# Interaction of N-Trimethylsilylimidazole with Electrophilic Trimethylsilyl Compounds. Part 2.[1] Some Exchange Reactions Involving Bistrimethylsilyl-imidazolium Salts

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The dynamic and equilibrium properties of bistrimethylsilylimidazolium salts (1) have been investigated by n.m.r. spectroscopy. The salts (1) are highly susceptible to nucleophilic attack. The exchange reactions of (1) with electrophilic silanes (TMSX) have also been studied, in one example by the dynamic n.m.r. method of total line-shape analysis. The rates of the exchange reaction decrease (X = Cl > Br > CF_3SO_3 > I,ClO_4). The equilibrium constants for formation of (1) were found to decrease in the order Me_3SiClO_4 > $Me_3SiOSO_2CF_3$ > Me_3SiI > Me_3SiBr > Me_3SiCl. These results are shown to be consistent with silylation mechanisms involving silylated nucleophiles as intermediates.

In the preceding paper[1] we established that N-trimethylsilylimidazole (NTMSIm) and electrophilic silanes (TMSX; X = $OClO_3$, OSO_2CF_3, Br, or I) form bis-silylimidazolium salts (1) as the major species in solution. Silylated amines such as (1)
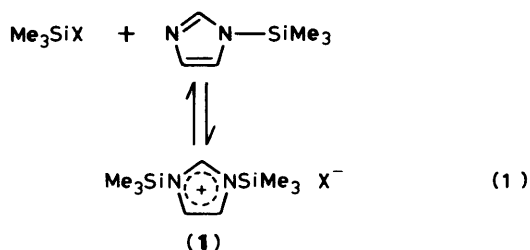
have frequently been postulated as the active intermediates in silylations,[1] as the neutral amine provides an excellent leaving group in nucleophilic substitutions at silicon. The role of these salts in the mechanism of nucleophilic substitution at silicon is beginning to be evaluated, especially with the advent of the highly electrophilic silanes, such as trimethylsilyl trifluoro-methanesulphonate[2] (TMST), trimethylsilyl iodide[3] (TMSI) and, to a lesser extent trimethylsilyl perchlorate[4] (TMSP). Although the mechanism of nucleophilic substitution at silicon has been thoroughly studied and reviewed,[5,6] scant attention has been paid to the highly electrophilic reagents. The only relevant study of which we are aware is by Hergott and Simchen,[7] and concerns the relative rates of silyl enol ether formation by Me_3SiX-Et_3N mixtures. The rate of reaction decreased, with varying X groups, in the order I > OSO_2CF_3 > Br > Cl. A mechanism for this reaction, in agreement with our previous studies,[8] is given in the Scheme.

Before this or alternative mechanisms can be validated much more information is needed on the interaction of silanes with nucleophiles, and a complete kinetic study is called for. If the mechanism shown in the Scheme is appropriate to silyl enol ether formation and, with minor modifications, to other amine-assisted silylations, the quaternised silylamine salt should be extremely susceptible to nucleophilic attack. Indeed, if the amine is intimately involved in the rate-determining step then species such as (1) should be more susceptible to nucleophilic attack than Me_3SiX.

The aim of this study was to probe the dynamic behaviour and equilibrium properties of the salts (1) by n.m.r. spectroscopy. The particular problems addressed were: the dynamics of nucleophilic attack on (1); the interaction in solution of (1) and
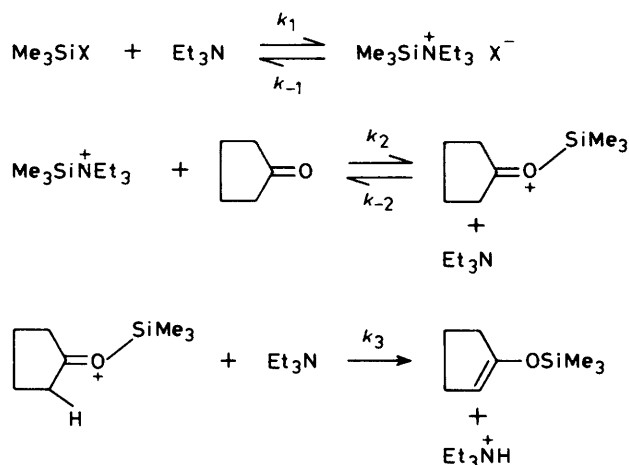
Scheme. A mechanism for silyl enol ether formation from Me_3SiX–Et_3N-ketone mixtures

Me_3SiX; and the relative equilibrium constants for formation of (1) with different X groups. The conditions chosen were intended to relate as closely as possible to common silylation conditions, with solvents such as chloroform, dichloromethane, and acetonitrile.

