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Rates of solvolysis of the compounds $(Me_3Si)_2(Ph_2MeSi)CSiMe_2X$, $X = I$, OSO_2CF_3 and OCN. Mechanistic implications [☆]

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Abstract

Comparisons of the rates of reaction of the compounds $(Me_3Si)_3CSiMe_2X$, with X = I (**1a**), OSO_2CF_3 (**1b**) or OCN (**1c**), with those of the corresponding compounds $(Me_3Si)_2(Ph_2MeSi)CSiMe_2X$ (**2a–c**), point to the following conclusions. (a) With 3 : 1 (v/v) $MeOH–CCl_4$ the iodide **2a** reacts by an ionization process, in which a γ-Ph group assists leaving of I^-, whereas **1a** reacts by a direct bimolecular displacement mechanism. (b) With 5% H_2O–dioxane or 6% H_2O in 4 : 1 $MeCN–CCl_4$, reactions of both **2a** and **1a** involve direct nucleophilic attack at silicon, as does that of the cyanate **2c** with 10 : 1 $CD_3OD–CDCl_3$ (containing a little water), towards which **2c** is > 600 times as reactive as the iodide **2a**. (c) With 1 : 3 $CF_3CO_2H–CDCl_3$, 1 : 3 $(CF_3)_2CHOH–CDCl_3$ and 3 : 1 $CF_3CH_2OH–CDCl_3$, **2a** (which is much more reactive than **1a** in all these media) reacts by the ionization mechanism. (d) The triflate **2b** probably reacts with all three fluorine-containing media by the ionization mechanism (although much less readily than the iodide **2a**) but by the bimolecular mechanism with 3 : 1 $MeOH–CCl_4$.

Keywords: Silicon; Mechanism; Solvolysis

1. Introduction

For solvolysis of compounds of the type $(Me_3Si)_3CSiRR'_2X$ and $(Me_3Si)_2(ZMe_2Si)CSiRR'X$, in which the normally very ready nucleophilic attack on the Si of an Si–X bond is severely sterically inhibited, three classes of mechanism have been suggested [1,2], viz.:

(a) Straightforward bimolecular, S_N2, substitution (possibly involving a five-coordinate silicon intermediate) as, for example, in the methanolysis of the compounds $(Me_3Si)_3CSiPhHX$ with X = Br, ONO_2, O_2CMe, F, etc. (but probably not I; see later), for which there is substantial acceleration by NaOMe.

(b) A process, not yet fully identified, which operates in the methanolysis of the compounds $(Me_3Si)_3CSiMe_2X$ in which X is one of the very good leaving groups $OClO_3$, OSO_2CF_3 or OCN. The rates of the reactions in MeOH are not significantly increased by addition of NaOMe but are markedly raised by the addition of water, which also diverts the reaction towards the formation of the hydroxide to a much greater extent than would be expected from the overall rate increase. The reactions do not involve ionization, but seem not to be wholly straightforward bimolecular nucleophilic substitutions, and it has been suggested that preassociation of a solvent molecule with the substrate, specifically with the group X, may account for some special features.

(c) Substitution involving rate-determing ionization with anchimeric assistance by a γ-Me or other group Z, to give a bridged cationic intermediate of type I, which is then attacked by the solvent. Examples are the solvolysis of $(Me_3Si)_3CSiMe_2I$ in CF_3CO_2H [3], of $(Me_3Si)_2(PhMe_2Si)CSiMe_2I$ in CF_3CH_2OH or $(CF_3)_2CHOH$ [4] and of $(Me_3Si)_2(MeOMe_2Si)CSiMe_2Cl$ in MeOH [5], the increasing anchimeric assistance in this series more than compensating for the decreasing ionizing power of the medium. Rates are little affected by the presence of lyate ion. In some cases the mechanism can operate alongside a bimolecular process, e.g. in the methanoly-

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[☆] Dedicated to Professor Hidekai Sakurai, an outstanding organosilicon chemist, on the occasion of his retirement from the post at Tohoku University that he filled with such distinction.

