyl chloride had produced a sulphinyl chloride in a manner similar to that described by Patai et al³⁸.

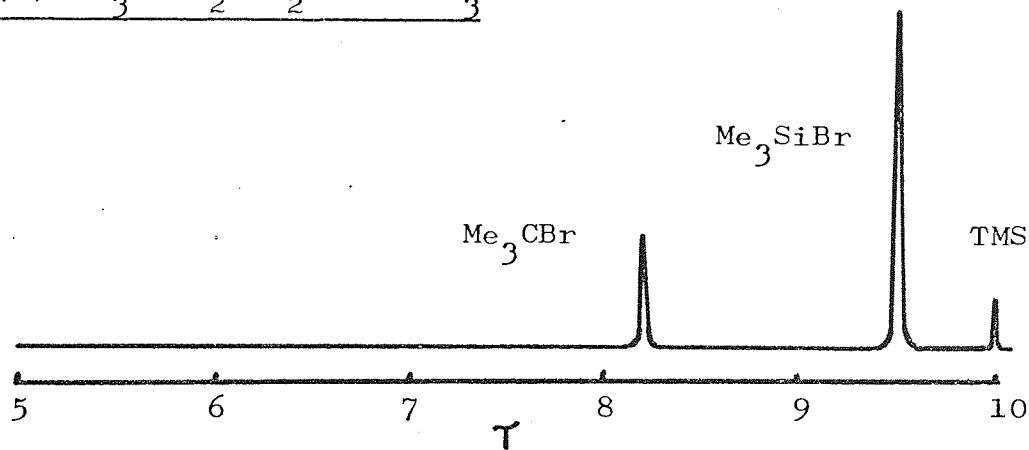
FIG. 2.

NMR spectra of reactions between (2-hydroxypropyl-2-methyl)-trimethylsilane and phosphorus tribromide or thionyl chloride

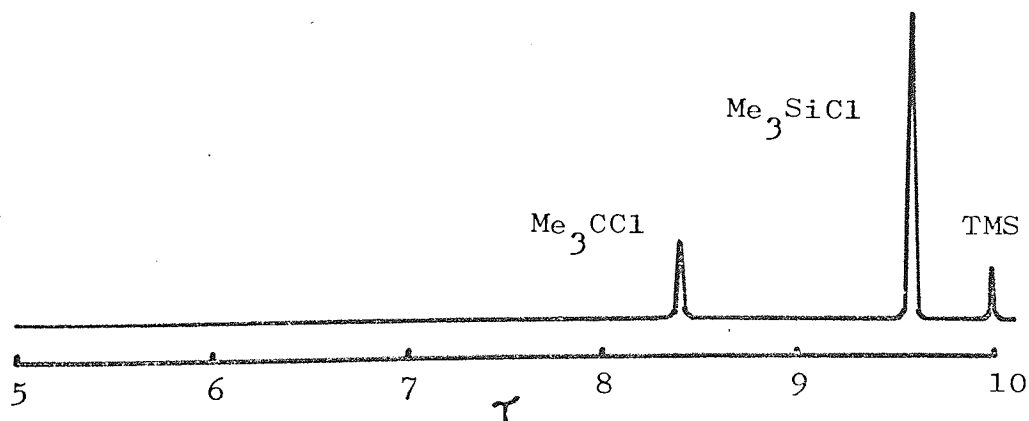
(a) $\text{Me}_3\text{SiCH}_2\text{CMe}_2\text{OH}$

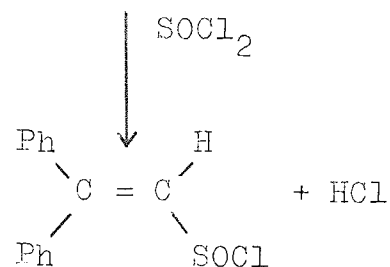
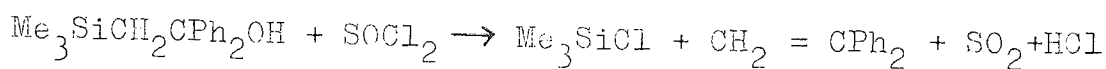


(b) $\text{Me}_3\text{SiCH}_2\text{CMe}_2\text{OH} + \text{PBr}_3$



(c) $\text{Me}_3\text{SiCH}_2\text{CMe}_2\text{OH} + \text{SOCl}_2$





The increased tendency of tertiary compounds to undergo elimination rather than substitution is commonly observed³⁹ and the explanation for this trend has been much debated. Two principal arguments have been presented. In the one case olefin formation is said to be favoured because of the relief of steric strain obtained for sp^2 hybridised carbon atoms where the bond angles are 120° as opposed to those of the substitution product which are about 109° . The alternative explanation is that the more branched cations undergo fragmentation rather than substitution because the substituents stabilize the incipient double bond of the transition state either by conjugation or hyperconjugation. Either of these explanations might be applied to our systems.

4. An attempt to trap the 2-(trimethylsilyl)ethyl cation.

Some of the more highly stabilized carbonium ions have been identified by isolation of their salts (e.g. $\text{Ar}_3\text{C}^+ \text{ClO}_4^-$) but the most widely used technique has been

detection by spectroscopic means in highly acidic media. The triarylmethyl and certain substituted allylic cations are stable in sulphuric acid solution but many of the simple aliphatic cations can only be observed in anhydrous hydrofluoric acid containing antimony pentafluoride or fluorosulphonic acid.⁴⁰ Evidence for the existence of carbonium ions under these conditions has been obtained mainly from their NMR spectra, since protons attached to a positively charged carbon atom are deshielded and consequently observed at lower field than in the neutral molecule. IR and UV spectra also provide evidence for the existence of such ions in these solutions. Most of the recorded alkyl carbonium ions are tertiary since although primary and secondary ions are formed in these media, rearrangement to the more stable tertiary ions occurs.

In view of the apparent stabilization of the carbonium ion $R_3SiCH_2CH_2^+$, it seemed possible that such an ion might be detectable under suitable experimental conditions. However, because of the inherent instability of the (2-hydroxyalkyl)trialkylsilanes the detection of these ions in highly acidic media seemed unlikely. The technique of silane hydride transfer offered obvious advantages in that carbonium ions had been detected under relatively mild conditions.

Since silicon is more electropositive than carbon, silanes are good hydride donors to carbonium ions:-

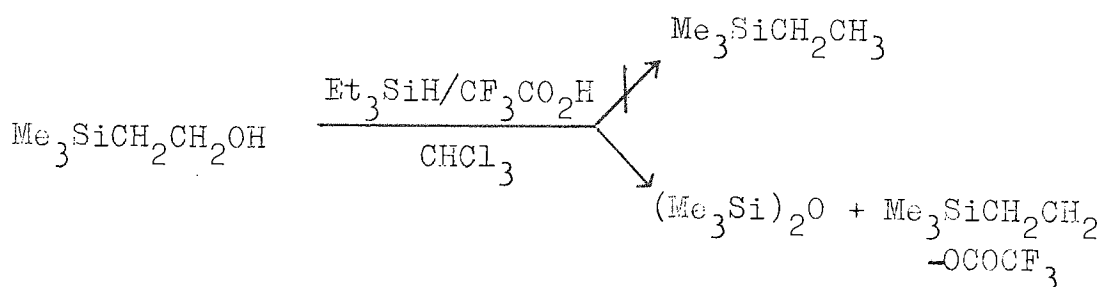


and such reactions have been used to establish formation of these ions. Thus, Whitmore et al⁴¹ obtained hexane from n-hexyl chloride, isopentane from neopentyl bromide and 2,3-dimethylbutane from neopentylcarbonyl bromide using triethylsilane in the presence of aluminium chloride (N.B. in the latter two reactions rearrangement had occurred). More recently, Carey and Trenper^{42,43,44} have used the technique in methylene chloride or chloroform by generating the carbonium ion with trifluoroacetic acid and the appropriate alcohol. In this manner, they have detected carbonium ions of the arylmethyl type, some tertiary alkyl and some cyclopropylmethyl cations. They have suggested that only those alcohols which form relatively stable carbonium ions are reduced to the corresponding alkane and that a significant concentration of free carbonium ion must be formed for transfer to occur.

It was decided to attempt a silane hydride transfer reaction using initially the trimethyl - substituted alcohol $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{OH}$ but it was thought possible that fragmentation of this compound to siloxane might necessitate the use of alcohols substituted by phenyl groups at the silicon atom for efficient reaction to occur.

Analysis of the products of a reaction performed at -15° using the alcohol, triethylsilane and trifluoroacetic acid in methylene chloride, indicated that no reaction had occurred. A similar reaction in chloro-

form gave the same results. Reaction at -5° gave a small amount of the ester $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{OCOCF}_3$ without evidence of hydride transfer or formation of hexamethyldisiloxane. Several other experiments were performed under a variety of conditions of temperature, concentration of alcohol, silane or acid and using triphenylsilane as the potential hydride donor (see Experimental, section B2). In none of these experiments was there evidence of ethyltrimethylsilane, formed by hydride transfer to the carbonium ion $\text{Me}_3\text{SiCH}_2\text{CH}_2^+$. Hexamethyldisiloxane and the trifluoroacetate ester $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{OCOCF}_3$ were the only products detected.



As might be expected the yield of siloxane increased with increasing temperature, alcohol concentration and concentration of trifluoroacetic acid. Reactions performed in the absence of silane allowed accurate determination of the relative proportions of 2-(trimethylsilyl)ethyl trifluoroacetate (ester), (2-hydroxyethyl)trimethylsilane (alcohol) and hexamethyldisiloxane (HMDS) from the NMR spectra obtained. The yield of these products in four such reactions are recorded in Table 2.

TABLE 2

Products of the reaction of (2-hydroxyethyl)trimethylsilane and trifluoroacetic acid in methylene chloride or chloroform.*

solvent	temperature	% composition		
		ester	alcohol	HMDS
CH ₂ Cl ₂	-10°	7	93	0
CH ₂ Cl ₂	R.T.	69	19	12
CHCl ₃	-10°	16	84	0
CHCl ₃	R.T.	78	17	5

*alcohol in solvent - 8% v/v.

Reaction time - 1h R.T. = room temperature.

The results indicate that a high yield of ester may be obtained under suitable experimental conditions and it seems possible that other reactions involving beta-substituted alkylsilanes might take place with less fragmentation if carried out under mild conditions.

Examination of the reaction products from the di-deuterated alcohol Me₃SiCH₂CD₂OH indicated that rearranged structures of the type Me₃SiCD₂CH₂X (X = OH, OCOF₃) had not been formed and provided additional evidence that the carbonium ion Me₃SiCH₂CD₂⁺ had not been produced under these conditions. It was concluded that reactions in these media were not sufficiently alike to those in phosphorus tribromide or thionyl

chloride to allow formation of this intermediate. It was unlikely that the triphenylsilyl systems would prove any more satisfactory and the work was discontinued.

It seems likely that a study of the reactions of phosphorus tribromide or thionyl chloride with the compounds $\text{Me}_3\text{SiCMe}_2\text{CH}_2\text{OH}$, $\text{Me}_3\text{SiCPh}_2\text{CH}_2\text{OH}$ and $\text{Ph}_3\text{SiCH}_2\text{-CMe}_2\text{OH}$ might provide additional information about the rearrangement. Attempts were in fact made to prepare the ester precursor ($\text{Me}_3\text{SiCMe}_2\text{CO}_2\text{Et}$) of the first compound but did not prove successful.

With regard to detection of carbonium ions of the type $\text{R}_3\text{SiCH}_2\overset{+}{\text{C}}\text{H}_2$, it is possible that the greater stability of the alcohol $\text{Ph}_3\text{SiCH}_2\text{CH}_2\text{OH}$ might make possible its use in strongly acid solutions and allow spectroscopic identification of such ions. It is interesting that in addition to the results described in this chapter, Gilman and Wittenberg⁴⁵ have successfully oxidised this alcohol to the corresponding acid in 20% yield using a mixture of chromic and glacial acetic acids and Gray and Davis⁴⁶ have established that the compound is completely stable in 8M acid at 60°.

Chapter Two

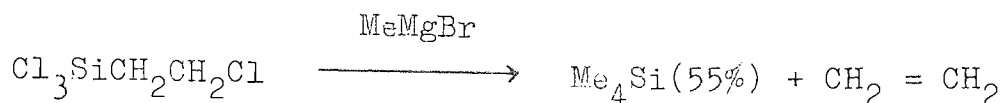
THE REACTION OF (2-HALOGENOALKYL)SILANES WITH GRIGNARD

REAGENTS

1. Introduction

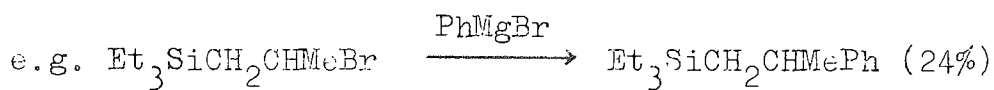
Having established that in the reaction between (2-hydroxyalkyl)silanes and thionyl chloride or phosphorus tribromide the proportion of fragmentation decreased with increasing phenyl substitution at the silicon atom, it was of interest to discover whether this behaviour was observed in other processes involving beta-functional organosilanes. Previous investigations with such compounds have been mainly confined to the trialkylsilyl systems. One of the reactions it was decided to study was that of the (2-halogenoalkyl)silanes with Grignard reagents in which the only previously recorded phenyl-substituted compound investigated was $\text{Me}_2\text{PhSiCH}_2\text{CHMeBr}$. Accordingly, the reactions of (2-halogenoalkyl)triphenylsilanes with Grignard reagents and magnesium metal were undertaken.

Sommer and his coworkers³ were the first to study reactions between Grignard compounds and (2-halogenoalkyl)silanes. They found that during the reaction of (2-chloroethyl)trichlorosilane with methylmagnesium bromide, stepwise addition of the latter proceeded smoothly to replace three chlorine atoms but that addition of a further equivalent gave ethylene and tetramethylsilane.

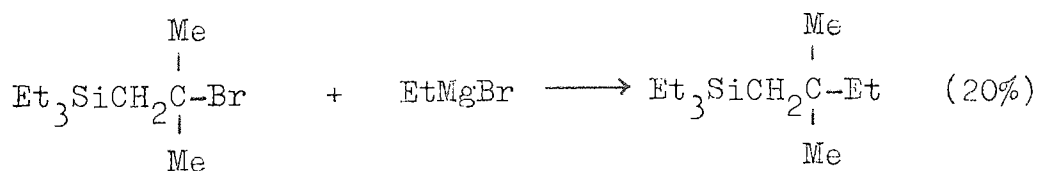


Similar fragmentation was observed using ethylmagnesium bromide and the American workers concluded that the (2-halogenoalkyl)silanes were unsuitable for Grignard-Wurtz coupling reactions.

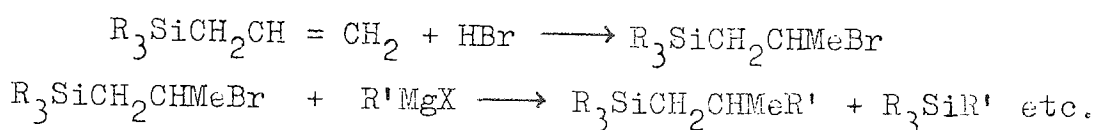
Petrov and Mironov⁴⁷ showed that this conclusion was unduly pessimistic and by choosing a suitable combination of Grignard reagent and halide obtained significant quantities of coupled products.



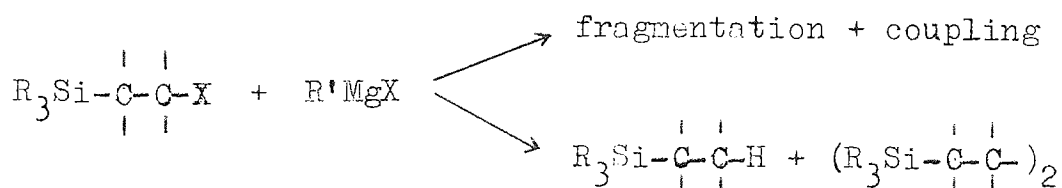
It is unfortunate that their work is marred by the use of crude starting materials and that their experimental reports lack detail. Nevertheless, since this is the only major investigation in the field, their results are worthy of note. They found that the amount of fragmentation relative to coupling was greater for bromides than chlorides and decreased in the series primary > secondary > tertiary (2-halogenoalkyl)silane. Hardly any fragmentation was said to accompany the following reaction:-



but the other products are not recorded. The Russian workers studied the behaviour of secondary (2-halogeno-alkyl)silanes in detail and determined the effect of the nature of the groups attached to silicon and the Grignard reagent employed on the coupling reaction.



Their results are summarised in Table 3. On the basis of these results, they concluded that the proportion of coupled product ($R_3SiCH_2CH_2R'$) increased as R was varied in the series Ph, Me, Et, n-Pr, n-Bu and as R' was varied in the series Et, n-Pr, Ph, $CH_2CH=CH_2$. Mironov⁹ has also reported the isolation of products which might have arisen by way of a halogen-metal exchange process but does not indicate the extent of such reactions or the systems in which they were observed.

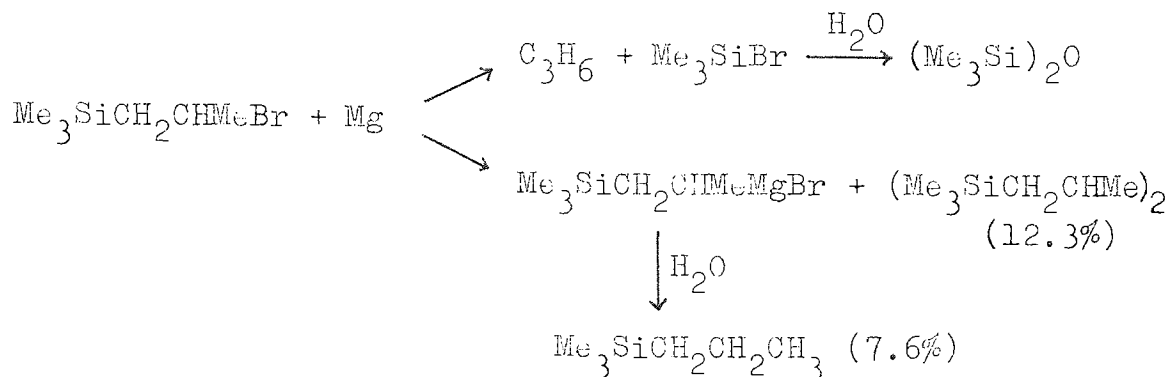


Petrov and Lavrishev⁴⁸ established that higher yields of coupled products can be obtained by using alkyl-lithium reagents in place of the Grignard compounds and that such reactions are also accompanied by the formation of by-products possibly from a halogen-metal exchange process.

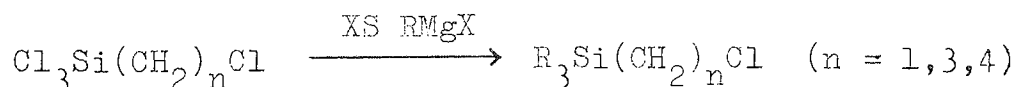
TABLE 3
 Yields of R_3SiCH_2CHMeR' (% based on $R_3SiCH_2CH=CH_2$)⁴⁷

R_3	R'				CH ₂ CH=CH ₂
	Et	n-Pr	Ph		
Me ₂ Ph	5	-	-		24
Me ₃	5	6	9		35
Et ₃	12	25	23		50
n-Pr ₃	12	20	-		38
n-Bu ₃	20	-	-		50

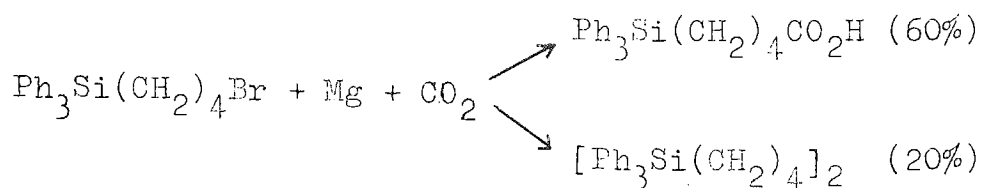
An attempt⁴⁷ to prepare the Grignard reagent from (2-bromopropyl)trimethylsilane was accompanied by appreciable fragmentation and hexamethyldisiloxane, n-propyltrimethylsilane and dimer were the products obtained.