Results and Discussion

The degenerate trimethylsilyl exchange reaction [equation (2)] was used as a model for nucleophilic substitution at silicon in (1). This is a convenient system for study as NTMS is a good nucleophile towards silicon, and has n.m.r. chemical shifts for all nuclei that differ significantly from those of (1). It was found
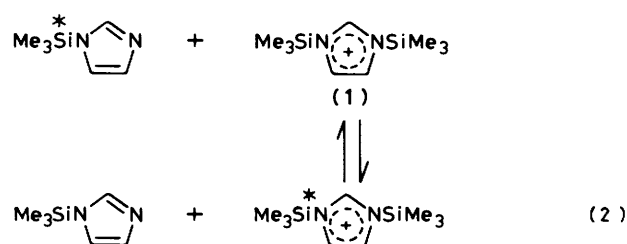
Table 1. N.m.r. spectra of equimolar mixtures of NTMSIm and (1) in CD_2Cl_2[a]

X	δ(^1H)			δ(^{13}C)			δ(^{29}Si)
	H-2	H-4, -5	$SiCH_3$	C-2	C-4, -5	$SiCH_3$	
Br	8.70	7.25	0.60	142.0	125.0	−0.20	20.0
I	8.40	7.25	0.59	141.4	125.0	0.22	20.2
CF_3SO_3	8.14	7.20	0.55	141.0	125.0	−0.62	20.2
ClO_4	8.00	7.20	0.57	141.5	125.1	−0.60	20.1
NTMSIm	7.60	7.07	0.45	140.2	125.5	−0.46	13.5

[a] Chemical shifts are averaged values for those of NTMSIm and (1); see ref. 1 for chemical shifts of (1).

that when NTMSIm and (1; X = OSO_2CF_3, $OClO_3$, Br, or I) were mixed in solution, the n.m.r. spectra of all nuclei (^{29}Si, ^{13}C, and ^1H) consisted of sharp, averaged signals, intermediate between those of NTMSIm and (1) (Table 1). The positions of the resonances depended on the molar proportions of the reagents but the linewidths were always insignificantly different from the natural linewidth. The usual dynamic n.m.r. method[8,9] can therefore be applied to the system shown in equation (2); The sharp, averaged signals demonstrate that the exchange is rapid on the n.m.r. time-scale for all counterions. The minimum first-order rate constant k (*i.e.* the inverse of the mean lifetime) for the exchange of each TMS group can be estimated using the relationship shown[8,9] in equation (3), where $v_A - v_B$ is the separation (Hz) of the two resonances, in the absence of exchange.

$$k = 2\pi(v_A - v_B)/\sqrt{2} \qquad (3)$$

The ^{29}Si n.m.r. chemical shift difference between (1) (δ 26.6) and NTMSIm (δ 13.6) is 231 Hz at 17.76 MHz which, when substituted in equation (3), gives a minimum rate constant for NTMSIm of 1.02×10^3 s^{-1} in the presence of (1; X = Br, I, CF_3SO_3, or ClO_4) at 30 °C. It was not possible to distinguish any difference in the effects of the various counterions, as all exchanges were very fast on the n.m.r. time-scale. A similar result was obtained for the exchange of NTMSIm–Me_3SiCl in the presence of (1; X = Cl) at low temperatures.[1]

Taken alone, these results are not *a priori* evidence for fast nucleophilic attack by NTMSIm on (1). An alternative mechanism for trimethylsilyl group exchange must be ruled out first. If dissociation of (1) [right to left in equation (1)] were the rate-determining step, and this was followed by a rapid reassociation, then exchange of trimethylsilyl groups could occur, without nucleophilic attack at (1). Another alternative mechanism [fast dissociation of (1) followed by slow recombination] can be excluded for (1; X = Br, I, CF_3SO_3, or ClO_4), as the equilibrium in equation (1) lies well to the right hand side.[1]