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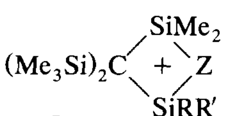
sis and hydrolysis of the iodides $(Me_3Si)_2(YC_6H_4Me_2Si)CSiMe_2I$ [4].



I

To throw further light on these mechanisms, we have now compared the rates of solvolysis of the compounds $(Me_3Si)_3CSiMe_2X$ (**1a–c**) with X = I, OSO_2CF_3 and OCN, respectively, with those of the corresponding compounds $(Me_3Si)_2(Ph_2MeSi)CSiMe_2X$ (**2a–c**) and in some cases $(Me_3Si)_2(PhMe_2Si)CSiMe_2X$ (**3a–c**). In compounds **2** and **3**, the γ-Ph groups can under appropriate conditions be expected to provide substantial anchimeric assistance to the leaving of X^-; such assistance was observed previously for reactions of the iodides **2a** and **3a** with silver salts and with ICl [6].

$(Me_3Si)_3CSiMe_2X$	$(Me_3Si)_2(Ph_2MeSi)CSiMe_2X$	$(Me_3Si)_2(PhMe_2Si)CSiMe_2X$
1a X = I	**2a** X = I	**3a** X = I
1b = OSO_2CF_3	**2b** = OSO_2CF_3	**3b** = OSO_2CF_3
1c = OCN	**2c** = OCN	**3c** = OCN
1d = OH	**2d** = OH	**3d** = OH
1d′ = OD	**2d′** = OD	**3d′** = OD
1e = OMe	**2e** = OMe	**3e** = OMe
1e′ = OCD_3	**2e′** = OCD_3	**3e′** = OCD_3
1f = OCH_2CF_3	**2f** = OCH_2CF_3	**3f** = OCH_2CF_3
1g = O_2CCF_3	**2g** = O_2CCF_3	

2. Results and Discussion

The media chosen for the solvolyses were H_2O–dioxane, H_2O–MeCN, MeOH (or CD_3OD), CF_3CH_2OH, $(CF_3)_2CHOH$ and CF_3CO_2H, in most cases containing CCl_4 or $CDCl_3$ to aid dissolution of the substrate (the exact composition of each medium is specified in the Experimental section). In the fluorine-containing media some Et_3N was also present to neutralize the generated acid HX, which otherwise would cleave the Si–Ph bonds in compounds **2** and **3** [4]. We confirmed that prolonged reaction of the iodide **2a** or triflate **2b** with CF_3CH_2OH–$CDCl_3$ in the absence of the base gave the tris(trifluoroethoxy) derivative (see, e.g., Eq. 1).

$$(Me_3Si)_2(Ph_2MeSi)CSiMe_2I + CF_3CH_2OH \rightarrow (Me_3Si)_2[(CF_3CH_2O)_2MeSi]CSiMe_2OCH_2CF_3 \quad (1)$$

For the iodides **1a** and **2a** and the trifluoromethanesulphonates (triflates) **1b** and **2b**, in most cases the progress of the reaction was monitored by ^1H NMR spectroscopy up to at least 75% completion, and unless indicated otherwise the data yielded a good first-order plot, from which was derived the half-life $t_{1/2}$. Values of the latter are given in Table 1; they could be in error by as much as ±10%, but the uncertainty does not affect the validity of the discussion below. A slightly different procedure (see later) was used for the iodide **3a** and triflate **3b** and also for all three cyanates, which were studied only in methanolysis.

2.1. Reactions of the iodides

The main features of the results shown in Table 1 for the solvolyses of the iodides **1a** and **2a**, with comments, are as follows.