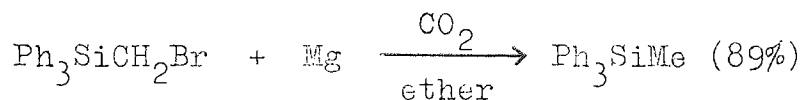
The reactivity of the halide atom in (2-halogeno-alkyl)silanes is of course in marked contrast to the alpha, gamma and delta-substituted compounds. Mironov and Pogonkina⁴⁹ have shown that cleavage of the silicon-carbon bond does not occur in reactions of the compounds $\text{Cl}_3\text{Si}(\text{CH}_2)_n\text{Cl}$ with Grignard reagents when $n = 1, 3$ or 4 and the carbon-halogen bond is also unreactive in such experiments.



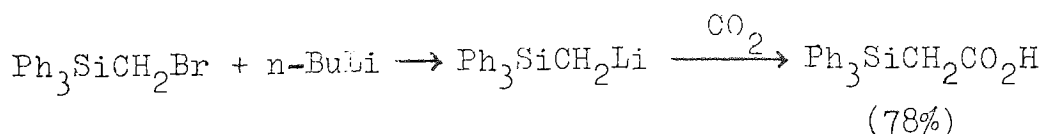
Similarly, Grignard reagents of the (1,3- and 4-halogenoalkyl)silanes may be obtained in high yields (e.g. $\text{Me}_3\text{SiCH}_2\text{MgCl} - 95\%$ ⁵⁰) although their formation is sometimes accompanied by significant quantities of dimer⁵¹:-



However, it is relevant to note that some unusual reactions of the triphenylsilyl-substituted compounds have been reported. Thus, Brook and his coworkers⁵² observed the following reaction:-



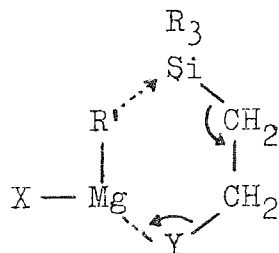
and Gilman et al⁴⁵ in a similar reaction with the gamma-substituted compound $\text{Ph}_3\text{Si}(\text{CH}_2)_3\text{Br}$ obtained the acid $\text{Ph}_3\text{Si}(\text{CH}_2)_3\text{CO}_2\text{H}$ in only 8% yield but do not record the other products formed. Brook also found that the alpha compound underwent halogen-metal exchange with n-butyllithium. In this case carbonation of the intermediate organolithium compound gave the acid in high yield.



Our intention at the onset of this present investigation was to study one or two reactions of (2-bromoethyl)triphenylsilane $\text{Ph}_3\text{SiCH}_2\text{CH}_2\text{Br}$ with Grignard reagents and magnesium. It was anticipated that high

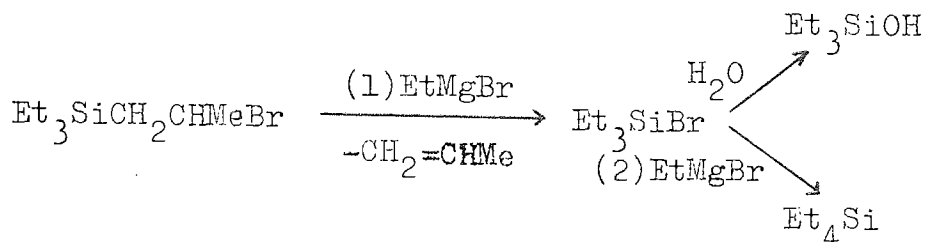
yields of coupled products might be obtained in the former reactions and that the latter might occur without appreciable fragmentation. In fact, fragmentation was not considerable in either of these reactions but in addition to coupled products, high yields of ethyltri-phenylsilane ('exchange' product) were isolated from interaction with the Grignard compounds. In view of this, our attention was diverted to the mechanism of formation of the products of coupling, 'exchange', fragmentation and dimerization. What had been intended as a few simple experiments, designed to establish stability in these systems, became the initiators of most of the remaining work described in this text.

Excluding the postulates of the American and the Russian workers on the fragmentation process, there have been no reported studies concerning the mechanism of reaction between Grignard compounds and (2-halogeno-alkyl)silanes. Sommer et al³ suggested that fragmentation occurred via a cyclic intermediate

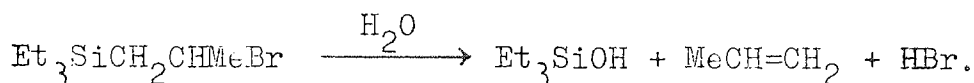


but Petrov and Mironov⁴⁷ proposed an alternative scheme. They found that if the reaction between ethylmagnesium bromide and (2-bromopropyl)triethylsilane is hydrolysed soon after mixing the reagents, little or no tetraethyl-

silane is observed and hydroxytriethylsilane is isolated. This was interpreted as evidence for a two stage process



in contrast to the simultaneous mechanism of the American authors. However, the quantity of recovered starting material is not recorded and it is possible that hydroxytriethylsilane may have been formed by hydrolysis of this compound.

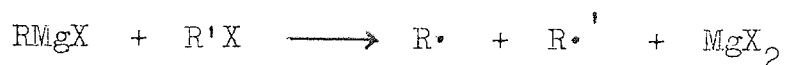


The fragmentation process will be discussed again later in this chapter.

Although Grignard reagents were first discovered at the beginning of this century, many of their reactions are still not completely understood. This is particularly true of their reactions with alkyl halides. In recent years new evidence has been obtained concerning the mechanism of these reactions much of which not been included in standard texts such as Kharasch and Reinmuth⁵³ or Nesmeyanov and Kocheshkov⁵⁴. In many cases the results have been treated in isolation and there seems to be a need for such evidence

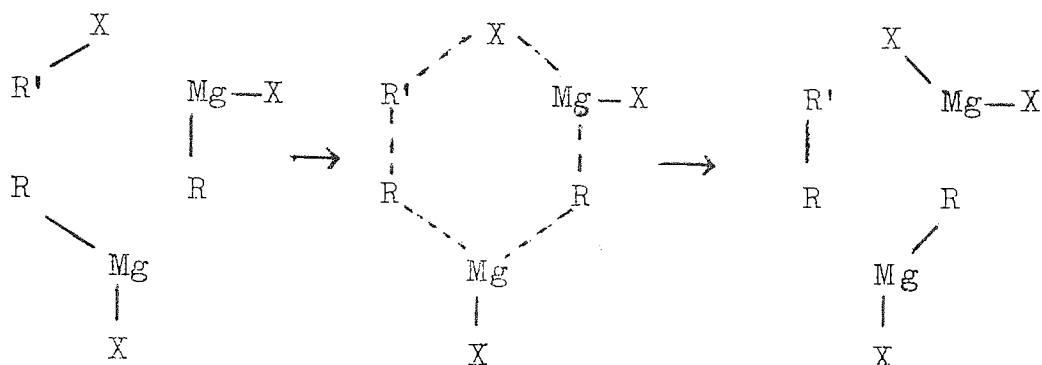
to be collected and critically reviewed. Since these results are pertinent to our argument an attempt (though of necessity a brief one) has been made to summarise some of the relevant data.

The first systematic investigation of the interaction of Grignard reagents with alkyl halides was undertaken by Spath⁵⁵ in 1913. In contrast to Abegg⁵⁶, who considered the fundamental reactions of organo-magnesium compounds to be ionic, Spath⁵⁵ concluded that reaction took place via free radical formation.



It is characteristic of this reaction that when primary alkyl halides and Grignard reagents are employed in diethyl ether, practically no coupling is observed (except when R and R' are CH₃). The major products obtained are alkanes (RH and R'H) and alkenes (R-H and R'-H). The yield of coupled product increases when R' is secondary or tertiary and appreciable amounts of RR' are formed only with allylic or highly branched compounds. Kharasch and Reinmuth⁵³ have argued that a free radical process would require a more nearly statistical product distribution and that highly reactive radicals such as phenyl or methyl would be expected to react with the solvent long before encountering or reacting with one another. They suggest that when formation of coupled product does occur (for

example with benzyl halides) the following is a possible mechanism:-

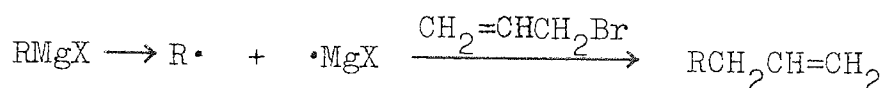


However, Letsinger⁵⁷ has shown that there is 91% racemisation in the reaction between benzylmagnesium chloride and L-2-bromooctane which is evidence against such a mechanism. In the case of triarylmethyl halides reaction is said to be predominantly of the S_N1 type⁵³. Zakharkin, Bilevich and Okhlobystin⁵⁸ obtained good yields of coupled products using primary alkyl halides in dioxane and suggested that reaction (at least in solvating solvents) proceeds by a heterolytic mechanism. They also suggested that the dimeric products RR and R'R' formed in the reaction were not due to free radical participation but were obtained from a parallel exchange process:-

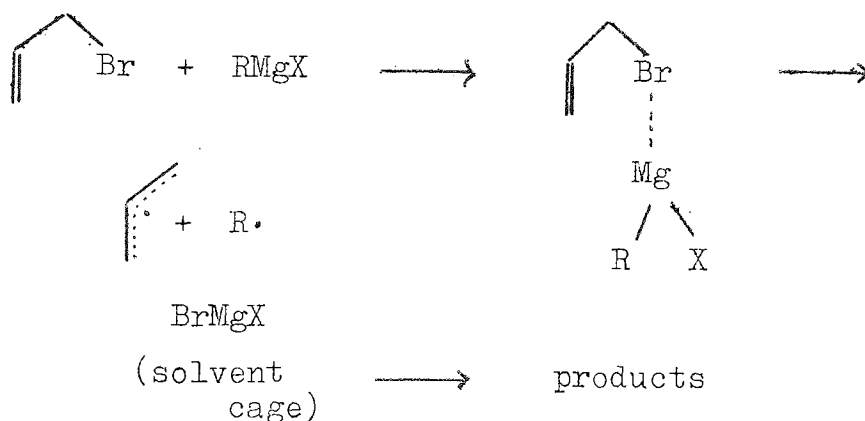


followed by normal coupling. Similarly, the use of hexamethylphosphotriamide⁵⁹ as solvent increases the yield of coupled products. In contrast, Hobbs and

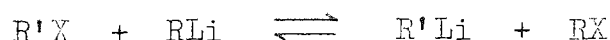
Hannann⁶⁰ obtained higher yields of coupled materials in non-polar media than in diethyl ether and suggested that radical formation had occurred. Gough and Dixon⁶¹ have presented evidence that reaction between alkyl-magnesium halides and allyl bromide may proceed by a radical mechanism. They did not consider the following reaction sequence consistent with the high yields of coupled product $RCH_2CH=CH_2$ obtained (85-90%):-



but proposed an alternative solvent cage type reaction:-



Halogen-metal exchange reactions are commonly encountered in organolithium chemistry⁶².



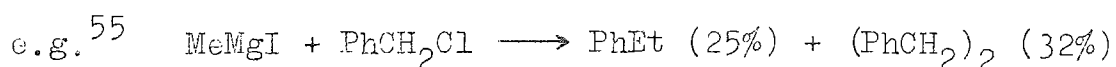
The reactions have generally been interpreted as heterolytic processes and it appears that at equilibrium lithium becomes attached to the most electronegative

organic group. A few such exchanges have been established using organomagnesium compounds⁶³⁻⁶⁷ but all these involve strongly electronegative substituents which can stabilize a carbanionic state. Attempts to observe exchange involving simple alkyl or aryl groups were apparently unsuccessful^{68,69} and Kharasch and Reinmuth⁵³ have suggested that 'functional exchange between an organic halide and an organomagnesium compound is a relatively rare reaction and when it does not involve a positive halide atom is a free radical process initiated by metallic impurities, by the presence of magnesium halides or other factors giving rise to free radicals'. In 1964 Zakharkin, Okhlobystin and Bilevich⁷⁰ reported halogen-metal exchange between Grignard reagents and some alkyl and aryl halides in various ether media. They found that exchange between *n*-arylmagnesium bromide and methyl iodide increased according to the solvent used, diethyl ether < diethoxyethane < methoxyethoxyethane < diglyme < tetrahydrofuran < dioxethoxyethane, was greater with alkyl iodides than bromides and also increased with increasing electronegativity of the alkyl group. On the basis of these results, they concluded that the mechanisms of exchange reactions for organolithium and organomagnesium compounds are very similar and that differences between them are due to the fact that organolithium compounds are stronger nucleophiles and consequently more suitable for exchange. However, it is not clear from their report

whether these authors actually detected the alkyl halide formed by exchange and thus established that their reactions were truly halogen-metal exchange processes.

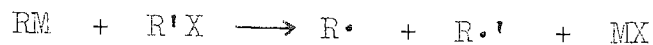
Discussion of reactions between alkyl halides and Grignard compounds in the presence of added metallic halides is really beyond the scope of this work but it perhaps should be pointed out that such halides have been used to accomplish coupling reactions⁷¹, exchange⁶⁸ and dimerization⁷². In the former reaction, the halides are believed to function as Lewis acids (e.g. FeCl_3) whilst the latter two processes are thought to proceed via free radicals. It is obvious that metallic impurities in the magnesium may affect the course of many Grignard reactions.

One explanation for the dimerization reaction (formation of $\text{R}'\text{R}'$) has already been recorded⁵⁸ (see page 34) but Kharasch and Reinmuth⁵³ believe that free radicals are involved. A tendency towards dimerization is encountered with the arylmethyl compounds:-



and in many ways these systems closely resemble the (2-halogenoalkyl)silane reactions. Morrison and his coworkers⁷³ have established the formation of radical intermediates in the benzyl system and in recent years evidence for radical participation in many Grignard reactions has been reported. Russell⁷⁴ has suggested

that numerous reactions between organometallic compounds and alkyl halides may proceed by electron transfer



and his arguments are supported by the following observations:-

- (1) the formation of 2,3-dimethyl-2,3-diphenylbutane in the presence of cumene⁷⁵.
- (2) the formation and detection of the trityl radical from trityl chloride⁷⁶.
- (3) nuclear polarisation (CIDNP) of the olefinic product or of the alkyl halide⁷⁷.
- (4) detection of alkyl radicals by ESR techniques⁷⁴.

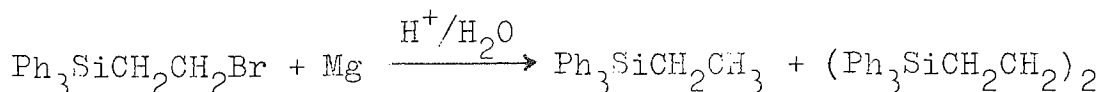
Bilevich and Okhlobystin⁷⁸ have put forward similar arguments and indeed have suggested that many nucleophilic substitutions may occur by an initial one electron transfer step⁷⁹. Shirley and Hendrix⁸⁰ have rationalised the metalation reaction in terms of radical anion formation and Screttas⁸¹ has interpreted several of the reactions of organolithium reagents as proceeding by a single electron transfer process. Other examples of free radical formation in these type of reactions are to be found in the literature⁸²⁻⁸⁶.

It is apparent from the foregoing discussion that a wide variety of interpretations concerning the mechanism of reaction between alkyl halides and organometallic compounds have been put forward. Our

investigation of the reaction between (2-bromoalkyl)-triphenylsilanes and Grignard compounds was carried out with a view to determining whether these processes involve ionic or radical intermediates. The results of this work will now be discussed.

2. The reactions of (2-bromoethyl)triphenylsilane and (2-bromopropyl)triphenylsilane with magnesium in tetrahydrofuran.

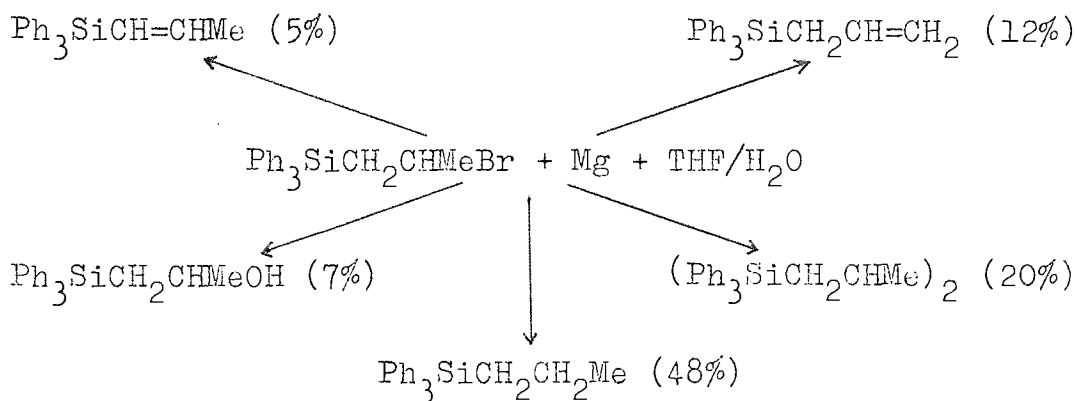
These experiments were conducted in tetrahydrofuran due to the low solubility of the primary compound in diethyl ether. A reaction between (2-bromoethyl)triphenylsilane and excess magnesium, performed in the absence of nitrogen, gave ethyltriphenylsilane (42%) and 1,4-bis(triphenylsilyl)butane (39%)



There was no evidence for the formation of the type of cleavage products (e.g. hexaphenyldisiloxane or hydroxytriphenylsilane) normally observed in the reactions of (2-halogenoalkyl)silanes. In the presence of a nitrogen atmosphere, the same products were obtained in different proportions - ethyltriphenylsilane (64%) and the dimer (21%). The effect of an inert atmosphere in reducing the quantity of dimerization in Grignard preparations has been previously noted⁸⁷. When a reaction was quenched after 1.5h with deuterium oxide, the ethyltri-

phenylsilane isolated contained 100% of one deuterium atom. From these results, the Grignard reagent derived from (2-bromoethyl)triphenylsilane would appear to be a potentially useful synthetic intermediate. It is possible that the interfering dimerization reaction might be further decreased using conditions of higher dilution, slower addition of halide etc. (cf. the preparation of allylmagnesium bromide⁵³) but this was not investigated

Reaction between (2-bromopropyl)triphenylsilane and magnesium, in the presence of nitrogen, proceeded according to the following scheme:-



Once again, there was no evidence of silicon-carbon bond cleavage. Dehydrohalogenation is commonly observed with secondary and tertiary halides during Grignard reagent preparations⁵³. Formation of (2-hydroxypropyl)triphenylsilane may have occurred by hydrolysis of the starting material during the separation of products by column chromatography rather than during the course of reaction (see Experimental, section C2). In contrast to the

primary compound, attempted deuterolysis gave n-propyl-triphenylsilane which did not contain deuterium. Thus, although fragmentation is not a problem in this reaction, a preliminary examination suggests that the process is not suitable for synthetic applications. The lack of deuterium incorporation may indicate that the Grignard reagent $\text{Ph}_3\text{SiCH}_2\text{CHMeMgBr}$ is unstable under the conditions of the experiment or that transfer of a second electron to form a carbanion from a radical intermediate does not take place in this system. One might anticipate that the radical intermediate would be more stable than the carbanion.

3. The influence of solvent and Grignard reagent on the products of the reaction between (2-bromoalkyl)tri-phenylsilanes and Grignard compounds.

Reactions were studied in three solvents - benzene, diethyl ether and tetrahydrofuran (THF). The results of these experiments are recorded in Tables 4,5 and 6. All of the reactions were carried out under standard conditions using excess organometallic reagent, as described in the Experimental section. They were initially performed for periods of about three days but later work indicated that such lengthy reaction times were unnecessary and that 5h was usually quite sufficient for complete reaction. Exceptions to this were some experiments performed in diethyl ether, where reaction proceeded in non-homogeneous solution.

TABLE 4

Reactions of (2-bromoalkyl)triphenylsilanes with Grignard reagents in diethyl ether.