If the dissociation–recombination mechanism were operating for the system in equation (2), it should apply *a fortiori* to the related system shown in equation (4), where no nucleophile is
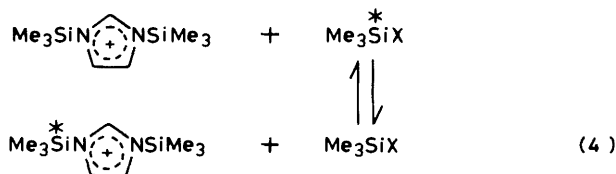
present. The exchange shown in equations (2) and (4) would therefore take place through a common rate-determining step; the dissociation of (1). It therefore follows that the reaction

rates should be essentially identical when the concentration of NTMSIm in reaction (2) is equal to the concentration of Me_3SiX in reaction (4) [with equal concentrations of (1) in each case]. We have therefore examined the rates of the exchanges shown in equation (4) (Table 2) and find that they are strongly influenced by the concentration as discussed in the following paragraphs. As the degenerate exchanges of reactions (2) and (4) take place at significantly different rates, under identical conditions, a common rate-determining step can be discounted. The leaving group in reaction (2) is a neutral molecule, NTMSIm, and the exchanging group, also NTMSIm, is a good nucleophile towards silicon. Taken together the evidence strongly supports the suggestion that the salts (1) are highly susceptible to nucleophilic attack. The related protonated aminosilanes have been shown to be very reactive and are the active silylation species in the alcoholysis of aminosilanes.[10]

The dynamics of the exchange reaction shown in equation (4), for the Me_3SiX–(1) system, were examined by n.m.r. spectroscopy, using the trimethylsilyl resonances in particular. These are singlets, of natural linewidth, for isolated samples of (1) and Me_3SiX in the ^1H, ^{13}C, and ^{29}Si n.m.r. spectra. By examination of the n.m.r. spectra, and application of equation (3), maximum or minimum first-order rate constants could be estimated for different groups X.

The exchange rates for reaction (4) are strongly dependent on X, and decrease in the order X = Br > CF_3SO_3 > I,ClO_4. The rates of exchange of trimethylsilyl groups in the reaction are also quite solvent dependent, with the rate increasing as the solvent polarity decreases. Thus exchange is significantly faster in $CDCl_3$ than in CD_3CN.

For X = Br, I, or ClO_4 it was not possible to carry out accurate rate studies by total lineshape analysis as the available temperature range of CD_2Cl_2 and CD_3CN is small and inappropriate to the rates.[9] For the system (1; X = CF_3SO_3) + TMST in $CDCl_3$ the rate was amenable to study and a total lineshape analysis was carried out. The results are discussed later (Table 3).

The only system for reaction (4) for which fast exchange rates were evident for all nuclei was (1; X = Br) + TMSBr (Table 2), in both acetonitrile and dichloromethane. The best estimate for the maximum half-life for exchange was derived from the ^{13}C n.m.r. spectrum, where the TMS groups gave rise to a sharp singlet intermediate in position between those for TMSBr and (1; X = Br). The peak separation, in the absence of exchange, is 94.5 Hz (4.2 p.p.m.) in CD_2Cl_2, and application of equation (3) gives a rate constant of 4.2×10^2 s^{-1} at coalescence. Therefore the half-life of (1; X = Br) must be significantly shorter than 1.65×10^{-3} s at ambient temperature. For this system the exchange was too fast for a solvent effect to be distinguished.

The reaction between (1; X = CF_3SO_3) and trimethylsilyl trifluoromethanesulphonate gave rather different spectra (Table 2). In CD_2Cl_2 there are two separate trimethylsilyl resonances, in the ^1H 90 MHz and ^{29}Si n.m.r. spectra, corresponding to (1) and TMST, but in each case they are broadened. In the 90 MHz ^1H n.m.r. spectrum the trimethylsilyl resonances have a half-height width of *ca.* 8 Hz, at 30 °C, to be compared with the natural line-width of 0.75 Hz. In the 60 MHz ^1H n.m.r. spectrum the trimethylsilyl resonances have coalesced to a broad singlet (*ca.* 11 Hz). The two ^{29}Si resonances are broad (*ca.* 15 Hz) in $CDCl_3$, less broad in CD_2Cl_2 (*ca.* 8 Hz), and almost of natural line-width in CD_3CN (*ca.* 2 Hz). The proton n.m.r. spectra of (1) and TMST in CD_3CN show separate, sharp, natural width lines. Thus the solvent polarity affects the reaction rate as already described. A total line-shape analysis,[11] using DNMR-4, gave the parameters for the (1)–TMST exchange in $CDCl_3$ shown in Table 3. The first-order rate constant for the dissociation of (1; X = CF_3SO_3) was 13.25 s^{-1} at 300 K, corresponding to a half-life of 5.2×10^{-2} s; the activation energy was

