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Review

THE SILICONIUM ION QUESTION

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Introduction

There have been many attempts to prove the existence of siliconium ions with an sp^2 structure analogous to carbonium ions:

$$\overset{+}{M} \qquad M = C, Si$$

Silicon is less electronegative than carbon [1] (respective electronegativities 1.8 and 2.5), and one would expect ion formation to be at least as easy as that of R_3C^+. This is true in the gas phase, as shown by appearance potentials and an abundance of Si^+ fragments in mass spectra [1—3]. However in solution, all attempts to obtain this ionic species have failed.

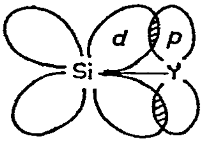
The following different methods which demonstrated the existence of carbonium ions have been applied: (a) detection by physicochemical measurements, (b) preparation of stable salts, (c) intervention as an intermediate in reaction mechanisms.

The problem of the cation Si^+ has been briefly reviewed by O'Brien and Hairston [4], in the conclusion to a recent article on reactions between organosilanes and Lewis acids. We thus only summarise the essential results allowing us to emphasise the study of optically active organosilanes.

Before tackling the problem, the difference in chemical behaviour between carbon and silicon compounds needs underlining. The behaviour of silicon is influenced by the presence of vacant *d*-orbitals; these allow extension of coordination, and a large number of penta- and hexa-coordinate complexes are known.

It seems that the chemistry of silicon compounds tends towards coordination extension (the hybridisation state passing from sp^3 to sp^3d or sp^3d^2) rather than contraction as in the case of carbon (passage to the state sp^2). Thus stable double bonds such as Si=C have still not been observed for silicon, although their existence has been postulated for reaction intermediates [5].

Many types of evidence (dipole moments, bond angles and distances, spectroscopic data, etc. [1,6—9]) prove the existence of a bond type unknown for carbon which consists of a partial $d_\pi—p_\pi$ bond, resulting from an overlap of a silicon *d*-orbital with the *p*-orbital of a neighbouring atom Y (Y = X = Hal, O, N, Ar, etc.)



I. Attempts to prove the existence of R_3Si^+ ions by physicochemical methods

Various physicochemical methods, particularly cryoscopy, conductometry and spectroscopy have been used to show the presence of carbonium ions in different media. Some cryoscopic and conductivity measurements on organosilanes in H_2SO_4 solution, have shown a chemical reaction with the solvent [10]:

$$(Me_3Si)_2O + 3\ H_2SO_4 \rightarrow 2\ Me_3SiHSO_4 + H_3O^+ + HSO_4^-$$

$$Me_3SiOEt + 3\ H_2SO_4 \rightarrow Me_3SiHSO_4 + EtHSO_4 + H_3O^+ + HSO_4^-$$

In no case has the formation of Si^+ ions been confirmed [1—4], as previously proposed [11].

A number of workers have tried to demonstrate the presence of an ion Ph_3Si^+ by an analogous method to that used for triphenylmethyl compounds Ph_3CX.

The conductivity measurements indicated no appreciable ionisation of Ph_3SiCl in pyridine, nitrobenzene—aluminium tribromide, or liquid sulphur dioxide [12]. It is however well known that these solvents cause ionisation of Ph_3CCl [12,13]:

$$Ph_3CCl \rightarrow Ph_3C^+Cl^-$$

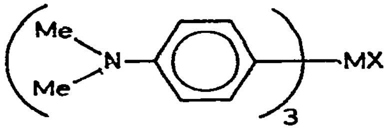
It has also been shown that the conductivities originally measured for solutions of Ph_3SiCl in dimethylformamide (DMF) are due to impurities present in the solvent [14,15].

Similarly solutions of the silanol Ph_3SiOH in liquid HCl do not conduct, whilst under the same conditions, the corresponding carbinol Ph_3COH gives the cation Ph_3C^+ [16].

$$Ph_3COH \xrightarrow{\text{liq. HCl}} Ph_3C^+Cl^- + H_2O$$

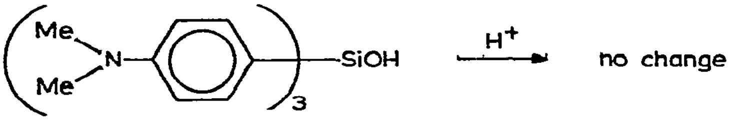
$$Ph_3SiOH \xrightarrow{\text{liq. HCl}} \text{no conductivity}$$

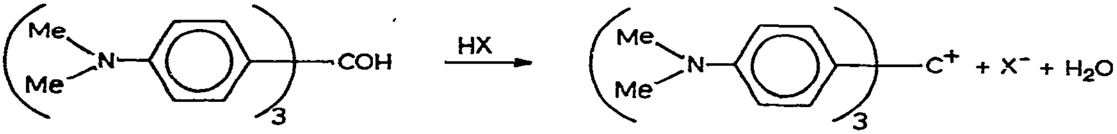
Tris(*p*-dimethylaminophenyl)chloromethane (I, M = C, X = Cl) is an ionic compound, but the silicon analogue (II, X = Cl, M = Si) which was prepared by Wannagat and Brandmair [17,18], behaved as a covalent compound (conductivity, IR spectra, X-ray diffraction, chemical behaviour, etc.).



(I) X=Cl, M=C
(II) X=Cl, M=Si
(III) X=OH, M=C
(IV) X=OH, M=Si

Similarly when the silanol IV is placed in an acid medium, one observes only a slight change in the UV spectrum due to protonation of the amino groups. In contrast, the initially colourless solutions of the corresponding carbinol III become deep violet, the colour characteristic of the cation $(p\text{-}Me_2N\text{-}C_6H_4)_3C^+$ [19].



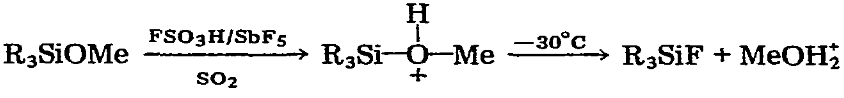


λ_{max} 264,300 nm, colourless

λ_{max} 319,441 nm, deep violet

The UV spectrum of the solution thus shows an important bathochromic displacement in the last case. Wannagat has also shown that silyl perchlorates R_3SiClO_4 (V, R = Me, Et, n-Pr, Ph, p-MeC_6H_4) are perchloric esters of covalent structure [20], in contrast to the highly colored crystalline triarylmethyl perchlorates.

NMR is useful for studying carbonium ions. Thus using a super-acidic medium such as $FSO_3H/SbF_5/SO_2$ Olah has been able to study a large variety of stable carbonium ions [21]. This author has recently studied alkoxysilane (R_3SiOR') and siloxane ($R_3Si{-}O{-}SiR'_3$) solutions by NMR at low temperature in the system mentioned above, and observed protonation of oxygen followed by a substitution reaction leading to fluorosilanes:

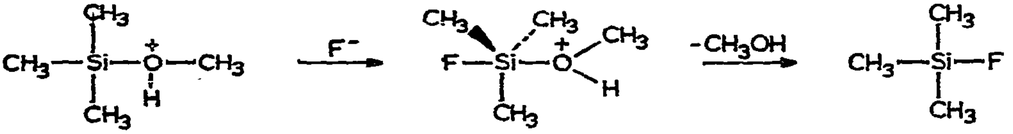


$$R_3SiOMe \xrightarrow[SO_2]{FSO_3H/SbF_5} R_3Si{-}\underset{+}{\overset{\overset{\displaystyle H}{|}}{O}}{-}Me \xrightarrow{-30^\circ C} R_3SiF + MeOH_2^+$$

$Me_2Si(OEt)_2 \rightarrow Me_2SiF_2 + EtOH_2^+$

$Me_3Si{-}O{-}SiPh_3 \rightarrow Me_3SiF + Ph_3SiOH_2^+ \rightarrow Ph_3SiF$

NMR studies showed that R_3Si^+ ions were not formed. The formation of fluorosilanes is adequately explained by assuming a pentavalent intermediate:



(ref. 22)

Another factor is the strength of the Si—F bond (130—135 kcal/mole), which makes the possibility of stable ions in these media highly unlikely.

Olah has also studied the behaviour of a fluorosilane Me_3SiF in the weakly nucleophilic medium SbF_5/SO_2ClF [23], which allowed direct observation of stable trivalent carbonium ions. However Me_3SiF remained unionised and formed a complex with SbF_5; the fluorine atom exchange could be observed. The authors propose a complex of the following structure:

$R^1 = R^2 = Me$; $R^1 = Me$, $R^2 = F$; $R^1 = R^2 = F$.

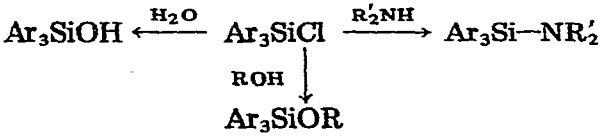
II. Preparation of stable salts

With carbon compounds, many reactions lead to stable carbonium ion salts (frequently Ph_3C^+) e.g.:

$Ph_3CBr \xrightarrow{BBr_3} Ph_3C^+BBr_4^-$ (ref. 24)

Attempts have been made to repeat these reactions for silicon compounds, but with Ph_3SiX, no salts containing the Ph_3Si^+ ion were isolated [25].

Likewise the covalent silicon analogue of I (violet crystals) has, as we have already seen, the classic reactivity of compounds Ar_3SiCl [17,18].



$$Ar_3SiOH \xleftarrow{H_2O} Ar_3SiCl \xrightarrow{R_2'NH} Ar_3Si{-}NR_2' \qquad Ar_3SiCl \xrightarrow{ROH} Ar_3SiOR$$

The only products isolated from the reaction of II with $AgClO_4$, $Ba(ClO_4)_2$, $Ba(BF_4)_2$, NaI, etc. were those resulting from aminophenyl group cleavage, and no salts of the type $Ar_3Si^+Y^-$ ($Y = ClO_4, BF_4, I$) [17,18] have been isolated.

The ability of carbonium ions to act as hydride ion acceptors has been used to obtain other carbonium ions [25,27]. For example:

(ref. 25)

As Si—H bonds (70—76 kcal/mole) are weaker than C—H bonds (99 kcal/mole) attempts to transfer H^- ions from Ph_3SiH have been made [26—28]. This reaction does not occur and one observes the formation of bromosilane:

$$Ph_3SiH + Ph_3C^+ BBr_4^- \rightarrow Ph_3SiBr + Ph_3CH + BBr_3$$

Triphenylbromosilane and boron tribromide do not interact to form the siliconium bromoborate ion pair. The same products may be obtained without the intervention of BBr_3:

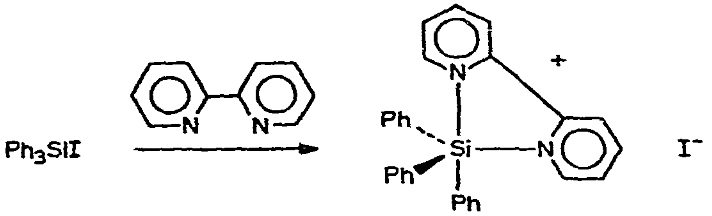
$$Ar_3SiH + Ph_3CX \rightarrow Ar_3SiX + Ph_3CH \qquad \text{(ref. 26,28)}$$

$X = Cl, Br, I$

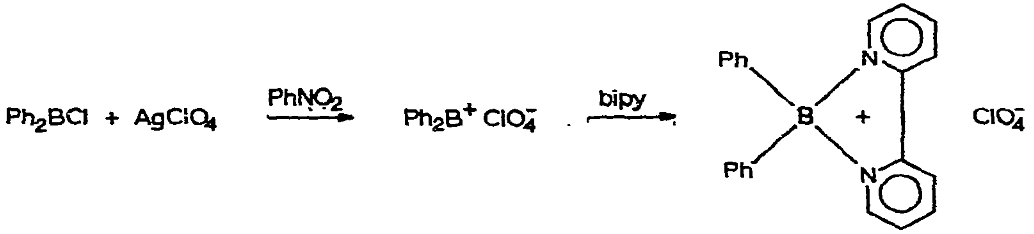
We know that the halosilanes thus formed have no ionic character, and this reaction mechanism will be discussed later.