(a) Compound **2a** is only ca. four times as reactive as **1a** towards water in dioxane or MeCN (the latter containing CCl_4, see Table 1), in line with our earlier conclusion that hydrolysis under such conditions is essentially a bimolecular process. (The higher reactivity of **2a** can be attributed to inductive electron withdrawal by the Ph groups [4].) In contrast, towards 3 : 1 MeOH–CCl_4, **2a** is ca. 30 times as reactive as **1a**, suggesting

Table 1
Approximate values of the half-life, $t_{1/2}$, for solvolyses of the iodides **1a** and **2a** and triflates **1b** and **2b**

Medium (ratio) [a]	Temperature (°C)	$t_{1/2}$		Temperature (°C)	$t_{1/2}$	
		2a	**1a**		**2b**	**1b**
5% H_2O–dioxane	61	6.0 h	27 h	35	8.3 min	13 min
6% H_2O–MeCN–CCl_4 (3 : 1)	61	8.4 h	34 h	30	19 min	20 min
MeOH–CCl_4 (3 : 1)	61	5.6 h	170 h	35	10.5 h	13.5 h
CF_3CH_2OH–$CDCl_3$ (3 : 1)	35	5 min	nr [b]	45	19 h	nr [b]
$(CF_3)_2CHOH$–$CDCl_3$ (1 : 3)	35	3.1 h	nr [c]			
$(CF_3)_2CHOH$–$CDCl_3$ (3 : 1)				35	10.5 h	nr [d]
CF_3CO_2H–$CDCl_3$ (1 : 3)	35	7.7 min	> 50 days [e]	35	5.2 h	nr [f]

[a] The denominator in the ratio refers to volume of CCl_4 or $CDCl_3$; for the exact composition of the medium, see the Experimental section.
[b] No reaction in 30 days at 61°C.
[c] No reaction in 3 : 1 $(CF_3)_2CHOH$–$CDCl_3$ during 20 days at 45°C.
[d] No reaction in $(CF_3)_2CHOH$–$CDCl_3$ (7 : 1) during 20 days at 45°C.
[e] $t_{1/2}$ ca. 14 days at 61°C.
[f] No reaction in 10 days at 61°C.

that in the case of **2a** there a significant contribution from the ionization, S_N1, process; this supports our suggestion that there is a small contribution from such a process in the methanolysis of the related iodide $(Me_3Si)_2(PhMe_2Si)CSiMe_2I$, in which only one γ-Ph group is available to provide assistance [4].

It is noteworthy that the chloride $(Me_3Si)_2(Ph_2MeSi)CSiMe_2Cl$ was found to undergo no reaction with 3:1 CF_3CH_2OH–$CDCl_3$ (again containing a small proportion of Et_3N) during 15 days at 61°C, showing that the anchimeric assistance by the Ph groups (unlike that by a γ-OMe group [5]) is not sufficient to induce departure of the much poorer leaving group Cl^-. Likewise, and as expected, the chloride was also inert towards MeOH or 5% H_2O–dioxane.

For a separate set of reactivity comparisons undertaken to include iodide **3a**, a continuous-wave NMR spectrometer was no longer available to us and it was necessary to use CD_3OD (containing 10 vol.% CCl_4 to increase solubility) rather than CH_3OH, and this deuteriated solvent (even after being kept over 3A molecular sieve) evidently contained a significant, and unknown, amount of water that it would have been too costly to remove. As it turned out, this contamination had the advantage that it revealed a difference between **1a** on the one hand and **2a** and **3a** on the other in respect of the amount of the corresponding hydroxide formed at the expense of the methoxide. Determination of the approximate extents of solvolysis at three or four points yielded the following rough values of $t_{1/2}$ at 61°C: for **1a**, 76 h; for **2a**, 7 h; and for **3a**, 32 h. Again, the data are consistent with predominant operation of the ionization mechanism for **2a** and a bimolecular mechanism for **1a**, and with concurrent operation of both mechanisms for **3a**. In line with this, **1a** yielded hydroxide and methoxide in a ratio of ca. 3:2 (as judged from the ^1H NMR spectrum), whereas only the methoxide appeared to be formed from **2a** and **3a**, although perhaps up to 10% of the hydroxide could have escaped detection. Formation of a substantial amount of hydroxide from **1a** is in keeping with the selectivity towards traces of water in the (bimolecular) solvolysis of the compounds $(Me_3Si)_3CSiMe_2X$ with $X = OClO_3$, OSO_2CF_3 or OCN in MeOH [1], whereas the highly reactive cationic intermediates formed from **2a** and **3a** would not be expected to show such high selectivity.