Grignard	reaction time (h)	'exchange'	dimerization	product yields (%)	coupling	fragmentation	others
Reaction with $\text{Ph}_3\text{SiCH}_2\text{CH}_2\text{Br}$		Ph_3SiEt	$(\text{Ph}_3\text{SiCH}_2\text{CH}_2)_2$	$\text{Ph}_3\text{SiCH}_2\text{CH}_2\text{R}^1$			
(1) PhMgBr	68	8	4	40	$\text{Ph}_3\text{SiOH-17}$ $\text{Ph}_4\text{Si} < 8$	-	-
(2) EtMgBr	66	57	15	5	uncertain ^a	-	-
(3) $n\text{-PrMgBr}$	3	68	8	4	$\text{Ph}_3\text{SiPr-2}$	-	-
(4) $n\text{-BuMgBr}$	3	50	4	5	-	$\text{Ph}_3\text{SiCH}_2\text{CH}_2\text{Br-17}$	
(5) $t\text{-BuMgBr}$	4	18	-	3	-	$\text{Ph}_3\text{SiCH}_2\text{CH}_2\text{Br-53}$	
Reaction with $\text{Ph}_3\text{SiCH}_2\text{CHMeBr}$		Ph_3SiPr	$(\text{Ph}_3\text{SiCH}_2\text{CHMe})_2$	$\text{Ph}_3\text{SiCH}_2\text{CHMeR}^1$			
(6) PhMgBr	48	0.5	3	79	$\text{Ph}_3\text{SiOH-12}$ $\text{Ph}_4\text{Si} < 3$	$\text{Ph}_3\text{SiCH}_2\text{CH=CH}_2\text{-1}$	

a. 'exchange' and fragmentation both yield Ph_3SiEt .

TABLE 5

Reactions of (2-bromoalkyl)triphenylsilanes with Grignard reagents in tetrahydrofuran.

Grignard	reaction time (h)	'exchange' dimerization	product yields (%)	coupling	fragmentation	others
Reaction with $\text{Ph}_3\text{SiCH}_2\text{CH}_2\text{Br}$		Ph_3SiEt	$(\text{Ph}_3\text{SiCH}_2\text{CH}_2)_2$	$\text{Ph}_3\text{SiCH}_2\text{CH}_2\text{R}^a$		
(7) n-PrMgBr	1.5	52	15	2	-	$\text{Ph}_3\text{SiCH}=\text{CH}_2$ -4
(8) PhMgBr	1.5	40	13	5	uncertain ^b	$\text{Ph}_3\text{SiCH}_2\text{CH}_2\text{Br}$ -12
Reaction with $\text{Ph}_3\text{SiCH}_2\text{CHMeBr}$		Ph_3SiPr	$(\text{Ph}_3\text{SiCH}_2\text{CHMe})_2$	$\text{Ph}_3\text{SiCH}_2\text{CHMeR}^a$		
(9) PhMgBr	22	22	24	13	Ph_3SiOH -4 $\text{Ph}_4\text{Si} < 6$	$\text{Ph}_3\text{SiCH}_2\text{CHMeOH}$ -5 $\text{Ph}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ -9 $\text{Ph}_3\text{SiCH}=\text{CHMe}$ -6

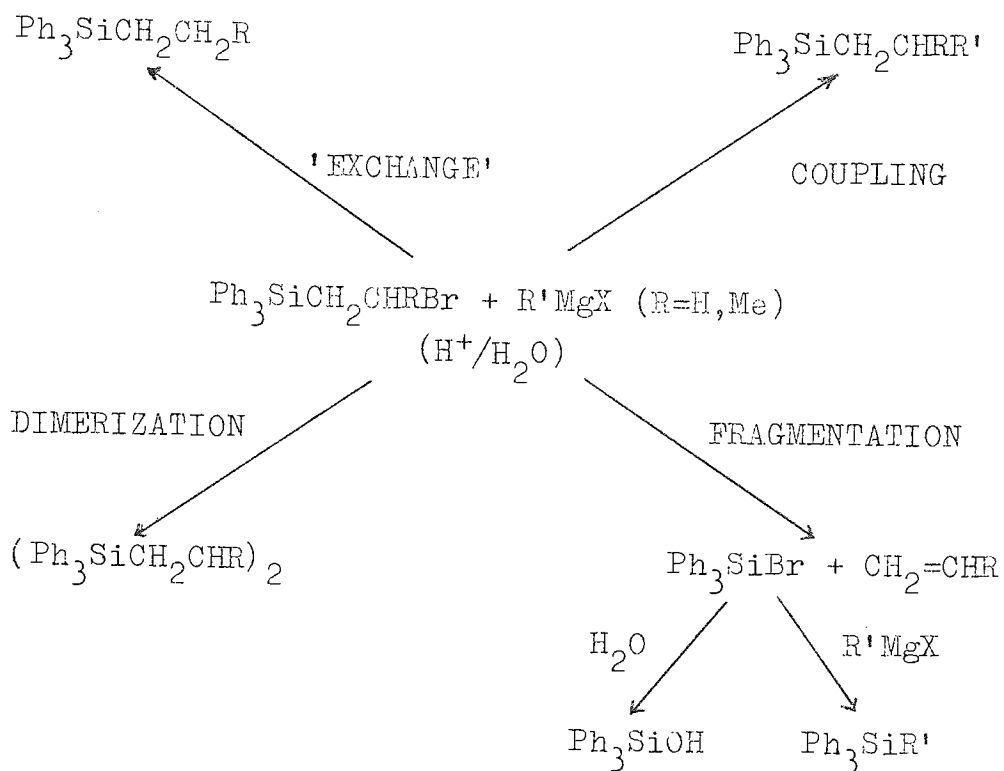
b. some fragmentation may have occurred followed by reaction with tetrahydrofuran.

TABLE 6

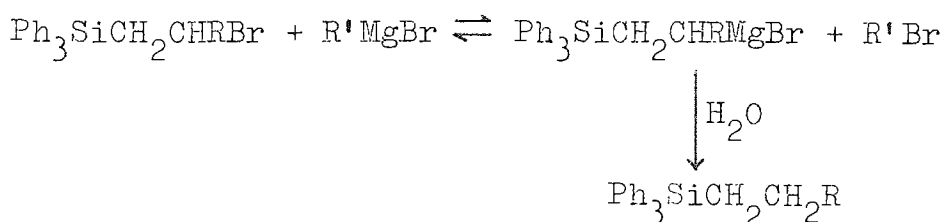
Reactions of (2-bromoalkyl)triphenylsilanes with Grignard reagents in benzene.

Grignard	reaction time (h)	'exchange'	dimerization	product yields (%)	coupling	fragmentation	others
Reaction with $\text{Ph}_3\text{SiCH}_2\text{CH}_2\text{Br}$		Ph_3SiEt	$(\text{Ph}_3\text{SiCH}_2\text{CH}_2)_2$	$\text{Ph}_3\text{SiCH}_2\text{CH}_2\text{R}'$			
(10) PhMgBr	48	<4	-	90	$\text{Ph}_3\text{SiOH-3}$	-	-
(11) $\text{CH}_2=\text{CHCH}_2\text{-MgBr}^{107}$	48	-	-	94	-	-	-
(12) β -Butenyl- MgBr^{107}	48	66	1	3	-	-	$\text{Ph}_3\text{SiCH}=\text{CH}_2\text{-12}$
(13) $n\text{-PrMgBr}$	40	40	15	9	-	-	$\text{Ph}_3\text{SiCH}=\text{CH}_2\text{-26}$
(14) $n\text{-BuMgBr}$	3	46	11	4	-	-	$\text{Ph}_3\text{SiCH}=\text{CH}_2\text{-28}$
Reaction with $\text{Ph}_3\text{SiCH}_2\text{CHMeBr}$		Ph_3SiPr	$(\text{Ph}_3\text{SiCH}_2\text{CHMe})_2$	$\text{Ph}_3\text{SiCH}_2\text{CHMeR}^*$			
(15) PhMgBr	48	-	-	88	$\text{Ph}_3\text{SiOH-8}$	-	$\text{Ph}_3\text{SiCH}_2\text{CH}=\text{CH}_2\text{-trace}$

Such experiments were more susceptible to variation when short reaction times were employed. Reactions were generally performed using 'magnesium for Grignard reactions' (purity > 99.75%, for principal impurities see Experimental, section C1) and good reproducibility was achieved in duplicate studies. The effect of the rate of stirring, the rate of addition of reagents or the relative concentration of reagents upon the reactions was not critically investigated. However, it appeared that the order of addition of reagents (i.e. Grignard to halide or vice-versa) was not important. The recovery of products derived from the silane was usually greater than 75% and the difference from theoretical was due both to inevitable losses during the separation procedure and to an inability to characterise all of the materials isolated. In many cases a hydrocarbon product or mixture of products was isolated which contained silicon-phenyl and aliphatic linkages and when tetrahydrofuran was employed as the solvent a material containing silicon-phenyl, aliphatic and hydroxyl groups was detected. The precise nature of these materials was not established. Products derived from the Grignard reagent were not determined. A summary of the principal classes of compounds obtained from such experiments is given in the scheme overleaf.



In addition, the olefinic products $\text{Ph}_3\text{SiCH}=\text{CH}_2$ and $\text{Ph}_3\text{SiCH}=\text{CHMe}/\text{Ph}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ were obtained in some of the reactions from the primary and secondary compounds respectively. It should be noted at this point, that the term 'exchange' is used simply for convenience and is not intended to imply any mechanistic pathway. The so called 'exchange process' may have occurred by true halogen-metal exchange:-

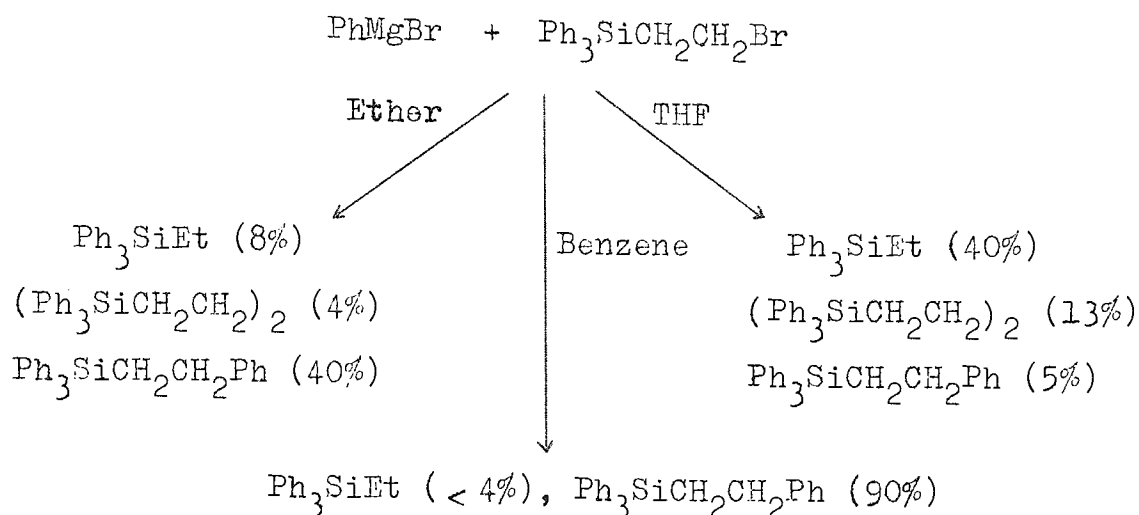


but the hydrocarbon product might equally well have

arisen by formation of the radical $\text{Ph}_3\text{SiCH}_2\text{CHR}\cdot$ followed by proton abstraction from the solvent etc. or by direct reduction of the (2-bromoalkyl)triphenylsilane by the Grignard reagent.

Examination of Tables 4, 5 and 6 reveals several important points:-

- (a) The extent of fragmentation in these reactions is small. Thus, the position of the phenyl group attached to silicon in the series proposed by Petrov and Mironov⁴⁷, (see page 27) for the stabilization of (2-halogenoalkyl)silanes in their reactions with Grignard compounds, would seem to be in error. The lack of fragmentation is in marked contrast to the behaviour of the corresponding carbon analogue $\text{Ph}_3\text{CCH}_2\text{CH}_2\text{Br}$ which is reported to undergo elimination of ethylene on reaction with magnesium, Grignard reagents or n-butyllithium⁸⁸. Fischer et al have explained this reaction as due to the stability of the triphenylmethyl carbanion intermediate formed in such a process. It would appear that the stability of the triphenylsilyl anion relative to the anion $\text{Ph}_3\text{SiCH}_2\text{CHR}^-$ is not as great.
- (b) The products obtained using a specific Grignard reagent may vary markedly with the solvent employed. Thus, reaction between phenylmagnesium bromide and (2-bromoethyl)triphenylsilane in ether, tetrahydrofuran or benzene proceeds in different directions as indicated overleaf (expts. 1,8 and 10).



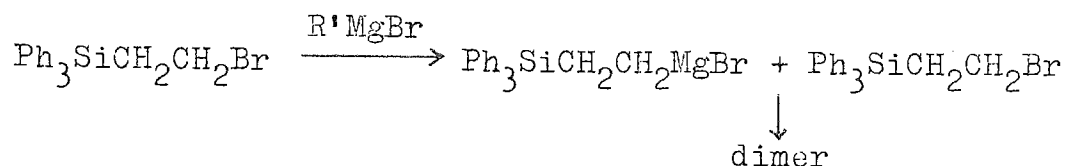
(c) The reaction pathway in a particular solvent may also vary according to the Grignard reagent used. For example, in benzene allyl and phenylmagnesium bromide react with the primary halide to give high yields of coupled materials (expts. 11 and 10) whilst n-propyl or n-butylmagnesium bromides give rise predominantly to the products of 'exchange' (expts. 13 and 14).

(d) In accordance with the results of Petrov and Mironov⁴⁷; it appears that coupling is greater with the secondary halide than with the primary (cf. expts. 1 and 6).

The poor reaction observed using t-butylmagnesium bromide (expt. 5) is probably due to conducting the process for too short a time.

At a cursory glance, it seems possible to explain all of these results by a heterolytic reaction mechanism. The 'exchange' products might be envisaged as formed by true halogen-metal interconversion since

the extent of exchange (as monitored by the quantity of ethyltriphenylsilane isolated) decreases in the case of the phenyl Grignard reagent from tetrahydrofuran to ether to benzene (expts. 1,8 and 10) and occurs more readily with alkylmagnesium halides than phenylmagnesium compounds (i.e. with the less electronegative groups). Such observations are completely in accord with the conclusions of Zakharkin, Okhlobystin and Bilevich⁷⁰. Dimerization could occur by reaction of the silane with its own Grignard reagent (formed by exchange):-



and there is no necessity to explain the formation of olefinic products by a radical mechanism. However, it seems rather surprising that a heterolytic halogen-metal exchange process might occur so readily in the non-polar benzene solvent when alkylmagnesium compounds are used (expts. 13 and 14).

(4) The influence of high purity magnesium.

The effect of metallic impurities on the course of Grignard reactions has already been mentioned. The principal impurity contained in the sample of magnesium used in the experiments of Table 4-6 was manganese (see Experimental, section C1). In order to assess the influence of these impurities, experiments were carried

out using magnesium metal of high purity (> 99.995%). The results of such reactions with (2-bromoethyl)triphenylsilane are recorded in Table 7. Comparison of expts. 16-19 with those of expts. 3,8,10 and 13 shows that the reactions of phenylmagnesium bromide are not much influenced by the sample of magnesium employed but that with n-propylmagnesium bromide in benzene the proportion of coupled material is considerably increased (apparently at the expense of olefin formation). Since metallic impurities are usually considered to give rise to radical intermediates, such an observation may indicate that the coupling reaction is not a homolytic process. However, the 'exchange' reaction is still considerable in these experiments and cannot be attributed to impurities contained in the magnesium.

Since the majority of Grignard reactions (at least in this country) are performed using 'magnesium for Grignard' grade metal, it was decided to continue our experiments with this type of magnesium but in the knowledge that the reaction pathways might be somewhat influenced by the presence of impurities.

5. Reaction of (2-bromoalkyl)triphenylsilanes and ethyltriphenylsilane with n-butyllithium.

If the 'exchange' process were a true example of halogen-metal interconversion, one might expect that the yield of corresponding hydrocarbon (Ph_3SiEt or Ph_3SiPr - according to the silane used) might increase when the

TABLE 7

Reactions with high purity magnesium

Grignard	solvent	reaction time (h)	'exchange' dimerization	product yields (%)	fragmentation	others
(16) PhMgBr	THF	4	57	9	7	-
(17) n-PrMgBr	Ether	5	31	-	8	Ph ₃ SiCH ₂ CH ₂ Br-46
(18) PhMgBr	Benzene	20	-	-	94	-
(19) n-PrMgBr	Benzene	20	41	11	38	Ph ₃ SiCH=CH ₂ -3

more nucleophilic organolithium compounds were employed in place of the Grignard reagents. In order to investigate this possibility, the reactions of (2-bromoalkyl)-triphenylsilanes with n-butyllithium were studied and the results of these experiments are recorded in Table 8. Such experiments, had they not been complicated by side reactions, might have provided a method for the determination of carbanion stability and allowed correlation with the data of Applequist and O'Brien⁸⁹. In none of the experiments was there any evidence of products derived from silicon-carbon bond cleavage. However, in contrast to the (alpha-halogenoalkyl)silane $\text{Ph}_3\text{SiCH}_2\text{Br}$ studied by Brook and his coworkers⁵², which apparently underwent halogen-metal exchange at -70° , there was no reaction at low temperatures. At higher temperatures, the rate of coupling was rapid and it was not possible to observe the products of 'exchange' in the absence of this coupling process. Since this competing reaction is not normally observed in reactions between alkyl halides and organolithium reagents under the conditions employed^{62,89}, one cannot draw any conclusions regarding the carbanion stabilities of $\text{Ph}_3\text{SiCH}_2\text{CHR}^-$ from these experiments. In view of this, it was decided to attempt the metalation of ethyltriphenylsilane, since this process might be expected to involve the same carbanion intermediate⁹⁰ without the complication of side reactions.

Gilman and Morton⁹⁰ have stressed the need to investigate the influence of solvent and temperature on

TABLE 8

Reaction of (2-bromoalkyl)triphenylsilanes with n-butyllithium

solvent	experimental conditions temperature	react ⁿ time(h)	'exchange' dimerization	product yields (%) coupling	others
Reaction with $\text{Ph}_3\text{SiCH}_2\text{CH}_2\text{Br}$					
Ether	-20°	1.0	-	-	$\text{Ph}_3\text{SiCH}_2\text{CH}_2\text{Br}$ 100
Ether	-20°	1.0	12	16	32
	and R.T.	0.25			25
Ether	-20°	0.5	19	16	45
	and R.T.	1.5			-
Ether/THF (3/1)	-45°	0.5	14	30	33
Reaction with $\text{Ph}_3\text{SiCH}_2\text{CHMeBr}$					
Ether	-20°	1.0	16	13	$\text{Ph}_3\text{SiCH}_2\text{CH=CH}_2$ -17 $\text{Ph}_3\text{SiCH=CHMe}$ -12
	and R.T.	0.5			29

R.T. = Room Temperature (20-25°)

metalation reactions and the experiments with ethyl-triphenylsilane were performed under a variety of conditions. Termination of the reactions was achieved using both deuterium oxide and carbon dioxide but in none of the experiments were products isolated which indicated significant metalation. The results are recorded in Table 9. If the so called 'exchange' products observed in the Grignard reaction were formed by a halogen-metal interconversion process, one might anticipate that the carbanion $\text{Ph}_3\text{SiCH}_2\text{CH}_2^-$ was at least of the same order of stability as the benzyl carbanion⁹¹ (or expressing this another way, that the hydrocarbon acidity of ethyltriphenylsilane should be similar to that of toluene). Although metalation of toluene is almost negligible in diethyl ether⁹⁰, using mixtures of ether and tetrahydrofuran approximately 20% metalation has been observed⁹². However, metalation of ethyltriphenylsilane did not occur even under these conditions. It is possible that the use of complexing agents such as tetramethylethylenediamine might facilitate the reaction.