Clearly, all these attempts to isolate a trivalent sp^2 siliconium ion R_3Si^+ were unsuccessful.

In another approach, Corey and West tried to stabilize a positive charge by coordination with a basic species [26,29]. The reaction of Ph_3SiI with 2,2′-bipyridyl allows isolation of the following five-coordinated complex ion [29]:



Analogous compounds have been formed with Ph_3SiBr [29], and also with o-phenanthroline [26]; a similar reaction exists in boron chemistry [30]:



The only way to isolate the ion Ph_2B^+ is by nucleophilic addition of bipyridyl.

Since this work, other ions $Si^{V,+}$ of the same type have been prepared [31—34], always by complexation with basic ligands:

$$H_3SiM(CO)_n \xrightarrow{R_3N} [SiH_3, 2NR_3]^+ \, M(CO)_n^- \qquad \text{(ref. 31)}$$

$M = Mn, n = 5$ $\qquad$ $R_3N = Me_3N$, pyridine
$M = Co, n = 4$ $\qquad$ $2R_3N = 2,2'$-bipy

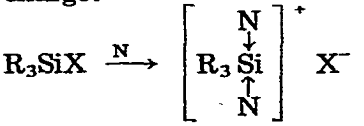
$$SiCl_3I + AgClO_4 \xrightarrow{Me_3N} [SiCl_3, 2NMe_3]^+ \, ClO_4^- \qquad \text{(ref. 32,33)}$$

$$[SiCl_3, 2NMe_3]^+ \xrightarrow[-2Me_3N]{+2Me_3P} [SiCl_3, 2Me_3P]^+$$

It is necessary to underline the fundamental difference in behaviour from carbon compounds where the dominant factor in the ionisation of a CX bond is the electrophilic assistance for X:

$$R{-}X + HOR' \rightarrow [\overset{\delta+}{R} \cdots\cdots \overset{\delta-}{X} \cdots\cdots H \cdots\cdots OR'] \rightarrow R^+X^- \cdots\cdots HOR'$$

In the case of silicon, the Si—X bond cleavage is promoted by nucleophilic reaction at the silicon atom. It is only this attack which gives rise to the positive charge:



$$R_3SiX \xrightarrow{N} \left[\begin{matrix} N \\ \downarrow \\ R_3\,Si \\ \uparrow \\ N \end{matrix}\right]^+ X^-$$ [*]

III. R_3 S^+ as a reaction intermediate

In spite of the failure to demonstrate the existence of a stable R_3Si^+ ion, this species has often been invoked as a reaction intermediate. This is reasonable since such an intermediate occurring generally at a high energy level would be difficult to trap.

The reaction types which might involve this intermediate are discussed in sections A—E.

We will consider each of these different categories, and particular attention will be paid to the last, that of reactions accompanied by racemisation.

A. Solvolysis reactions

One of the first experiments to prove the intervention of a Si^+ ion by kinetic studies was that of Swain who studied the hydrolysis of triphenylfluorosilanes Ph_3SiF [36]:

$$Ph_3SiF + H_2O \rightleftharpoons Ph_3SiOH + HF$$

The results showed that solvolysis did not occur via a Si^+ cation intermediate. This is particularly important, because the structure of the substrate, Ph_3SiF, should favour such a reaction. One can summarise the results as follows:

(1) the reaction is very dependent upon the nucleophilic strength of the reactant. Thus Ph_3SiF reacts 10^6 times faster in the presence of OH^- ions than in a neutral medium (acetone—water), whilst the rate of reaction of Ph_3CF is independent of the pH of the medium.

(2) $(p\text{-}MeC_6H_4)_3SiF$ reacts 5 times more slowly than Ph_3SiF. The opposite is observed for the corresponding carbon compounds. This result shows that no positive charge is developed on silicon in the transition state.

(3) Ph_3SiF is much less reactive than Ph_3SiCl, indicating that Si—X bond cleavage is still a rate-determining step of the reaction.

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[*] In the recent nomenclature introduced by Olah [35], such a pentacoordinated ion would be designated as a "siliconium" and a tricoordinated ion R_3Si^+ as a "silicenium" by analogy with "carbonium" and "carbenium". The term "onium" is applied to the ion of higher valence and "enium" to the cation of planar structure. However, to avoid confusion, we will not use this terminology, which is not as yet well known in the literature.

The authors proposed a mechanism with a rapid initial equilibrium, leading to a pentacoordinate intermediate:

$$Ph_3SiF + H_2O \overset{\text{fast}}{\rightleftharpoons} (Ph_3SiF, OH_2)$$

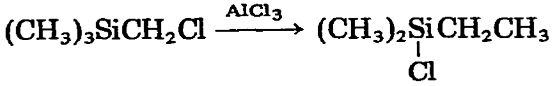
$$(Ph_3SiF, OH_2) \xrightarrow{\text{slow}} Ph_3SiOH_2^+ + F^- \rightarrow Ph_3SiOH + FH$$

This mechanism is confirmed by subsequent work of Sommer et al. on the racemisation of optically active fluorosilanes [37]; they showed the reaction to be highly dependent upon the solvent's nucleophilic power (CH_3NO_2, $CH_3CN <$ $ROH < H_2O$).

Moreover, in water racemisation was 10^5 times as fast as hydrolysis. A common intermediate for the two reactions would be formed, implying coordination to the silicon atom. This intermediate leads rapidly to racemisation whilst solvolysis is limited by the slow Si—F bond cleavage.

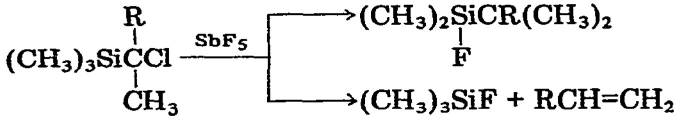
B. Reactions at C α to Si

This reaction type has been well studied. For example various workers including Sommer and then Eaborn investigated the rearrangement of chloromethyltrimethylsilane [38,39].



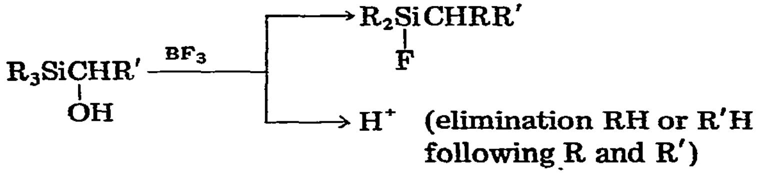
$$(CH_3)_3SiCH_2Cl \xrightarrow{AlCl_3} (CH_3)_2\underset{\displaystyle Cl}{Si}CH_2CH_3$$

O'Brien observed the behaviour of α-haloalkylsilanes in the presence of SbF_5 [40,41].



$$(CH_3)_3Si\overset{\displaystyle R}{\underset{\displaystyle CH_3}{C}}Cl \xrightarrow{SbF_5} \begin{cases} (CH_3)_2\underset{\displaystyle F}{Si}CR(CH_3)_2 \\ (CH_3)_3SiF + RCH{=}CH_2 \end{cases}$$

Finally the reaction of α-silylcarbinols with BF_3 has been carried out by Brook et al. [42,43].

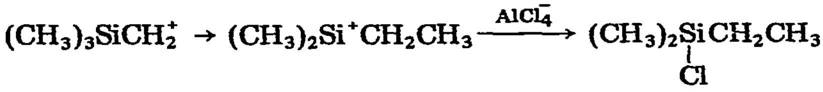


$$R_3Si\underset{\displaystyle OH}{C}HR' \xrightarrow{BF_3} \begin{cases} R_2\underset{\displaystyle F}{Si}CHRR' \\ H^+ \end{cases}$$

(elimination RH or R'H following R and R')

A Wagner—Merwein mechanism was initially suggested for this type of rearrangement [38]:

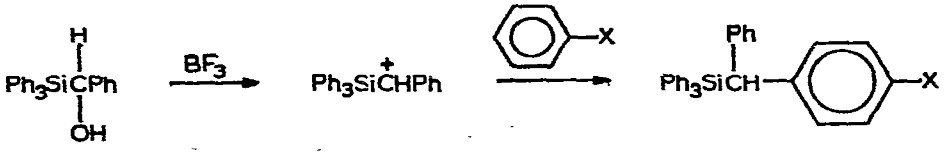
$$(CH_3)_3SiCH_2Cl \xrightarrow{AlCl_3} (CH_3)_3SiCH_2^+ + AlCl_4^-$$



$$(CH_3)_3SiCH_2^+ \rightarrow (CH_3)_2Si^+CH_2CH_3 \xrightarrow{AlCl_4^-} (CH_3)_2\underset{\displaystyle Cl}{Si}CH_2CH_3$$

There have now been further studies:

(1) There seems to be stabilization of carbonium ions α to a silicon atom. Their formation has been proved by direct observation [40,41], or by Friedel—Crafts reaction on an aromatic substrate [42,43]:



(2) Formation of the carbonium ion may be followed by further reaction: either migration of a group R (alkyl or aryl) from Si to the C^+, or elimination. This rearrangement is always promoted by nucleophilic attack of the Lewis aci anion on Si, and its concentration appears in the rate equation [40,41].

$$V_R = k\,[\equiv \mathrm{Si}-\overset{+}{\mathrm{C}}\!<]\,[\mathrm{SbX_6}]^-$$

$$(k = k_{\text{migration}} + k_{\text{elimination}})$$

The formation of Si^+ in the system has never been proved. In an aromatic medium, one sees only the Friedel—Crafts reaction with the silylcarbonium ion ($\equiv \mathrm{Si}-\overset{+}{\mathrm{C}}\!<$), and no reaction product from a silicon ion. Moreover Russell could not cause Me_3SiBr and C_6H_6 to react in the presence of $AlBr_3$, and he conclude that ion formation does not occur below 80° C.

