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Reactions of the highly sterically hindered compounds $(Me_3Si)_3CSiMe_2X$ (X = Cl, Br, I, or ONO_2) with NaN_3, CsF, KSCN, and KOCN in MeOH

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Abstract

The reaction of the nitrate $TsiSiMe_2ONO_2$, **9**, (Tsi = $(Me_3Si)_3C$) with 0.25 M solutions of salts MY, *viz.* NaN_3, CsF, and KSCN, in MeOH at 45°C and 60°C give exclusively the corresponding substitution products $TsiSiMe_2Y$, but in the case of the halides $TsiSiMe_2X$, with X = I (**1**), Br (**2**), or Cl (**3**), some side-products are formed, mainly the fragmentation product $(Me_3Si)_2CHSiMe_2$-OMe; the proportion of these side-products increases in the sequence (X =) I < Br < Cl, in line with the decreasing reactivity of the substrate towards the salts. With KOCN, the least reactive of the salts used, substantial amounts of the side-products are formed even from the reactions of the nitrate. The rough relative reactivities of **3**, **2**, **1**, and **9** at 60°C are: 0.1/1.0/4.5/83 towards NaN_3; 0.5/1.0/2.6/115 towards CsF; and 0.13/1.0/4.2/120 towards KSCN. (The rather small spread of rates for the halides is noteworthy.) Examples of rough relative rates of reaction with NaN_3, CsF, and KSCN at 60°C are 0.5/1.0/0.3 for the nitrate and 1.3/1.0/0.45 for the iodide. Sodium methoxide in MeOH, which is ineffective in bringing about substitution of the $TsiSiMe_2X$ compounds, involving attack at the $SiMe_2X$ centre, is roughly comparable with NaN_3 and CsF in bringing about fragmentation, involving attack at an $SiMe_3$ centre. Features of the substitution reactions are consistent with a rate-determining transition state close to the very crowded five-coordinate silicon species $[TsiSiMe_2XY]^-$. Reaction of the compounds **1**–**3** and **9** with 0.25 M KSCN in MeCN are some 15–30 times as fast as those in MeOH, and give solely the isothiocyanate $TsiSiMe_2NCS$.

1. Introduction

The bulky group $(Me_3Si)_3C$, the 'trisyl' group, usually denoted below by the symbol Tsi, greatly inhibits nucleophilic attack at a silicon centre to which it is attached [1–3]. For example, the halides $TsiSiMe_2X$ with X = I, Br, Cl, or F (compounds **1**–**4**) were found [4] to react only slowly with boiling 2 M NaOMe–MeOH, and to give not the simple substitution product $TsiSiMe_2OMe$, **5**, but instead the fragmentation product $(Me_3Si)_2CHSiMe_2OMe$, thought to be formed, as depicted in Scheme 1, by initial attack of MeO^- at a Me_3Si group to give a sila-olefin, which rapidly undergoes addition of MeOH. The iodide $TsiSiMe_2I$ did react slowly ($t\frac{1}{2}$ *ca.* 5 days) with boiling methanol alone to give the methoxide **5**, but addition of NaOMe had little effect of the rate of this simple substitution [5].

$TsiSiMe_2X$	**1**	X = I	$(Me_3Si)_2CHSiMe_2OMe$ **11**
	2	Br	$(Me_3Si)_2CHSiMe_2OSiMe_3$ **12**
	3	Cl	
	4	F	
	5	OMe	
	6	NCS	
	7	N_3	
	8	NCO	
	9	ONO_2	
	10	OH	

Later it was shown that other strongly nucleophilic anions, in the salts MY, could bring about direct displacement of I^- from the iodide **1**, to give $TsiSiMe_2Y$, this displacement occurring alongside methanolysis to give the methoxide **5** [6]. Thus, when **1** was treated with

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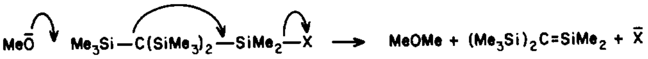

$(Me_3Si)_2C{=}SiMe_2 + MeOH \rightarrow (Me_3Si)_2CHSiMe_2OMe + MeO^-$

Scheme 1.