We previously suggested that since the rate of solvolysis of **1a** in MeOH is not substantially increased by the presence of water, it was possible that the methanolysis of the iodide had a different mechanism from that of the compounds $(Me_3Si)_3CSiMe_2X$ with $X = OClO_3$, OSO_2CF_3 or OCN [1]. However, the observation that in the reaction of **1a** with CD_3OD there is marked selectivity towards water (although smaller than that observed for the more reactive compounds), when considered along with the fact that for all four compounds the rate is insensitive to the presence of base, leads us now to favour a common mechanism for all four substrates. We tentatively suggested that the increase in the rate on addition of water and the selectivity towards water arise from preferential preassociation of water with X of the Si–X bond, perhaps largely by hydrogen bonding to X, and this effect, and thus its consequences, would be expected to be smaller for X = I.

(b) In 1:3 CF_3CO_2H–$CHCl_3$, the half-life for **2a** is only ca. 8 min at 35°C, whereas that for **1a** is ca. 14 days at 61°C, indicating that **2a** is $> 10^4$ times the more reactive. This is consistent with our view that even the reaction of **1a** with CF_3CO_2H involves ionization, as indicated by the formation of rearranged $(Me_3Si)_2$-$(Et_2MeSi)CSiMe_2O_2CCF_3$ along with the unrearranged $(Me_3Si)_3CSiEt_2O_2CCF_3$ in the reaction of $(Me_3Si)_3$-
$CSiEt_2I$ with refluxing CF_3CO_2H [3].

(c) In 1:3 $(CF_3)_2CHOH$–$CDCl_3$, **2a** has a half-life of ca. 3 h at 35°C whereas **1a** undergoes no detectable reaction even in the 3:1 mixture during 20 days at 45°C. Likewise, in 3:1 CF_3CH_2OH–$CHCl_3$, **2a** has a half-life of only 5 min at 35°C, whereas **1a** undergoes no detectable reaction in 30 days at 61°C. The reactions of **2a** evidently involve the ionization process (as confirmed by the small effect of added water, discussed later). In the reaction of **2a** with $(CF_3)_2CHOH$ the product was the hydroxide $(Me_3Si)_2(Ph_2MeSi)CSiMe_2OH$ (**2d**), showing that there must have been traces of water in the alcohol (even though it had been dried by a standard method) and that the intermediate cation discriminates effectively between water and the weakly nucleophilic and bulky alcohol; a similar result was observed for the reaction of **3a** in this medium [4].

2.2. Reactions of the triflates

The features of the results for the triflates shown in Table 1 are as follows:

(a) Towards H_2O–dioxane, H_2O–$MeCN$–CCl_4 or $MeOH$–CCl_4, **2b** is only slightly more reactive than **1b**, indicating that for both compounds the reactions involve direct nucleophilic substitution, not ionization; again, the slightly higher reactivity of **2b** can be attributed to electron withdrawal by the Ph groups. Towards water and MeOH the triflates **1b** and **2b** are much more reactive than the corresponding iodides. Hence the fact that the iodide **2a** reacts with MeOH by the ionization mechanism whereas the triflate **2b** does not can probably be attributed to the much greater ease of bimolecular attack on **2b** and not necessarily to a lower ability to undergo ionization. (As in the case of the iodides, in order to include the monophenyl derivative rough half-lives were determined for the triflates **1b**, **2b** and **3b** in 10:1 CD_3OD–CCl_4 at 61°C, and all were found to be about 30 min, confirming that there is no anchimeric assistance. As expected from the reasoning advanced in the discussion of the corresponding reactions of the iodides above, a substantial proportion of the hydroxide (ca. 30% for **1a**, 25% for **2a** and > 15% for **3a**) was formed in each case.)