C. Reactions on β-functional compounds

β-Functional silicon compounds ($R_3SiCH_2CH_2X$) are much more reactive than α or γ functional derivatives [45]. We will only discuss the two following cases for which the possibility of a silicon ion has been proposed:

$$R_3SiCH_2CH_2Cl \xrightarrow{AlCl_3} R_3SiCl + CH_2{=}CH_2 \quad \text{(ref. 46)} \qquad (1$$

$$R_3SiCH_2CH_2Cl \xrightarrow[H^+ \text{ or } OH^-]{EtOH/H_2O} R_3SiOEt + CH_2{=}CH_2 + HCl \quad \text{(ref. 47,48)} \qquad (2$$

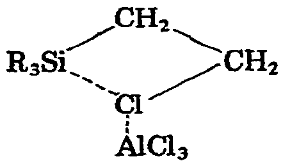
(1) For reaction 1, the original mechanism proposed was as follows [46]:

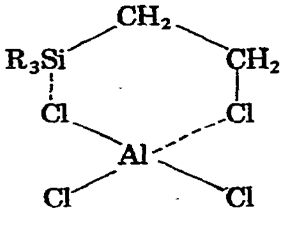
$$R_3SiCH_2CH_2Cl \xrightarrow{AlCl_3} R_3SiCH_2CH_2^+ + AlCl_4^-$$

$$R_3SiCH_2CH_2^+ \rightarrow R_3Si^+ + CH_2{=}CH_2$$

$$R_3Si^+ + AlCl_4^- \rightarrow R_3SiCl + AlCl_3$$

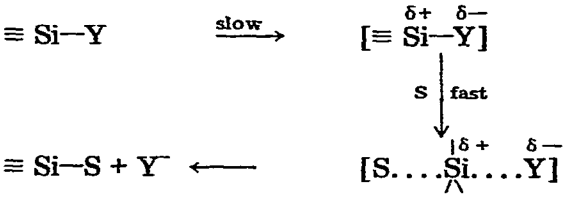
As with the α-haloalkylsilanes previously discussed, a 4- or 6-centre mechanism seems more plausible [39]:





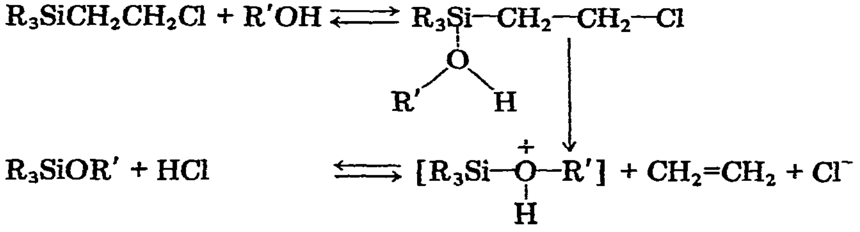
(2) The solvolysis reaction mechanism 2 has been successively studied by different authors. Baughmann and Sommer [47,48], observed the following facts:
(a) The reaction is unaffected by the nucleophilic character of the solvent, but depends on the solvent-ionising power, as for t-butyl chloride solvolysis;
(b) There is no basic catalysis, and (c) Electron-attracting substituents slow down the reaction.

From this, a mechanism via a "limiting siliconium ion" has been postulated:



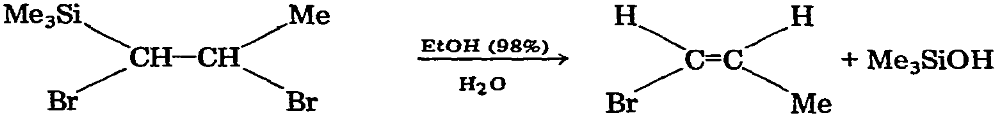
This mechanism has been criticised, in particular because the carbon ion Y^- cannot possibly be stabilised.

An initial equilibrium for the solvent coordination adequately explains the experimental data:



(ref. 49)

Jarvie et al. have shown that a *trans*-stereochemistry occurs in the elimination of the olefin [50]:



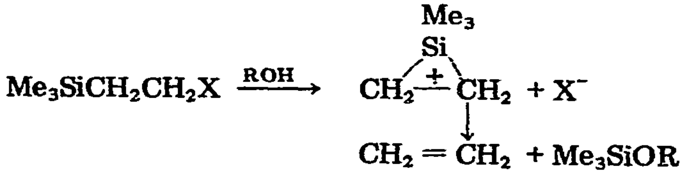
Moreover a trimethylsilyl group migration has sometimes been observed [50,51]:

$$\mathrm{Me_3Si{-}CH_2{-}CD_2OH \xrightarrow[SO_2Cl_2]{PBr_3} Me_3Si{-}CH_2{-}CD_2X + Me_3Si{-}CD_2{-}CH_2X} \quad \text{(ref. 50)}$$

$$\mathrm{Me_3Si{-}CH_2{-}CD_2Br \xrightarrow[H_2O]{MeOH} Me_3Si{-}CH_2{-}CD_2Br + Me_3Si{-}CD_2{-}CH_2Br} \quad \text{(ref. 51)}$$

(Products recovered after 50% reaction)

These results all lead to a mechanism involving a non-classical carbonium ion (silacyclopropenium)



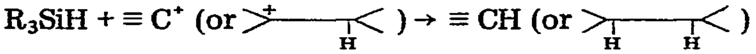
The reactivity of these compounds is much higher than one would expect from the simple inductive effect of the Me_3SiCH_2-group; this suggests assistance by the Me_3Si group in the C—Cl bond cleavage [51]. A non-classical carbonium ion is not essential; the assistance may arise from delocalisation of the adjacent σ-bonds (vertical stabilization), a concept recently discussed [52].

D. Hydride transfer

The hydride ion from a Si—H compound may be abstracted by an existing carbonium ion; such a transfer is found for example in halogen exchange between triphenylmethyl halides Ph_3CX and triarylsilanes Ar_3SiH (1):

$$Ph_3SiH + Ph_3C^+X^- \rightarrow Ph_3SiX + Ph_3CH \quad \text{(ref. 28,53,54)} \qquad (1)$$

and in olefin or alcohol reduction by a silane in acid solution (2):

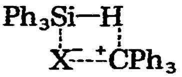


$$R_3SiH + \equiv C^+ \;(\text{or } >\overset{+}{C}-\underset{H}{C}<) \rightarrow \equiv CH \;(\text{or } >\underset{H}{C}-\underset{H}{C}<) \quad \text{(ref. 55—57)} \qquad (2)$$

The first reaction has been studied several times, but none of the results favour a mechanism involving Si—H bond ionisation. The reaction is first-order with respect to each reactant:

$$V = k_2 \; [Ph_3SiH] \; [Ph_3CX]$$

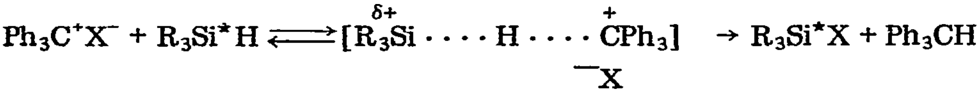
Corey and West proposed a 4 centre-mechanism [28]:



$$\begin{array}{ll} Ph_3Si & -H \\ \vdots & \vdots \\ X & \cdots {}^{+}CPh_3 \end{array}$$

This mechanism is supported by the high stereospecificity observed when the reaction is carried out with (+)-MePh-1-NpSiH [53], when the transfer occurs with retention of configuration. One would not observe a stereospecific reaction with an ionic mechanism.

However, Bauman and Sommer [54] have observed that the reaction stereochemistry varies according to the solvent (for example: inversion of configuration in $CHCl_3$ and retention in C_6H_6). It is difficult to explain clearly the results, but the author proposed a concerted mechanism somewhat similar to the one proposed by Corey and West [28]:

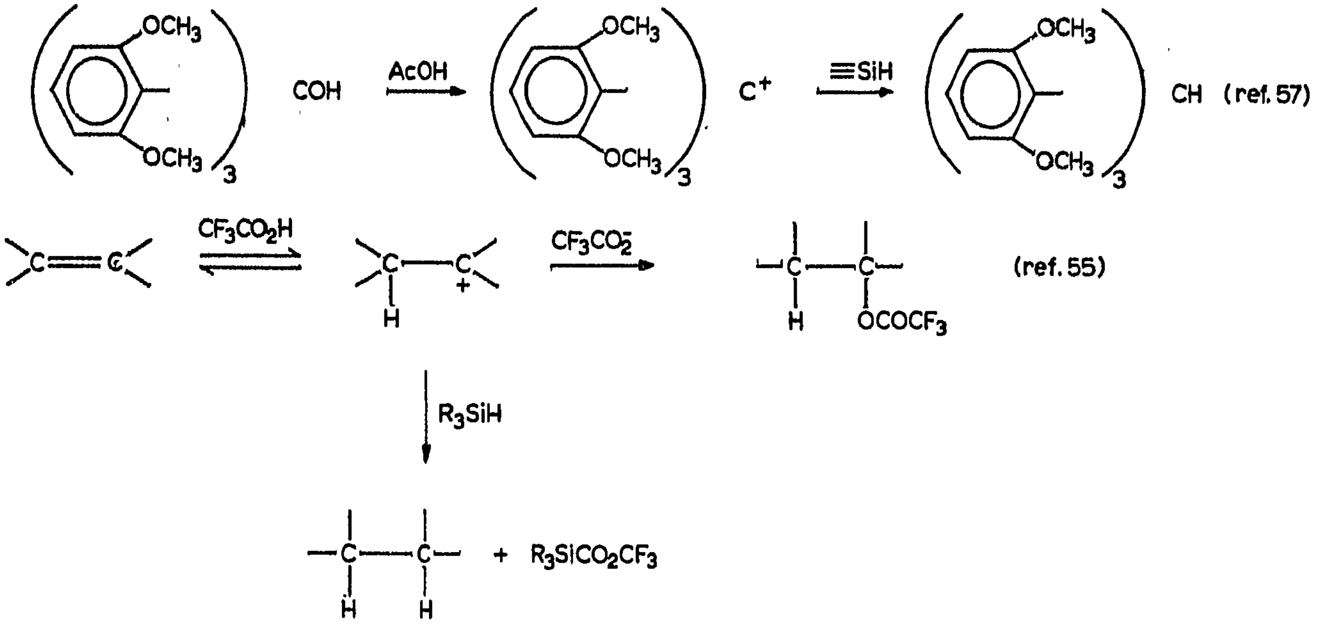


$$Ph_3C^+X^- + R_3Si^*H \rightleftharpoons [\overset{\delta+}{R_3Si} \cdots\cdots H \cdots\cdots \underset{^-X}{\overset{+}{CPh_3}}] \rightarrow R_3Si^*X + Ph_3CH$$

The different stereochemistries are related to the degree of dissociation of the ion pair $Ph_3C^+X^-$.

A reaction of the same type is hydrogenation of an olefin or alcohol by a silane in an acid medium. The reaction passes through a carbonium ion intermediate which abstracts an ion H^- from the silane [55—57] (Scheme 1).

SCHEME 1


OCH3
OCH3
3
COH
AcOH
C+
≡SiH
CH
(ref. 57)
CF3CO2H
CF3CO2-
OCOCF3
(ref. 55)
R3SiH
R3SiCO2CF3

This second reaction is normally carried out in trifluoroacetic acid and the silane is converted to trifluoroacetoxysilane.

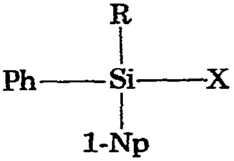
The results of a kinetic study carried out by Carey [57] support the 4-centre mechanism of Corey and West [28]. In this mechanism the silane forms a pentacovalent intermediate with the nucleophilic solvent (AcOH or $CF_3CO_2^-$):

Such an intermediate could transfer the hydride ion to the cation $\equiv C^+$. The coordination of a nucleophile with silicon would labilise the $\equiv$Si—H bond and facilitate the H^- ion departure.

E. Reactions with racemisation

Finally, the case of reactions involving racemisation; here the existence of a siliconium ion can be proposed from stereochemical data. When racemisation occurs for carbon compounds, it generally indicates a sp^2 carbonium ion intermediate.