It is difficult to draw any definite conclusions from the results of the reactions with n-butyllithium. The stability of the organolithium compound $\text{Ph}_3\text{SiCH}_2\text{CH}_2\text{Li}$ in diethyl ether or ether/THF mixtures has not been determined and it is possible that this compound might react rapidly with the solvent and defy its detection by deuterium oxide or carbon dioxide. Certainly, attempts to identify the organolithium intermediate in

TABLE 9

The attempted metalation of ethyltriphenylsilane

solvent	experimental conditions		method of termination	
	temperature	react ⁿ time (h)	D ₂ O addition	CO ₂ addition
Ether	R.T.	20	-	Ph ₃ SiEt - 92% Ph ₃ SiCH ₂ CH ₂ CO ₂ H < 0.5%
Ether	reflux	16	Ph ₃ SiEt - 89% (no deuterium detected)	Ph ₃ SiEt - 84% Ph ₃ SiCH ₂ CH ₂ CO ₂ H < 1.5%
Ether/THF (3/2)	R.T.	1.5	Ph ₃ SiEt - 87% (no deuterium detected)	-
Ether/THF (3/1)	R.T.	24	Ph ₃ SiEt - 85% (no deuterium detected)	Ph ₃ SiEt - 85% Ph ₃ SiCH ₂ CH ₂ CO ₂ H < 3%

R.T. = Room Temperature (20-25°).

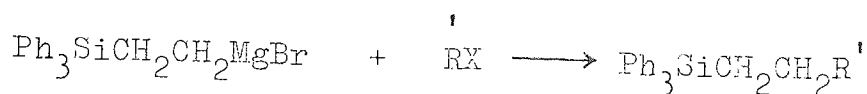
reactions with both (2-bromoalkyl)triphenylsilanes and ethyltriphenylsilane using NMR spectroscopy were unsuccessful but its absorption may have been masked by those of solvent or n-butyllithium or its relative concentration too low to allow detection. Perhaps the only conclusive evidence to emerge from these experiments is that, as in the Grignard process, fragmentation is not an important pathway with the (2-bromoalkyl)triphenylsilanes.

6. Evidence concerning the mechanism of reaction between (2-bromoalkyl)triphenylsilanes and Grignard reagents.

In order to classify a reaction as a genuine halogen-metal interconversion process ($\text{RMgX} + \text{R}'\text{X} \rightleftharpoons \text{R}'\text{MgX} + \text{RX}$), it is necessary to establish two factors:-

- (a) formation of the Grignard reagent $\text{R}'\text{MgX}$.
- (b) formation of an equivalent quantity of the alkyl halide RX .

Experiments were carried out with (2-bromoethyl)-triphenylsilane in an attempt to detect the alkyl halides anticipated from a halogen-metal exchange reaction. n-Butyl and phenylmagnesium bromides were used in these experiments. Bach⁷³ has shown that any bromobutane formed would not be significantly consumed by side reactions (e.g. formation of octane etc) and our experiments with bromobenzene gave similar results. Examination of Tables 4-6 shows that the coupling reaction,



if it occurs, does so only to a minor extent. Thus, if alkyl or aryl halides were formed from these Grignard reagents by a heterolytic process, their detection should be possible. In none of the systems investigated were the quantities of halide detected similar to that of the ethyltriphenylsilane formed in the same reaction. The results are recorded in Table 10 and other products were as reported in the corresponding experiments of Tables 4-6. Clearly, these results alone indicate that formation of ethyltriphenylsilane does not occur by a genuine halogen-metal interconversion process.

The next priority was to discover whether any of the ethyltriphenylsilane isolated had been formed from the carbanion $\text{Ph}_3\text{SiCH}_2\text{CH}_2^-$ or whether it had been derived from other reaction pathways. The fact that the Grignard reagent $\text{Ph}_3\text{SiCH}_2\text{CH}_2\text{MgBr}$ is apparently stable in the solutions employed enabled us to investigate the extent of involvement of the organometallic intermediate. In order to do this reactions were quenched with deuterium oxide and the proportion of deuterium contained in the sample of ethyltriphenylsilane obtained was determined. The results are summarised in Table 11. Examination of the table reveals that only in the cases of *t*-butylmagnesium bromide in ether and *n*-propylmagnesium bromide in benzene does the extent of deuteration approach 100%.

TABLE 10

The search for alkyl/aryl halide formation in reactions between (2-bromoethyl)triphenylsilane and Grignard reagents (RMgX).

Grignard reagent	solvent	halide (RX) remaining after Grignard formation	halide (RX) detected after reaction with (2-bromoethyl)-triphenylsilane	halide (RX) expected, assuming all the Ph ₃ SiEt were formed by halogen-metal exchange.
PhMgBr	THF	0	0	0.90g
n-BuMgBr	diethyl ether	0.14g	0.08g	0.93g
n-BuMgBr	benzene	0.10g	0	0.84g

TABLE 11

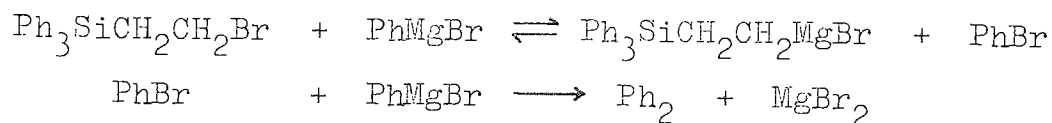
Reactions between (2-bromoethyl)triphenylsilane and Grignard reagents
quenched with deuterium oxide.

Grignard reagent	solvent	reaction time (h)	% deuteration of the ethyltriphenylsilane isolated
PhMgBr	THF	1.5	10
n-PrMgBr	THF	1.5	39
n-PrMgBr	ether	3	50
t-BuMgBr	ether	4	100
n-PrMgBr	benzene	40	96

It is apparent that in the reactions with n-propylmagnesium bromide in THF or ether and with phenylmagnesium bromide in THF, the ethyltriphenylsilane isolated is not solely derived from an intermediate carbanion. The full significance of these results will be discussed later in this chapter.

An explanation for the results obtained using deuterium oxide was that some of the 'exchange' hydrocarbon had been formed from a free radical process. Experiments were therefore carried out to investigate the possible participation of radical intermediates in these systems. It was hoped that the experiments might shed light not only on the 'exchange' process but also on the related dimerization and coupling reactions. Normally the detection of free radicals is achieved using ESR techniques but unfortunately the instrument available was not suitable for such studies. Another commonly used method of radical detection is addition of a scavenger and two experiments were performed in the presence of styrene. This monomer has recently been successfully used in Grignard systems by Tamura and Kochi⁹³. A reaction between phenylmagnesium bromide and (2-bromoethyl)triphenylsilane in benzene in the presence of styrene gave (2-phenylethyl)triphenylsilane in 95% yield and was thus unaffected by the presence of this scavenger (cf. expt. 10, Table 6). In contrast, the presence of styrene in the reaction between n-propylmagnesium bromide and the silane in THF decreased the

yield of ethyltriphenylsilane to 16% (cf. expt. 7, Table 5 - Ph_3SiEt 52%) whilst the proportion of dimerization remained virtually unchanged (17%). No starting halide was recovered and the only other product isolated was a polymeric material containing both silicon-phenyl and aliphatic linkages. It would appear that styrene has successfully trapped free radical intermediates in the latter reaction but not in the former. The results may indicate that the 'exchange' process is partly radical but that dimerization and coupling do not involve such intermediates. However, a more detailed discussion will be presented later. Further indirect evidence suggesting the participation of radical intermediates in the 'exchange' process was obtained from a study of the reactions of (2-bromoalkyl)triphenylsilanes with phenylmagnesium bromide in tetrahydrofuran. It was observed that high yields of biphenyl were formed in these reactions. One possible explanation was that halogen-metal exchange had occurred followed by consumption of bromobenzene in a coupling reaction:-



However, this seemed unlikely since coupling between phenylmagnesium bromide and bromobenzene is known to be a sluggish process^{53,54} and obviously this exchange reaction would conflict with the evidence thus far

presented. In fact, experiments confirmed that negligible yields of biphenyl were obtained in the formation of phenylmagnesium bromide and in its reaction with bromobenzene in the presence or absence of magnesium bromide. In the latter two cases, high recoveries of the added bromobenzene could be achieved. The results are summarised in Table 12 and would seem to indicate that the biphenyl is probably formed by the coupling of phenyl radicals. These experiments were the only ones in which the fate of products derived solely from the Grignard reagent were determined.

The results obtained using deuterium oxide, styrene and the estimation of biphenyl in reactions with phenylmagnesium bromide seemed to suggest the participation of free radicals in the 'exchange' process. In order to determine whether the products obtained were consistent with the formation of such intermediates, a reaction was performed under conditions believed to generate free radicals. The reaction between Grignard compounds and alkyl halides in the presence of cobaltous chloride has generally been interpreted as a radical process^{53,54,94}. Wilt and his coworkers^{94,95} have investigated the reactions of (alpha, gamma and delta-halogenoalkyl)-silanes under radical conditions and found that the gamma and delta compounds undergo rearrangement:-

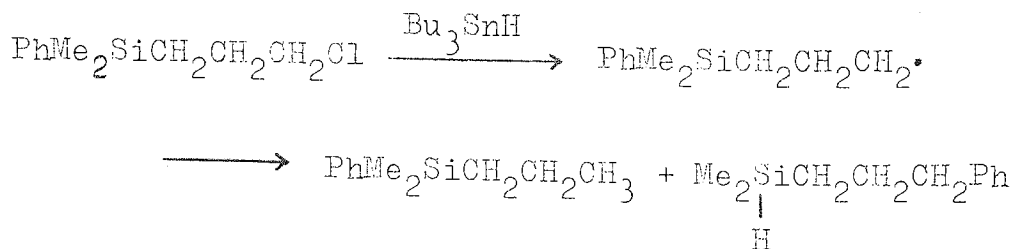
TABLE 12

Determination of the biphenyl formed from reactions between (2-bromoalkyl)triphenylsilanes and phenylmagnesium bromide in THF.

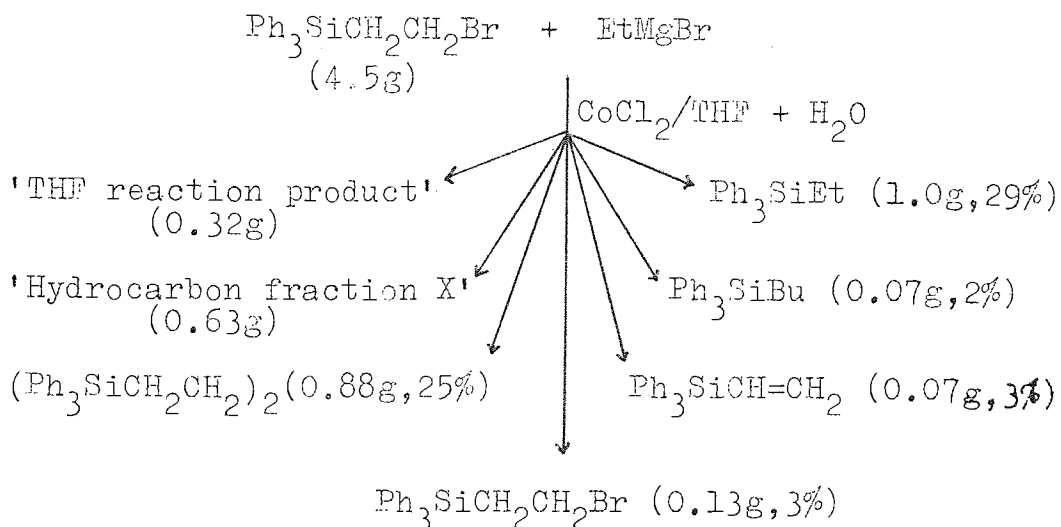
Reaction	biphenyl formed during Grignard preparation	biphenyl formed in* reaction with PhBr	biphenyl formed in reaction with $\text{Ph}_3\text{SiCH}_2\text{CHRR}$
$\text{PhMgBr} + \text{Ph}_3\text{SiCH}_2\text{CH}_2\text{Br}$	0.027g	0.013g	0.330g
$\text{PhMgBr} + \text{Ph}_3\text{SiCH}_2\text{CHMeBr}$	0.022g	0.007g	0.240g

Reaction in the presence of MgBr_2 - no silicon cpds.	0.024g	0.009g	React ⁿ with MgBr_2 0.012g

* These reactions were carried out using a quantity of bromobenzene similar to that of the ethyltriphenylsilane isolated.



In contrast, the alpha compound $\text{Ph}_3\text{SiCH}_2\text{Cl}$ does not rearrange under similar conditions and it was suggested that either steric hindrance or $d\pi - p\pi$ bonding in this compound prevented rearrangement. In none of the experiments with (2-bromoethyl)triphenylsilane, in the absence of added metallic halide, was there any evidence for the formation of the rearranged product $\text{Ph}_2\text{HSiCH}_2\text{-CH}_2\text{Ph}$. In an attempt to discover whether such rearrangement might be anticipated if the Grignard reactions involved radical intermediates, an experiment between ethylmagnesium bromide and (2-bromoethyl)triphenylsilane in tetrahydrofuran in the presence of cobalt chloride was performed. The products obtained are summarised in the scheme below:-

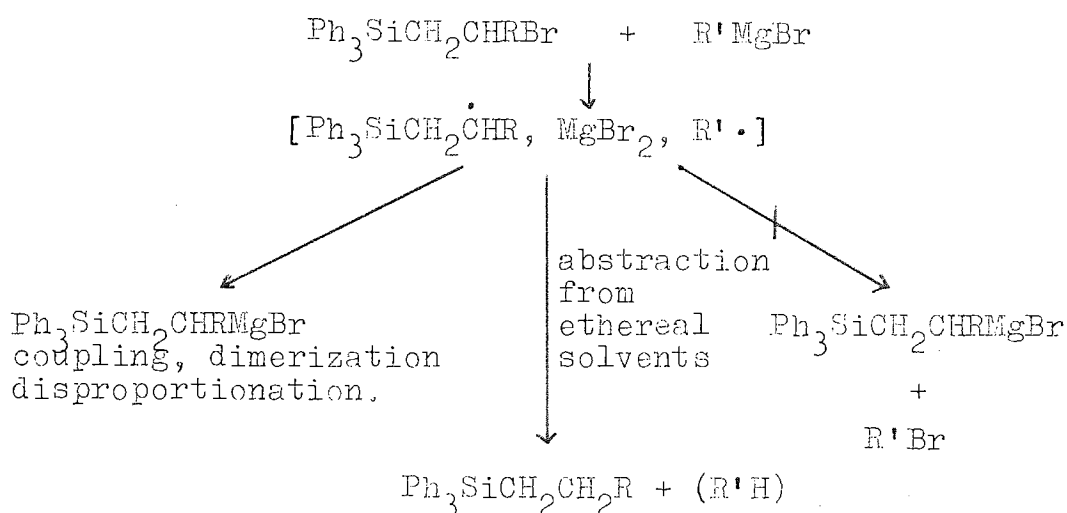


The 'hydrocarbon fraction X' and the 'THF reaction product' were similar to those obtained in the experiments recorded in Tables 4-6 (see page 45). There was no evidence for the formation of the rearranged compound. Although the relative proportions differ, the principal types of compounds obtained are similar to those using alkylmagnesium halides in the absence of metallic halide (cf. expt. 7, Table 5). Thus, provided that reactions in the presence of cobaltous chloride are accepted as radical processes, the results of this experiment are consistent with the hypothesis that interactions between Grignard reagents and (2-bromoalkyl)silanes (in the absence of CoCl_2) involve radical intermediates.

7. Rationalisation of the foregoing results.

It is apparent from the results obtained that the 'exchange' process is not a genuine example of halogen-metal interconversion and that in some cases, at least, proceeds via free radical formation. Classification of the coupling and dimerization reactions is not so clear cut. Clearly, a more detailed picture of these processes would emerge from a study of the products derived from the Grignard reagent - necessitating a system of gas analysis. It should also be pointed out that products obtained from attack of radicals on the solvent (e.g. compounds of the type $\text{Ph}_3\text{SiCH}_2\text{CH}_2\text{CHCH}_3\text{OC}_2\text{H}_5$) when diethyl ether is employed, have not been detected. Such compounds were identified by Kumada et al⁹⁶ in their

reactions of organosilylmethylmagnesium chlorides with silver halides. Nevertheless, the data presented in this text is most simply rationalised by a mechanism in which a one electron transfer gives a caged radical pair which can then react further in a variety of ways:-

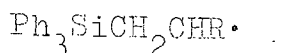


The radical derived from the Grignard reagent is bracketed because the products from this reagent were not determined. The particular reaction pathway followed and the products obtained are envisaged as being governed by:-

- (1) The ease of transfer of a second electron to produce the carbanion $\text{Ph}_3\text{SiCH}_2\text{CHR}^-$ (i.e. on the electron donor ability of the organometallic compound).



- (2) The relative stability of the intermediate radical



- (3) The ease of proton abstraction from the solvent employed.

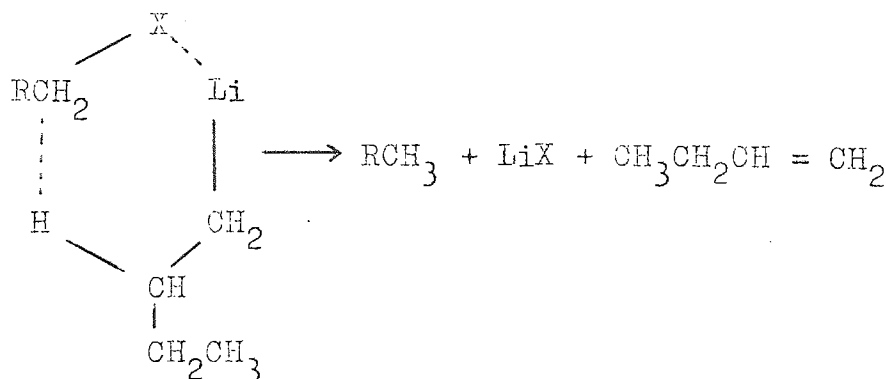
The results obtained with deuterium oxide are readily explained by this scheme. The 'exchange' hydrocarbons (Ph_3SiEt and Ph_3SiPr) are formed not only from an organometallic compound but also by proton abstraction from the medium by the intermediate free radical. Thus, reaction in tetrahydrofuran between (2-bromoethyl)triphenylsilane and phenylmagnesium bromide (a poor electron donor) gives rise to ethyltriphenylsilane of which little is derived from the carbanion and most is formed by a radical abstraction process. When n-propylmagnesium bromide (a somewhat better electron donor than phenyl) is employed in this solvent, the principal source of 'exchange' hydrocarbon is still proton abstraction by the radical but rather more of the product is obtained via the organometallic intermediate. Using n-propylmagnesium bromide in ether, approximately 50% of the 'exchange' product is derived from the carbanion and with the strongly donating reagent t-BuMgBr, carbanion formation is the exclusive process.

Whether coupling or 'exchange' occurs is governed by similar considerations. The yield of coupled material might be expected to increase as:-

- (a) the donor ability of the Grignard reagent decreases and (b) the ease of removal of a proton from the solvent decreases.

Examination of the results obtained using phenylmagnesium bromide and (2-bromoethyl)triphenylsilane shows that these conclusions are borne out. Thus, coupling is the major process in benzene and diethyl ether but decreases in that order whereas in tetrahydrofuran (where proton abstraction might be expected to be rapid) dimerization and 'exchange' predominate. With alkylmagnesium compounds coupling is not observed in any significant extent irrespective of the solvent used. The negligible yield of 'exchange' hydrocarbon from reaction of the secondary halide with phenylmagnesium bromide in ether (expt. 6, Table 4), is presumably the result of the decreased tendency of the more stable secondary radical to undergo a second electron transfer or abstract a proton from the medium.

The foregoing argument adequately explains the 'exchange' process. However, there is at least one other possible mechanism by which the 'exchange' hydrocarbon might be partially formed. This involves direct reduction of the halide by the Grignard reagent. Eastham and Gibson⁹⁷ have claimed to have observed such processes in the reactions between 1-bromooctane or bromocyclohexane and n-butyllithium.



Obviously, this cannot be an important pathway in any of the reactions involving phenylmagnesium bromide or in any of the experiments where quantitative carbanion formation is observed. However, in the experiments with alkylmagnesium compounds, where deuteration of the 'exchange' hydrocarbon does not approach 100%, some of the non-deuterated product may have arisen by this process and our experiments have not eliminated this possibility.