(b) No reaction of **1b** even with 3:1 CF_3CO_2H–$CDCl_3$ was observed during 10 days at 61°C, i.e. the triflate is much less reactive towards the acid than is the iodide **1a**, and it seems that this acid is much less effective in promoting ionization of an $Si–OSO_2CF_3$ than that of an Si–I bond. Towards the alcohols CF_3CH_2OH and $(CF_3)_2CHOH$, **1b**, like **1a**, was unreactive under the conditions used (The triflate **1b** was previously shown to undergo no significant reaction during 24 h in refluxing CF_3CH_2OH [7].) However, **2b** did react with both the acid and the alcohols, and the fact that it is much more reactive than **1b** suggests that even in media seemingly unfavourable for ionization of a triflate, formation of a cationic intermediate can be induced by the anchimeric assistance from the γ-Ph groups. Again, however, **2b** is less reactive than the corresponding iodide **2a**. Unless the presence of $CDCl_3$ has a seriously distorting effect, which is unlikely, it is puzzling that CF_3CO_2H, CF_3CH_2OH and $(CF_3)_2CHOH$ are all so much less effective than MeOH at promoting ionization of the triflates, in contrast to that of the iodides, since S_N1 reactions of adamantyl triflates (and *p*-toluenesulphonates) are much faster than those of corresponding iodides in both the fluorinated solvents and MeOH [8].

2.3. Reactions of the cyanates with MeOH

For studies of reactions of the cyanates again a Fourier transform NMR spectrometer had to be used, and so reactions were carried out in 10:1 CD_3OD–$CDCl_3$ evidently containing a little water. It was shown previously that **1c** reacts extremely selectively with traces of water in MeOH [1], and so it was not surprising that in the reactions in CD_3OD–$CDCl_3$ the products from all three cyanates were exclusively the corresponding hydroxides (containing Si–OD bonds). Reactions were not monitored continuously to yield first-order plots but the approximate extents of solvolysis after various times at 25°C were as follows: for **1c**, 30% after 40 min and 75% after 2.5 h; for **2c**, 35% after 35 min and 73% after 2.5 h; and for **3c**, 33% after 45 min. The rough values of $t_{1/2}$ (70–80 min) that can be derived from these results do not differ significantly, showing that the Ph groups do not provide assistance; this is in line with the conclusion that the methanolysis of **1c** involves direct nucleophilic attack at silicon [1], and indicates that this is also the case for **2c** and **3c**. The rate of reaction of the cyanate **2c**, at 25°C is ca. 60 times that of the iodide **2a** at 61°C, implying that the cyanate is > 600 times the more reactive.

3. Experimental section

Compounds **1a** [9], **1b** [1], **1c** [10], **2a** [6], **2b** [6], **2c** [11], **3a** [6] and **3c** [12] were prepared as described elsewhere.

Aldrich Gold-Label Anhydrous MeOH and MeCN were used as received; CF_3CH_2OH [4] and $(CF_3)_2CHOH$ [4] were dried as described previously; CF_3CO_2H was refluxed for 2 h with concentrated sulphuric acid, distilled out and redistilled from AgO_2CCF_3, with exclusion of moisture at all stages; CD_3OD was stored over 3A molecular sieve under argon before use.

The ^1H NMR spectra were recorded at 90 MHz on a Perkin-Elmer R32 spectrometer or, for reactions in CD_3OD, at 360 MHz on a Bruker WP360 instrument.