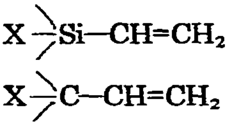
However for silicon, the reactions are found to be very stereospecific, even for a substituted silicon atom in the allylic position [58]. Some nucleophilic substitution reactions at Si have been studied with functional vinylsilanes III:



$$\mathrm{Ph{-}\overset{R}{\underset{1\text{-}Np}{Si}}{-}X}$$

(I) R = Me, (II) R = Et, (III) R = $CH{=}CH_2$
(X = Cl, F, H, OR′, OCOR′ etc.; Ph = phenyl, 1-Np = 1-naphthyl)

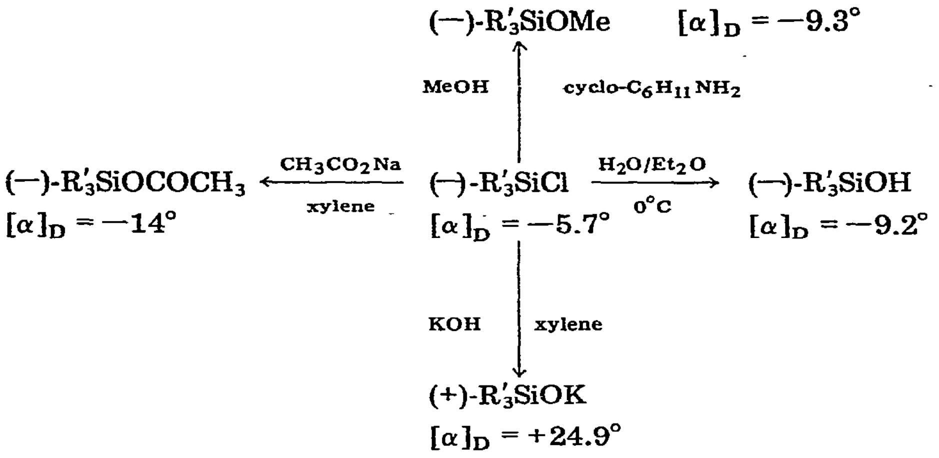
This structure is known to favour sp^2 ion formation due to stabilisation from the π-bond electrons:



The homologous halo—carbon compounds rapidly racemise under the solvolysis conditions where allylic rearrangement is observed.

For silicon compounds, all the reactions are highly stereospecific (> 95%), both for retention and inversion of configuration. The vinylsilanes behave as compounds in the series I (R = Me) and II (R = Et); for example, some reactions of III where X = Cl and R'_3 = $CH{=}CH_2$, Ph, 1-Np, as in Scheme·2.

SCHEME 2



Racemisation was only observed for solvolysis of this chlorosilane in homogeneous solutions. This point will be discussed later; the racemisation arises from a secondary reaction of the products formed [58,72].

Some optically active halosilanes do racemise under certain conditions, and Sommer et al. have observed that methylphenylnaphthylfluorosilane is racemised by hydroxylic reagents (H_2O and ROH) [59,60]. They explained the reaction by a mechanism involving a pentacoordinate intermediate [60]. They have also shown that (—)-MePh-1-Np*SiCl (R_3 SiCl)* loses its optical activity in certain media [1], as do other chlorosilanes and the equivalent chlorogermanes.

Racemisation may be promoted by a number of solvents and by the presence of salts.

(1) Racemisation in the presence of salts. Sommer et al. have found that the ions Cl^-, Br^- and I^- can cause racemisation of (—)-R_3SiCl, and the reaction has only a slight dependence on the halide ion X^- [61]. The rapid chloride—chloride ion exchange with chlorosilane is already known; Allen and Modena showed that the exchange between Cl^- and Ph_3SiCl was much faster than solvolysis:

$$Ph_3SiCl + {}^{36}Cl^- \rightleftharpoons Ph_3Si^{36}Cl \pm Cl^- \qquad \text{(ref. 62)}$$

The first kinetic study of the former reaction showed the rates of exchange (k_E) and racemisation (k_R) to be equal [61]:

$$(-)\text{-}R_3SiCl + {}^{36}Cl^- \xrightleftharpoons{k_E, k_R} (\pm)\text{-}R_3Si^{36}Cl + Cl^-$$

The reaction scheme proposes a siliconium ion existing as an ion pair, with exchange occurring within the pair:

$$(-)\text{-}R_3SiCl \rightleftharpoons [R_3Si^+Cl^-] \xrightleftharpoons{{}^{36}Cl^-} [R_3Si^+\,{}^{36}Cl^-] \rightleftharpoons (+)\text{-}R_3Si^{36}Cl$$

This mechanism is not consistent with equal rates for racemisation and ex-

---

* In the following text R_3 = (Me, Ph, 1-Np).

change. For carbon compounds, a factor indicating solvolysis reactions proceeding by ion pairs, in the presence of chloride ions, is a higher rate for racemisation (k_R) than for incorporation of $^{36}Cl(k_E)$ [63], $k_R \gg k_E$.

The reaction has been further investigated on one hand by Prince and Grant [64—67], and more recently by Sommer et al. [68]. Their results show that the initially observed equality of exchange and racemisation rate was a unique case. Indeed, in the solvent mixture acetone—dioxan, Prince observed a racemisation rate double that of exchange, $k_R = 2\,k_E$ [66]. However in a slightly polar solvent such as benzene, he always found a higher exchange rate: $k_R \ll k_E$ [67].

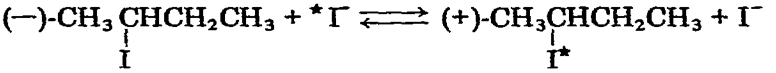
In more recent work, it has been found that the relationship between the rate of racemisation and exchange depends also on the nature of the chlorosilane: $1.3 \leqslant k_R/k_E \leqslant 2$ [68].

Overall, the results can be interpreted if one considers that the exchange occurs by two concurrent processes, one with retention, the other with inversion of configuration. The racemisation arises from an S_N2 substitution by the chloride ion, with inversion of configuration:

$$^{36}Cl^- + (-)\text{-}R_3SiCl \xrightleftharpoons{k_E = k_i} (+)\text{-}R_3Si^{36}Cl + Cl^-$$

(i = inversion)

Analogous reactions are observed for carbon; for example the racemisation of iodo-2-butane [69]:



$$(-)\text{-}CH_3\underset{\displaystyle I}{\underset{|}{C}}HCH_2CH_3 + {}^{*}I^- \rightleftharpoons (+)\text{-}CH_3\underset{\displaystyle I^{*}}{\underset{|}{C}}HCH_2CH_3 + I^-$$

In these reactions, the racemisation rate is twice the exchange rate (identical to the inversion rate), $k_R = 2\,k_E$.

Alongside this process the exchange may occur with retention, but this would not alter the optical activity of the medium:

$$^{*}Cl^- + (-)\text{-}R_3SiCl \xrightleftharpoons{k'_E \equiv k_i} Cl^- + (+)\text{-}R_3Si^{*}Cl \qquad \text{(a)}$$

$$^{*}Cl^- + (-)\text{-}R_3SiCl \xrightleftharpoons{k''_E \equiv k_r} Cl^- + (-)\text{-}R_3Si^{*}Cl \qquad \text{(b)}$$

(r = retention)

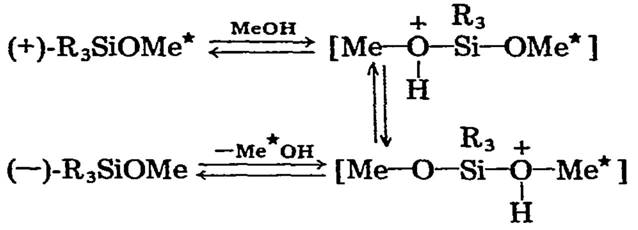
The relative rates of the two processes (a and b) depend on reaction conditions; thus in a slightly polar solvent such as benzene [67], retention (b) predominates. The exchange rate is higher than the racemisation rate:

$k_E = k'_E + k''_E \equiv k_R + k_i$ where $k_r > k_i$; $k_E > k_R$ $(= 2k_i)$.

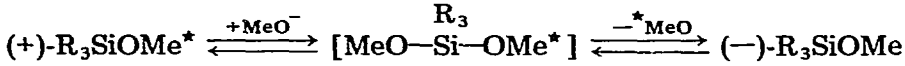
By contrast, in chloroform, it seems that the two processes (a and b) occur concurrently, since the relationship between the rates varies between 1 and 2. Finally in a medium such as acetone—dioxan, the exchange with retention (b) does not occur ($k_r = 0$). Only the S_N2 exchange (a) takes place giving the result $k_R = 2k_E$ [66].

Such concurrent processes have been observed in other cases. $LiAlD_4$ promotes racemisation of R_3SiH at a lower rate than that of H, D exchange. From the discussion above, this means that exchange with retention is operating in the reaction.

Another process of the type (a) is the racemisation of methoxysilanes by methanol in an acid medium as studied by Eaborn et al. [71]. They showed that racemisation arises from an S_N2 substitution of the OMe group by methanol (i). Racemisation by methoxy ions CH_3O^- (ii) is similar:



$$\begin{array}{l} (+)\text{-}R_3SiOMe^{*} \underset{}{\overset{MeOH}{\rightleftarrows}} [Me\text{-}\overset{+}{\underset{H}{O}}\text{-}\overset{R_3}{Si}\text{-}OMe^{*}] \\ \qquad\qquad\qquad\qquad\qquad \updownarrows \\ (-)\text{-}R_3SiOMe \overset{-Me^{*}OH}{\rightleftarrows} [Me\text{-}O\text{-}\overset{R_3}{Si}\text{-}\overset{+}{\underset{H}{O}}\text{-}Me^{*}] \end{array} \qquad (i)$$



$$(+)\text{-}R_3SiOMe^{*} \overset{+MeO^-}{\rightleftarrows} [MeO\text{-}\overset{R_3}{Si}\text{-}OMe^{*}] \overset{-{}^{*}MeO}{\rightleftarrows} (-)\text{-}R_3SiOMe \qquad (ii)$$

Overall, the exchange reactions resemble those known for carbon, resulting in stereospecific substitution with inversion of configuration. However, for organosilanes, there is also a possible exchange with retention and this certainly occurs uniquely in the chemistry of elements with vacant *d*-orbitals. The reaction mechanisms for such elements are evidently complex because a slight change in a medium alters the reaction stereochemistry.

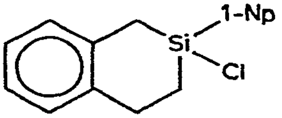
(2) Racemisation by solvents. Here we have two cases: (a) racemisation occurring simultaneously with a substitution reaction, and (b) racemisation without Si—Cl bond substitution.

(*2a*) Racemisation with substitution. This concerns the hydrolysis and alcoholysis of chlorosilanes [58,72]. Unless the chlorosilane is hydrolysed carefully the racemic compound is obtained, alcoholysis is similar.

$$(-)\text{-RPh-1-NpSiCl} \begin{array}{l} \xrightarrow{H_2O} (\pm)\text{-RPh-1-NpSiOH} \\ \xrightarrow{R'OH} (\pm)\text{-RPh-1-NpSiOR}' \end{array}$$

A priori, this could be an indication of siliconium ions existing in the medium since the hydroxylic solvents used are able to promote heterolytic Si—Cl bond cleavage. However, these reactions have been carried out with complete stereospecificity after a slight modification of the experimental conditions. Thus an alcoholysis carried out in the presence of an amine, which traps the liberated HCl, leads with high stereospecificity (> 95%) to an optically active alkoxysilane, e.g.:

$$\text{RPh-1-NpSiCl} \xrightarrow[\text{cyclo-}C_6H_{11}NH_2]{MeOH} \text{RPh-1-NpSiOMe}$$

R = Me	$[\alpha]_D = -6.3°$	$[\alpha]_D = -16°$	(ref. 73)
R = Et	$[\alpha]_D = -24°$	$[\alpha]_D = -13°$	(ref. 58)
	$[\alpha]_D = +28.5°$	$[\alpha]_D = -70°$	(ref. 74)

In the same way, hydrolysis in the heterogeneous medium Et_2O/H_2O (which eliminates HCl from the organic phase) gives a silanol of good optical purity.

