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# Nucleophile-assisted racemisations of halosilanes — kinetic studies

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**Abstract**

Kinetic studies have been carried out on the nucleophile-induced racemisation of $PhMeCHSiMe_2X$, **2**, X = triflate, Br or Cl. Thirteen nucleophiles were studied. The results are interpreted in terms of two competing mechanisms for racemisation: (a) nucleophile attack on a silane–nucleophile complex formed by displacement of the halide by the nucleophile, and (b) halide–halosilane exchange, with inversion of configuration. Solvent effects were examined, and kinetic orders in the nucleophile and in one case for the halosilane were determined. The order in added nucleophile varied between one and two, with strong nucleophiles in polar media. Anomalously high orders in nucleophile were observed in non-polar media and are ascribed to aggregation of the nucleophile. A kinetic analysis of the competing mechanisms was attempted, and was consistent with the experimental findings. In this particular series of reactions involving compounds with good leaving groups and relatively powerful nucleophiles there was no evidence for intermediates involving extracoordinate silicon.

*Keywords:* Silicon; Racemisation; Mechanism

## 1. Introduction

Diverse studies of the mechanism of nucleophilic substitution at silicon [1–3] have led to lively debate and controversy over many years. Recent questions about the mechanism of substitution at silicon have been concerned with the nature and extent of the involvement of extracoordinate intermediates or transition states. Although the most common coordination number of silicon is four, there are numerous examples of stable silicon compounds in which the coordination number is five or six, and very recently an example of a species in which the siliconation is approaching seven coordinate in the solid state has been observed [4]. Much of the mechanistic debate has concentrated on the superficially simple substitution in which one group, X, on a four-coordinate silicon is replaced by another group, Nu, in a nucleophilic substitution (Eq. 1).

$$R_3SiX + Nu = R_3SiNu + X \quad (1)$$

Sommer [1] described the mechanism and stereochemistry of such reactions in terms of $S_N$–Si reactions that were variations of the mechanisms of substitutions at carbon. Simple bimolecular nucleophilic substitution at carbon invariably occurs with inversion of configuration. Modification was necessary for silicon because, although bimolecular substitution was usually found to be stereoprecise, it could take place with either inversion or retention of configuration at silicon, depending principally on the nature of the nucleophilic reagent and the nucleofuge. The mechanistic framework delineated by Sommer remains the foundation for contemporary interpretation, although it has been refined and significantly extended by Corriu et al. [3]. For inversion of configuration, a trigonal bipyramidal intermediate (or transition state) is usually assumed in which the nucleophile attacks at the tetrahedral face opposite the nucleofuge, so that the entering and leaving groups occupy the axial positions. For retention of configuration the following sequence is considered to be the best description of events at the molecular level. Initial nucleophilic attack is at a face of the tetrahedron that contains the nucleofuge, to give an intermediate with the entering ligand taking an axial position and the nucleofuge occupying an equatorial position. A pseudorotation then occurs in which the nucleofuge takes an axial position and the nucleophile occupies an equa-

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torial site. The final step is the loss of the nucleofuge from the axial site to give a substitution with retention of relative configuration. This mechanism is very closely related to those described by the Westheimer rules for substitution in organophosphorus compounds [5]. Other pathways involving edge attack at silicon tetrahedra rather than face attack have been considered, but were ruled out following an elegant theoretical analysis by Deiters and Holmes [6], and the mechanisms described above are now considered to be established.

More recently, the phenomenon of nucleophilic activation of nucleophilic substitution has received significant attention [2,3,7–19]. This interest derives from the initial observation [8] that hydrolysis of halosilanes can be accelerated by the presence of nucleophiles, and the predominant stereochemistry changes from inversion of configuration at silicon to retention. The rate law was stated to be:

$$\text{Rate of hydrolysis} = k[\text{halosilane}][H_2O][\text{Nu}] \quad (2)$$

Similarly, chiral halosilanes are racemised in the presence of nucleophiles according to the expression [8,9]:

$$\text{Rate of racemisation} = k[\text{halosilane}][\text{Nu}]^2 \quad (3)$$

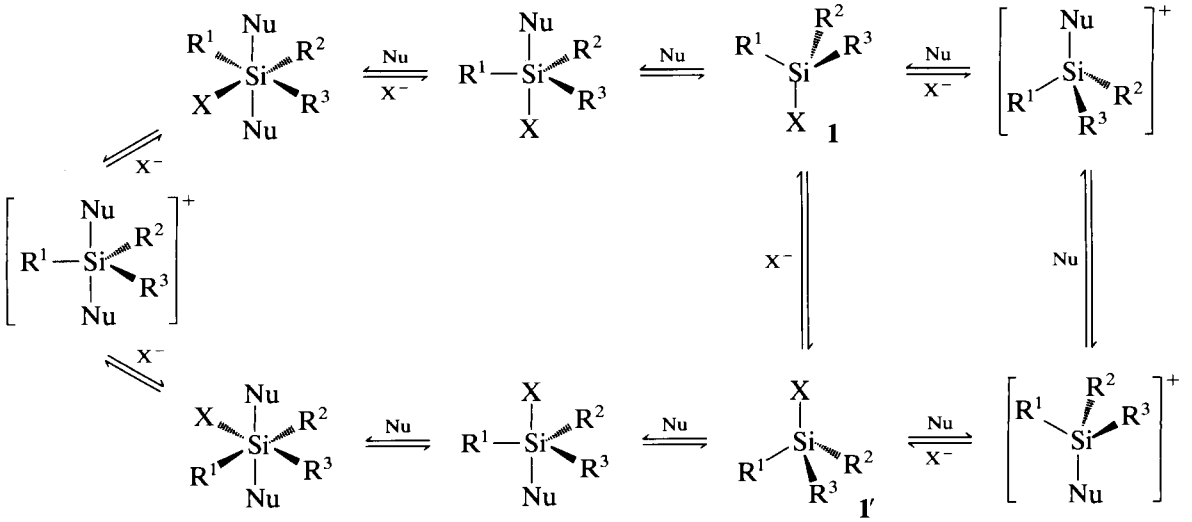
The interpretation of such apparently simple kinetic laws in mechanistic terms is by no means straightforward. Scheme 1 shows two kinetically equivalent mechanisms for racemisation, one of which involves substitution at an activated pentacoordinated silicon while the other involves consecutive substitutions at tetracoordinate silicon. The anti-clockwise route from **1** to **1′** shows an initial coordination of nucleophile to produce a pentacoordinate species that is activated to substitution. A second molecule of nucleophile then attacks the silicon to give the hexacoordinated silicon species that could either be an intermediate or a transition state (these are kinetically indistinguishable) which collapses to another pentacoordinate species that has a plane of symmetry. Chiral memory is therefore lost and racemisation is inevitable. The rate limiting step in this mechanism must be the attack of nucleophile on the activated pentacoordinated species if the rate expression is to be second order in nucleophile.

The clockwise route from **1** to **1′** in Scheme 1 is a double displacement [14] in which the nucleophile displaces $X^-$ with inversion of configuration, in the first step. The second, stereochemically determining step is attack by another molecule of nucleophile on the tetracoordinate silicon–nucleophile species, which again takes place with inversion of configuration. Racemisation is the eventual result, and a number of these inversions can occur before $X^-$ re-coordinates to the silicon to give **1** or **1′**.

Cartledge et al. [13] examined the nucleophile-induced *cis–trans* isomerisation of some halosilacyclobutanes and pentanes, which is a process directly analogous to the racemisation of acyclic halosilanes. Cartledge et al. also noted that halogen exchange took place at a rate comparable with racemisation. A substantial rate acceleration for racemisation was observed relative to the acyclic halosilanes, and the order in nucleophile (hexamethylphophoramide, HMPA) was found to be 1.23 for 1-chloro-1,2-dimethylsilacyclobutane and 1.6 for 1-chloro-1,2-dimethylsilacyclopentane. These data were interpreted in terms of competing first- and second-order reactions, in which $k_{obs}$ was assumed to be partitioned as expressed in Eq. 4.

$$k_{obs} = k_1[\text{Nu}] + k_2[\text{Nu}]^2 \quad (4)$$

The first-order process was postulated to proceed by a coordination of nucleophile, followed by a series of pseudorotations in which the configuration at silicon is inverted and interpreted in terms of the extension of