0.10 M NaN_3–MeOH at 60°C the azide **7** was virtually the sole product and the reaction was of first order with respect to the salt. The reactions with 0.1 M methanol solutions of other salts MY, namely CsF, KSCN, KOCN and KCN, were found to give mixtures of the corresponding products $TsiSiMe_2Y$, Y = F (**4**), NCS (**6**), NCO (**8**) and NC with the solvolysis product $TsiSiMe_2OMe$, **5**, the proportion of this last species increasing from 8% for CsF to 33% for KOCN. The effectiveness of the salts in bringing about the substitution fell in the sequence NaN_3, CsF > KCN > KSCN > KOCN. The iodide **1** was also found to react readily with the salts MY in MeCN to give exclusively the products $TsiSiMe_2Y$.

We have now made a detailed study of the reactions of the iodide, **1**, and of the related bromide, chloride, and nitrate with NaN_3, CsF, KSCN, and KOCN in MeOH and with KSCN in MeCN.

2. Results and discussion

The reactions in MeOH involved *ca.* 0.05 M $TsiSiMe_2X$ and 0.25 M MY (the high concentration of the salt being used to give rates as high as practicable for the less reactive compounds and to minimize competition from methanolysis). They were carried out in NMR tubes at 45°C and 60°C. When there was one greatly predominant product, $TsiSiMe_2Y$, the ratio h_x/h_y of the heights of the signal from the protons of the Me_3Si groups in the starting material and product were determined at intervals, and the approximate first order rate constant, k_y, for conversion of $TsiSiMe_2X$ into $TsiSiMe_2Y$ was then taken to be given by the slope of a plot of $\ln[(h_x + h_y)/h_x]$ against time. (This is not a strictly correct procedure, as noted in the Experimental section, but is an allowable approximation in view of the substantial margin of error in the experimental data.) At the end of the reaction (or at an earlier stage with very slow reactions) the composition of the product mixture was determined by GLC-MS, and if $TsiSiMe_2Y$ formed x% of the products the overall rate, k_T, of disappearance of the substrate was taken to be given by $100k_y/x$. In cases in which there were two or three major products, the ratio used was that of the height of the peak from the starting material to the

TABLE 1. Approximate composition of the product mixture for reactions of $TsiSiMe_2X$ with 0.25 M MY in MeOH, and approximate values of the (pseudo) first order rate constant, k_y, for conversion of $TsiSiMe_2X$ into $TsiSiMe_2Y$

MY	X	Temp./°C	$10k_y$/s^{-1}	k(rel) [a]	Product composition (%)
NaN_3	Cl	60	6.7	0.1	**7**(88), **11**(11), **12**(1)
		45	1.8		**7**(87), **11**(11), **12**(2)
	Br	60	65	1.0	**7**(88), **5**(2), **10**(1), **11**(9)
		45	19		**7**(90), **5**(1), **10**(1), **11**(8)
	I	60	290	4.5	**7**(95), **5**(2), **10**(3)
		45	105		**7**(96), **5**(2), **11**(2)
	NO_3	60	5400	83	**7**(100)
		45	3700		**7**(100)
CsF	Cl	60	44	0.5	**4**(85), **11**(15)
		45	0.88		**4**(95), **11**(5)
	Br	60	86	1.0	**4**(92), **11**(8)
		45	23		**4**(95), **11**(5)
	I	60	220	2.6	**4**(86), **5**(2), **11**(12)
		45	56		**4**(93), **5**(2), **11**(5)
	NO_3	60	9900	115	**4**(97), **10**(1), **11**(1), **12**(1)
		45	6400		**4**(95), **10**(1), **11**(2), **12**(2)
KSCN	Cl	60	3.0	0.13	**6**(75), **11**(25)
	Br	60	23	1.0	**6**(85), **5**(2), **10**(1), **11**(12)
		45	5.7		**6**(85), **5**(2), **10**(1), **11**(12)
	I	60	96	4.2	**6**(80), **5**(10), **10**(2), **11**(7), **12**(1)
		45	26		
	NO_3	60	2800	120	**6**(100)
		45	1650		**6**(100)

[a] Ratio of k_y for $TsiSiMe_2X$ to that for $TsiSiMe_2Br$.

combined heights of both or all three such products (see Experimental section). A value of k_c, the sum of the rate constants for formation of the two or three products, was derived as above, and the value of k_y was taken to be $yk_c/100$, where y was the percentage of $TsiSiMe_2Y$ in the product mixture, and the value of k_T to be $100k_c/z$, where z was the combined percentage of the two or three main products in the overall product mixture. The reasonable assumption made is that $TsiSiMe_2X$ is consumed in concurrent (pseudo) first order processes.