The solvolysis of the three following chlorosilanes was studied to determine whether racemisation arises from a siliconium ion intermediate or by a secondary reaction:

$$\mathrm{RPh\text{-}1\text{-}NpSi^{*}Cl} \xrightarrow[\text{Dioxan}]{H_2O} \mathrm{RPh\text{-}1\text{-}NpSi^{*}OH}$$

R = Me, R = Et [72], R = $CH_2{=}CH$ [58]

$$\mathrm{RPh\text{-}1\text{-}NpSi^{*}Cl} \xrightarrow{R'OH,\ Et_2O \text{ or } C_6H_6} \mathrm{RPh\text{-}1\text{-}NpSi^{*}OR'}$$

R′ = Me, Et, i-Pr, t-Bu.

The study of the substitution (alcoholysis without an amine and hydrolysis in homogeneous medium) parallel to the racemisation, showed the substitution reaction to be stereospecific; but it is easily shown that with an excess of alcohol, the alkoxysilanes are racemised by traces of HCl. This reaction was studied by Eaborn [71] who demonstrated an S_N2 exchange reaction between MeOH and the SiOMe group, in acid media (cf. the preceding paragraph).

The following kinetic scheme explains the experimental facts:

$$\begin{tikzcd}
(-)\text{-}R_3SiCl + R'OH \arrow[r, shift left, "k_1"] & (-)\text{-}R_3SiOR' + HCl \arrow[l, shift left, "k_{-1}"] \arrow[d, "k_2"', "R'OH"] \\
(\pm)\text{-}R_3SiCl + R'OH \arrow[r, shift right, "k_1"'] & (\pm)\text{-}R_3SiOR' \arrow[l, shift right, "k_{-1}"']
\end{tikzcd}$$

One observes an equilibrium for the solvolysis reaction. Figures 1 and 2 represent simultaneously the change in optical rotation (at 365 nm) with time and the percentage substitution for two experiments (the initial inversion of optical rotation occurs because the alkoxysilane has a rotation opposite in sign to that of the chlorosilane at 365 nm).

Two limiting cases may be proposed depending upon the alcohol used:

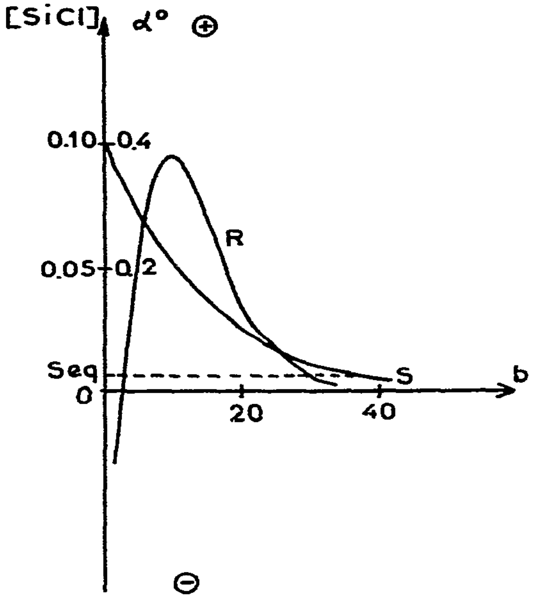
(*i*) The case of MeOH/EtOH in ether solvent for which the substitution is nearly complete (% Seq > 90). The two reactions are analogous and in the preceding scheme $k_2\,[R'OH] \gg k_{-1}$. The SiCl bond substitution is the rate-determining step.

(*ii*) The case of $t\text{-}BuOH/Et_2O$ where the equilibrium is rapidly attained $t = 2$ min, 40% substitution, whilst racemization is complete but very slow $t = 45$ min, thus $k_2\,[R'OH] \ll k_{-1}$.

The alkoxysilane racemisation is the slow step in the scheme. Indeed the t-butoxysilane racemises very slowly in the reaction medium which was used: $R_3Si^{*}O\text{-}t\text{-}Bu$, t-BuOH 80%, % Rac. 15, solvent C_6H_6, t 48 h; solvent Et_2O, t 15 h.

According to the nature of the solvent and the nature and concentration of the alcohol, the other cases studied fell between these two limiting ones.

This work has thus shown that, even in hydroxylic solvents there is no S_N1



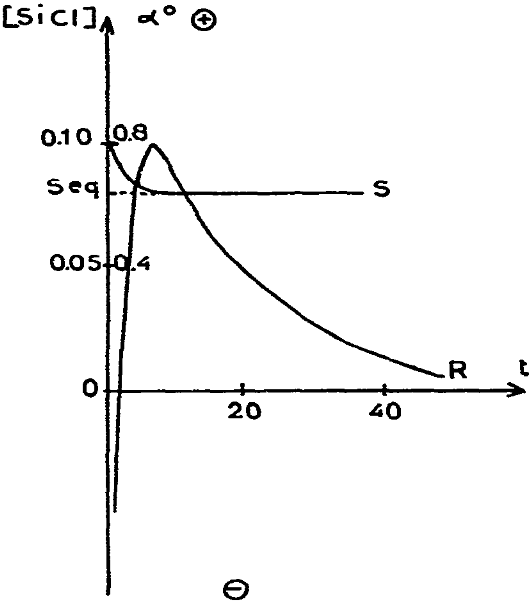


Fig. 1. Change in optical rotation (at 365 nm) and percentage of substitution of MePh1-NpSi*Cl with 5% MeOH in EtOH. S, substitution; Seq., substitution at equilibrium; R, racemisation.

Fig. 2. Change in optical rotation (at 365 nm) and percentage of substitution of MePh1-NpSi*Cl with 80% t-BuOH in EtOH. S, substitution; Seq., substitution at equilibrium; R, racemisation.

type reaction at Si. The observed racemisation is only a second step: that of the reaction products. A simple modification of the experimental conditions permits a totally specific substitution.

(*2b*) Racemisation without substitution. Sommer et al. were the first to observe that (—)-R_3SiCl racemises in certain solvents of rather high dielectric constant ($\epsilon > 30$) [1,75] (Table 1).

This racemisation takes place without substitution, and conductometric measurements indicated no appreciable ionisation. The authors showed a linear correlation between racemisation rate, and the constant ϵ using $CHCl_3/CH_3NO_2$ mixtures of various composition.

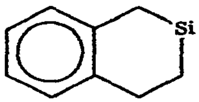
TABLE 1

EXAMPLES OF RACEMISATION SOLVENTS OF (—)-R_3SiCl

Racemising solvents	Non-racemising solvents
CH_3NO_2	$CHCl_3$
CH_3CN	CCl_4
$PhNO_2$	C_6H_6
CH_3COCH_3	hydrocarbons
$(CH_3CO)_2O$	*p*-dioxan

TABLE 2

SOLVENTS ABLE TO INDUCE RACEMISATION OF THE CHLOROSILANES RPh-1-NpSiCl [76]

Solvent	RPh-1-NpSiCl		
	R = Me	R = vinyl	RPh = 
Dioxan	-[a]	-	x
THF	-	x	x
GDME[b]	x	x	x
Ethyl esters[c]	x	x	x
Aprotic polars[d]	x	x	x

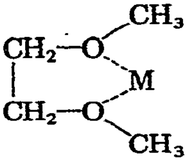
[a] x = racemisation, - = no racemisation. [b] GDME = glycol dimethyl ether. [c] Ethyl esters: $MeCO_2Et$, $PhCO_2Et$, $EtO_2CCH_2CO_2Et$, $EtO_2C(CH_2)_2CO_2Et$, $EtO_2CCH{=}CHCO_2Et$ (*cis*, *trans*), $MeCOCH_2CO_2Et$. [d] Aprotic polar solvents: HMPT [$O{=}P(NMe_2)_3$], DMF, DMSO (Me_2SO).

As an explanation, the formation of a siliconium ion in an ion pair has been proposed (the restriction is needed to explain the weak or non-existent conductivity of the reaction media).

$$(-)\text{-}R_3SiCl \rightleftharpoons [R_3Si^+\cdots Cl^-] \rightleftharpoons (\pm)\text{-}R_3SiCl$$

This work has been continued with 3 optically active chlorosilanes [76]. There are many solvents able to induce racemisation, including those studied by Sommer and the solvents listed in Table 2.

Amongst these are solvents of low dielectric constant, for example monoglyme, and esters ($\epsilon < 15$). The latter are interesting because in spite of their low polarity they are generally able to cause racemisation. This ability probably stems from the nucleophilic CO_2R group in the molecule; those compounds with more than one group easily induce racemisation. Thus ethyl acetoacetate gives immediate racemisation of the 3 chlorosilanes studied, and so does monoglyme (GDME) which can also solvate electrophilic species:



Aprotic polar solvents form an important class (HMPT, DMF, DMSO). They easily induce chlorosilane racemisation since a low concentration (0.1 to 0.5%) in CCl_4 or C_6H_6 gives a rapid reaction [76]. In such conditions, the Si—Cl bond cleavage is not the determining factor for the reaction; this factor may be the solvent's nucleophilic power.

The polar aprotic compounds are very good ligands for metals or elements with vacant 3*d* orbitals since they very easily form coordinate bonds.

A number of complexes with halosilanes are known, such as SiF_4, 2DMF, SiX_4, 2DMSO (X = F, Cl, Br) [77a], and $R^1R^2SiF_2$, *n*DMF (R^1 = Ph, R^2 = F, R^1 = R^2 = Ph; R^1 = Me, R^2 = Ph) [77b].

In view of the fact that polar aprotic solvents induce chlorosilane racemisation, one can suggest that the reaction involves extension of coordination through the vacant 3*d* silicon orbitals.

Analogous results have been obtained for optically active germanium compounds R_3GeCl [78].

The following points may be deduced:

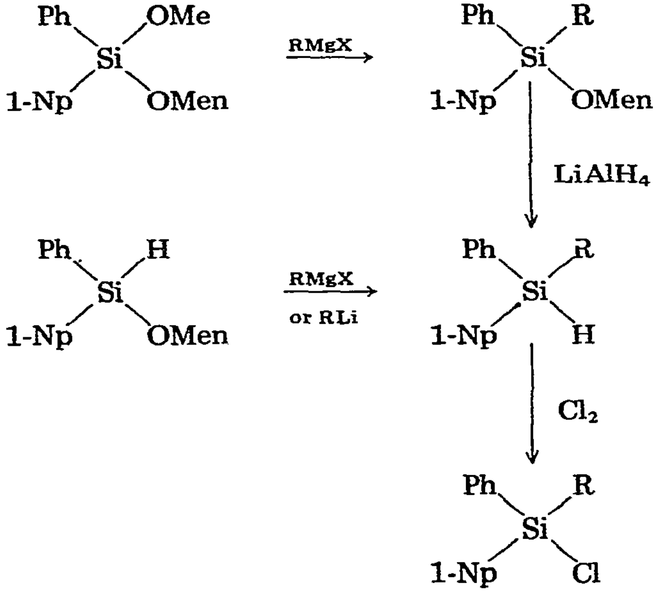
(1) Racemisation by solvent is certainly not due to a heterolytic Si—Cl bond cleavage.

(2) The efficiency of the racemising reagent is completely independent of its dielectric constant.

(3) The essential characteristic is the presence of one or more nucleophilic groups in the molecule; thus a reaction pathway involving extension of coordination at the silicon atom may be envisaged.

To prove this, a series of compounds with a group R of increasing steric hindrance have been studied [79] viz. RPh-1-NpSiCl (R = Me, Et, n-Pr, i-Pr, t-Bu).

The preparation of these compounds from bifunctional asymmetric organosilanes has been recently described [80]:



The racemisation rates of these chlorosilanes were measured with different solvents diluted with CCl_4 (DMF, HMPT, CH_3COCH_3, CH_3CN, CH_3CO_2Et, GDME, etc.) and we found the following order of rate constants: (k_R) R = Me > Et > Pr > i-Pr > t-Bu; and k_R/k_R equals for R = Me, 1; R = Et, $2 \cdot 10^{-1}$; R = i-Pr, 10^{-2}—10^{-3}; R = t-Bu, very small.