Table 2. N.m.r. spectra of 1:1 molar mixtures of Me₃SiX and (1)

Solvent	X	δ(¹H)			δ(¹³C)			δ(²⁹Si)
		H-2	H-4, -5	SiCH₃	C-2	C-4, -5	SiCH₃	
CD₃CN	Br	8.96	7.60	0.61	143.3	125.1	—0.46	27.5
CD₃CN	I	8.80	7.62	0.79,[a] 0.65				26.4, 12.1
CD₃CN	CF₃SO₃	8.47	7.58	0.61, 0.49	143.1	125.5	0.30, −1.0	26.5, 46.1
CD₂Cl₂	Br	9.79	7.48	0.72	144.1	124.5	3.1	27.5
CD₂Cl₂	I	9.48	7.53	0.79, 0.75	144.0	124.9	5.6, −0.8	26.9, 10.7
CD₂Cl₂	CF₃SO₃	8.66	7.44	0.63, 0.52[b]	142.7	120	0.1, −0.75	44.3,[b] 26.6
CD₂Cl₂	ClO₄	8.55	7.30	0.58, 0.40	143.7	124.3	1.0, −0.97	45.9, 26.6
CDCl₃	CF₃SO₃	8.80	7.46	0.65[c]				43.6, 26.7[d]
CDCl₃	Br	9.95	7.78	0.74	142.6	123.7	0.8	26.8

[a] All lines approximately natural linewidth unless stated otherwise. [b] Each line ca. 8 Hz half-height width. [c] Single line ca. 6 Hz half-height width. [d] Each line ca. 15 Hz half-height width.

Table 3. Variable-temperature ¹H n.m.r. study on a 2:1 mixture of TMST and (1; X = CF₃SO₃) in CDCl₃[a]

T/K	$10^3 T^{-1}$/K⁻¹	Rate (s⁻¹)	ln (rate)
296	3.378	11.7	2.460
298—299	3.35	12.85	2.553
300	3.33	13.25	2.584
301	3.322	13.8	2.625
302—303	3.306	13.8	2.625
304	3.29	16.4	2.797
306	3.268	17.0	2.833
307	3.257	19.5	2.970
308	3.247	23.0	3.136
312	3.205	38.0	3.638
314	3.185	42.0	3.738

[a] Coalescence temperature 308 K; A = 2.4 × 10⁸; E_a = 40 kJ mol⁻¹.

Table 4. N.m.r. spectra of equimolar mixtures of Me₃SiX and Me₃SiY

Solvent	X	Y	δ(¹H)	δ(¹³C)	δ(²⁹Si)
CDCl₃	I	Br	0.8,[a] 0.6	5.6, 4.1	9.6, 27.8
CDCl₃	I	CF₃SO₃	0.8, 0.50	5.6, 0.34	9.7, 43.3
CD₂Cl₂	ClO₄	CF₃SO₃	0.4	1.0	44.1
CD₂Cl₂	ClO₄	Br	0.35, 0.52	0.69, 4.8	45.0, 27.2
CD₂Cl₂	ClO₄	I	0.40, 0.75	0.63, 5.6	45.3, 9.8
CD₃CN	CF₃SO₃	I	0.63	2.75	ca. 23[b]

[a] All lines of natural linewidth unless otherwise stated. [b] ca. 100 Hz half-height width.

40 ± 2 kJ mol⁻¹, and the Arrhenius A factor was 2.4 × 10⁸. The lineshape analysis was carried out over a 20 °C range, and although this is relatively small, the readings were taken at, or around, the coalescence temperature, which gives the most accurate information. The thermodynamic data are consistent with a process largely controlled by the entropy change. There are too many factors involved, such as solvent reorganisation, transition state structure, desolvation of ions, etc. for the data to be analysed in detail. There is good evidence, however, that the exchange process involves dissociation of (1) followed by reaction of NTMSIm with TMST. When the solution of (1; X = CF₃SO₃) and TMST was diluted four-fold with CDCl₃ the reaction rate increased slightly. This observation is not compatible with direct attack of TMST on (1), for which a significant rate lowering would be observed on dilution. We interpret this observation in the following way. On dilution the medium becomes less polar, and the equilibrium of equation (1) moves slightly to the left. There is therefore more NTMSIm in solution and the exchange shown in equation (4) increases in rate. This dissociation–reassociation mechanism is also consistent with the solvent effect, where the rate is faster in non-polar solvents.