Satisfactory first-order plots were obtained in all cases in which the reaction could be taken to a degree of completion that allowed meaningful plots. Where $TsiSiMe_2Y$ formed more than 90% of the products the rate constants k_y are probably reliable to within about ±10%; in other cases the possible error could be as high as ±20%, but the level of uncertainty is not such as to affect significantly any conclusions reached below.

The simplest results (see Table 1) were obtained with NaN_3, the azide **7** apparently forming > 85% of the products even in the case of the chloride **3**, which was in general the most prone to undergo side-reactions. The reaction of the most reactive substrate, the nitrate **9**, gave only the azide **7** within the limits of detection, but even the iodide **1** gave also small amounts of the methoxide **5** and the fragmentation product $(Me_3Si)_2CHSiMe_2OMe$, **11**. The bromide **2** also gave the side products **5** and **11**, and in addition a trace of the hydroxide, **10**, while the chloride **3** gave, along with **5**, some **11** and a trace of the rearranged product $(Me_3Si)_2CHSiMe_2OSiMe_3$, **12**. In general similar variations in the product composition were observed in the reactions with CsF, but the proportion of the fragmentation product **11** from the halides **1**–**3** was significantly higher.

In the light of these results it is evident that reaction of the iodide **1** with 0.1 M solutions of the salts MY in MeOH [5] must have given some of the fragmentation species **11** along with the observed side product **5**, but the proportion of the latter would have been substantially larger than in the present work in which use of a higher concentration of the salt reduced the effect of competition by methanolysis. (In the earlier, preliminary, study the analysis was solely by ^1H NMR spectroscopy, and the presence of **11** could easily have been overlooked.)

The small amounts of the hydroxide **10** formed in several of the reactions with NaN_3 or CsF evidently arise from the presence of a little water in the MeOH (see later). The base-catalysed rearrangement of **10**, a well established process [7], accounts for the formation of a little **12**.

The nitrate **9** reacts roughly 1.5 times as rapidly with CsF as with NaN_3 at both 45°C and 60°C. The chloride **3** is less reactive towards CsF than NaN_3 at 45°C but the reverse is the case at 60°C. The spread of rate constants k_y for the halides **1**–**3** is substantially larger for the reactions with NaN_3 than for those with CsF; in the reaction with the latter at 60°C the iodide **1** is only *ca.* 4.5 times as reactive as the chloride **3**. We previously considered the small spread of rates for the halides towards KSCN in MeCN in terms of a rate-determining step involving loss of X^- from an initially formed five-coordinate anion $[TsiSiMe_2XY]^-$, with a transition state not far removed from the latter [8]. The energy required to form this intermediate, and so increase its stationary concentration, would be lower the greater the electron withdrawal by X, and in terms of this effect the rate would tend to increase in the order (X =) I < Br < Cl. However, the tendency of X^- to separate from the intermediate would increase in line with the usual leaving group ability, and with increase in the relief of steric strain, in the order I > Br > Cl, and so overall only a small rate variation might be observed. (In the case of the even more sterically hindered halides $^tBu_3SiX$ the iodide is actually less reactive than the chloride towards KSCN in MeCN [8].)