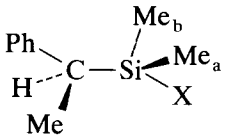
Scheme 1.

coordination mechanism shown in Scheme 1. There are some lingering problems with these interpretations. A mechanism change was postulated as the concentration of HMPA was varied, but the plot of log $k_{obs}$ against log [HMPA] was a straight line for all concentrations of HMPA for both compounds. We have previously commented on this discrepancy [2]. It appears that the data are not accurately defined by a second-order polynomial of the type shown in Eq. 4, but are more accurately represented by Eq. 5:

$$k_{obs} = k_n[Nu]^n \quad (5)$$

Since the work described above was reported, the enhanced reactivity of many penta- and even hexa-coordinated silicon compounds towards nucleophilic substitution has been observed many times [20] and is part of the currency of organosilicon chemistry. It is also apparent that nucleophilic activation of silicon does not necessarily always involve activated extra-coordinated silicon species and in some cases the double displacement mechanism is preferred [2]. The challenge now is to establish the nature and limits of nucleophilic activation.

We are attempting to throw light on the mechanism of nucleophilic substitution at silicon by studying the behaviour, in solution, of various silicon compounds in the presence of nucleophiles [21–24] to obtain information about the structure and equilibria of penta- and hexa-coordinated species. In addition we are examining the kinetics and thermodynamics of a series of substitutions in which extracoordinate silicon could feature [25]. In a previous paper [25] we showed how NMR spectroscopy could be used to examine the mechanism of nucleophile-induced racemisation by observing the effect of added nucleophile on the resonances of the diastereotopic methyl groups in **2**. The use of such compounds avoids the need for resolution of chiral organosilicon compounds and enables stereochemical investigations to be made on racemic compounds.




**2**

Under conditions in which inversion of configuration at the silicon centre is slow on the NMR time-scale, the diastereotopic methyl groups, $Me_a$ and $Me_b$, give separate, distinct signals in the $^{13}C$ NMR spectrum. When inversion of configuration at silicon is fast the signals collapse to a frequency-averaged singlet. At intermediate rates of inversion of configuration the lifetime of the silicon species can be determined by simulation of the spectrum using a commercially available program such as DNMR4 [26]. The pseudo-first-order rate constant $k_{obs}$ is given by:

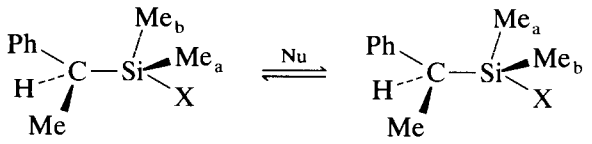
$$\text{Rate of reaction}/[R_3SiX] = d[R_3SiX]/dt.1/[R_3SiX] = k_{obs} \quad (6)$$

In our previous paper [25] we showed how this method could be successfully applied to racemisation at silicon in **2** (X = Cl, Br; Nu = HMPA). NMR studies also showed that a racemisation mechanism involving direct attack of halide on halosilane was operating in addition to the double displacement mechanism. The direct route is shown in Scheme 1 by the vertical arrows between **1** and **1′**. In the examples studied there was no evidence to suggest that the extension of coordination route was operating. For $R_3SiX$, where R = alkyl, the available evidence favours simple reaction mechanisms, with nucleophilic attack at four-coordinate silicon being the favoured route for substitution. For R = Oalkyl, halide, and other electron-withdrawing groups, substitution at extra-coordinated intermediates is more common.

The purpose of the present work was to extend the kinetic studies on compounds **2** to encompass a variety of nucleophiles and solvents so that more details of the simpler mechanisms could be revealed. An additional aim was to examine the kinetic schemes in more detail, partly to include the direct halide attack mechanism and partly to try to resolve the problem of fractional orders in nucleophile.

## 2. Results and discussion

The reaction shown in Eq. 7 was studied under a variety of conditions for X = Cl, Br, or $OSO_2CF_3$, and Nu = hexamethylphosphoramide, (HMPA); *N*-methylimidazole, (NMI); pyridine, (py); dimethylformamide, (DMF); 2,4-, 2,6- and 3,5-dimethylpyridine (2,4-, 2,6- and 3,5-DMP); *N*,*N*′-dimethylethyleneurea (DMEU); *N*,*N*′-dimethylpropyleneurea (DMPU); 1-methyl-2-pyrrolidone (NMP); 1-methyl-2-pyridone (NMPO); triethylamine ($Et_3N$); or 1,1,3,3-tetramethylurea (TMU).