Summing up the evidence regarding the 'exchange' reaction, one might conclude that a process involving single electron transfer provides a workable explanation for the results obtained using phenylmagnesium bromide and can be used to explain the remaining data in a satisfactory manner but that an alternative pathway for the latter cannot be entirely excluded.

Concerning the coupling reaction there are three relevant pieces of evidence:-

- (1) In the presence of styrene, the reaction between (2-bromoethyl)triphenylsilane and phenylmagnesium bromide giving (2-phenylethyl)triphenylsilane is not significantly altered. This might be interpreted as indicating that the coupling reaction is not homolytic. Alternatively, it is possible that reaction takes place within the solvent cage and that few of the radicals escape into the medium for detection.
- (2) The use of high purity magnesium appears to increase the yield of coupled product in the

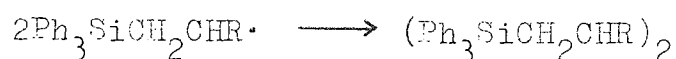
reaction between (2-bromoethyl)triphenylsilane and n-propylmagnesium bromide in benzene. If the metallic impurities contained in the magnesium generally employed are assumed to facilitate a homolytic process, one might conclude that the coupling reaction is heterolytic. However, it is by no means certain that such impurities induce a radical process and coupling between the silane and phenylmagnesium bromide in THF or n-propylmagnesium bromide in ether is not significantly increased using high purity magnesium (see Table 7).

- (3) Petrov and Mironov⁴⁷ concluded that the extent of coupling increased from primary to secondary to tertiary halide and the results presented in this text are in agreement with this conclusion (cf. expts. 1 and 6, Table 4). It will be recalled that in the reactions between (2-hydroxyalkyl)silanes and phosphorus tribromide or thionyl chloride, extensive fragmentation was observed with the tertiary compounds. Since these reactions were believed to proceed via carbonium ions of the type $R_3SiCH_2CR_2^+$, it seems unlikely that explanation of the coupling process by a heterolytic mechanism, which would involve similar intermediates, is valid. In other words, if the coupling reaction were heterolytic, one might anticipate that its extent should increase in the reverse order to that observed.

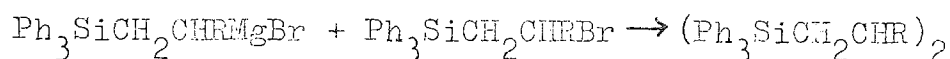
Although the data is not completely decisive, it is concluded that coupling is probably a radical process. The reaction between n-propylmagnesium bromide and (2-bromoethyl)triphenylsilane in benzene with high purity magnesium remains an anomaly.

Two possible mechanisms may be envisaged for the dimerization reaction:-

(a) radical combination



(b) coupling of the halide with its own organometallic compound



In the reaction between n-propylmagnesium bromide and (2-bromoethyl)triphenylsilane in THF containing added styrene, although the proportion of 'exchange' hydrocarbon was decreased, the quantity of dimer was unaffected. This might suggest that dimerization is not a radical phenomenon but once again it is possible that reaction occurs within the solvent cage. It is noticeable that dimerization is not observed in the absence of 'exchange' and is maximal in tetrahydrofuran. The results may indicate a heterolytic mechanism but are not conclusive.

Without knowing the fate of the products derived from the Grignard reagents it is not possible to offer

explanation for the formation of olefinic materials. The fact that in the reaction of n-propylmagnesium bromide and (2-bromoethyl)triphenylsilane in benzene (expt. 13, Table 6), the quantity of non-deuterated ethyltriphenylsilane does not balance that of triphenylvinylsilane indicates that the following disproportionation reaction is unimportant.

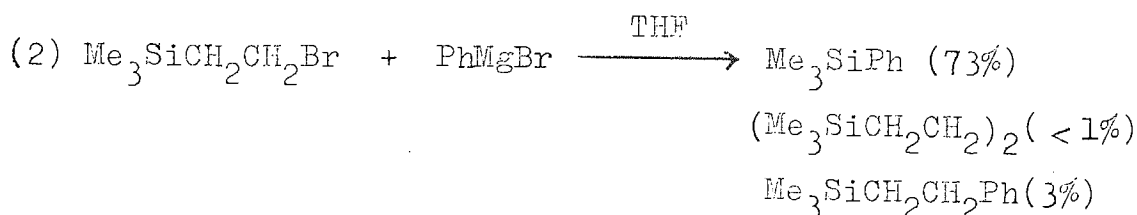
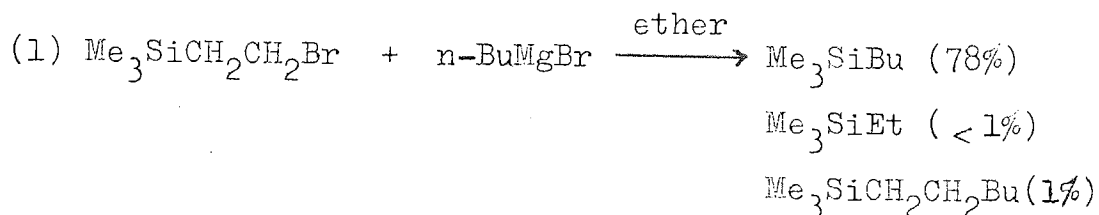


Since significant triphenylvinylsilane formation is not observed in ether or THF, it may also be concluded that the process is negligible in these systems. The formation of the olefin in benzene may well be explained by cross disproportionation between $\text{Ph}_3\text{SiCH}_2\text{CH}_2$ radicals and alkyl radicals derived from the Grignard reagent but proof of such a process would require gas analysis and labelling experiments.

Out of curiosity (rather than scientific reason!), the reaction between (bromomethyl)triphenylsilane and n-propylmagnesium bromide in diethyl ether was studied. Only two products were recovered in significant proportions - methyltriphenylsilane (20%) and starting material (59%). Time did not allow a study of the mechanism of this reaction but in view of the results of Brook and his coworkers⁵², an investigation of this system might prove interesting.

8. Attempts to determine the mechanism of fragmentation.

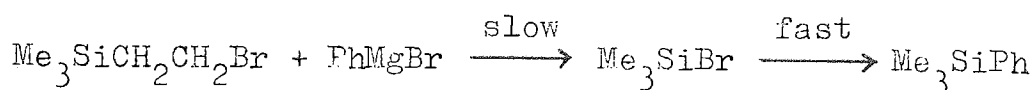
Since the reactions between (2-halogenoalkyl)tri-phenylsilanes and Grignard compounds did not involve significant silicon-carbon bond cleavage, it was necessary to return to the trialkylsilyl systems in order to study the fragmentation process. As a preliminary to this work, two reactions were studied and a thorough search for the products of 'exchange', dimerization and coupling (in addition to those of fragmentation) was made. In previous investigations complete product analysis has not been reported^{3,47}. The reactions are summarised below:-



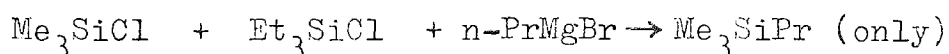
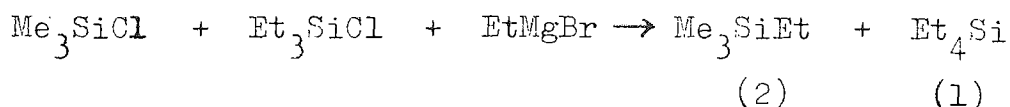
It is apparent that 'exchange', dimerization and coupling do not compete with fragmentation in these systems.

It will be recalled that two mechanisms have been proposed for the fragmentation process^{3,47}. In order to distinguish between them a search was made for the intermediate halide which would be anticipated in the Russian scheme. Reaction (2) appeared to be a particularly suitable system for study by NMR

spectroscopy since the trimethylsilyl protons of starting material $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{Br}$, intermediate Me_3SiBr (if it were formed) and product Me_3SiPh were well defined singlet absorptions, clearly detectable in a mixture of the three components. However, although absorptions attributable to product and starting material were detected at various time intervals, there was no evidence for the formation of bromotrimethylsilane during a reaction. In spite of this, the experiment does not constitute definite evidence against the Russian scheme since it was found that reaction between Me_3SiBr and PhMgBr occurs extremely rapidly and that only an absorption due to product (Me_3SiPh) is detected when the two are mixed in an NMR tube at 35° . Thus, reaction with the (2-halogenoalkyl)silane might well proceed in the following manner:-



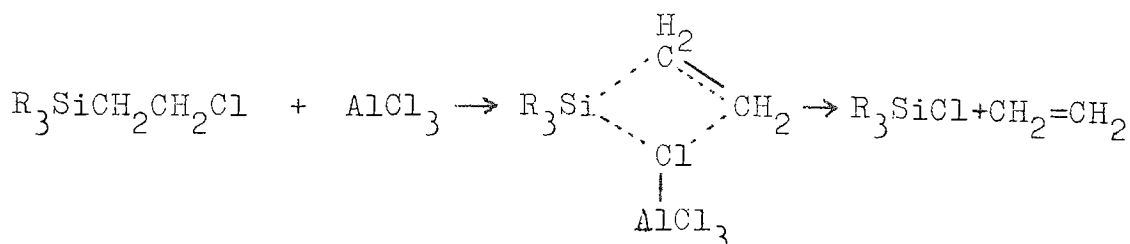
It is possible that the Russian workers chose an exceptionally good system for study ($\text{Et}_3\text{SiCH}_2\text{CHMeBr}$ and EtMgBr) in that coupling between halogenotriethylsilanes and Grignard reagents is known to be a much slower process than with the trimethyl analogues⁹⁸.



Unfortunately, their system is not suitable for a detailed investigation by NMR techniques.

In an attempt to discover whether the hydroxytriethylsilane obtained by Petrov and Mironov might have been formed merely by hydrolysis of the starting material during the work up procedure (see page 32), the preparation of (2-bromopropyl)triethylsilane was undertaken. It was hoped to study the stability of this compound in a diethyl ether/water mixture. Every precaution was taken during the preparation and storage of the halide but the precise constitution of the product obtained was uncertain. It is possible that fragmentation to bromotriethylsilane had occurred. The product obtained by reaction with an ether/water mixture was identified as hydroxytriethylsilane but in view of the uncertainty of the nature of the starting material no conclusions may be drawn from this experiment. It seems likely that the halide $\text{Et}_3\text{SiCH}_2\text{CH}_2\text{Br}$ is fairly unstable but our experiments have not contributed to the already known facts concerning the fragmentation process.

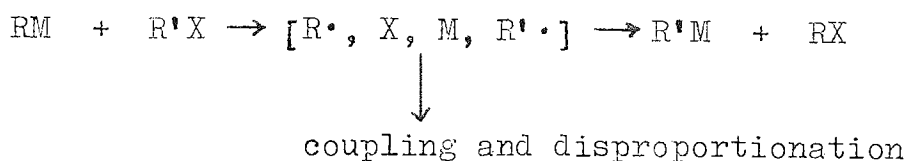
It is probable that the Russian scheme is the correct one and that decomposition occurs in a manner similar to that proposed for reactions between (2-halogenoalkyl)silanes and aluminium chloride⁹⁹



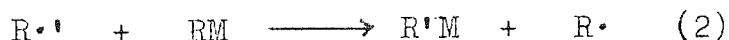
but unequivocal evidence is still awaited.

9. Reactions between alkyl halides and organometallic reagents.

The results presented in this dissertation are in agreement with the now emerging pattern of single electron transfer processes in organic chemistry. As was noted in the introduction to this chapter, much evidence suggesting radical participation in reactions where such intermediates were not previously considered important is now accumulating. It seems likely that many reactions of alkyl halides with organometallic compounds can be explained by such processes. Ward, Lawler and Cooper⁷⁷ and Russell and Lamson⁷⁴ have proposed schemes essentially similar to that suggested in this text, from studies with organolithium reagents.



Undoubtedly, true halogen-metal exchange processes do occur (in the sense that both a new organometallic compound and alkyl halide are formed). In these cases the following reactions may take place:-



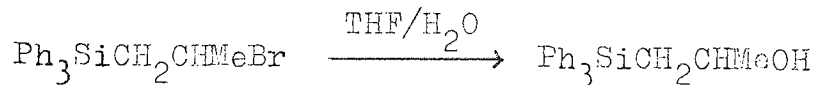
In the (2-halogenoalkyl)triphenylsilane systems, reaction (1) is obviously unimportant but in others it may occur to a significant extent.

It is hoped that the work described in this chapter may contribute in a small way towards the further understanding of these processes.

Chapter Three

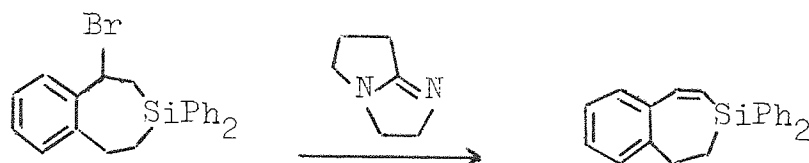
THE DECREASE IN SILICON-CARBON BOND CLEAVAGE OBSERVED
IN REACTIONS OF BETA-FUNCTIONAL TRIPHENYLSILANES.

The results described in Chapters 1 and 2 have demonstrated the decreased tendency of beta-functional organosilanes to undergo fragmentation when phenyl groups replace alkyl groups at the silicon atom. Similar observations were recorded when the (2-bromo-alkyl)triphenylsilanes were added to protic solvents, in which the trialkylsilyl analogues readily decompose. (2-Bromoethyl)triphenylsilane was recovered unchanged from a variety of solvolytic media and (2-bromopropyl)triphenylsilane did not eliminate propylene in tetrahydrofuran/water (50/50) but gave (2-hydroxypropyl)triphenylsilane in almost quantitative yield.



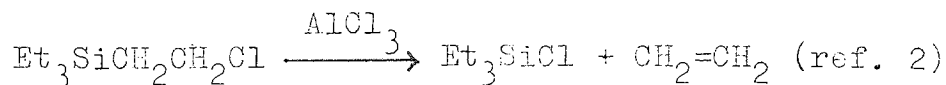
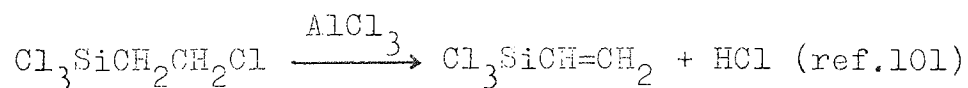
Corriu and coworkers³⁵ found that (2-chloroethyl)triphenylsilane was stable in ethanol/water and dioxan/water mixtures below 200°. All of these results are consistent with those of Sommer²¹ who studied the neutral solvolysis of the compounds $\text{R}_3\text{SiCH}_2\text{CH}_2\text{Cl}$ in 70% ethanol at 50° and found that the rates were $\text{Me}_3\text{Si} > \text{Et}_2\text{MeSi} > \text{PhMe}_2\text{Si} > (\text{m-CF}_3\text{C}_6\text{H}_4)\text{Me}_2\text{Si}$. A similar rate order was obtained from a study of the acid catalysed solvolysis of $\text{R}_3\text{SiCH}_2\text{CH}_2\text{OH}$. Oxidation of (2-hydroxyethyl)triphenyl-

silane to the corresponding acid⁴⁵ and the results of Davis and Gray^{10,46} have already been mentioned. Yet another example of phenyl groups stabilizing the silicon-carbon bond is shown in the following reaction:-



In the presence of base, the diphenyl substituted bromide undergoes dehydrohalogenation whereas the corresponding compound with methyl groups on silicon undergoes complete desilicohalogenation¹⁰⁰.

The trichlorosilyl group exerts a similar stabilizing influence. When the compound $\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{Cl}$ is treated with methylmagnesium bromide, elimination of ethylene is not observed until the third chlorine atom at silicon has been replaced³ and (in contrast to the trialkyl analogues) this compound eliminates hydrogen halide when reacted with aluminium chloride.



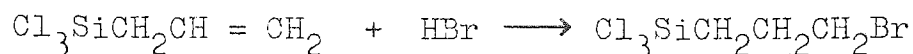
The reactivity and ready cleavage of the silicon-carbon bond of beta-functional trialkylsilanes has sometimes been attributed to the high inductive electron release by the group R_3SiCH_2 . The Taft σ^* value for the

Me_3SiCH_2 group (-0.26)³⁰ is considerably higher than for the analogous carbon group¹⁰² Me_3CCH_2 ($\sigma^* = -0.17$) and is comparable to that of the t-butyl substituent¹⁰² Me_3C ($\sigma^* = -0.30$). The ease of formation of the carbonium ion $\text{Me}_3\text{SiCH}_2\text{CH}_2^+$ in solvolytic and other reactions is thus increased and following the accumulation of positive charge at the beta-carbon atom, fragmentation is observed. In contrast, the group Cl_3SiCH_2 is believed to be electron withdrawing and leads to a more stable system. A similar argument might explain the behaviour of the triphenylsilyl compounds (i.e. the group Ph_3SiCH_2 might be expected to display electron withdrawal or, at least, decreased electron donation compared to that of R_3SiCH_2 groups). At the onset of this work, the only reported data on the electronic effects of the Ph_3SiCH_2 group was that of Brook and Pannell¹⁰³ ($\sigma^* = +0.09$). This would indicate that the group is electron donating. One manifestation of the differences in the inductive effects of the groups Cl_3SiCH_2 and Me_3SiCH_2 is observed on addition of hydrogen bromide to the corresponding allyl compounds. Thus, addition to allyltrimethylsilane occurs exclusively according to Markownikoff's rule even in the presence of peroxide^{104,105}.



whereas addition to allyltrichlorosilane occurs in an anti-Markownikoff fashion and the incorporation of

inhibitors is without effect¹⁰⁶.



If the value derived by Brook and Pannell were in error (the constant was not determined directly) and the group Ph_3SiCH_2 were electron withdrawing, one might anticipate that addition of hydrogen bromide to allyltriphenylsilane should occur as in the latter reaction. Since there appeared to be no published evidence of this reaction, it was performed in the presence and absence of peroxide. In both instances (2-bromopropyl)triphenylsilane was the product obtained.

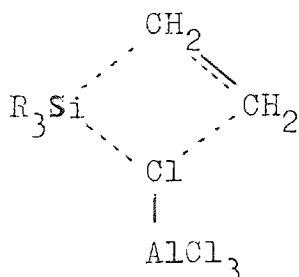


Recently, Rowley¹⁰⁷ has obtained a value of σ^* similar to that of Brook and Pannell and one must conclude that the group Ph_3SiCH_2 is electron donating.

Another commonly used concept to explain the high reactivity of beta-functional trialkylsilanes is that of $\sigma-\pi$ conjugation (see Chapter 1). The decreased reactivity in ionic addition reactions observed with the trichlorosilyl compounds has been attributed to decreased $\sigma-\pi$ conjugation with the accumulation of electronegative groups at silicon. It seems unlikely that the effect of the triphenylsilyl group may be similarly explained but it is possible that this type of conjugation may be decreased in such compounds by

other factors (steric hindrance).

Other possible explanations exist. In reactions involving carbonium ion intermediates the build up of positive charge may be prevented by delocalisation in the aromatic rings (see Chapter 1). Reactions of (2-halogenoalkyl)trialkylsilanes with aluminium chloride and Grignard reagents and their thermal decompositions probably proceed via a cyclic transition state involving interaction between silicon and the group attached to the beta-carbon atom



It is possible that in the triphenyl-substituted compounds steric factors may prevent such interaction. Alternatively, steric effects may prevent rearside attack at the silicon atom by an incoming nucleophile - an argument presented by Corriu et al³⁵.

At the present time, the relative importance of inductive and resonance effects on the reactions of beta-functional organosilanes has not been determined. It might be concluded that whilst the differences in the reactions of the trialkyl and triphenyl-substituted compounds may be explained by the contrasting inductive effects of the groups Ph₃SiCH₂ and Me₃SiCH₂, steric and resonance factors may also be important.