In the reactions with KSCN, the nitrate gave only the isothiocyanate **8**, but, at the other extreme, the chloride gave *ca.* 25% of the fragmentation product **11** at 60°C. The reactions are slower than those with NaN_3 and CsF, but in the case of the nitrate only by factors of *ca.* 2 and 3.5, respectively, at 60°C. There is, indeed, a remarkably small variation in the effectiveness of the various salts as nucleophiles. Thus, in reactions with the nitrate **9** the ratios of the approximate values of k_y at 60°C for CsF, NaN_3, and KSCN, respectively, are *ca.* 3.5/2/1, and the corresponding ratios are *ca.* 3/2.3/1 for the iodide **1**, 2.8/3.7/1 for the bromide **2**, and 2/3.3/1 for the chloride **3**. Since the chloride is some 800 times less reactive towards NaN_3 than the nitrate, it would normally be expected to discriminate between the various anions markedly more effectively than the latter, and it is probably mechanistically significant that it does not.

In the reaction with KOCN at 60°C, even the nitrate **9** gave only 60% of the direct substitution product **8** (see Table 2). This substitution is only *ca.* 6 times as slow as that with KSCN, but this factor is sufficient to permit concurrent formation of significant amounts of the methoxide **5** and the hydroxide **10** by solvolysis. In addition there was *ca.* 9% of a product with a mass spectrum consistent with its being the carbamate $TsiSiMe_2NHCO_2H$, formed by addition of water to the cyanate **8**. The species **5** and **10** formed an even higher proportion of the products from the iodide **1**, and the bromide **2** gave only a very small amount of the isocyanate. The apparent preference for formation of the

TABLE 2. Approximate composition of product mixtures and approximate values of the (pseudo) first order rate constants, k_D, for disappearance of $TsiSiMe_2X$ in reactions with KOCN in MeOH at 60°C

X	10^8k_D/ s^{-1}	10^8k_y/ s^{-1} [a]	Product composition (%)
Cl	– [b]	–	– [b]
Br	3.7	–	**8**(4), **5**(12), **10**(63), **11**(20), **12**(1)
I	43	140	**8**(33), **5**(39), **10**(3), **11**(23), **12**(2)
NO_3	890	530	**8**(61), **5**(15), **10**(7), **11**(4), **12**(4), A(9) [c]

[a] Given by $k_D \times x/100$, where x = percentage of $TsiSiMe_2NCO$, **8**, in the product.

[b] Only 7% of **3** had reacted after 7 days; the only product detected was **10**.

[c] Probably $TsiMe_2SiNHCO_2H$.

hydroxide rather than the methoxide in a solution containing only a very low concentration of water would be surprising if the effect had not been observed previously in the solvolysis in 'dried' MeOH of the very reactive compounds $TsiSiMe_2X$ with X = OCN, OSO_2CF_3, or $OClO_3$; thus the cyanate (X = OCN) gave exclusively the hydroxide **10** in the reaction with MeOH containing 0.05 vol-% of added water [9].

Since NaOMe is very much less effective than the salts NaN_3 and CsF in bringing about substitution of the halides **1**–**3** in MeOH, it is of interest to make some comparison, however rough, of the relative effectiveness of these reagents in bringing about the fragmentation, involving attack on an Me_3Si rather than an Me_2XSi centre. The outcomes of reactions of the halides **1**–**3** with 0.25 M NaOMe in MeOH at 60°C are shown in Table 3. Disappearance of 70% of the iodide **1** in 7 days corresponds to a first-order rate constant of *ca.* 20×10^{-7} s^{-1} (which compares with a value of 290×10^{-7} s^{-1} for the reaction with NaN_3), and of this *ca.* 10×10^{-7} s^{-1} is attributable to the formation of the methoxide **5** (this value being essentially the same as that which can be estimated from the data for methanolysis in MeOH alone at 50°C [5]) and *ca.* 9×10^{-7} s^{-1} to the fragmentation to give **11**. For the reaction with NaN_3, which gave between, say, 2.5 and 10% of **11** (the observed percentage was *ca.* 5), the value of the corresponding rate constant is *ca.* $8–30 \times 10^{-7}$ s^{-1}. Thus, the rate constants for the fragmentation brought about by NaOMe and NaN_3 are comparable, and a similar conclusion is reached if the comparison is made with the reaction involving CsF. Likewise, for reaction of the chloride **3** with NaOMe in MeOH the disappearance of *ca.* 18% of **3** in 17 days corresponds to a rate constant of *ca.* 1.35×10^{-7} s^{-1}, of which *ca.* 1.3×10^{-7} is attributable to the fragmentation. The formation of, say, 6–20% of **11** (the observed percentage was *ca.* 11) in the reaction with NaN_3 corresponds to a rate constant of *ca.* $0.45–1.5 \times 10^{-7}$ s^{-1}, so that again NaOMe is roughly as effective as NaN_3. We have suggested that the inability of NaOMe to catalyse the methanolysis of **1** (or that of the compounds $TsiSiMe_2X$ with X = $OClO_3$, OCN, or OSO_2CF_3) may be due to severe steric hindrance to attack at the $SiMe_2X$ centre arising from the bulk of the solvated MeO^- anion, and the relative absence of such an effect in the attack on an Me_3Si centre is consistent with our view that in this case the steric hindrance in the (rate-determining) transition state is markedly reduced by the stretching (partial breaking) of the $Me_3Si–C$ bond [4].