Mass spectra (at 70 eV) were obtained with a Kratos MS-25 spectrometer. For GLC–MS a column of 5% OV-101 on GasChrom (100–200 mesh) was used.

3.1. Preparation of $(Me_3Si)_2(PhMe_2Si)CSiMe_2OSO_2CF_3$ (3b)

A mixture of the iodide **3a** (0.20 g, 0.42 mmol) and $AgOSO_2CF_3$ (0.20 g, 0.78 mmol) in CH_2Cl_2 (20 cm^3) was stirred under dry nitrogen for 2 h at room temperature. The solution was then filtered and the solvent was evaporated from the filtrate to leave a solid, which was recrystallized from pentane to give **3b** (0.16 g, 80%): δ(H) ($CDCl_3$) 0.30 (18H, s, $SiMe_3$), 0.59 (6H, s, $SiMe_2Ph$), 0.64 ($SiMe_2O$), 7.2–7.8 (5H, m, Ph); *m/z* 485 (50%, M − Me), 423 (2%, M − Ph), 351 (10), 335 (95), 135 (60), 73 (100).

A similar procedure, but with Et_2O as solvent and stirring for only 0.5 h, gave essentially identical results.

*3.2. Reaction of the iodide **2a** and triflate **2b** with CF_3CH_2OH*

The iodide **2a** (0.010 g) was dissolved in $CDCl_3$ (0.10 cm^3) in an NMR tube and CF_3CH_2OH (0.30 cm^3) was added. The tube was capped and kept at 61°C. The ^1H NMR spectrum was recorded periodically in order to monitor the progress of the reaction. After 1 day the solvent was removed and the residue was taken up in $CDCl_3$ for recording of the ^1H NMR and mass spectra, which showed the product to be $(Me_3Si)_2[(CF_3CH_2O)_2MeSi)]CSiMe_2OCH_2CF_3$: δ(H) 0.17 (18H, s, $SiMe_3$), 0.19 (9H, s, $SiMe_2$ plus SiMe), 3.8 (6H, q, $J = 9.4$ Hz, CH_2CF_3); δ(F) −75.8 to −76.5 (m); *m/z* 541 (90%, M − Me), 457 (15, M − OCH_2CF_3), 301 (95), 213 (45), 209 (95), 193 (15), 143 (25), 73 (100, $SiMe_3$), 54 (25).

An identical result was obtained when a solution of **2b** in a mixture of $CDCl_3$ (0.10 cm^3) and CF_3CO_2H (0.50 cm^3) was kept at 61°C for 5 days.

3.3. Rate studies

(a) For reactions of the iodides **1a** and **2a** and triflates **1b** and **2b** (except for those with CD_3OD) a solution of the substrate (ca. 10 mg) in the relevant medium was made up in an NMR tube, which was then securely capped and placed either in the probe of the spectrometer or (for half-lives > 1 h) in a thermostatically controlled water-bath, from which it was removed at intervals for rapid recording of the spectrum. From the relative heights of the signals from the $SiMe_3$ protons in the substrate and product at various times, a first-order plot was constructed, and in all cases was satisfactorily linear over the range studied (usually at least 75% completion of the reaction). Unless indicated otherwise, the solution was kept at the reaction temperature for at least five half-lives and the product was identified from its ^1H NMR spectrum in the reaction mixture and, after isolation by evaporation of the solvent under reduced pressure, in CCl_4. Authentic samples of all the products were available. Specific details are as follows:

(i) For reactions with H_2O in MeCN–CCl_4, to a solution of the substrate in CCl_4 (0.100 cm^3) was added MeCN (0.375 cm^3) followed by H_2O (0.025 cm^3). The signals from $SiMe_3$ protons were at δ 0.36 for **1a**, 0.32 for **2a**, 0.20 for **1d** and 0.18 for **2d**.