The other exchanges studied are also compatible with a dissociation–reassociation mechanism rather than a four-centre or other bimolecular attack of TMSX on (1). The reactions between TMSI and (1; X = I), and between trimethylsilyl perchlorate (TMSP) and (1; X = ClO₄), are very slow on the n.m.r. time-scale, for all nuclei in CD₂Cl₂ solutions. Sharp, separate resonances of natural linewidth were observed for (1) and TMSX in each case. Similarly the exchange of (1; X = I) and TMSI is immeasurably slow in CD₃CN solution. The exchange of TMSP with (1; X = ClO₄) in CD₃CN is compli-

cated by reaction of TMSP with the solvent.[1] The proton n.m.r. spectra, together with the application of equation (3), show that the half lives of (1; X = I or ClO₄) are appreciably longer than 58 × 10⁻³ s.

At 180 K a 2:1 mixture of TMSCl and NTMSIm gave a ²⁹Si resonance at δ 29.5, whereas at 300 K the resonance is at δ 25. This is consistent with formation of (1; X = Cl) at low temperature, rapidly exchanging ($t_½$ ≪ 2.8 × 10⁻³ s) with TMSCl, even at 180 K.

The rates of silyl-group exchange in reaction (4) therefore decrease in the order (Cl) > Br > CF₃SO₃ > I,ClO₄, and decrease with solvent in the order CDCl₃ > CD₂Cl₂ > CD₃CN.
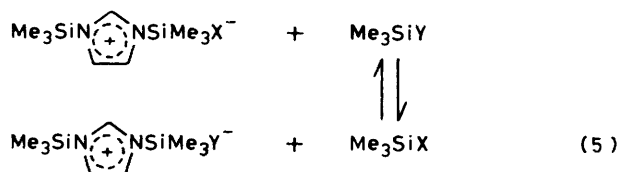
These results are compatible with the dissociation of (1) being rate-determining in reaction (4). The rate is highly dependent on counterion X⁻, being slower for good leaving groups from silicon. We are unable to offer a complete rationalisation of the order of reactivity in reaction (4). There is a reasonable inverse correlation of rate with the relative equilibrium constants for reaction (1), which increase in the order Cl < Br < I < CF₃SO₃ < ClO₄ (see later). This supports the proposition that dissociation of (1) is important. However, the equilibrium constant for reaction (1) is slightly greater for X = CF₃SO₃ than for X = I, whereas exchange of TMST with (1; X = CF₃SO₃) is faster than the related exchange of TMSI. The relative rates of the iodide and trifluoromethanesulphonate exchange reactions can be rationalised if the latter anion is both a better leaving group and a better silicon nucleophile than iodide. The rates of reaction (4) therefore reflect a complex combination of the leaving group ability of X, the solvation energies of X⁻, and the silicon nucleophilicity of X⁻.

Finally, we investigated the relative ability of TMSX to form the salts (1). This information is of some importance in the design of better silylation reagents if such salts are the active species in silylations. The relative order of equilibrium constants for reaction (1) was obtained through the system shown in equation (5).

Table 5. N.m.r. spectra of 1:1:1 molar mixtures of Me₃SiX, Me₃SiY, and NTMSIm[a]