TABLE 3. Products from reactions of $TsiSiMe_2X$ with 0.25 M NaOMe in MeOH at 60°C

X	Time/days	Composition (%) of reaction mixture
I (**1**)	7.0	**1**(29), **5**(36), **11**(31), **12**(4)
Br (**2**)	7.0	**2**(92), **11**(7), **12**(1)
Cl (**3**)	7.0	**3**(93), **11**(7)
Cl (**3**)	17.0	**3**(82), **11**(17), **12**(1)

3. Activation parameters

Rough values of the activation energy ΔE, log A (where A is the frequency factor), of the activation entropy, ΔS, calculated from the data in Table 1, are shown in Table 4. Because of the possible errors in the rate constants and because studies were made at only two temperatures these parameters are subject to substantial error and can be used only for gross comparisons, but some aspects merit comment.

TABLE 4. Approximate values of Arrhenius parameters for reactions of compounds $TsiSiMe_2X$ with salts MY in MeOH [a]

MY	X	$10^{-3}\Delta E$/ kcal mol^{-1}	log(A/s^{-1})	$-\Delta S$/ cal K^{-1} mol^{-1}
NaN_3	Cl	18	6.5	29
	Br	17	7	27
	I	14	4	40
	NO_3	5	1	57
CsF	Cl	22	10	13
	Br	18	7	27
	I	18	8	22
	NO_3	6	1.5	53
KSCN	Br	19	7	27
	I	18	7	27
	NO_3	7	2	50

[a] For calculation of approximate values of $-\Delta S$, the specific second order rate constants, given by $k_y/0.25$, were used.

The most striking feature is the marked difference between the data for the halides **1**–**3** and those for the nitrate, **9**. Except for that for the reaction of the iodide with NaN_3 (which looks anomalously low and probably reflects the possible errors in k_y) the values of ΔE for the halides fall in the range 18–22 kcal mol^{-1} whereas those for the nitrate lie between 5 and 7 kcal mol^{-1}, an unexpectedly large difference when it is remembered that the nitrate is only *ca.* 20–40 times as reactive as the iodide. The low values of ΔE for the nitrate are matched by very unusually low values of A (and correspondingly high values of $-\Delta S$).