**2** **2′** (7)

The method was the same for each reaction and consisted of measuring and simulating the $^{13}C$ NMR spectrum of a concentrated solution of **2** as the concentration of nucleophile, Nu, was incrementally increased. Rate constants for each concentration of nucleophile were obtained by visual comparison of the

simulated lineshapes [26] of the $^{13}C$ resonances of the SiMe groups with the observed line shapes. Kinetic orders were obtained by plotting ln $k_{obs}$ against ln [Nu] where the gradient of the straight line gives directly the order, $n$, in nucleophile. Application of Eq. 5 shows that the intercept is ln $k_n$, and so the rate constant for the reaction is also readily obtained.

The results were analysed in terms of the two competing racemisation mechanisms: double displacement, and attack of $X^-$ on $R_3SiX$, as previously established for this system [25].

### 2.1. Influence of the group X

It did not prove possible to compare quantitatively the effects of the groups X on racemisation as there was found to be a difference of several orders of magnitude in the racemisation rate between the groups X = Cl, Br and OTf. A semi-quantitative measure of the difference between these groups is given by the following comparison. For a 90% solution of **2** (X = OTf) in benzene-$d_6$ the diagnostic SiMe doublet in the $^{13}C$ NMR spectrum of **2** had collapsed to a singlet (indicating rapid racemisation by inversion of configuration at silicon) on the addition of 0.008 molar equivalents of pyridine. By contrast, for **2**, (X = Br) an equimolar amount of pyridine was needed for coalescence to occur, and for **2**, (X = Cl) the coalescence of the SiMe resonances was not complete even at a molar ratio of more than ten pyridine to one chlorosilane. We have shown that the equilibrium for the substitution shown in Eq. 1 lies progressively to the right for the series Cl, Br, OTf. It was established by NMR spectroscopy that for **2** (X = Br) under these conditions there was an equilibrium mixture of salt and starting bromide resulting from mixing equimolar quantities of bromosilane and pyridine. For **2** (X = Cl) there was no salt formation detectable by NMR spectroscopy in a mixture of ten parts pyridine to one part chlorosilane. It is reasonable to suggest that for the triflate, because the nucleophile is almost completely consumed to form the salt, the racemisation is predominantly through reaction of triflate anion on the silyl triflate. The implication of the immeasurably high rate constant for racemisation is that attack of triflate anion on the silyl triflate is very fast indeed. That is consistent with a low-energy pentacoordinate intermediate/transition state with the two triflate groups occupying axial positions. For the bromide and chloride, both the double displacement and halide/halosilane routes are possible.

### 2.2. Influence of nucleophile, Nu

Quantitative information on the influence on rates and kinetic orders for racemisation of **2** (X = Cl and Br) in the presence of thirteen nucleophiles was obtained. (It was not possible to determine such parameters for X = OTf because the rates were too high). The results are given in Table 1. Under the conditions of these experiments the reaction orders in nucleophile for the racemisation of the chloride, which are reproducible to at least ±10%, are very high, with values between 2.33 and 9. These are attributed to self association of the nucleophiles in the non-polar reaction media. If the kinetically active form of the nucleophile is an aggregate then the number of molecules in the aggregate will be reflected in the order of the reaction. In the examples reported here the order is assumed to be a complex function of three factors, viz the intrinsic