CONCLUSIONS

The decrease in silicon-carbon bond cleavage observed in the reactions of beta-functional organosilanes when triphenylsilyl compounds are employed in place of the trialkylsilyl analogues has been established. Reaction of (2-hydroxyalkyl)silanes with phosphorus tribromide or thionyl chloride is consistent with a carbonium ion mechanism and demonstrates the ability of silicon to stabilize such intermediates by interaction with the developing charge at the beta-carbon atom. The reaction between (2-bromoalkyl)triphenylsilanes and Grignard reagents was studied with a view towards the better understanding of the interactions of alkyl halides with organometallic compounds but in such a vast field it is possible merely to scratch the surface. Many important questions remain unanswered (e.g. the precise role of the solvent in these reactions has not been determined) and the manner in which several of the products are obtained has not been firmly established. Clearly, the formation of 'exchange' hydrocarbon is not a genuine example of halogen-metal interconversion and the data presented is adequately explained by a mechanism of single electron transfer. It is possible that many reactions in organic chemistry may proceed by such processes. In the past, reactions have been rigidly divided into homolytic and heterolytic processes and the formation of radicals in a heterolytic system (or the production

of ions in a free radical system) have been regarded as side reactions proceeding in parallel with the main reaction. This phenomenon might be better explained if it is assumed that the formation of a new bond is preceded by single electron transfer from one reacting species to another. Evidence is now accumulating in this area but there is scope for many more investigations. In conclusion one might echo the words of Julian Huxley that 'truth is not revealed as a whole but has to be progressively discovered'.

EXPERIMENTAL

Melting points and boiling points quoted in this section are uncorrected. The elemental analyses of liquid materials were carried out at the Alfred Bernhardt Laboratory (W. Germany). Organosilanes were kindly donated by Midland Silicones Ltd. and the remaining chemicals were purchased from Messrs. Hopkin and Williams Ltd. or the alternative supplier indicated.

UV spectra were recorded with a Perkin-Elmer 137 spectrometer.

GLC analyses were performed on a Pye-Unicam 104 instrument using an SE30 silicone gum column (9ft. x 1/8 in. o.d.) with helium as a carrier gas at a flow rate of 50ml/min. Temperatures for individual separations are recorded in the text.

NMR spectra were determined at 35° (unless otherwise stated). Routine spectra were recorded at 60 MHz/sec using either a Varian Associates A-60A spectrometer or a Perkin-Elmer R-10 model. For the accurate integration of dilute solutions (10% w/v or less), spectra were recorded at 100 MHz/sec with a Perkin-Elmer R-14 spectrometer. Tetramethylsilane was used as an internal reference and spectral assignments were based on the data of Mathieson¹⁰⁸.

IR spectra were obtained using a Perkin-Elmer Infracord 237 and the interpretation of absorption bands was based on the texts of Bellamy¹⁰⁹ and Flett¹¹⁰. The anticipated silicon-methyl or silicon-phenyl absorptions were observed in all compounds and are not individually recorded.

A. THE REACTION OF (2-HYDROXYALKYL)SILANES WITH THIONYL CHLORIDE OR PHOSPHORUS TRIBROMIDE.

1. Preparation of alpha-silylacetates.

Ethyl (trimethylsilyl)acetate, ethyl (diphenylmethylsilyl)acetate and ethyl (triphenylsilyl)acetate were prepared from ethyl bromoacetate, zinc and chlorosilane using the method outlined by Pratt¹¹¹.

Ethyl (trimethylsilyl)acetate. Yield 47%; b.p. 74-76°/42mm.

Ethyl (diphenylmethylsilyl)acetate. Yield 62%; b.p. 143-148°/0.1mm. (Found: C, 71.88; H, 7.03; Si, 9.62. C₁₇H₂₀O₂Si calcd.: C, 71.80; H, 7.09; Si, 9.88%).

Ethyl (triphenylsilyl)acetate. This ester was separated from hydroxytriphenylsilane, formed by hydrolysis of unconsumed chlorotriphenylsilane, by elution with benzene from a column of silica gel. Yield 28%; m.p. 74-76°. (Found: C, 75.50; H, 6.30. C₂₂H₂₂O₂Si calcd.: C, 76.25; H, 6.40%).

Ethyl (dimethylphenylsilyl)acetate was prepared by a method similar to that of Gold et al⁷. Reaction of phenylmagnesium bromide and (chloromethyl)dimethylchlorosilane in diethyl ether gave (chloromethyl)dimethylphenylsilane. The Grignard reagent of the latter reacted with ethyl chloroformate to give the desired ester in 53% yield, b.p. 93-99°/3mm.

The physical properties and the IR and NMR spectra of these esters were consistent with those recorded by Fessenden and Fessenden¹¹².

Repeated attempts to prepare ethyl (trimethylsilyl)-propionate and ethyl (trimethylsilyl)isobutyrate by the modified Reformatsky procedure were unsuccessful.

2. Preparation of (2-hydroxyalkyl)silanes.

The deuterated alcohols were obtained by reduction of the alpha-silylacetates with lithium aluminium deuteride (99% isotopic purity - ex CIBA) in diethyl ether. The procedure using ethyl (trimethylsilyl)acetate is typical of those performed:-

Ethyl (trimethylsilyl)acetate (8.0g, 0.050 mole) in diethyl ether (20ml) was slowly added to a stirred suspension of lithium aluminium deuteride (2.0g, 0.048 mole) in ether (40ml). The resulting mixture was stirred for 1h after which the excess reducing agent was destroyed by careful hydrolysis with water. The aqueous layer was extracted with ether and the combined extracts dried over magnesium sulphate. Fractionation gave (2-hydroxyethyl-2,2-d₂)trimethylsilane (3.6g, 61%).

The IR spectra of all the deuterated alcohols showed characteristic carbon-deuterium absorptions at 2180cm⁻¹ and 2080cm⁻¹. Other properties of these compounds are summarised in Table 13.

(2-Hydroxypropyl)triphenylsilane was prepared by the method of Gilman et al¹¹³. M.p. 85-88° (lit.¹¹³ 86-88°); NMR (CCl₄ soln.): multiplet τ 2.6 (intensity 15), multiplet τ 6.0 (intensity 1), multiplet τ 8.3 (intensity 2), singlet τ 8.4 (intensity 1), doublet τ 8.9 (intensity 3).

TABLE 13

Properties of (2-hydroxyethyl - 2,2 - d₂)silanes.

Alcohol	b.p.	NMR absorptions* (τ values)				Analysis
		Si-Ph	Si-Me	Si-CH ₂	OH	
Me ₃ SiCH ₂ CD ₂ OH (Yield 61%)	68°/30 mm (lit. 114 95°/100mm)	-	10.0	9.1	5.0	Found: C, 50.65; H, 11.71; Si, 23.55. C ₅ H ₁₂ D ₂ O ₂ Si calcd: C, 50.01; H, 11.86; Si, 23.35%.
Me ₂ PhSiCH ₂ CD ₂ OH (Yield 49%)	96-100°/4mm	2.5	9.8	8.8	5.9	Found: C, 66.83; H, 8.72; Si, 15.27. C ₁₀ H ₁₄ D ₂ O ₂ Si calcd: C, 65.90; H, 8.85; Si, 15.41%.
MePh ₂ SiCH ₂ CD ₂ OH (Yield 67%)	145-8°/0.2mm	2.6	9.5	8.6	6.7	Found: C, 74.33; H, 7.47; Si, 11.41. C ₁₅ H ₁₆ D ₂ O ₂ Si calcd: C, 73.77; H, 7.42; Si, 11.49%.
Ph ₃ SiCH ₂ CD ₂ OH (Yield 90%)	m.p. 97-98° (lit. 114 99-100°)	2.6	-	8.4	7.8	Found: C, 77.85; H, 6.53; C ₂₀ H ₁₈ D ₂ O ₂ Si calcd: C, 78.43; H, 6.54%.

* All singlet absorptions except the aromatic.

(2-Hydroxypropyl-2-methyl)trimethylsilane was obtained in low yield by reaction of ethyl (trimethylsilyl)-acetate and methylmagnesium iodide in refluxing diethyl ether for 15h. B.p. 85-90°/90mm (lit.¹¹⁴ 91-92°/98mm); NMR (neat liquid): singlet τ 6.6 (intensity 1), singlet τ 8.8 (intensity 6), singlet τ 9.0 (intensity 2), singlet τ 10.0 (intensity 9).

(2,2-Diphenyl-2-hydroxyethyl)trimethylsilane was obtained in 37% yield by reaction of phenylmagnesium bromide and ethyl (trimethylsilyl)acetate in refluxing diethyl ether for 48h. The alcohol distilled at 144-148°/0.1-0.2mm and then solidified. Recrystallisation from light petroleum (b.p. 60-80°) gave a product, m.p. 67-69°; NMR (CCl₄ soln.): multiplet τ 2.5 (intensity 10), singlet τ 7.9 (intensity 1), singlet τ 8.1 (intensity 2), singlet τ 10.0 (intensity 9). (Found: C, 76.22; H, 8.38. C₁₇H₂₂OSi calcd.: C, 75.54; H, 8.15%).

3. Reaction of (2-hydroxyalkyl)silanes with thionyl chloride or phosphorus tribromide.

Thionyl chloride or phosphorus tribromide was added dropwise, in excess, to the alcohol at 0° and after addition was complete NMR spectra of the resulting solutions were recorded at 35°. From these spectra the proportion of rearrangement (from the intensities of the methylene groups attached to bromine and silicon respectively) and of substitution relative to elimination (from the intensities of the (2-halogenoalkyl)silane and halogenosilane produced) were determined. The extents

of these reactions are recorded in Table 1 and the corresponding absorption positions of the products formed in Table 14.

Separation of the substituted products of the reaction of (2-hydroxyethyl-2,2-d₂)trimethylsilane and (2-hydroxyethyl-2,2-d₂)triphenylsilane with thionyl chloride was possible and allowed their analyses.

a) Isolation of (2-chloroethyl-2,2-d₂)trimethylsilane + (2-chloroethyl-1,1-d₂)trimethylsilane.

B.p. 60°/60mm; NMR (neat liquid): singlet τ 6.4 (intensity_<1), singlet τ 8.8 (intensity_>1), singlet τ 10.0 (intensity 9). (Found: titratable Cl, 25.9. C₅H₁₁D₂ClSi calcd.: titratable Cl, 25.6%).

b) Isolation of (2-chloroethyl-2,2-d₂)triphenylsilane + (2-chloroethyl-1,1-d₂)triphenylsilane.

Recrystallisation from light petroleum (b.p. 60-80°) gave a white solid, m.p. 128-130°; NMR (CCl₄ soln.): singlet τ 2.5 (intensity 15), singlet τ 6.3 (intensity < 1), singlet τ 8.0 (intensity_>1). (Found: C, 74.50; H, 5.90; Cl, 10.93. C₂₀H₁₇D₂ClSi calcd.: C, 73.96; H, 5.86; Cl, 10.91%).

c) Reaction of (2-hydroxyethyl-2,2-d₂)triphenylsilane with phosphorus tribromide.

Reaction as described above gave rise to absorptions at τ 2.5, 6.4, 7.9 and 8.1 in the NMR spectrum. The intensity of the latter peak decreased with time whilst those at τ 6.4 and 7.9 increased until constant proportions were obtained which then remained unchanged even after 7 days. After this period, the material

TABLE 14

NMR spectral absorption positions of the products from reaction of (2-hydroxyethyl - 2,2 - d₂)-silanes and phosphorus tribromide or thionyl chloride (τ values).

Alcohol	Si-Ph	Si-Me	Si-CH ₂	CH ₂ -X	Fragmentation Products ^a
Reaction with thionyl chloride (X=Cl)					
Me ₃ SiCH ₂ CD ₂ OH	-	10.0	8.8	6.4	9.6 (Me ₃ SiCl-9.6)
Me ₂ PhSiCH ₂ CD ₂ OH	2.5	9.8	8.7	6.5	9.4
MePh ₂ SiCH ₂ CD ₂ OH	2.5	9.5	8.3	6.4	9.3 (MePh ₂ SiCl-9.3)
Ph ₃ SiCH ₂ CD ₂ OH	2.5	-	8.0	6.3	2.5
Reaction with phosphorus tribromide (X=Br)					
Me ₃ SiCH ₂ CD ₂ OH	-	10.0	8.7	6.5	9.5 (Me ₃ SiBr-9.5)
Me ₂ PhSiCH ₂ CD ₂ OH	2.7	9.8	8.5	6.6	9.4
MePh ₂ SiCH ₂ CD ₂ OH	2.7	9.5	8.2	6.6	9.3
Ph ₃ SiCH ₂ CD ₂ OH	2.5	-	7.9	6.4	2.5

a. The absorption positions in brackets are those of authentic samples which were available.

absorbing at τ 8.1 was present to approximately 40%.

d) Reactions with (2-hydroxypropyl)triphenylsilane.

Examination of the NMR spectrum of the resulting solution from reaction of (2-hydroxypropyl)triphenylsilane and phosphorus tribromide revealed the following absorptions: multiplet τ 2.5 (intensity >15), multiplet τ 5.6 (intensity 1), multiplet τ 7.7 (intensity 2), doublet τ 8.4 (intensity 3). Such absorptions were consistent with the formation of (2-bromopropyl)triphenylsilane and possibly a small quantity of bromotriphenylsilane produced by fragmentation. Any such fragmentation did not exceed 7%. No absorptions were observed in the region τ 6.0-7.0 suggesting an absence of the rearranged compound $\text{Ph}_3\text{SiCHMeCH}_2\text{Br}$ (expected methylene absorption τ 6.4).

Reaction with thionyl chloride gave rise to the following absorptions: multiplet τ 2.6 (intensity >15), multiplet τ 5.5 (intensity 1), multiplet τ 7.8 (intensity 2), doublet τ 8.5 (intensity 3). These absorptions were consistent with the formation of (2-chloropropyl)triphenylsilane and possibly a small amount of chlorotriphenylsilane (not greater than 6%). There was no evidence of formation of the rearranged halide $\text{Ph}_3\text{SiCHMeCH}_2\text{Cl}$ (anticipated methylene absorption τ 6.3).

e) Reaction with (2-hydroxypropyl-2-methyl)trimethylsilane.

Addition of phosphorus tribromide gave a mixture whose NMR spectrum showed only singlet absorptions at τ 8.2 and 9.5 (authentic samples of t-butyl bromide and

bromotrimethylsilane absorbed at τ 8.2 and 9.5 respectively).

Reaction with thionyl chloride gave rise to absorptions at τ 8.4 and 9.6 (pure samples of *t*-butyl chloride and chlorotrimethylsilane absorbed at τ 8.4 and 9.6 respectively).

f) Reaction with (2,2-diphenyl-2-hydroxyethyl)trimethylsilane.

Reaction with phosphorus tribromide gave a mixture absorbing at τ 2.6 (aromatic protons), τ 9.5 (bromotrimethylsilane) and at τ 7.6 and 4.6. By analogy with reaction (e), the latter two peaks were assigned to 1-bromo-1,1-diphenylethane (methyl protons) and 1,1-diphenylethylene (olefinic protons) respectively. Calculations^{108,115} indicated that these two compounds would be expected to absorb at τ 7.6 and 4.5 and that the absorption positions were not those anticipated for the rearranged and unrearranged bromides formed by substitution.

Reaction with thionyl chloride appeared normal at 0° but on warming to room temperature vigorous gas evolution occurred and the solution turned from yellow to dark brown. Absorptions at τ 2.7 (aromatic protons) and 9.6 (chlorotrimethylsilane) were observed. Removal of the latter and excess thionyl chloride, under vacuum, gave a product absorbing only at τ 2.7. Its IR spectrum was not superimposable on those of diphenylethylene or *cis/trans* stilbene (possibly formed by olefinic rearrangement) but indicated a trisubstituted ethylene.

Lassaigne tests confirmed the presence of sulphur and chlorine.

B. THE ATTEMPTED TRAPPING OF THE 2-(TRIMETHYLSILYL)ETHYL CATION BY SILANE HYDRIDE TRANSFER.

1. Preparation and purification of reagents.

Technical grade methylene chloride and chloroform were purified as described by Vogel¹¹⁶ and the distilled liquids stored over molecular sieves. Trifluoroacetic acid (ex Koch-Light) was used without further purification.

(2-Hydroxyethyl)trimethylsilane and its dideuterated analogue, (2-hydroxyethyl-2,2-d₂)trimethylsilane, were prepared as described in section A2.

Triethylsilane was obtained by the method of Eaborn¹¹⁷; b.p. 107° (lit.¹¹⁷ 107°); IR (neat liquid): Si-H absorption 2090cm⁻¹; NMR (neat liquid): multiplet τ 6.3 (intensity 1), complex multiplet τ 8.8-9.7 (intensity 15).

Triphenylsilane was prepared by the method of Reynolds et al¹¹⁸; m.p. 36-37° (lit.¹¹⁸ 36-37°); IR (thin film): Si-H absorption 2120cm⁻¹; NMR (CCl₄ soln.): multiplet τ 2.6 (intensity 15), singlet τ 4.6 (intensity 1).

Ethyltrimethylsilane was prepared following the procedure of Whitmore et al¹¹⁹; b.p. 63° (lit.¹¹⁹ 62.7-63.2°/736mm); NMR (neat liquid): complex multiplet τ 8.9-9.6 (intensity 5), singlet τ 10.0 (intensity 9).

Hexamethyldisiloxane was obtained by hydrolysis of chlorotrimethylsilane; b.p. 99-100° (lit.¹¹⁴ 99.6°); IR (neat liquid): Si-O-Si absorption 1050cm⁻¹; NMR (neat liquid): singlet τ 9.9.

2. Reaction conditions for attempted silane hydride transfer.

The conditions employed were similar to those of Carey and Tremper⁴³. A typical reaction is described:-

Trifluoroacetic acid (0.80g, 0.0070 mole) was added to a mixture of (2-hydroxyethyl)trimethylsilane (0.42g, 0.0035 mole) and triethylsilane (0.49g, 0.0042 mole) in methylene chloride (alcohol/solvent, 8% w/v) at -15° . This temperature was maintained for 30 min, after which the reaction was quenched with sodium carbonate and the products analysed.

Other reactions were carried out with the following variations in conditions:-

- a) using chloroform as the solvent.
- b) reaction in chloroform at -5° for 1h, 3h and 60h.
- c) (2-hydroxyethyl)trimethylsilane in chloroform or methylene chloride (4,8,16% w/v) at room temperature for 1h and 24h.
- d) reaction in chloroform or methylene chloride at room temperature for 3h, using triphenylsilane as potential hydride transfer agent.
- e) reaction in chloroform or methylene chloride at room temperature for 1h, using a triethylsilane/alcohol molar ratio of 3/1.
- f) reaction in chloroform or methylene chloride at room temperature for 1h, using a trifluoroacetic acid/alcohol molar ratio of 5/1.

In all experiments only hexamethyldisiloxane, 2-(trimethylsilyl)ethyl trifluoroacetate and starting compounds

were identified as products. Ethyltrimethylsilane was not detected. The yield of hexamethyldisiloxane increased with increasing alcohol concentration, temperature and trifluoroacetic acid/alcohol concentration.

Reactions were also performed in the absence of hydride transfer agent and are summarised in Table 2. Examination of the NMR spectra of the alcohol and ester obtained from reactions in which (2-hydroxyethyl-2,2-d₂)-trimethylsilane was used indicated that skeletal rearrangement ($XCH_2CD_2Y \rightarrow XCD_2CH_2Z$) did not occur under the conditions employed.

3. Identification of products.

This was achieved by the combined use of NMR, IR and GLC analyses. A mixture of authentic samples of ethyltrimethylsilane, hexamethyldisiloxane and triethylsilane in chloroform or methylene chloride was readily separable into individual components using GLC at 36°. This temperature was therefore used in all analyses. (2-Hydroxyethyl)trimethylsilane and 2-(trimethylsilyl)ethyl trifluoroacetate had much greater retention times at this temperature and were observed as broad peaks. GLC was used simply to indicate the presence or absence of ethyltrimethylsilane in the reaction mixture and the relative proportions of hexamethyldisiloxane, triethylsilane, triphenylsilane, (2-hydroxyethyl)trimethylsilane and 2-(trimethylsilyl)ethyl trifluoroacetate were determined from their corresponding absorptions (recorded in section B1) in the NMR spectrum.

2-(Trimethylsilyl)ethyl trifluoroacetate was identified from the following physical data:- IR : strong absorption 1780cm^{-1} (cf. Carey and Tremper⁴³ - trifluoroacetate compounds 1780cm^{-1}); NMR : multiplet τ 5.6* (intensity 2), multiplet τ 8.9 (intensity 2), singlet τ 10.0 (intensity 9).