It is instructive to compare the values of ΔE and log A in Table 4 with those for cleavage of Si–R bonds in various compounds of the type Me_3SiR (where R is, *e.g.*, $CH_2C_6H_4X$, $CHPh_2$, *etc.*) by NaOMe in MeOH, a reaction also involving bimolecular nucleophilic displacement by an anion [10]. For a *ca.* 10^7-fold range of rate constants in that reaction the values of ΔE range from 14 to 26 kcal mol^{-1} and those of log (A/s^{-1}) from 9 to 11 ($-\Delta S = 9.5$–23). For cleavage of the compound m-$ClC_6H_4CH_2SiMe_3$, the specific (second order) rate constant, k_s, at 60°C is within a factor of 2 of that for reaction of the bromide **2** with CsF in MeOH, the similarity in rates arising from the presence of a sterically unhindered silicon centre along with a very poor leaving group in the m-$ClC_6H_4CH_2SiMe_3$ and that of a highly sterically hindered silicon centre along with a much better leaving group in **2**. For the cleavage the values of ΔE, log (A/s^{-1}) and $-\Delta S$ are 22.6 kcal mol^{-1}, 10.6, and 12, respectively; these are not greatly different from those of 18, 7, and 27 for the reaction of **2**, but clearly the similarity in rates arises from a higher activation energy for the cleavage coupled with a lower activation entropy. In contrast, for cleavage of 3,5-$Cl_2C_6H_3CH_2SiMe_3$ (for which the value of k_s at 60°C is within a factor of 2 of that for reaction of the nitrate **9** with CsF in MeOH) the values of ΔE, log (A/s^{-1}), and $-\Delta S$ are 21.2 kcal mol^{-1}, 11.1, and 0.95 cal mol^{-1} K^{-1}, very different from those for the reaction of **9**, *viz*, 6, 1.5, and 53, respectively. Even when allowance is made for the possible errors in the latter values it is evident that the severe steric hindrance to attack on the silicon atom in **9** gives rise to an unusually high entropy of activation. This is consistent with a very crowded transition state in which molecular motions are very restricted, but it is puzzling that the activation energy is so low. The difference between the activation parameters for the reactions of the halides **1**–**3** on the one hand and those of the nitrate **9** on the other are so large as to suggest a change in mechanism, but it is difficult to see what this might involve. It is possible that at least part of the difference arises from much more effective solvation of the transition state in the case of **9**, especially by hydrogen-bonding to the oxygen atoms of the leaving ONO_2^- ion, since the binding of solvent molecules would both lower the activation energy and significantly raise the activation entropy, but it seems unlikely that this effect alone would be large enough to account for the abnormal parameters observed.

TABLE 5. Approximate (pseudo) first order rate constants, k_y, for reactions of $TsiSiMe_2X$ with 0.25 M KSCN in MeCN to give $TsiSiMe_2NCS$

X	Temp./ °C	10^7k_y/ s^{-1}	k_y(rel) (60°C)	k_y(rel) (35°C)
Cl	60	85	0.12	
Br	60	700	1.0	
I	75	5000		
I	60	1520	2.2	
I	35	(150) [a]		1.0
NO_3	35	25,000	(400) [b]	170

[a] By extrapolation from 75°C and 60°C.

[b] Estimated from rate relative to that for the iodide at 35°C.

4. Reactions with KSCN in MeCN

The rates of reactions of the halides **1**–**3** and the nitrate **9** with 0.25 M KSCN in MeCN were determined, and the results are shown in Table 5. (The other salts are not sufficiently soluble to allow rate studies under similar conditions.) The isothiocyanate **6** was the only product in each case.

The iodide reacts *ca.* 16 times as fast in MeCN as in MeOH at 60°C, and this can be attributed to the poorer solvation of the anion SCN^- in MeCN. The corresponding factors for the chloride, the bromide, and the nitrate (in this last case at 35°C) are roughly 20–30. Rough values of the activation energy and log (A/s^{-1}) of 18.4 kcal mol^{-1} and 8 can be derived for the reaction of the iodide, not significantly different from those for the reaction in MeOH.

5. Experimental details

5.1. Materials

The preparations of the compounds $TsiSiMe_2X$, **1**–**10**, have been described previously [5,11,12], as have those of **11** [4] and **12** [11].

Methanol was refluxed over and distilled from $Mg(OMe)_2$, and stored over 3A molecular sieves. Acetonitrile was boiled with CaH_2 for 2 h then distilled, and stored over 4A molecular sieves.

5.2. Product analyses

Product analyses were carried out by GLC by use of a Pye Unicam GCD Chromatograph fitted with a 2 m column of 3% OVIOI on Chromasorb G at 180°C and linked to a Kratos MS-25 mass spectrometer. Retention times and mass spectra for authentic samples of reactants and products were available. Reactions were usually taken effectively to completion before analysis, but for reaction with KOCN only to 7% completion for reaction of **3** and 73% for the reaction of **2**. The reaction of **9** gave 9% of a product with a mass spectrum consistent with its being $TsiSiMe_2NHCO_2H$: the main peaks were: m/z 349 (80%, M), 305 (90, M − CO_2), 289 (10, M − $NHCO_2H$), 275 (10), 217 (15), 201 (40), 187 (20), 129 (10), 89 (10), 73 (100), and 59 (38).