The observed decrease in rate is most important for the t-BuPh-1-NpSiCl. Thus in HMPT 20%/CCl_4, there is only 50% racemisation after 2 h, whilst this point is achieved in less than 5 min for MePh-1-NpSiCl with only 1% of HMPT [81].

This rate order is not consistent with a R_3Si^+ intermediate of sp^2 structure. A reaction involving such a cation should show an increase in racemisation speed with increasing steric hindrance of the group R, or at least no change with increasing group size.

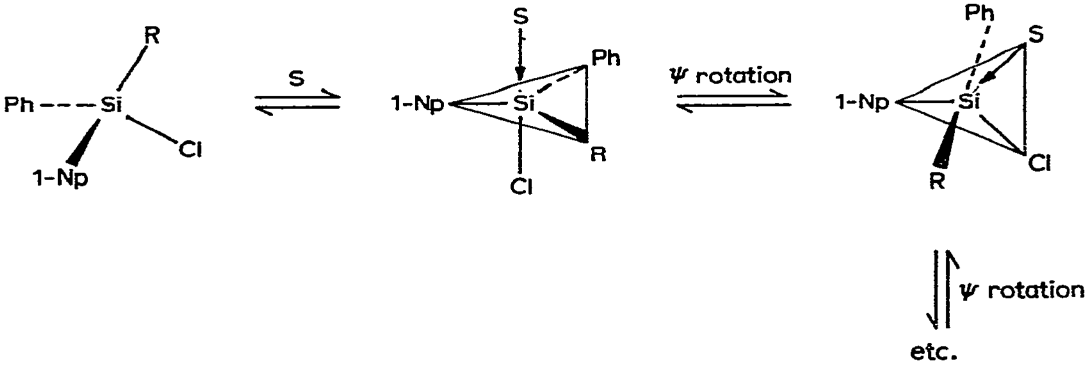
The results however agree with a scheme involving coordination of the solvent with the silicon atom. If this becomes five- or six-coordinated during the reaction, a bulky group R would be expected to slow down the reaction.

Analogous results have been observed with two germanium compounds [79]: RPh-1-NpGeCl where R = Me and i-Pr. The same rate decrease is found when the methyl group is replaced by an isopropyl group. From this it follows that the racemisation of the chlorosilanes and germanes occurs by extension of coordination around the central atom. Such a mechanism has also been proposed for aminosilane racemisation [82].

Three pathways may be considered for this mechanism [83]:

(1) By coordination of a racemising molecule, a five-coordinated complex Si^V is formed, which undergoes pseudo-rotation:

SCHEME 3



Rather than this pseudo-rotation mechanism several alternative mechanisms have been proposed, all leading to the same results.

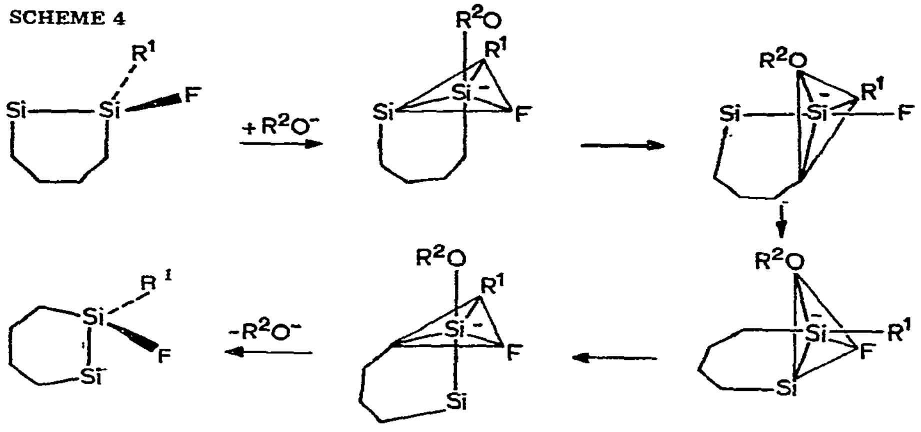
This process has been demonstrated by Muetterties for the silicon anions SiF_5 and $RSiF_4$ [84]; low-temperature NMR has shown the fluorine atoms to be equivalent, as with the fluorophosphoranes PF_5, RPF_4 [85]. Such an equivalence is not due to an intermolecular exchange since the $^{29}Si—^{19}F$ coupling is unchanged. $R_2SiF_3^-$ does not exhibit the process. Pseudo-rotation has been used by Kumada to explain the *cis—trans* isomerisation of difluorodisilacyclohexanes (Scheme 4) [87] and by Sommer in fluorosilane racemisation (Scheme 5) [60].

This mechanism applied to chlorosilanes does not follow the electronegativity rules. As can be seen in Scheme 3, the Cl and S groups are in equatorial position of the bipyramid and this contradicts the normal observations [84—85]. A bimolecular rearrangement between pentacoordinated intermediates, such as that recently suggested by Musher would lead to the same result [86].

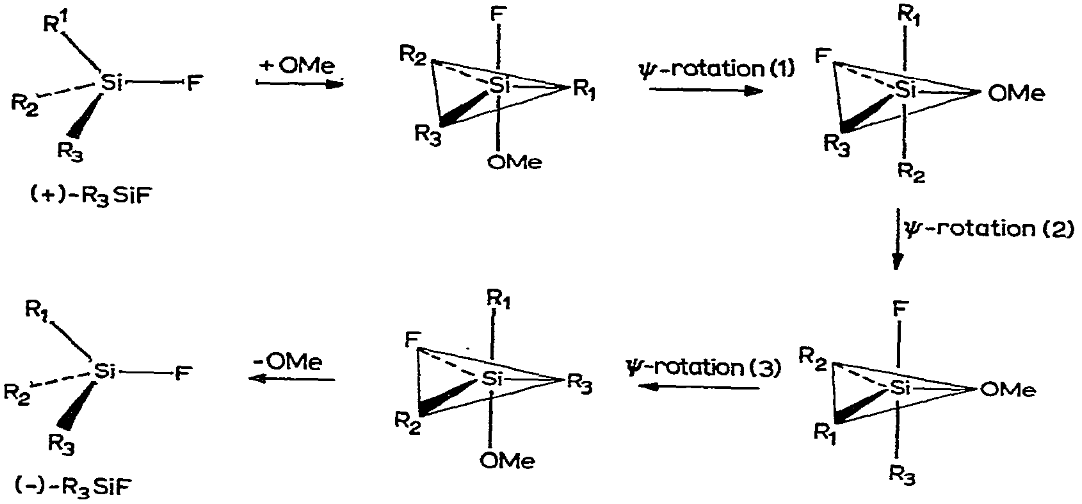
(2) The intervention of two reactant molecules could form an octahedral intermediate Si^{VI} (Scheme 6).

(3) One can envisage that coordination of the second reactant molecule causes Si—Cl bond cleavage and forms a pentacoordinated siliconium ion (Si^V). The two reactant molecules occupy axial positions (Scheme 7).

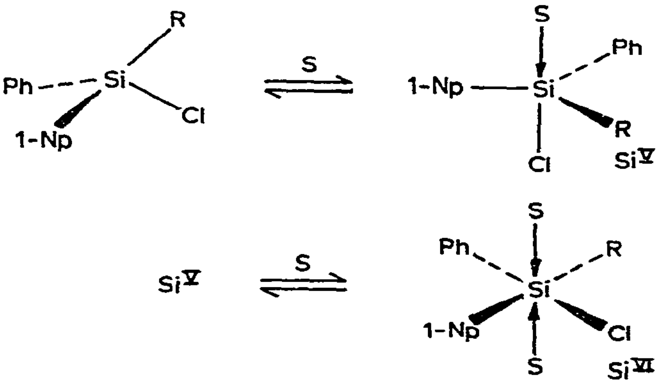
SCHEME 4



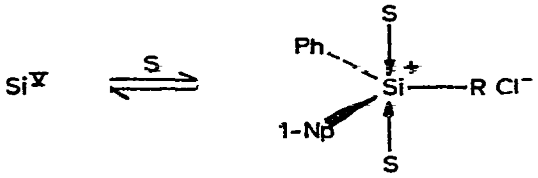
SCHEME 5



SCHEME 6



SCHEME 7



Such a mechanism must be examined, since this type of complex ion is formed by a nucleophilic attack at ^{29}Si [31—34].

To distinguish whether racemisation occurs by pseudo-rotation (1) or by coordination of two solvent molecules (2,3), the reaction order with respect to reactant was determined by kinetics. This was possible only with aprotic polar solvents since a low concentration in CCl_4 or hydrocarbons will cause racemisation [76]. The experiments carried out are stated in Table 3.

The rate is first-order in chlorosilane and in all cases is second-order in the racemising reagent; this was shown by variation of the first-order rate constant k_1 as a function of reagent concentration.

Figure 3 gives the variation of k_1 with the square of concentration for (MenO)Ph-1-NpSiCl.

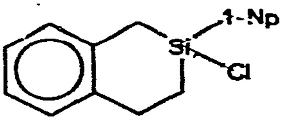
The results shown in Fig. 3 obey the following rate law:

$$V = k_3[R_3Si^*Cl]\,[S]^2 \qquad S = \text{reagent}$$

An analogous equation exists for the racemisation of t-butylphenyl-1-

TABLE 3

LIST OF KINETIC EXPERIMENTS

≡SiCl	Reactant	Solvent
EtPh-1-NpSiCl	DMF	CCl_4
	HMPT	
	DMSO	
	DMSO	PhMe
MePh-1-NpSiCl	DMF	PhMe
iPrPh-1-NpSiCl	HMPT	CCl_4
(MenO)Ph-1-NpSiCl	HMPT	CCl_4
(MenO)(p-$MeOC_6H_4$)-1-NpSiCl	HMPT	CCl_4
$[(CH_3)_3CCH_2]$Ph-1-NpSiCl	HMPT	CCl_4
	DMF	PhMe

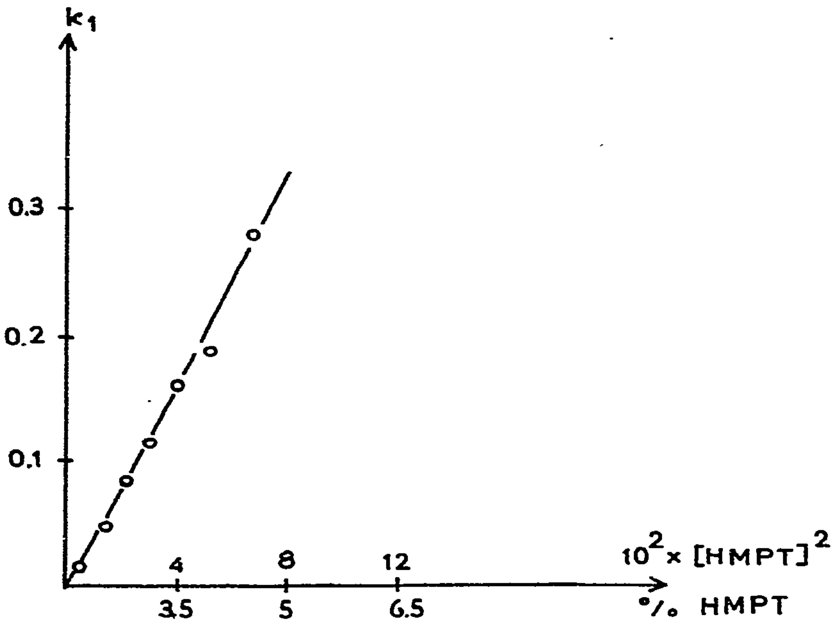


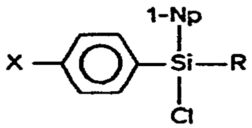
Fig. 3. Variation of k_1 with the square of concentration of solvent for (MenO)Ph-1-NpSiCl.

naphthylbromosilane [88]. The only difference observed is in the reaction rate which is higher for the bromosilane.