Table 1
Kinetic data for the racemisation of $PhCHMeSiMe_2X$ (X = Cl, Br) by nucleophiles, Nu [a]

| Nucleophile | Molar ratio silane : Nu at coalesce X = Cl [a] | Kinetic order in Nu X = Cl | $k_n/l^{-n}$ mol$^{-n}$ s$^{-1}$ X = Cl [b] | Molar ratio silane : Nu at coalesce X = Br [a] | Kinetic order in Nu X = Br | $k_n/l^{-n}$ mol$^{-n}$ s$^{-1}$ X = Br [a] |
|---|---|---|---|---|---|---|
| HMPA | 1 : 0.08 | 2.33 | 602 | 1 : < 0.01 [c] | – | |
| NMI | 1 : 0.13 | 3.37 | 308 | 1 : < 0.02 [c] | – | |
| NMPO | 1 : 0.34 | 3.74 | 13.5 | 1 : < 0.03 [c] | – | |
| DMPU | 1 : 0.37 | 4.74 | 8.2 | 1 : 0.03 | 1.1 | 812 |
| DMEU | 1 : 0.86 | 4.38 | 0.5 | 1 : 0.1 | 1.7 | 298 |
| DMF | 1 : 1 | 7.58 | 0.004 | 1 : 0.07 | 2.33 | 899 |
| NMP | 1 : 1.18 | 4.4 | 0.20 | 1 : 0.09 | 2.02 | 440 |
| TMU | 1 : 1.02 | 4.69 | 0.26 | 1 : 0.22 | 1.65 | 70.5 |
| 3,5 DMP | 1 : 6.23 | 3.76 | 0.03 | 1 : 0.76 | 2.07 | 9.5 |
| py | 1 : 10 | 9 | | 1 : 1.31 | 2.42 | 0.55 |
| 2,4 DMP | > 1 : 10 | – | – | 1 : 1.68 | 1.8 | 4.7 |
| 2,6 DMP | ≫ 1.20 | – | – | ≫ 1.20 | | – |
| $Et_3N$ | ≫ 1.20 | – | – | ≫ 1.20 | | – |

[a] Measurements carried out in $C_6D_6$ solution with silane concentrations 3 mol $l^{-1}$.
[b] $k$ is the observed rate constant determined as described in the text.

reaction order; an average value for aggregation, and the polarity of the medium. On dilution of the solutions with more solvent benzene the order in nucleophile increases, and we conclude that the nucleophile aggregation is increased in the less polar solution. Despite the difficulty of making quantitative comparisons, the relative amounts of nucleophile needed to effect coalescence of the diastereotopic SiMe signals in the $^{13}C$ NMR spectra was closely related to the Taft nucleophilicities, $\beta$, of the nucleophiles [27], with the most nucleophilic reagent being needed in the smallest amounts.

The results for racemisation of the bromide do not appear to be so affected by nucleophile aggregation, probably because the polarity of the medium is greater owing to the larger equilibrium constants for salt formation. For bromide racemisation with benzene as solvent there is relatively little change in rate constants or orders on dilution, supporting the suggestion that nucleophile aggregation is unimportant in these cases. Once again the relative amounts of nucleophile needed for coalescence follow the order of Taft nucleophilicity, with smaller quantities required than for the chloride. The orders in nucleophile are almost all fractional, with values between about one and two. It was observed here and elsewhere that the kinetic orders in the most powerful nucleophile for the racemisation of bromide **2** were closest to unity and those for the weakest nucleophiles were closer to two. This is examined in more detail later. As the orders of reaction differ, the rate constants have different units and direct comparison is therefore impossible. It is therefore not useful to attempt quantitative comparisons of these data with related data, such as the equilibrium constants for salt formation [21] (eq. 1, R=Me) or the rate constants for nucleophile-catalysed substitution of $Ph_2SiCl_2$ [15]. It is, however, noteworthy that plots of ln $k_n$ for nucleophile-induced racemisation of **2** (X=Br, Table 1) when plotted against ln K [21] or Frye's ln $k_1$ [15] gave fair straight lines. This lends support to the conclusions reached on other grounds [25] that the particular racemisations being studied here are proceeding by double displacement mechanisms and halide–halosilane exchange, because the formation of a four-coordinate salt is the crucial step in each of the other processes [15,21].

It was of considerable interest and importance to be able to compare the rate of racemisation of **2** (X=Br) promoted by bromide ion alone with the rates of the various nucleophile-induced racemisations. The rate of bromide ion attack on **2** (X=Br) was at least as fast as the fastest nucleophile-induced racemisation. The molar ratio of **2** (X=Br) to $Bu_4N^+Br^-$ was less than 1:0.01 at coalescence under the same conditions as those given in Table 1. The significance of this result is that for the strongest nucleophiles, where the equilibrium for salt formation lies almost entirely in favour of the salt, the limiting rate for racemisation is determined by the rate of bromide attack on bromosilane. Even though it is possible, and indeed probable, that attack of nucleophile on salt has a higher rate constant than the bromosilane–bromide reaction, the concentration of nucleophiles such as HMPA will be so small as to be kinetically inconsequential.