(ii) For the reactions with H_2O in dioxane, to the substrate in an NMR tube was added dioxane (0.380 cm^3) followed by H_2O (0.020 cm^3). The signals from $SiMe_3$ protons were at δ 0.36 for **1a**, 0.38 for **2a**, 0.33 for **1b**, 0.38 for **2b**, 0.23 for **1d** and 0.21 for **2d**.

(iii) For the reactions in MeOH–CCl_4, MeOH (0.300 cm^3) was added to a solution of the substrate in CCl_4 (0.100 cm^3). The relevant $SiMe_3$ signals were at δ 0.36 for **1a**, 0.38 for **2a**, 0.23 for **1e** and 0.19 for **2e**.

(iv) For reactions in CF_3CH_2OH, the substrate was dissolved in $CDCl_3$ (0.100 cm^3), then CF_3CH_2OH (0.300 cm^3) and Et_3N (0.005 cm^3) were added. The signals from the $SiMe_3$ protons were at δ 0.38 for **2a**, 0.31 for **2b** and 0.24 for **2f**.

(v) For reaction of **1a** and **2b** with $(CF_3)_2CHOH$–$CDCl_3$, the solution was prepared as described for CF_3CH_2OH under (iv), but for **2a** the volume of $CDCl_3$ was 0.300 cm^3 and that of $(CF_3)_2CHOH$ was 0.100 cm^3. The signals from $SiMe_3$ protons were at δ 0.38 for **2a**, 0.32 for **2b** and 0.20 for **2e**. For **1a** in 3 : 1 $(CF_3)_2CHOH$–$CDCl_3$ and **1b** in 7 : 1 $(CF_3)_2CHOH$–$CDCl_3$, there was no reaction during 20 days at 45°C.

(vi) For reactions in CF_3CO_2H–$CDCl_3$, the substrate was dissolved in $CDCl_3$ (0.100 cm^3) and Et_3N (0.0050 cm^3) and CF_3CO_2H (0.300 cm^3) were added. The signals from $SiMe_3$ protons were at δ 0.36 for **1a**, 0.38 for **2a**, 0.29 for **1g** and 0.30 for **2g**. For the reaction of **1a** at 61°C, the reaction was stopped after 40 days and the recovered solid was shown to contain **1a** and **1f** in a ca. 85 : 15 ratio. In the case of **1b** there was no reaction during 10 days at 61°C, as shown by isolation of the recovered substrate and confirmation of its identity from its ^1H and ^{29}Si NMR spectra and the absence of ^{19}F signals.

(b) For the reactions of the iodides and triflates in CD_3OD–CCl_4, the substrate (10 mg) was dissolved in CCl_4 (0.050 cm^3) and CD_3OD (0.500 cm^3) was added. For the cyanates $CDCl_3$ was used in place of CCl_4. The solution was kept at the selected temperature (61°C for the iodides and triflates and 25°C for the cyanates) and the ^1H NMR spectrum was recorded at three or four points during the reaction. When both hydroxide (actually the OD species) and methoxide (actually the OCD_3 species) were formed, the combined height of the signals from the $SiMe_3$ protons of both was used in deriving the approximate extent of reaction.

The signals from the $SiMe_3$ protons were at δ 0.36 for **1a** and **3a**, 0.38 for **2a**, 0.33 for **1b**, 0.29 for **2b**, 0.30 for **3b** and **3c**, 0.26 for **1c** and **2c**, 0.20 for **1d′** and **2d′**, 0.19 for **3d′** and 0.23 for **1e′**.

After the last spectrum had been recorded, the identities of the products were confirmed by GLC–MS, which also gave the ratio of methoxide to hydroxide. From the iodides **2a** and **3a** only methoxides were formed, and from all three cyanates only hydroxides. For other substrates the approximate methoxide to hydroxide ratios were as follows: **1a**, 2.5 : 1; **1b**, 3 : 1; and **3b**, 6 : 1.

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