(*lit.⁴³ - $\text{RCH}_2\text{OCOCF}_3$, methylene protons τ 5.5-5.8).

C. ORGANOMETALLIC REACTIONS.

1. Preparation and purification of reagents.

a) Purity of magnesium.

Unless otherwise stated, experiments were performed using 'magnesium turnings for Grignard reaction' having the following batch analysis (%):-

minimum assay - 99.75

zinc	- 0.01	nickel	- 0.001
aluminium	- 0.007	lead	- 0.003
silicon	- 0.007	calcium	- 0.003
copper	- 0.001	cadmium	- 0.0003
manganese	- 0.004	iron	- 0.008
tin	- 0.001	manganese dioxide	- 0.1

In the experiments of Table 7 a high purity grade magnesium was used, supplied by New Metals and Chemicals Limited, purity > 99.995%.

b) Purification of solvents and alkyl halides.

Technical grade diethyl ether and tetrahydrofuran were initially dried over sodium wire and then distilled from lithium aluminium hydride, immediately prior to use. Dibutyl ether was dried over calcium chloride and distilled at 142-144°. AnalaR benzene was stored over sodium wire and used without further purification.

All alkyl halides were distilled and dried over magnesium sulphate.

c) Preparation of allyl- and vinylsilanes.

Allyltriphenylsilane - An ethereal solution of chloro-

triphenylsilane was prepared by addition of phenyllithium to an equimolar solution of dichlorodiphenylsilane and was then refluxed with allylmagnesium bromide (50% molar excess) for 48h. The resulting mixture was hydrolysed with ammonium chloride solution and the ethereal layer separated and dried over magnesium sulphate. Removal of the solvent and recrystallisation from ligroin gave the required compound in 80% yield. M.p. 88-90° (lit.¹¹⁴ 90°); NMR (CCl₄ soln.): multiplet τ 2.5 (intensity 15), multiplet τ 4.2 (intensity 1), multiplet τ 5.1 (intensity 2), doublet τ 7.7 (intensity 2).

Trimethylvinylsilane was prepared as described by Nagel and Post¹²⁰; b.p. 54-56° (lit.¹²⁰ 54.4°/745.4mm); NMR (neat liquid): complex multiplet τ 3.7-4.6 (intensity 3), singlet τ 9.9 (intensity 9).

Triphenylvinylsilane was obtained using the method of Cason and Brooks¹²¹; m.p. 68-70° (lit.¹²¹ 67-68°); IR identical to that recorded by Henry and Noltes¹²²; NMR (CCl₄ soln.): multiplet τ 2.6 (intensity 15), complex multiplet τ 3.0-4.5 (intensity 3).

d) Preparation of (2-bromoalkyl)silanes.

In the following preparations, hydrogen bromide was generated by addition of water to phosphorus tribromide and dried by passing through a trap at -40°. Carbon tetrachloride was distilled and stored over molecular sieves.

(2-Bromoethyl)trimethylsilane was prepared from tri-

methylvinylsilane and hydrogen bromide using the method of Sommer et al¹²³; b.p. 72°/45mm (lit.¹²³ 64-65°/39mm); NMR (neat liquid): multiplet τ 6.5 (intensity 2), multiplet τ 8.7 (intensity 2), singlet τ 10.0 (intensity 9). (Found: titratable Br, 44.57. C₅H₁₃BrSi calcd.: titratable Br, 44.11%).

(2-Bromoethyl)triphenylsilane was obtained by passing hydrogen bromide through a solution of triphenylvinylsilane in carbon tetrachloride (20% w/v) containing a small quantity of benzoyl peroxide. Removal of the solvent and recrystallisation from light petroleum (b.p. 60-80°) gave the compound in 82% yield. M.p. 142-144° (lit.¹¹⁴ 144°); NMR (CCl₄ soln.): multiplet τ 2.5 (intensity 15), multiplet τ 6.4 (intensity 2), multiplet τ 7.9 (intensity 2). (Found: C, 65.75; H, 5.48; Br, 21.50. C₂₀H₁₉BrSi calcd.: C, 65.39; H, 5.21; Br, 21.75%).

(2-Bromopropyl)triphenylsilane was prepared by reaction between allyltriphenylsilane (20% w/v in carbon tetrachloride solution) and hydrogen bromide. The solvent was removed and the product obtained was recrystallised from ligroin to give the desired halide in 68% yield. M.p. 89-92°; NMR (CCl₄ soln.): multiplet τ 2.5 (intensity 15), multiplet τ 5.6 (intensity 1), multiplet τ 7.7 (intensity 2), doublet τ 8.4 (intensity 3). (Found: C, 65.76; H, 5.48; Br, 20.50. C₂₁H₂₁BrSi calcd.: C, 66.13; H, 5.55; Br, 20.95%).

e) Preparation of ethyltriphenylsilane.

This compound was prepared by reaction between

chlorotriphenylsilane and ethylmagnesium bromide (50% excess) in diethyl ether for 72h. The mixture was hydrolysed and the ethereal layer separated and dried. After the removal of solvent, a small quantity of light petroleum was added and the insoluble material filtered and discarded. On cooling the filtrate to 0°, a compound crystallised in 65% yield, m.p. 68-72°. Elution with light petroleum/benzene (90/10, v/v) from a column of silica gel gave a 94% recovery of material: m.p. 75-77° (lit.¹¹⁴ 76°); NMR (CCl₄ soln.): multiplet τ 2.6 (intensity 15), complex multiplet τ 8.5-9.0 (intensity 5). (Found: C, 83.55; H, 6.70. C₂₀H₂₀Si calcd.: C, 83.25; H, 6.99%).

f) Preparation of anhydrous metal halides.

Anhydrous cobalt chloride was obtained by distillation of acetic anhydride from 'cobaltous chloride-dried, blue', followed by several hours heating of the solid remaining, at 130° under vacuum.

Anhydrous magnesium bromide - Bromine (80g, 0.5 mole), freshly distilled from phosphorus pentoxide, was added slowly with vigorous stirring to magnesium (12.1g, 0.5 mole) in anhydrous ether (100ml). The resulting brown solution was evaporated and the solid obtained washed with several portions of carbon tetrachloride and then heated at 130° under vacuum.

2. Reactions of (2-bromoethyl)triphenylsilane and (2-bromopropyl)triphenylsilane with magnesium.

A solution of (2-bromoethyl)triphenylsilane (3.00g, 0.0082 mole) in tetrahydrofuran (9.0ml) was added dropwise to magnesium metal (0.60g, 0.025g atoms) in tetrahydrofuran (3.0ml) under an atmosphere of nitrogen ('White Spot' - ex British Oxygen Company). Reaction was initiated using 2 drops of ethylene dibromide and stirring, under reflux conditions, was continued for 1h. The resulting mixture was hydrolysed with dilute hydrochloric acid (10% v/v) and washed with sodium bicarbonate solution and water. The organic phase was dried over magnesium sulphate and evaporation gave a low melting solid (2.39g). Separation and identification as described in sections C5 and 6 showed that this mixture contained ethyltriphenylsilane (1.50g, 64%) and 1,4-bis(triphenylsilyl)butane (0.50g, 21%).

Reaction with (2-bromopropyl)triphenylsilane was carried out in a similar manner.

3. Reactions of (2-bromoalkyl)silanes with Grignard reagents.

Grignard reagents were prepared in the conventional manner⁵³ from alkyl bromides in ether (diethyl or dibutyl) or tetrahydrofuran using an alkyl halide/solvent ratio of 1/3 (v/v). For the reactions conducted in benzene, the organometallic compounds were initially prepared in diethyl ether which was then removed by distillation and replaced by benzene until a constant temperature of 76° was obtained. In all experiments

a Grignard reagent/(2-bromoalkyl)silane molar ratio 3/1 was used and a nitrogen atmosphere was maintained throughout. The following is a typical reaction:-

A solution of n-propylmagnesium bromide (approx. 0.05 mole) in diethyl ether was filtered free of excess magnesium through a plug of glass wool and made up to a total of 20.0ml. An aliquot of this solution (10.0ml, approx. 0.025 mole) was transferred by pipette to a dropping funnel and then added slowly to a stirred suspension of (2-bromoethyl)triphenylsilane (3.00g, 0.0082 mole) in ether (11.0ml). After refluxing for 3h the mixture was washed with dilute hydrochloric acid, sodium bicarbonate and water. The organic layer was separated, dried over magnesium sulphate and the solvent removed to yield an oil (2.50g). Individual components of this mixture were separated and identified as described in sections C5 and 6.

Reactions of (2-bromoethyl)triphenylsilane and (2-bromopropyl)triphenylsilane with a variety of Grignard reagents and in different solvents are summarised in Tables 4, 5 and 6.

4. Reactions with n-butyllithium.

A solution of n-butyllithium in diethyl ether (approx. 1.0 M) was prepared by the method of Gilman and Jones⁶².

a) Reaction with ethyltriphenylsilane.

The following is an example of such reactions:-

n-Butyllithium (15.0 ml, approx. 0.015 mole) was added dropwise to ethyltriphenylsilane (3.00g, 0.0104 mole) dissolved in a mixture of tetrahydrofuran (9.0 ml) and ether (12.0 ml) at 0°. After stirring at room temperature for 24h under an atmosphere of nitrogen, deuterium oxide (10.0 ml, ex Koch-Light, purity > 99.75%) was added and the stirring continued for 20 min. Lithium salts were then dissolved by addition of water, the aqueous layer was extracted with ether and the combined extracts dried over magnesium sulphate. Removal of the solvent gave a solid material (2.75g) which after elution from a column of silica gel using light petroleum/benzene (90/10, v/v) was identified as ethyltriphenylsilane (87%). There was no evidence of deuterium in this compound.

A similar reaction was quenched at -50° with carbon dioxide, generated from 'drikold' and dried by passing through towers of silica gel and calcium chloride. Dilute acid was added and the solution extracted with ether. The organic layer was separated, washed with ice cold sodium hydroxide (5%, w/v) and dried over magnesium sulphate. Evaporation of solvent and separation by column chromatography gave ethyltriphenylsilane (85%). The fraction extracted with sodium hydroxide was neutralised at 0°, extracted with ether and dried. Examination of the product isolated after the removal of solvent indicated that the yield of carboxylic acid did not exceed 3%.

Other reactions carried out under a variety of

conditions are summarised in Table 9.

b) Reaction with (2-bromoethyl)triphenylsilane and (2-bromopropyl)triphenylsilane.

A typical reaction is described:-

n-Butyllithium (12.0 ml, approx. 0.012 mole) was added over a period of 20 min to a suspension of (2-bromoethyl)triphenylsilane (3.00g, 0.0082 mole) in diethyl ether (75 ml) at -20° . This temperature was maintained for 30 min and the reaction then allowed to warm to room temperature at which point a clear yellow colouration was observed. After stirring for a further 1.5h the mixture was hydrolysed, extracted with ether and the extracts dried over magnesium sulphate. Removal of the solvent gave a mixture (2.59g), the components of which were separated and identified as described in sections C5 and 6. The results of this and other reactions are summarised in Table 8.

5. Separation of reaction products.

The products of reactions between (2-bromoalkyl)-silanes and Grignard reagents or n-butyllithium were separated as described below.

TLC was carried out using silica gel (ex Camlab Ltd.) spread to a thickness of 0.25mm according to the manufacturer's instructions. Chromatographic separations were performed on a column (approximately 1ft. x lin. diameter) using 'silica gel M.F.C.' AnalaR grade solvents were employed in all chromatographic experiments.

a) Reaction products from (2-bromoethyl)trimethylsilane.

Mixtures were fractionally distilled and examined by the techniques IR, NMR and GLC. Thus after removal of the low boiling liquids, distillation of the products obtained from reaction between the halide (10.4g, 0.057 mole) and phenylmagnesium bromide in tetrahydrofuran gave 2 fractions:-

Fraction A - b.p. 168-174° (6.0g). Analysis by GLC indicated only a single component and the material was identified as phenyltrimethylsilane from its NMR spectrum.

Fraction B - undistilled material (0.74g). The combined use of GLC and NMR spectroscopy showed that the mixture consisted of biphenyl (0.14g), phenyltrimethylsilane (0.29g), (2-phenylethyl)trimethylsilane (0.27g) and one other component, possibly 1,4-bis(trimethylsilyl)butane (0.04g).

b) Reaction products from (2-bromoethyl)triphenylsilane.

Products were separated by addition of a precipitant or by column chromatography and identified using the techniques of TLC, UV, IR, NMR and GLC.

Initial experiments indicated that (2-bromoethyl)triphenylsilane could be recovered quantitatively after:-

- (1) refluxing in tetrahydrofuran, diethyl ether or benzene for 24h.
- (2) washing an ethereal solution with dilute acid

(10%, v/v), sodium bicarbonate and water, as in a normal 'work-up' procedure.

(3) elution from a column of silica gel.

These results indicated that the products obtained after separation did not contain materials formed by decomposition of the halide during the isolation process.

The addition of small quantities of diethyl ether or ethanol precipitated 1,4-bis(triphenylsilyl)butane and allowed its separation from the remaining components of the mixture. The soluble fraction was then further separated by column chromatography using various mixtures of light petroleum/benzene as eluant. Separation of the following fractions could be achieved:-

- (a) biphenyl*.
- (b) mixtures of alkyltriphenylsilanes and triphenylvinylsilane.
- (c) (2-bromoethyl)triphenylsilane and (2-phenylethyl)triphenylsilane*.

* these products were only formed when phenylmagnesium bromide was the Grignard reagent employed.

Alcohols and hydroxysilanes which remained on the column were then removed with ether. By eluting at a slow rate and collecting several samples, further separation of fraction (b) could be achieved. The higher alkyltriphenylsilanes were eluted before the lower ones (e.g. n-hexyltriphenylsilane before ethyltriphenylsilane) and individual components of the remaining fractions were determined by NMR and GLC analyses.

The following procedure for the separation of the products obtained by reaction of the halide (3.00g, 0.0082 mole) with n-butyllithium is an example of such a process:-

Evaporation of the solvent gave a viscous material (2.76g). TLC of this mixture gave single spots at positions similar to those of authentic samples of 1,4-bis(triphenylsilyl)butane, (2-bromoethyl)triphenylsilane and what appeared to be the superimposition of two or more spots at positions similar to those of the alkyl-triphenylsilanes. Addition of diethyl ether (30 ml) precipitated pure 1,4-bis(triphenylsilyl)butane (0.27g). A further quantity of solid material (0.45g), obtained by addition of ethanol (25 ml), was shown by its NMR spectrum to consist of 1,4-bis(triphenylsilyl)butane (0.10g) and (2-bromoethyl)triphenylsilane (0.35g). A portion of the soluble fraction (0.705g) was separated into its components by column chromatography using light petroleum/benzene (90/10, v/v) as eluant and the fractions were identified:-

Fractions A-C - n-hexyltriphenylsilane (total weight 0.287g).

Fraction D - A mixture of n-hexyltriphenylsilane (0.059g) and ethyltriphenylsilane (0.014g).

Fraction E - ethyltriphenylsilane (0.107g).

Thus, the ratio of total n-hexyltriphenylsilane/ethyltriphenylsilane was 0.35/0.12 (74/26) and was in good

agreement with analysis by GLC at 275° of a sample before column separation (75/25). (2-Bromoethyl)triphenylsilane (0.150g) was removed from the column using benzene as the eluant and a further material (0.073g), isolated with ether, was not identified.

Other separations were similarly performed. When triphenylvinylsilane was formed it was eluted with the ethyltriphenylsilane and the relative proportions of each determined by NMR spectroscopy. In the reaction with phenylmagnesium bromide in tetrahydrofuran a product was formed by reaction with the solvent. This material was soluble in diethyl ether and ethanol and was separated from the remaining constituents of the mixture by its insolubility in light petroleum.

c) Reaction products from (2-bromopropyl)triphenylsilane.

A similar procedure to that of section 5(b) was employed:-

Although stable to the 'work-up' process and to heating with tetrahydrofuran, ether and benzene, this halide underwent some decomposition to hydroxytriphenylsilane and (2-hydroxypropyl)triphenylsilane when eluted with benzene from a column of silica gel. Thus isolation of these two compounds did not necessarily imply their formation in the organometallic reaction.

Using suitable mixtures of light petroleum/benzene, separation of the following fractions could be achieved:-

- (a) biphenyl*
- (b) mixtures of alkyltriphenylsilanes, allyltriphenyl-

silane and propenyltriphenylsilane

(c) (2-phenylpropyl)triphenylsilane *

(d) 1,4-bis(triphenylsilyl)- 2,3 - dimethylbutane.

* these products were formed only when phenylmagnesium bromide was the Grignard reagent employed.

The separation of products from reaction of the halide (3.00g, 0.0078 mole) with phenylmagnesium bromide in tetrahydrofuran is described:-

An NMR spectrum of the mixture (2.54g) indicated the presence of allyltriphenylsilane, propenyltriphenylsilane and one or more alkyltriphenylsilanes. TLC confirmed these observations and also indicated the presence of biphenyl. A portion of the mixture (0.701g) was separated by column chromatography and the following fractions were identified:-

- | | | | |
|-----------|-----|---|---|
| Fractions | 1-3 | - | biphenyl (0.072g). |
| Fraction | 4 | - | n-propyltriphenylsilane (0.056g). |
| Fraction | 5 | - | n-propyltriphenylsilane (0.098g),
allyltriphenylsilane (0.059g),
propenyltriphenylsilane (0.040g). |
| Fraction | 6 | - | (2-phenylpropyl)triphenylsilane
(0.070g) and 1,4-bis(triphenyl-
silyl)- 2,3 - dimethylbutane
(0.030g). |
| Fraction | 7 | - | 1,4-bis(triphenylsilyl)- 2,3 -
dimethylbutane (0.150g). |
| Fraction | 8 | - | hydroxytriphenylsilane and (2-
hydroxypropyl)triphenylsilane |

(0.065g total) in roughly equal proportions.

Fractions 1-6 were eluted using light petroleum/benzene (90/10, v/v), fraction 7 with light petroleum/benzene (70/30, v/v) and fraction 8 using diethyl ether.

6. Identification of reaction products.

Products from the reactions of (2-bromoalkyl)silanes with Grignard reagents or n-butyllithium were identified by comparison with authentic samples (where available) using GLC and TLC and also from the properties listed below. The elemental analyses and melting points quoted are typical of the samples isolated.

The properties of (2-bromoethyl)triphenylsilane, ethyltriphenylsilane, ethyltrimethylsilane, allyltriphenylsilane, triphenylvinylsilane and (2-hydroxypropyl)triphenylsilane have already been recorded.

Phenyltrimethylsilane - b.p. 168-174° (lit.¹¹⁴ 170.6°/760mm); NMR (neat liquid): multiplet τ 2.6 (intensity 5), singlet τ 9.8 (intensity 9).

n-Butyltrimethylsilane - b.p. 114-116° (lit.¹¹⁴ 115.4°/758.2mm); NMR (neat liquid); multiplet τ 8.7 (intensity 4), multiplet τ 9.1 (intensity 3), multiplet τ 9.4 (intensity 2), singlet τ 10.0 (intensity 9).

(2-Phenylethyl)trimethylsilane was not isolated in a pure state but was identified as a component of a mixture from the following NMR spectrum: multiplet τ 2.6 (intensity 5), multiplet τ 7.4 (intensity 2), multiplet τ 9.1 (intensity

2), singlet τ 10.0 (intensity 9).

Biphenyl - m.p. 69-71 $^{\circ}$ (lit.¹²⁴ 70 $^{\circ}$); IR identical to that of an authentic sample¹²⁵; UV (hexane soln.): wavelength of maximum absorption 247 μ , molar extinction coefficient 19,000 (lit.¹¹⁰ wavelength of maximum absorption 246 μ , molar extinction coefficient 20,000).