Solvent	X	Y	δ(¹H)			δ(¹³C)			δ(²⁹Si)
			H-2	H-4, -5	SiCH₃	C-2	C-4, -5	SiCH₃	
CD₃CN	Br	I	8.75	7.63	0.63	143.1	125.2	2.0	27.2
CD₃CN	Br	CF₃SO₃	8.55	7.54	0.60	142.7	125.2	0.4	27.2
CD₃CN	Br	ClO₄	8.38	7.50	0.59	143.9	125.1	0.92	26.7
CD₃CN	I	CF₃SO₃	8.57	7.59	0.71, 0.62	143.5	125.6	4.2, −0.8	26.5, 21.6
CD₃CN	I	ClO₄	8.34	7.51	0.78, 0.59	143.3	125.7	5.2, −0.98	26.4, 12.9
CD₃CN	Cl[b]	I	8.65	7.48	0.43	142.0	124.2	2.3	30.9
CD₃CN	CF₃SO₃	ClO₄	8.35	7.46	0.59, 0.49				
CD₂Cl₂	CF₃SO₃	ClO₄	8.5	7.4	0.58, 0.44	142.6	125.4	0.3, −0.8	44.4, 26.6
CD₂Cl₂	ClO₄	I	8.71	7.40	0.76, 0.63	143.6	125.8	5.8, −0.84	26.7, 10.8
CD₂Cl₂	ClO₄	Br	8.56	7.31	0.52	142.8	125.5	4.07, −0.97	27.3

[a] The chemical shifts of (1) and TMSX are given in ref. 1. For assistance in interpreting these data the following points should be noted: where only one TMS resonance is observed (*i.e.* with X = Br or Cl) these resonances are approximately at the average positions of TMSX and (1); where two TMS peaks are observed these correspond to (1) and TMSX or TMSY, except in the case of I or CF₃SO₃ where one resonance corresponds to (1) and the other to exchanging TMST and TMSI (see text): in cases where assignment was uncertain TMSX and TMSY were added to separate solutions of the mixture, and the enhancement of one peak and/or the appearance of a new one was used to confirm the interpretation given in the text. [b] In this case TMSCl:TMSI was 2:1.

$$Me_3SiN\overset{\frown}{\underset{\smile}{N}}SiMe_3X^- \quad + \quad Me_3SiY$$

$$\updownarrow$$

$$Me_3SiN\overset{\frown}{\underset{\smile}{N}}SiMe_3Y^- \quad + \quad Me_3SiX \qquad (5)$$

Before presenting and interpreting the results for this system it is necessary to describe some experiments on the interaction of Me₃SiX and Me₃SiY in solution. These experiments were necessary to determine whether fast equilibration of silyl groups, as shown in equation (6), was occurring. Table 4 shows

$$Me_3SiY + Me_3\overset{*}{Si}X \Longrightarrow Me_3SiX + Me_3\overset{*}{Si}Y \qquad (6)$$
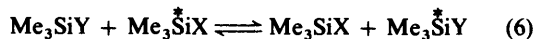
that exchange of silyl groups, as shown by separate ²⁹Si, ¹³C, and ¹H resonances, was slow for all mixtures of silanes except TMSI–TMST and TMSP–TMST in CD₂Cl₂ or CD₃CN solution. For the TMSI–TMST mixture, exchange was moderately fast in CD₃CN; the averaged ¹³C and ¹H resonances were slightly broadened singlets, and the ²⁹Si resonance was a very broad (*ca.* 100 Hz half-height width) singlet. Exchange in this example was slower in CD₂Cl₂ but became fast on addition of a trace of NTMSIm. The exchange between TMSP and TMST was fast even in CD₂Cl₂. Little is known about such ready silyl exchanges at ambient temperature,[12,13] but we have found them to be more common than previously reported.[14]

Once equilibrium has been established in the system shown in equation (5) the relative order of equilibrium constants for equation (1) can be determined from the relative amounts of Me₃SiX and Me₃SiY in solution, as measured by n.m.r. spectroscopy. As it was important to ensure that the system was at equilibrium, three separate routes to the equilibrium were studied. These were (*a*) adding an equimolar solution of Me₃SiX and Me₃SiY (*ca.* 2M in each) to a solution of NTMSIm (*ca.* 2M), (*b*) mixing equimolar solutions of Me₃SiY and (1) with anion X⁻, and (*c*) mixing equimolar solutions of Me₃SiX and (1) with anion Y⁻. In each case the ²⁹Si, ¹³C, and ¹H n.m.r. spectra were essentially identical, confirming that the system was at equilibrium. The results are given in Table 5, and are the values obtained from route (*a*). The complete series of exchanges was carried out in CD₃CN solution, but because of the problems with CD₃CN–TMSP[1] this series was repeated in CD₂Cl₂. The whole series could not be carried out in CD₂Cl₂

because in some examples precipitation of the salt (1) interfered with the observations.