If the hypothesis is correct that the limiting rate of racemisation in the presence of the strongest nucleophiles is the bromide–bromosilane reaction, then in appropriate conditions the rates and orders should be identical for different nucleophiles. That was found to be the case within the limits of measurement for the racemisation of **2** (X=Br; 1 M in $CD_2Cl_2$), for which the kinetic order was $1.5 \pm 0.15$ and ln $k_n$ was $9.6 \pm 0.3$ for each of the nucleophiles NMI, HMPA, NMPO and DMPU.

### 2.3. Effect of medium and concentration of silane

The racemisations are unusually susceptible to changes in solvent polarity, and even in very highly concentrated solutions the orders and rate constants varied greatly with solvent. Some examples for racemisations of the chloride **2** are given in Table 2. It is

Table 2
The effect of solvent [a] on the racemisation of $PhCHMeSiMe_2X$ (X = Cl) by nucleophiles, Nu

| Nucleophile | Solvent | Solvent dielectric constant | Ratio silane : Nu at coalescence | Order of reaction in Nu | $k_n$/ $l^{-n}$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|
| HMPA | $C_6D_6$ | 2.3 | 1:0.075 | 3.0 | 640 |
| HMPA | $C_6D_5CD_3$ | 2.4 | 1:0.08 | 2.3 | 700 |
| HMPA | $CD_2Cl_2$ | 8.9 | 1:0.05 | 1.7 | 680 |
| HMPA | $CD_3NO_2$ | 35.9 | 1:0.012 | 1.25 | 1930 |
| NMI | $C_6D_6$ | 2.3 | 1:0.13 | 3.3 | 318 |
| NMI | $C_6D_5CD_3$ | 2.4 | 1:0.13 | 2.6 | 219 |
| NMI | $CD_2Cl_2$ | 8.9 | 1:0.08 | 1.9 | 399 |
| NMI | $CD_3NO_2$ | 35.9 | 1:0.03 | 1.1 | 426 |

[a] In these experiments the "solvent" was actually little more than an NMR lock because it was present only to the extent of 9% by volume in each case.

Table 3
The effect of concentration on the racemisation of **2** (X = Cl) by HMPA in $CD_2Cl_2$

| Concentration of **2**/ mole $l^{-1}$ | Ratio of **2** to HMPA at coalescence | Kinetic order in HMPA, $n$ | Rate constant/ $l^{-n}$ $mol^{-n}$ $s^{-1}$ |
|---|---|---|---|
| 4.6 | 1:0.052 | 1.75 | 670 |
| 3.0 | 1:0.05 | 1.5 | 800 |
| 1.0 | 1:0.07 | 1.24 | 946 |
| 0.5 | 1:0.15 | 1.2 | 940 |
| 0.1 | 1:0.7 | 1.3 | 1100 |

notable that the amount of nucleophile necessary for coalescence decreased as the solvent polarity increased, and the order in nucleophile also decreased as the solvent polarity increased. Once again this is very typical of a reaction in which charged intermediates are involved. The amount of salt present in the mixture increases as the polarity of the medium increases, driving the equilibrium of Eq. 1 to the right.

In some time-consuming, but useful, experiments with dilute solutions in $CD_2Cl_2$, the reaction order in chlorosilane for racemisation of **2** by HMPA was shown to be unity. In concentrated solutions in this solvent the reaction order in HMPA was 1.75, and this value fell incrementally to a limiting value of about 1.25 in more dilute solution (see Table 3). The rate constant for racemisation in dilute solution was constant (independent of the concentration of silane). Application of Eq. 6 to a reaction with a rate equation of the form of Eq. 8 gives Eq. 9, which shows that the observation of a constant $k_{obs}$ is only consistent with a reaction in which the kinetic order in silane concentration is one.