(Ethyl-2-d)triphenylsilane - m.p. 74-76 $^{\circ}$; IR (KBr disc): carbon-deuterium absorption 2180 cm^{-1} ; NMR (CCl_4 soln.): multiplet τ 2.6 (intensity 15), doublet τ 8.7 (intensity 2), doublet τ 8.9 (intensity 2).

n-Propyltriphenylsilane - m.p. 83-85 $^{\circ}$ (lit.¹¹⁴ 84 $^{\circ}$); NMR (CCl_4 soln.): multiplet τ 2.5 (intensity 15), multiplet τ 8.6 (intensity 4), distorted triplet τ 9.0 (intensity 3). (Found: C, 83.41; H, 7.30. $\text{C}_{21}\text{H}_{22}\text{Si}$ calcd.: C, 83.38; H, 7.33%).

n-Amyltriphenylsilane - m.p. 45-47 $^{\circ}$ (lit.¹¹⁴ 47 $^{\circ}$); NMR (CCl_4 soln.): multiplet τ 2.5 (intensity 15), multiplet τ 8.6 (intensity 8), distorted triplet τ 9.1 (intensity 3).

n-Hexyltriphenylsilane - m.p. 77-79 $^{\circ}$ (lit.¹¹⁴ 77-78 $^{\circ}$); NMR (CCl_4 soln.): multiplet τ 2.5 (intensity 15), multiplet τ 8.7 (intensity 10), multiplet τ 9.2 (intensity 3).

(2-Methylhexyl)triphenylsilane - a viscous material was obtained by column chromatography; NMR (CCl_4 soln.): multiplet τ 2.6 (intensity 15), complex multiplet τ 8.3-9.1 (intensity 12), doublet τ 9.2 (intensity 3).

1,4-Bis(triphenylsilyl)butane - m.p. 213-215 $^{\circ}$ (lit.¹¹⁴

215-216°); NMR (CDCl₃ soln.): multiplet τ 2.6 (intensity 30), multiplet τ 8.5 (intensity 8). (Found: C, 82.82; H, 6.64. C₄₀H₃₈Si₂ calcd.: C, 83.57; H, 6.65%).

1,4-Bis(triphenylsilyl)-2,3-dimethylbutane - m.p. 128-131°; NMR (CDCl₃ soln.): multiplet τ 2.6 (intensity 30), multiplet τ 8.2 (intensity 2), multiplet τ 8.7 (intensity 4), doublet τ 9.3 (intensity 6). (Found: C, 83.10; H, 6.95. C₄₂H₄₂Si₂ calcd.: C, 83.66; H, 7.02%).

(2-Phenylethyl)triphenylsilane - m.p. 144-146° (lit.¹¹⁴ 147-148°); NMR (CCl₄ soln.): multiplet τ 2.6 (intensity 20), multiplet τ 7.2 (intensity 2), multiplet τ 8.3 (intensity 2). (Found: C, 85.85; H, 7.05. C₂₆H₂₄Si calcd.: C, 85.66; H, 6.64%).

(2-Phenylpropyl)triphenylsilane - m.p. 92-94°; NMR (CCl₄ soln.): multiplet τ 2.6 (intensity 20), multiplet τ 7.0 (intensity 1), multiplet τ 8.2 (intensity 2), doublet τ 8.8 (intensity 3). (Found: C, 85.57; H, 7.03. C₂₇H₂₆Si calcd.: C, 85.66; H, 6.92%).

Propenyltriphenylsilane was not isolated in a pure state but was identified as a component of a mixture from its NMR spectrum; multiplet τ 2.6 (intensity 15), complex multiplet τ 3.8 (intensity 2), multiplet τ 8.1 (intensity 3).

Hydroxytriphenylsilane - m.p. 151-153° (lit.¹¹⁴ 151-153°); IR identical to that of an authentic sample¹²⁶.

n-Hexyltrimethylsilane and n-butyltriphenylsilane were identified as components of mixtures from their retention times using GLC. In reactions with phenyl-

magnesium bromide, the presence of tetraphenylsilane was sometimes inferred by an excess of aromatic absorption in the NMR spectra of certain fractions. Thus the yields quoted for this compound represent the maximum amount formed.

7. The search for bromotrimethylsilane as an intermediate in reactions between (2-bromoethyl)trimethylsilane and Grignard reagents.

Experiments indicated that all the methyl protons in an authentic mixture of bromotrimethylsilane (prepared by the method of McCusker and Reilly¹²⁷), phenyltrimethylsilane and (2-bromoethyl)trimethylsilane were visible as distinct individual singlet absorptions in the NMR spectrum at τ 9.5, 9.8 and 10.0 respectively.

a) Reaction between (2-bromoethyl)trimethylsilane and phenylmagnesium bromide.

Reaction between the halide and phenylmagnesium bromide in tetrahydrofuran was carried out in a manner similar to that described in section C3. Samples were periodically removed by syringe, under an atmosphere of nitrogen, and their NMR spectra recorded. A sample after 10 min indicated only the presence of starting halide and another after 1h had absorptions attributable to starting material and phenyltrimethylsilane. Examination of a sample taken after 24h indicated predominant formation of phenyltrimethylsilane and a small quantity of (2-bromoethyl)trimethylsilane remained.

There was no evidence for the formation of bromotrimethylsilane in any of the samples taken.

b) Reaction between bromotrimethylsilane and phenylmagnesium bromide.

Grignard reagents were added, in excess, to the halide contained in an NMR tube and the spectra of the resulting mixtures immediately recorded. Reactions with phenylmagnesium bromide in tetrahydrofuran or benzene occurred rapidly with the evolution of heat and only coupled products were observed without evidence of any remaining bromotrimethylsilane.

8. Termination of Grignard reactions with deuterium oxide.

Reactions with (2-bromoalkyl)triphenylsilanes (3.00g, approx. 0.008 mole) were carried out as described in sections C2 or 3. When completed, deuterium oxide (10.0g, 0.5 mole) was added dropwise and the resulting mixture stirred for 30 min. (The deuterium oxide was supplied by Koch-Light, purity > 99.75% and a fresh ampoule was opened for each experiment).

Magnesium salts were dissolved by addition of dilute hydrochloric acid (10%, v/v) and the organic phase was washed with sodium bicarbonate solution and water and dried over magnesium sulphate. The products of these reactions were separated and identified as described in sections C5 and 6 and are recorded in Table 11. The relative proportions of deuterated

products were determined from the intensity of the carbon-deuterium absorption in the IR spectrum (2180 cm^{-1}) and from the NMR spectra.

9. Determination of the biphenyl formed during reactions with phenylmagnesium bromide.

A solution of phenylmagnesium bromide (approx. 0.20 mole) in tetrahydrofuran (80.0 ml) was prepared by slow addition (over 2h) of bromobenzene to magnesium metal. Two aliquots (20.0 ml) of this solution were hydrolysed and the organic phases separated and dried. Removal of the solvent gave solid materials (0.209g and 0.239g). Elution from a column of silica gel using light petroleum /benzene (90/10, v/v) gave biphenyl (0.040g, 1.0%) and (0.043g, 1.1%) respectively. The remaining material appeared to consist mainly of an alcoholic component probably formed by reaction between the Grignard reagent and tetrahydrofuran. An authentic sample of biphenyl (0.197g) was eluted under identical conditions and gave 0.184g (94% recovery) of material.

Another aliquot of the Grignard solution (20.0 ml, approx. 0.050 mole) was added to bromobenzene (2.60g, 0.0165 mole) in tetrahydrofuran (28 ml). After refluxing for 3h, the mixture was hydrolysed and the organic phase separated and dried. Analysis of this mixture by GLC before the removal of solvent indicated the presence of bromobenzene. Evaporation of the solvent gave a material (0.260g) which after separation by column

chromatography was shown to consist of biphenyl (0.057g, 0.6% yield in this reaction).

Reaction between (2-bromopropyl)triphenylsilane (3.00g, 0.0078 mole) and the Grignard solution (10.0 ml, approx. 0.025 mole) in tetrahydrofuran (15 ml) for 3h gave a viscous material (2.76g) which contained biphenyl (0.262g).

In another series of reactions, the Grignard solution (20.0 ml, approx. 0.050 mole) was added to bromobenzene (1.30g, 0.0083 mole) and anhydrous magnesium bromide (1.20g, 0.0062 mole) in tetrahydrofuran (28 ml) and the mixture refluxed for 3h. Following hydrolysis and separation and drying of the organic phase, a material (0.440g) was obtained which contained biphenyl (0.072g, 2.06%). Analysis by GLC of the products before the removal of solvent indicated the presence of bromobenzene.

The results of this and other similar reactions are summarised in Table 12.

10. The search for alkyl halide formation during reaction between Grignard reagents and (2-bromoethyl)triphenylsilane.

Trial experiments indicated that ethylene dibromide was a suitable internal standard for the determination of both 1-bromobutane and bromobenzene by GLC at 71°. The reaction between n-butylmagnesium bromide and the halide in diethyl ether is described:-

The Grignard reagent (approx. 0.20 mole) in ether (80 ml) was prepared by slow addition (over 2h) of 1-bromobutane to magnesium turnings. A portion of this solution (32.0 ml) was hydrolysed and the organic phase separated and dried. The solution was then reduced in volume to about 30 ml, by careful fractionation through a 6 in. column of glass helices. The temperature of the distilling liquid did not rise above 35° throughout the fractionation. Ethylene dibromide (0.50 ml) was added and the mixture analysed by GLC at 71°. 1-Bromobutane (0.28g) was detected.

Reaction between the Grignard reagent (16.0 ml, approx. 0.040 mole) and (2-bromoethyl)triphenylsilane (5.00g, 0.013 mole) was carried out in the normal manner. After separation and drying, the organic phase was reduced in volume to about 30 ml (as described above) and ethylene dibromide (0.50 ml) added. Analysis by GLC at 71° indicated the presence of 1-bromobutane (0.08g). Other products of the reaction were separated and identified as described in sections 05 and 6.

The results of similar determinations taken from reactions between (2-bromoethyl)triphenylsilane and phenylmagnesium bromide in tetrahydrofuran and n-butylmagnesium bromide in benzene are recorded in Table 10.

11. Reactions between (2-bromoethyl)triphenylsilane and Grignard reagents in the presence of styrene.

The reaction between (2-bromoethyl)triphenylsilane

and n-propylmagnesium bromide in tetrahydrofuran is described:-

A solution of n-propylmagnesium bromide (approx. 0.025 mole) in tetrahydrofuran (10.0 ml) was added dropwise to a solution of (2-bromoethyl)triphenylsilane (3.00g, 0.0082 mole) in a mixture of tetrahydrofuran (11.0 ml) and freshly distilled styrene (1.5 ml, 0.0115 mole). The mixture was stirred at reflux for 3h, quenched, and the organic phase separated in the normal manner. Removal of the solvent gave a solid material (3.62g). Addition of diethyl ether (30 ml) precipitated 1,4-bis(triphenylsilyl)butane (0.39g, 17%) and the soluble fraction was evaporated to dryness. This was insoluble in ethanol and a portion of the material was separated by column chromatography. Ethyltriphenylsilane (0.38g, 16%) was isolated and the remaining product appeared to be polymeric and contained both silicon-phenyl and benzylic groupings. No starting material was recovered.

A reaction was also carried out between (2-bromoethyl)triphenylsilane (3.00g, 0.0082 mole) and phenylmagnesium bromide (approx. 0.025 mole) in benzene in the presence of styrene (1.5 ml). Separation and isolation in the usual manner indicated that (2-phenylethyl)triphenylsilane (2.84g, 95%) was formed. Another material (0.67g), which did not contain silicon-phenyl linkages, was identified as polystyrene.

12. Reaction between (2-bromoethyl)triphenylsilane and ethylmagnesium bromide in the presence of cobalt chloride.

The conditions employed were similar to those of Wilt et al⁹⁴ in their reactions with (chloromethyl)triphenylsilane. The Grignard solution (approx. 0.0122 mole) was slowly added to a mixture of the halide (4.50g, 0.0122 mole) and anhydrous cobaltous chloride (0.05g) in tetrahydrofuran (13.0 ml) at room temperature. The solution at first became dark blue, then black and effervescence was observed. After the addition was complete, the mixture was refluxed for 3h and then hydrolysed with ammonium chloride solution. The organic phase was separated and dried in the usual manner. Evaporation of the solvent gave a solid (3.81g) whose IR spectrum indicated the absence of silicon-hydrogen and benzyl absorptions. Rearrangement to a material of the type $\text{Ph}_2\text{SiHCH}_2\text{CH}_2\text{Ph}$ had evidently not occurred. Separation and identification of reaction products as described in sections C5 and 6 indicated the formation of ethyltriphenylsilane (29%) n-butyltriphenylsilane (2%), triphenylvinylsilane (2%) and 1,4-bis(triphenylsilyl)butane (25%). The recovery of starting material was 3%. In addition, a product formed by interaction with the solvent (0.32g) and another (0.63g), eluted from the 'silica gel column' using benzene, were isolated. The latter was not positively identified but displayed absorptions at τ 2.7 and τ 8.0-9.0 in the NMR spectrum. A similar material, but

in smaller quantities, was observed in several reactions in the absence of cobalt chloride and may be of a polymeric nature.

13. Reaction between (bromomethyl)triphenylsilane and n-propylmagnesium bromide.

The halide used in this reaction was kindly supplied by Mr R.J. Rowley (University of Aston). A solution of n-propylmagnesium bromide (approx. 0.025 mole) in diethyl ether (10.0 ml) was added to a suspension of the halide (3.00g, 0.0085 mole) in ether (10.0 ml) and the resulting solution refluxed for 6h. It was quenched with dilute acid and after washing with sodium bicarbonate solution and water, the organic phase was separated and dried. Removal of the solvent gave a solid (2.79g). The components of this mixture were separated by column chromatography (silica gel) using varying mixtures of light petroleum/benzene. n-Butyltriphenylsilane (0.01g, 0.5%), methyltriphenylsilane (0.46g, 20%) and (bromomethyl)triphenylsilane (1.77g, 59%) were isolated.

Methyltriphenylsilane was identified from the following data:- m.p. 68-69° (lit.¹¹⁴ 69.5-69.9°); NMR (CCl₄ soln.): multiplet τ 2.6 (intensity 15), singlet τ 9.2 (intensity 3).

D. MISCELLANEOUS REACTIONS.

1. The attempted solvolysis of (2-bromoethyl)triphenylsilane.

Solubility tests indicated that (2-bromoethyl)triphenylsilane was insoluble in ethanol, formic acid, acetone/water (50/50, v/v) and dioxan/water (50/50, v/v) but was soluble in acetone/water (90/10, v/v) and tetrahydrofuran/water (50/50, v/v).

The halide (0.50g, 0.0014 mole) was stirred at room temperature with tetrahydrofuran/water (50/50, v/v - total volume 136 ml) for 64h and the mixture then extracted with ether. After drying over magnesium sulphate, the ethereal layer was evaporated to yield a solid material (0.48g). Its m.p., NMR and IR spectra indicated that a quantitative recovery of starting halide had been achieved. A reaction in refluxing acetone/water (90/10, v/v) for 9h gave similar results. In neither experiment was there evidence of the formation of hydroxytriphenylsilane, (2-hydroxyethyl)triphenylsilane or hexaphenyldisiloxane.

In another series of reactions (2-bromoethyl)triphenylsilane (0.50g, 0.0014 mole) in diethyl ether (20 ml) was stirred with ethanol or water for 16h at room temperature. Separation and identification of the product obtained indicated that once again a quantitative recovery of the halide had been achieved.

2. The solvolysis of (2-bromopropyl)triphenylsilane.

(2-Bromopropyl)triphenylsilane (0.48g, 0.0013 mole) was dissolved in a mixture of tetrahydrofuran (65 ml) and water (65 ml) and refluxed for 114h. The solution was extracted with ether and the organic phase dried over magnesium sulphate. Removal of the solvent gave a solid (0.39g) whose IR and NMR spectra were identical to those of an authentic sample of (2-hydroxypropyl)triphenylsilane (see section A2). A reaction at room temperature gave similar results. There was no evidence of the formation of hydroxytriphenylsilane.

3. The attempted preparation and solvolysis of (2-bromopropyl)triethylsilane.

Allyltriethylsilane had previously been prepared in the laboratory; b.p. 171° (lit.¹¹⁴ $171^{\circ}/750\text{mm}$); NMR (neat liquid): multiplet τ 4.2 (intensity 1), multiplet τ 5.1 (intensity 2), doublet τ 8.6 (intensity 2), multiplet τ 9.0 (intensity 9), multiplet τ 9.4 (intensity 6).

Hydrogen bromide, generated from reaction between phosphorus tribromide and water, was passed through a trap at -60° in order to remove moisture and then bubbled into allyltriethylsilane, also at -60° . After reaction was complete, excess hydrogen bromide was removed under vacuum ($40\text{mm}/0^{\circ}$). The pale yellow liquid was stored overnight under vacuum at -70° . The NMR spectrum of this material (recorded at -25°) did not

seem consistent with the formation of (2-bromopropyl)-triethylsilane. Absorptions at τ 8.5 (a doublet) and at τ 9.0 (complex multiplet) were observed but none at lower field were detected. The relative intensities of the two absorptions were 1/9 respectively. The IR spectrum, recorded at room temperature, contained no hydroxyl or siloxane absorptions. Both spectra bore similarities to those of chlorotriethylsilane (those of bromotriethylsilane were not available).

Titration as described in section D4 gave the percentage bromine content as 31.54 ($\text{Et}_3\text{SiCH}_2\text{CHMeBr}$: calcd. Br, 33.68%. Et_3SiBr : calcd. Br, 40.94%). The precise nature of the material obtained was thus difficult to assess.

The product obtained (approx. 5 ml) was dissolved in diethyl ether (30 ml) and water (60 ml) was added dropwise over 20 min, with stirring at 0° . The organic layer was separated and the aqueous phase extracted with several portions of ether. After drying the ethereal over magnesium sulphate at 0° for 3h, the solvent was removed under vacuum and the product remaining was identified as hydroxytriethylsilane; IR: strong broad absorption 3320cm^{-1} ; NMR: singlet τ 4.1 (intensity 1), complex multiplet τ 8.8-9.6 (intensity 15).

In a similar experiment with (2-bromoethyl)trimethylsilane, the halide was recovered quantitatively.

4. The titration of (2-bromoalkyl)silanes.

The (2-bromoalkyl)trialkylsilanes (approx. 0.25g) were carefully weighed into acetone (25 ml) and standard sodium hydroxide solution (0.1 N, 25.0 ml) was added. Solutions were periodically shaken during 4h and then back titrated with standard acid using phenolphthalein as indicator. Blank determinations were also carried out in the absence of halide.

The (2-bromoalkyl)triphenylsilanes were insoluble in acetone and hydrolysis was performed using tetrahydrofuran/sodium hydroxide solutions (50/50, v/v). Extraction with ether, followed by the removal of solvent showed that hydroxytriphenylsilane was the product formed in such reactions.

5. The attempted addition of hydrogen bromide to allyltriphenylsilane in an anti-Markownikoff manner.

The conditions employed were similar to those of Petrov and Mironov¹⁰⁶ in their additions to allyltrichlorosilane. Dry hydrogen bromide was bubbled through a solution of allyltriphenylsilane (5.0g, 0.0166 mole) in bromopropane (30 ml), in the presence of benzoyl peroxide (0.045g, 1.0 mole %). The solution was gently refluxed throughout the addition. Removal of the solvent gave a material (6.3g) whose IR spectrum was similar to that of an authentic sample of (2-bromopropyl)triphenylsilane except for an additional absorption at 1630cm^{-1} . An NMR spectrum indicated that the material consisted

of (2-bromopropyl)triphenylsilane (89%) and propenyltriphenylsilane (11%). There was no evidence of an absorption attributable to the presence of (3-bromopropyl)triphenylsilane (expected position of a methylene group attached to bromine approx. τ 6.6).

ADDENDA

Recently, Rowley and Jarvie¹²⁸ have studied the reaction between (2-bromoethyl)triphenylsilane and the deuteriated Grignard reagent $\text{CH}_3\text{CH}_2\text{CD}_2\text{CH}_2\text{MgBr}$ in diethyl ether. They found that the sample of ethyltriphenylsilane isolated did not contain deuterium. Clearly, a mechanism of direct reduction by the Grignard reagent (cf. Eastham and Gibson⁹⁷) is not operative in this system.

Magid, Nieh and Gandour¹²⁹ have investigated coupling reactions between phenyllithium and a variety of allylic chlorides and suggest that a mechanism involving concerted C-Cl bond cleavage and C-C bond formation in a six-membered transition state is consistent with their experimental results.

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