Thus the racemisation is second-order in racemising solvent, allowing the first hypothesis to be dismissed i.e. formation of a pentacoordinated immediate (Si^V) followed by pseudo-rotation (Scheme 3). Another argument against the hypothesis came from the same kinetic study when the energy and entropy of activation were determined. The activation energy is very low ($\Delta H^{\ddagger} \leqslant 3$ kcal/mole) and the entropy has a high negative value ($\Delta S^{\ddagger} \sim -60$ e.u.). These differ considerably from literature values for the pseudo-rotation of organophosphoranes [85,89].

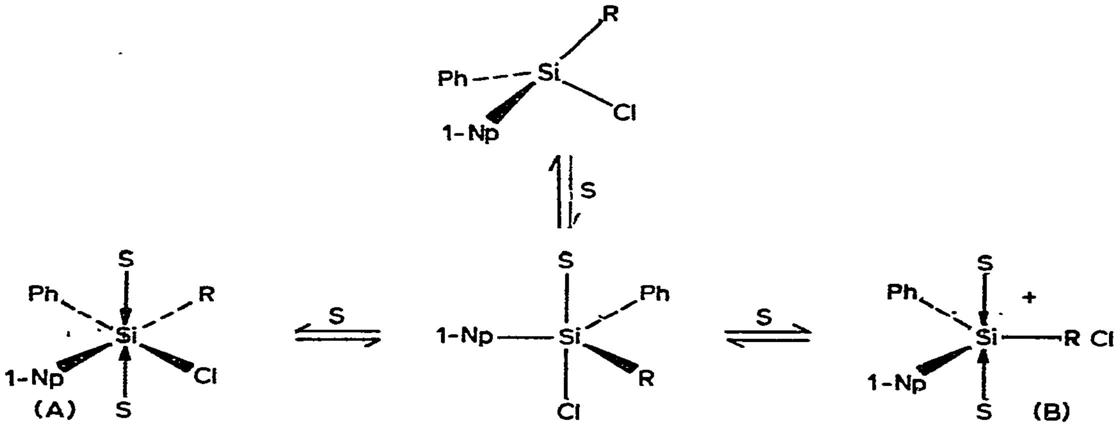
Para-substituents on the phenyl ring exert an electronic influence on the racemisation rate and can be used to give further information alowing one to choose between the two other posulates: an octahedral complex (A) or a pentacoordined siliconium ion (B) (Scheme 8).

The racemisation rates of the compounds



where X = H, OMe, CF_3 and R = OMen and Et, have been compared [90]. $k_X/k_H = 1.5$ when X = OMe, R = OMen and when X = OMe, R = Et, no racemisation occurred when X = CF_3. Thus the methoxy group has a negligible effect on the rate, but the highly electron-withdrawing CF_3 group prevents racemisation. A priori this could invoke the ion $(Si^V)^+$ (B); moreover, the reactivity order observed for halosilane racemisation $\equiv$SiBr > $\equiv$SiCl > $\equiv$SiF is also that of Si—X

SCHEME 8



bond lability. However the observation of no notable increase in reaction rate for the OMe group contradicts this argument. S_N1 reactions are generally strongly accelerated by substitution of an OMe group in the *para* position of a phenyl ring [91].

This study shows the difficulty in simply translating concepts from organic reaction mechanisms to those of silicon. The vacant *d* orbitals certainly modify the transmission of electronic effects. Unfortunately little is known about siliconium ion stabilisation by electron releasing groups: recent results from mass spectrometry [92] show that when substituted on the phenyl ring they stabilise the ions $PhSi^+Me_2$ by resonance interactions. However, this stabilisation is lower than for the carbon analogues [93]. But these results, concerning trivalent ions $(Si^{III})^+$ cannot be extended to pentacovalent ions $(Si^V)^+$. There is a fundamental difference between the two ions: the ion $(Si^V)^+$ is formed by double nucleophilic reaction at Si, whilst a carbonium ion (or $Si^{III})^+$ is formed by electrophilic assistance on bond cleavage, and it is thus difficult to apply results from organic mechanisms to silicon chemistry.

No definite conclusion is yet possible, but the arguments developed favour the second postulate i.e. formation of an octahedral Si complex, with no bond cleavage.

This mechanism agrees with the low activation energies measured ($\Delta H^{\ddagger} \leqslant$ 3 kcal/mole) and the highly negative activation entropy ($\Delta S^{\ddagger} \sim -60$ cal/mole/degree).

In addition the observed reactivity order ($\equiv$SiF < $\equiv$SiCl < $\equiv$SiBr), the same as the polarisability bond order, does not contradict the mechanism. During the slow step of the reaction (passage from Si^V to Si^{VI}):

$$R_3SiX + X \underset{}{\overset{\text{fast}}{\rightleftarrows}} Si^V$$

$$Si^V + S \underset{}{\overset{\text{slow}}{\rightleftarrows}} Si^{VI}$$

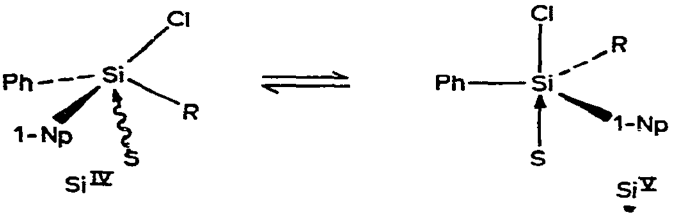
the attack of the second molecule of racemising solvent causes the Si—Cl bond to lengthen. This allows the silicon atom to become more electrophilic, and the bond lengthening is easier when it is more polarisable.

The influence of the CF_3 group can also be explained in the two-step mechanism. The CF_3 group certainly favours formation of the first intermediate (Si^V), since being highly inductive, it makes the Si more polar, facilitating attack by the first molecule. But it lowers the polarisability of the SiCl bond, making the second attack less favorable, thus explaining the slower rate of racemisation.

The second molecule has a number of possible modes of attack leading to the six-coordinated intermediate responsible for the racemisation.

We have always considered the first molecule as attacking on the side away from the Cl group (Scheme 9).

SCHEME 9

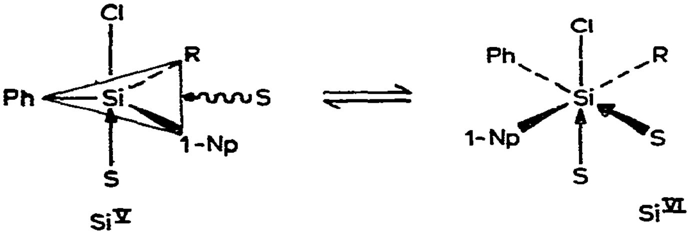


This structure is reasonable since the chlorosilanes react preferentially with inversion of configuration.

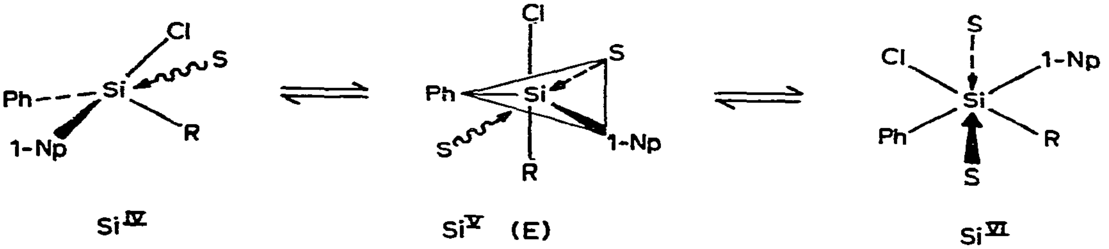
There are two possibilities for the second attack:

(*1*) Equatorial attack. The solvent molecule attacks the intermediate Si^V in the equatorial plane (Scheme 10)

SCHEME 10



SCHEME 11



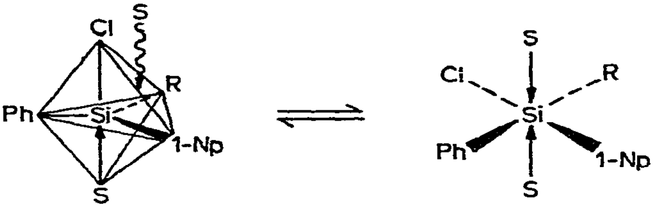
Such a mode of attack gives retention of configuration and cannot explain the racemisation. For racemisation to occur, the first intermediate must have the structure (E) (Scheme 11). (E) is obtained by frontal attack of the solvent on the chlorosilane (step 1) corresponding to retention of configuration. To give racemisation, it is necessary to have Schemes 10 and 11 acting concurrently, Scheme 10 corresponding to retention and Scheme 11 to racemisation. Such a dual stereochemistry has already been observed for example in the ion exchange between $^{36}Cl^-$ and a chlorosilane [66,67]:

$$(-)\text{-}R_3SiCl \overset{^{36}Cl^-}{\rightleftharpoons} (+)\text{- or } (-)\text{-}R_3Si^{36}Cl$$

However this mode of attack seems unlikely since the Si—Cl and Si—Br groups generally react with inversion of configuration.

(2) Attack on a bipyramidal face (Scheme 12).

SCHEME 12



In this mechanism, the second solvent molecule attacks at the face of the bipyramidal intermediate (Si^V) opposite to the first coordinate molecule. This attack places the Si—Cl bond in the equatorial plane of the octahedral intermediate, the two solvent molecules taking up axial positions.

Such a mechanism, although unusual, agrees with the experimental data. In the absence of other information, it is difficult to choose between the two modes of attack.

Conclusion

This analysis shows that the majority of results obtained in silicon chemistry can be interpreted without invoking siliconium ions $(Si^{III})^+$ analogous to carbonium ions. The high affinity of silicon for nucleophiles explains the failure to prove the presence of such ions, but one cannot exclude their possible existence. A medium, weakly nucleophilic towards silicon, could give an $(Si^{III})^+$ of sufficient lifetime to be characterised.

The unusual behaviour of silicon in giving rise to a new class of five-coordinated ions $(Si^V)^+$ should be noted. These ions are formed by double nucleophilic attack at silicon and are thus fundamentally different from $(Si^{III})^+$ ions which would result from electrophilic assistance to Si—Cl bond cleavage.

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References

1 L.H. Sommer, Stereochemistry, Mechanism and Silicon, McGraw-Hill, New York, 1965..
2 G.G. Hess, F.W. Lampe and L.H. Sommer, J. Amer. Chem. Soc., 86 (1964) 3174.
3 W.P. Weber, R.A. Felix and A.K. Willard, Tetrahedron Lett., (1970) 907 and references therein.
4 D.H. O'Brien and T.J. Hairston, Organometal. Chem. Rev. A, 7 (1971) 95.

5 (a) M.C. Flowers and L.E. Gusel'nikov, J. Chem. Soc. B, (1968) 419;

(b) A.W.P. Jarvie and R.J. Rowley, J. Organometal. Chem., 36 (1972) C7;

(c) R.P. Clifford, B.G. Gowenlock, C.A.F. Johnson and J. Stevenson, J. Organometal. Chem., 34 (1972) 53;

(d) T.J. Barton and E. Kline, J. Organometal. Chem., 42 (1972) C21; T.J. Barton, E. Kline and C.L. McIntosh, Chem. Commun., (1972) 861;

(e) P. Boudjouk and L.H. Sommer, Chem. Commun., (1973) 54; D.N. Roark and L.H. Sommer, ibid., (1973) 167.