5.3. Rate measurements

A sample of the compound $TsiSiMe_2X$ (*ca.* 8 mg) was dissolved in two microdrops (*ca.* 6 mm^3) of CCl_4 in an NMR tube and 0.50 cm^3 of a 0.25 M solution of MY in MeOH or MeCN was added. (For reactions with half lives of < 20 min the salt solution was prewarmed to close to the intended reaction temperature.) For reactions with half-lives of less than *ca.* 1.5 h the tube was firmly capped, shaken, and placed in the probe of a Perkin Elmer R32 spectrometer maintained at the selected temperature (± 0.1°C). For reactions of longer half-life the tube was sealed, shaken, and placed in a thermostated bath, and withdrawn at intervals for rapid recording of the ^1H NMR spectrum (at 90 MHz) at the relevant temperature.

The progress of the reaction was usually monitored by determining at intervals the relative heights of corresponding peaks from the starting material and products. When the substitution product $TsiSiMe_2Y$ formed more than *ca.* 90% of the products, the rate constant k_y was determined by plotting $\log[(h_x + h_y)/h_x]$ against the time t [where h_x is the height of the peak from $TsiSiMe_2X$ and h_y that from $TsiSiMe_2Y$]. Remarkably good first order plots were obtained for the extent of reaction monitored (usually > 70%). [Strictly, if $TsiSiMe_2Y$ forms x% of the products, $[h_y + (100 - x)h_y]$ should be used in place of h_y, and the value of k thus determined then multiplied by $x/100$ to give k_y, but the result is not significantly different from that derived directly from h_y.]

When substantial amounts of products other than $TsiSiMe_2Y$ were formed, the combined height of the relevant peaks of the products (with correction for the relevant number of protons where necessary) was used in place of h_y. The value of k thus determined was multiplied by $x/100$ to give k_y. Again remarkably good first order plots were obtained.

Details for specific reactions were as follows.

(a) For reactions of **1–3** with NaN_3 the Me_3Si peaks from **1** (δ 0.36), **2** (δ 0.35), **3** (δ 0.34), were used along with that from **7** (δ 0.30).

(b) For the reaction of **1–3** with CsF the combined height of Me_3Si peaks from **4** (δ 0.22) and **11** (δ 0.09) was used.

(c) For the reaction of **2** with KSCN in MeOH the height of the Me_3Si peak from **6** (δ 0.31) was used, and for the reaction of **1** this height combined with that of the Me_3Si peak from **5** plus **10** (at δ 0.23). For the reaction of **3** the $SiMe_2Cl$ peak from **3** (at δ 0.64) was used along with the combined height of the $SiMe_2NCS$ peak (δ 0.51) and the Me_3Si peak from **11** (δ 0.09).

(d) For reactions of **1**, **2** and **9** with KOCN the combined heights of the Me_3Si peaks from **8** (δ 0.27), **5** + **10** (at δ 0.23), and **11** (δ 0.09) were used. For the reaction of **3** the Me_3Si peak from the product **10** (δ 0.23) was used.

(e) For the reactions of **1** and **2** with KSCN in MeCN the Me_3Si peaks from **1** (δ 0.36) or **2** (δ 0.35) and the product **6** (δ 0.31) were used. For those of **2** and **9**, the $SiMe_2Cl$ peak from **2** (δ 0.64) or the $SiMe_2ONO_2$ peak of **9** (δ 0.65) was used along with the $SiMe_2NCS$ peak (δ 0.51).

5.4. Reactions with NaOMe in MeOH

To a sample of the halide **1**, **2**, or **3** (10 mg) in an NMR tube was added 1 cm^3 of a 0.25 M solution of NaOMe in MeOH followed by the minimum amount of CCl_4 needed to take all the solid into solution. The tube was sealed and kept for some days (see Table 3) in a bath at 60°C. The products were analysed by GLC in the way described above.

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