Analysis of the n.m.r. spectra led to the following relative order for effectiveness in forming (1), according to equation (1): Me₃SiClO₄ > Me₃SiOSO₂CF₃ > Me₃SiI > Me₃SiBr > Me₃SiCl. The interpretations of the spectra were, in most cases, quite straightforward. For example TMSP displaces any counterion from (1), as shown by the absence of a resonance at δ 46 in the ²⁹Si spectrum, and the appearance of a peak corresponding to TMSX (X ≠ ClO₄). The spectra showed that in all but one of the examples chosen the equilibrium fell to one side, within the limits of detection (*ca.* 2%). When mixtures of TMSBr, TMSX (X = ClO₄, CF₃SO₃, or I), and NTMSIm were examined, the ²⁹Si spectra consisted of a single line at about δ 26 as expected for TMSBr exchanging with (1). In no example was evidence for the presence of TMSX found from the ²⁹Si, ¹³C, or ¹H n.m.r. spectra.

The TMST–TMSI–NTMSIm system was a little more complicated to interpret because of exchange between TMST and TMSI in CD₂Cl₂ or CD₃CN in the presence of (1). In CD₃CN the ²⁹Si spectrum consisted of two resonances, one at δ 26.5 (1) and one at δ 21.6. The low-frequency resonance was assigned to a rapidly exchanging mixture of *ca.* 75% TMSI (δ 12.1) and 25% TMST (δ 46.1). The ¹³C and ¹H spectra were consistent with this interpretation. Therefore the equilibrium constants for reaction (1) are of similar magnitudes for TMST and TMSI, but slightly greater for TMST.

It was already known[1] that TMSCl does not form (1) at ambient temperature with NTMSIm. However, two experiments were carried out, in which TMSCl was added to (1; X = CF₃SO₃) in CD₃CN and to (1; X = I) in CD₃CN. In each case a single trimethylsilyl resonance was observed at δ 31 in the ²⁹Si spectra, illustrating fast exchange with (1; X = CF₃SO₃ or I).

In the preceding paper[1] we established that the equilibrium constant for reaction (1) lies substantially to the right for X = ClO₄, CF₃SO₃, I, or Br, and to the left for X = Cl, at ambient temperature. The order of relative equilibrium constants, as determined herein, is exactly in opposition[1] to the ¹H n.m.r. deshielding of H-2 in (1), and also follows the same trend as the conductivity of (1). These latter two observations were taken as evidence of ion pairing in (1), and strongly suggest that the solvation of X⁻ in organic solvents is a major determinant in the formation of (1). The entropy data also support this proposition. The Si–X bond enthalpy is another factor to be considered, and where bond energy terms are known[15] (for

Si–I, Si–Br, and Si–Cl) the equilibrium constants do increase with decreasing SiX bond enthalpies. Bonds between silicon and oxygen are generally strong,[15] but we could find no information on Si–OClO$_3$ or Si–OSO$_2$CF$_3$. The importance of bond energy in determining the extent of salt formation between electrophilic silanes and nucleophiles cannot therefore be properly assessed, through lack of relevant data.

At this stage we cannot make detailed comparisons between this work and Simchen's study,[7] as the nucleophiles in the two studies are different. The rate of formation of silyl enol ethers does however follow a similar trend to that of the equilibrium concentration of (1). There is an exact correspondence between the rate of enol ether formation and the rate of reaction (4), which suggests that the lifetime of species related to (1), particularly with weak nucleophiles, may be of importance.

In conclusion, we suggest that some useful information on the composition of nucleophile–silane mixtures has been obtained from this work. Silylated salts (1) are certainly present in such mixtures. The concentration of such salts is higher in more polar solvents, consistent with the use of highly polar solvents, such as dimethylformamide[16] in silylations. Silylated amines, like (1), are particularly susceptible to nucleophilic substitution and are strong candidates for the active species in silylations.

Experimental

Bistrimethylsilyl salts were prepared as described in the preceding paper.[1] Solvents were rigorously dried and distilled prior to use. Trimethylsilyl compounds were also distilled before use. All solutions were made up under nitrogen, and n.m.r. tubes were sealed under nitrogen, usually with a rubber septum cap, or kept in a specially designed tube with ground glass joints.

N.m.r. experiments were carried out with a JEOL FX90Q multinuclear Fourier transform spectrometer. [1]H N.m.r. spectra (60 MHz) were measured with a Perkin-Elmer R12B spectrometer. Tetramethylsilane was used as internal standard. Solutions were generally made up to about 0.3M in each component.

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