$$\text{Rate of reaction} = [\text{silane}][\text{nucleophile}]^n \quad (8)$$

$$k_{obs} = [\text{nucleophile}]^n \quad (9)$$

### 2.4. Effect of hydrolysis

In general, rigorous steps were taken to exclude moisture from the reaction mixtures, but when dealing with halosilanes, hydrolysis is an ever-present hazard. It was shown that 2,6-DMP and 2,6-di-*t*-butylpyridine did not catalyse racemisation of **2** (X=Cl, Br) when precautions had been taken to exclude moisture. When water was deliberately added to **2** (X=Cl, Br) NMR spectroscopy showed that in a closed system the equilibrium shown in Eq. 10 lies to the left in benzene solution.

$$R_3SiX + H_2O = R_3SiOH + HX \quad (10)$$

Racemisation of **2** took place on addition of traces of water, but rather slowly (quantitative measurements were not made), but the rate increased dramatically on addition of the non-coordinating but highly basic 2,4-DMP. That is consistent with the reaction of the base with HX to liberate $X^-$ and drive the equilibrium, (10) to the right. In highly polar solvents the equilibrium (10) lies further to the right, particularly with solvents such as acetonitrile that have some proton-acceptor properties. This leads us to ask the question whether some reported solvent-induced racemisations may have been halide-induced. (It is difficult to imagine solvents such as sulpholane coordinating to silicon to form either penta or tetra-coordinate adducts.) At present, there is no experimental evidence in favour of this possibility, but the fact that racemisation and halogen exchange took place at comparable rates in some of the reactions of Cartledge et al. [13] is suggestive.

### 2.5. Kinetic analysis of halosilane racemisation by nucleophiles

The kinetics of halogen exchange and nucleophile-salt reactions are different, and will be treated separately. The halide–halide racemisation kinetics are examined first.

A complication in the kinetic analysis is that particularly in non-polar solvents, we [22] and others have shown by electrical conductivity measurements that ion pairing of the silane-nucleophile salt with the halide counter ion can be significant. It is probable that the tight ion paired halide ion is less kinetically active than a solvent-separated or free halide ion.

The relevant kinetic scheme is:

$$R_3SiX + Nu \underset{k_{-1}}{\overset{k_1}{=}} R_3SiNu^+X^- \underset{k_{-2}}{\overset{k_2}{=}} R_3SiNu^+ + X^- \quad (11)$$

or for fully separated ions,

$$R_3SiX + Nu \underset{k^1_{-1}}{\overset{k^1_1}{=}} R_3SiNu^+ + X^- \quad (12)$$

and in both cases

$$R_3SiX^* + X^- \overset{k_3}{=} R_3SiX + X^{*-} \quad (13)$$

As the reactions are equilibria, with the concentrations remaining unchanged once equilibrium is established, we may define the following,

$$K_{eq} = k_1/k_{-1} = [R_3SiNu^+X^-]/[R_3SiX][Nu] \quad (14)$$

$$K^1_{eq} = k^1_1/k^1_{-1} = [R_3SiNu^+][X^-]/[R_3SiX][Nu] \quad (15)$$

and

$$K_d = k_2/k_{-2} = [R_3SiNu^+][X^-]/[R_3SiNu^+][X^-] \quad (16)$$

The rate of racemisation is,

$$\text{Rate} = 2k_3[X^-][R_3SiX] \quad (17)$$

and as $[X^-]$ necessarily = $[R_3SiNu^+]$, rearranging Eqs. (14) and (16) gives,

$$[X^-] = K_{eq}^{0.5} K_d^{0.5} [R_3SiX]^{0.5} [Nu]^{0.5} \quad (18)$$

or in the case of fully separated ions,

$$[X^-] = K^1{}_{eq}^{0.5} [R_3SiX]^{0.5} [Nu]^{0.5} \quad (19)$$

The rate of halide-induced racemisation with ion-paired salts is therefore

$$\text{Rate} = 2k_3 K_{eq}^{0.5} K_d^{0.5} [R_3SiX]^{1.5} [Nu]^{0.5} \quad (20)$$

or for separated ions

$$\text{Rate} = 2k_3 K^1{}_{eq}^{0.5} [R_3SiX]^{1.5} [Nu]^{0.5} \quad (21)$$

As the concentration of added nucleophile is generally very low, it is very difficult to measure in the reaction mixture. It is, however, possible to determine the kinetic order in halosilane.