6 C. Eaborn, Organosilicon compounds, Butterworth, London, 1960.

7 M.E. Freeburger and L. Spialter, J. Amer. Chem. Soc., 93 (1971) 1894 and references therein.

8 (a) C. Lageot, Y. Limouzin and J.C. Maire, J. Organometal. Chem., 38 (1972) 23;

(b) J.M. Angelleli, J.C. Maire and Y. Vignollet, ibid., 22 (1970) 313;

(c) Y. Vignollet, J.C. Maire and D.W. Turner, ibid., 18 (1969) 349;

(d) Y. Vignollet, J.C. Maire and M. Witanovski, Chem. Commun., (1968) 1187.

9 Y. Limouzin, Thèse Doctorat Sciences Physiques, Marseille, 1972.

10 R.H. Flowers, R.J. Gillespie and E.A. Robinson, Can. J. Chem., 41 (1963) 2464.

11 F.P. Price, J. Amer. Chem. Soc., 70 (1948) 871.

12 A.B. Thomas and E.G. Rochow, J. Inorg. Nucl. Chem., 4 (1957) 205.

13 N. Litchin and P.D. Bartlett, J. Amer. Chem. Soc., 73 (1951) 5530.

14 K. Gingold, E.G. Rochow, D. Seyferth, A.C. Smith and R. West, J. Amer. Chem. Soc., 74 (1952) 6306.

15 A.B. Thomas and E.G. Rochow, J. Amer. Chem. Soc., 79 (1957) 1843.

16 M.E. Peach and T.C. Waddington, J. Chem. Soc; (1961) 1238.

17 U. Wannagat and F. Brandmair, Z. Anorg. Allgem. Chem., 280 (1955) 223.

18 F. Brandmair and U. Wannagat, Z. Anorg. Allgem. Chem., 288 (1956) 91.

19 H. Gilman and G.E. Dunn, J. Amer. Chem. Soc., 72 (1950) 2178.

20 U. Wannagat and W. Liehr, Angew. Chem., 69 (1957) 783.

21 G.A. Olah and J. Lukas, J. Amer. Chem. Soc., 89 (1967) 2227, 4739.

22 G.A. Olah, D.H. O'Brien and C.Y. Lui, J. Amer. Chem. Soc., 91 (1969) 701.

23 G.A. Olah and Y.K. Mo, J. Amer. Chem. Soc., 93 (1971) 4942.

24 D.W.A. Sharp and N. Sheppard, J. Chem. Soc., (1957) 674.

25 K.M. Harmon and A.B. Harmon, J. Amer. Chem. Soc., 83 (1961) 865.

26 J.Y. Corey, University of Wisconsin, Unpublished work, 1964.

27 H.J. Dauben Jr., F.A. Gadecki, K.M. Harmon and D.L. Pearson, J. Amer. Chem. Soc., 79 (1957) 4557.

28 J.Y. Corey and R. West, J. Amer. Chem. Soc., 85 (1963) 2430.

29 J.Y. Corey and R. West, J. Amer. Chem. Soc., 85 (1963) 4034.

30 J.C. Davidson and C.M. French, J. Chem. Soc., (1958) 114.

31 B.J. Aylett and J.M. Campbell, Chem. Commun., (1967) 159.

32 G.A. Ozin, Chem. Commun., (1969) 104.

33 I.R. Beattie and G.A. Ozin, J. Chem. Soc. A, (1968) 2373.

34 I.R. Beattie, T.R. Gilson and G.A. Ozin, J. Chem. Soc. A, (1968) 1092, 2772.

35 G.A. Olah, J. Amer. Chem. Soc., 94 (1972) 808.

36 C.G. Swain, R.M. Esteve Jr. and R.H. Jones, J. Amer. Chem. Soc., 71 (1949) 965.

37 P.G. Rodewald, Pennsylvania State University, Unpublished work, 1963.

38 F.C. Whitmore, L.H. Sommer and J. Gold, J. Amer. Chem. Soc., 69 (1947) 1976.

39 R.W. Bott, C. Eaborn and B.M. Rushton, J. Organometal. Chem., 3 (1965) 455.

40 T.J.H. Hairston and D.H. O'Brien, J. Organometal. Chem., 23 (1970) C41.

41 T.J.H. Hairston and D.H. O'Brien, J. Organometal. Chem., 29 (1971) 79.

42 A.G. Brook, K.H. Pannel, G.E. Le Grow and J.J. Sheeto, J. Organometal. Chem., 2 (1964) 491.

43 A.G. Brook and K.H. Pannel, Can. J. Chem., 48 (1970) 3679.

44 G.A. Russel, J. Amer. Chem. Soc., 81 (1959) 4831.

45 A.W.P. Jarvie, Organometal. Chem. Rev., 6 (1970) 153.

46 L.H. Sommer, D.L. Bailey and F.C. Whitmore, J. Amer. Chem. Soc., 70 (1948) 2869.

47 L.H. Sommer and G.A. Baughman, J. Amer. Chem. Soc., 83 (1961) 3346.

48 G.A. Baughman, Dissert. Abstracts, 22 (1961) 2187.

49 F. Carre, R. Corriu and B. Henner, J. Organometal. Chem., 22 (1970) 589.

50 A.W.P. Jarvie, A. Holt and J. Thompson, J. Chem. Soc. B, (1969) 852.

51 M.A. Cook, C. Eaborn and D.R.M. Walton, J. Organometal. Chem., 24 (1970) 301.

52 (a) T.G. Traylor, W. Hanstein, H.J. Berwin, N.Y.A. Clinton and R.S. Brown, J. Amer. Chem. Soc., 93 (1971) 5715;

(b) U. Weidner and A. Schweig, Angew. Chem. Int. Ed., 11 (1972) 146.

53 J.D. Austin and C. Eaborn, J. Chem. Soc., (1964) 2279.

54 L.H. Sommer and D.L. Bauman, J. Amer. Chem. Soc., 91 (1969) 7076.

55 D.M. Kursanov and Z.N. Parnes, Russian Chem. Rev., 38 (1969) 812.

56 F.A. Carey and H.S. Tremper, J. Amer. Chem. Soc., 90 (1968) 2578; 91 (1969) 2967.

57 F.A. Carey and C.L. Wang Hsu, J. Organometal. Chem., 19 (1969) 29.

58 R. Corriu and G. Royo, J. Organometal. Chem., 14 (1968) 291.

59 L.H. Sommer and P.G. Rodewald, J. Amer. Chem. Soc., 85 (1963) 3898.

60 L.H. Sommer and D.L. Bauman, J. Amer. Chem. Soc., 91 (1969) 7045.

61 L.H. Sommer, F.O. Stark and K.W. Michael, J. Amer. Chem. Soc., 86 (1964) 5683.

62 A.D. Allen and G.D. Modena, J. Chem. Soc., (1957) 3671.

63 A. Ledwith, M. Hojo and S. Winstein, J. Amer. Chem. Soc., 82 (1960) 1010; S. Winstein and J.S. Gall, Tetrahedron Lett., 2 (1960) 31; W.C. Young, S. Winstein and H.L. Goering, J. Amer. Chem. Soc., 73 (1951) 1958; P.B.D. de la Mare and C.A. Vernon, J. Chem. Soc., (1954) 2504.
64 M.W. Grant and R.H. Prince, J. Chem. Soc. A, (1968) 2305.
65 M.W. Grant and R.H. Prince, J. Chem. Soc. A, (1969) 1138.
66 M.W. Grant and R.H. Prince, Chem. Commun., (1968) 1076.
67 M.W. Grant and R.H. Prince, Nature (London), 222 (1969) 1163.
68 L.H. Sommer, G.D. Homer, A.W. Messing, J.L. Kutchinsky, F.O. Stark and K.W. Michael, J. Amer. Chem. Soc., 93 (1971) 2093.
69 (a) E.D. Hughes, F. Juliusberger, S. Masterman, B. Tofley and J. Weiss, J. Chem. Soc., (1935) 1525;
(b) E.D. Hughes, F. Juliusberger, A.D. Scott, B. Tofley and J. Weiss, Ibid (1936) 1173;
(c) W.A. Cowdrey, E.D. Hughes, T.P. Newell and C.L. Wilson, Ibid (1938) 209.
70 A. Jean and M. Le Quan, Personnal communication, 1971.
71 R. Baker, R.W. Bott, C. Eaborn and P.W. Jones, J. Organometal. Chem., 1 (1963) 37.
72 R. Corriu and M. Leard, J. Organometal. Chem., 15 (1968) 25.
73 L.H. Sommer, C.L. Frye, G.A. Parker and K.W. Michael, J. Amer. Chem. Soc., 86 (1964) 3271.
74 R.J.P. Corriu and J.P. Masse, Chem. Commun., (1967) 1287.
75 F.O. Stark, Pennsylvania State University, Unpublished work, 1962.
76 R. Corriu, M. Leard and J. Masse, Bull. Soc. Chim. Fr., (1968) 2555.
77 (a) M. Gielen and N. Sprecher, Organometal. Chem. Rev., 1 (1966) 455;
(b) V.A. Drozdov, A.P. Kreshkov and A.D. Romanova, J. Gen. Chem. USSR Int. Ed., 40 (1970) 2574.
78 F.H. Carre, R.J.P. Corriu and R.B. Thomassin, Chem. Commun., (1968) 560.
79 F. Carre, R. Corriu and M. Leard, J. Organometal. Chem., 24 (1970) 101.
80 R.J.P. Corriu and G.F. Lanneau, Tetrahedron Lett., (1970) 165; R.J.P. Corriu and G.F. Lanneau, Tetrahedron Lett., (1971) 2771; R.J.P. Corriu, G.F. Lanneau and G.L. Royo, J. Organometal. Chem., 35 (1972) 35; R.J.P. Corriu, G.F. Lanneau and M. Leard, Chem. Commun., (1971) 1365.
81 R. Corriu and M. Leard, Unpublished work.
82 K.D. Kaufmann and K. Ruhlmann, Z. Chem., 7 (1967) 391.
83 R. Corriu and M. Henner-Leard, Chem. Commun., (1971) 1086; J. Organometal. Chem., 64 (1974) 351
84 F. Klanberg and E.L. Muetterties, Inorg. Chem., 7 (1968) 155.
85 E.L. Muetterties, W. Mahler and R. Schmultzer, Inorg. Chem., 2 (1963) 613.
86 J.I. Musher, Tetrahedron Lett., (1973) 1093.
87 K. Tamao, M. Ishikawa and M. Kumada, Chem. Commun., (1969) 73.
88 R. Corriu and M. Henner, J. Organometal. Chem., 65 (1974) C39.
89 (a) E.L. Muetterties, Accounts Chem. Res., 3 (1970) 266;
(b) D. Gorenstein, J. Amer. Chem. Soc., 92 (1970) 644;
(c) C.G. Moreland, G.O. Doak and L.B. Littlefield, J. Amer. Chem. Soc., 95 (1973) 255;
(d) A. Klaebe, J.F. Brazier, F. Mathis and R. Wolf, Tetrahedron Lett., (1972) 4367.
90 R. Corriu and M. Henner, in press.
91 (a) S. Altscher, R. Baltzly and S.W. Blackmann, J. Amer. Chem. Soc., 74 (1952) 3649;
(b) H.C. Brown, Y. Okomoto and G. Ham, J. Amer. Chem. Soc., 79 (1957) 1906.
92 H. Sakurai, M. Kira and T. Sato, J. Organometal. Chem., 42 (1972) C24.
93 F.W. McLafferty and M.M. Bursey, J. Amer. Chem. Soc., 90 (1968) 5299.