In the limiting case in which the equilibria for Eqs. 11 or 12 lie very far to the right, the concentration of halide ion is almost identical to the concentration of added nucleophile, $[Nu_0]$, so that

$$\text{Rate} = k_3 [R_3SiX][Nu_0] \quad (22)$$

The above analysis suggests that in the presence of very powerful silicon nucleophiles the rate equation for racemisation of halosilanes approximates to that shown in Eq. 22. For weaker nucleophiles the halide–halosilane component of the racemisation should show more complex kinetics, according to Eqs. 20 and 21.

For the nucleophile–salt component of the racemisation, the steps represented by Eqs. 11 and 12 are once again the preliminary steps, but in these cases the rate of racemisation is given by:

$$\text{Rate} = 2k_4 [R_3SiNu^+][Nu] \quad (23)$$

where $k_4$ is the rate constant for the invertive, chemically degenerate, reaction:

$$R_3SiNu^+ + Nu^* = R_3SiNu^{*+} + Nu \quad (24)$$

There are several ways of analysing this reaction, but the two most straightforward analyses yield (Eqs. 25, 26):

$$\text{Rate} = 2k_4 K_{eq} [R_3SiX][Nu_0]^2 \quad (25)$$

when the salt is produced to a small extent such that [Nu] is approximately the same as $[Nu_0]$ and the salt is extensively ion paired, and it is the ion paired form that undergoes exchange with Nu. In the second case:

$$\text{Rate} = 2k_4 K_{eq}^{0.5} K_d^{0.5} [R_3SiX][^{0.5}Nu_0]^{1.5} \quad (26)$$

when the salt is again produced to a small extent, with [Nu] approximately the same as $[Nu_0]$, but in this case the separated ion $R_3SiNu^+$ is assumed to be the only catalytically active form. From Eqs. 21 and 26, when salt formation is not the predominant reaction, the relative rates of racemisation via halide or nucleophile exchange is given by:

$$\frac{\text{Rate of nucleophile exchange}}{\text{Rate of halide exchange}} = \frac{k_{Nu}[R_3SiX]^{0.5}[Nu]^{1.5}}{k_{hal}[RSiX]^{1.5}[Nu]^{0.5}} \quad (27)$$

$$\frac{\text{Rate of nucleophile exchange}}{\text{Rate of halide exchange}} = \frac{k_{Nu}[Nu]}{k_{hal}[RSiX]} \quad (28)$$

For a given nucleophile or halogen, which mechanism predominates depends upon the relative rates of Eqs. 13 and 24. For X = triflate we would expect the rate of Eq. 13 to be faster than that of Eq. 24, so that exchange via attack of $X^-$ would predominate. For X=Cl or Br we would expect the rate of Eq. 24 to be faster than that of Eq. 13 for all nucleophiles, so that exchange via attack of Nu would predominate.

## 3. Conclusions

The kinetic analysis is not complete, but does illustrate the complexity of the apparently simple racemisation reaction, even when only four-coordinate intermediates are involved. Although it is not possible to make firm conclusions about the relative importance of halide–halosilane or nucleophile–salt mechanisms from the kinetic studies of our reactions, it can be concluded that the order in added nucleophile approaches two for nucleophile–salt mechanisms and unity for halide–halosilane mechanisms. We did observe that the order in nucleophile was closer to two for weak nucleophiles and chlorosilanes, where the predominant mechanism should be the more rapid nucleophile–salt mechanism because salt formation and production of halide ion would be small in these examples. By contrast, the order in added nucleophile was close to unity for strong nucleophiles, and particularly in polar solvents where the added nucleophile is more likely to be consumed fully in the production of halide ion.

Thermodynamic activation parameters for some of these reactions will be reported in a forthcoming publication.

## 4. Experimental details

The synthesis of starting materials and salts has been reported previously [25]. The methods used were also as previously described. Solvents and nucleophiles were rigorously dried by standard methods and stored under dinitrogen. NMR solutions were made up in a dry box in 10 mm stoppered tubes. Kinetic analyses were carried out by use of DNMR4.

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