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Preparation and reactions of some organosilicon cyanates

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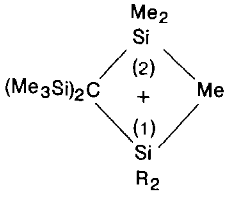
Abstract

Reactions of the iodides TsiSiRR'I (Tsi = $(Me_3Si)_3C$; RR' = Me_2, Me(OMe), $(OMe)_2$, Me(NCO)) with AgOCN in CH_2Cl_2 give the corresponding normal cyanates TsiSiRR'(OCN), which have been isolated but shown to isomerize when heated to give the corresponding isocyanates TsiSiRR'(NCO). Similar treatment of $TsiSiPh_2I$ gives the rearranged cyanate $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OCN)$, which also isomerizes to the isocyanate $(Me_3Si)_2C(SiPh_2Me)(SiMe_2NCO)$ when heated. Reaction of the less sterically-hindered iodide TsiSiMeHI with AgOCN in CH_2Cl_2 initially gives a mixture of the cyanate and isocyanate in solution but after more prolonged reaction only the isocyanate is present. The thermal isomerization of $TsiSiMe_2OCN$ (**1**) in Ph_2O (at 155–200 °C) is of second order with respect to **1**. The isomerization in CCl_4 is strongly catalysed by ICl, and the reaction is of second order with respect to both **1** and ICl. Isomerization occurs rapidly in MeOH containing NaOMe. Substitution to give the corresponding product $TsiSiMe_2X$ occurs rapidly and very predominantly when **1** is treated with salts MX, viz. NaN_3, CsF and KOCN in MeOH, but with LiCl under similar conditions some of the isocyanate is formed along with the chloride $TsiSiMe_2Cl$ and the related methoxide and hydroxide (the latter from traces of water). Reaction of **1** with KSCN in MeCN gives exclusively the substitution product $TsiSiMe_2NCS$, but CsF and NaN_3, which are only very slightly soluble, promote very predominant isomerization. Possible mechanisms of the isomerizations are discussed. Cyanate is a markedly better leaving group from silicon than iodide, and comparable with triflate.

Introduction

Ten years ago we reported briefly the first isolation of (normal) cyanates of silicon, all containing the very bulky group $(Me_3Si)_3C$ (subsequently denoted by Tsi), and showed that they readily isomerize to the corresponding isocyanates [1]. Later we noticed that the isomerization in solution was catalysed by a variety of reagents [2]. We delayed publication of the full details of the initial observations and of the results of further studies in the expectation of addressing further the questions remaining about the mechanism of the isomerization, but it now seems unlikely that we shall be able to undertake additional studies and so we present the available information below. We note that the cyanates Bu^tMe_2SiOCN [3] and Ph_3SiOCN [4] were probably generated in solution at low temperatures by reaction of the corresponding silanols with BrCN, but they were not isolated.



I

Results and discussion

Preparation and thermal isomerization

This study began when a solution of $TsiSiMe_2I$ in CH_2Cl_2 was stirred with an excess of AgOCN for 15 min, during which AgI separated. Work-up gave a white solid that analysed correctly for $TsiSiMe_2OCN$ (or, of course, $TsiSiMe_2NCO$) and which gave a ^1H NMR spectrum (in CCl_4) showing sharp singlets at δ 0.24 and 0.64 in a 9/2 integration ratio, and an IR spectrum showing a strong band at 2240 and a weaker one at 1160 cm^{-1}. When this solid was kept at 150 °C for 2 h the ^1H NMR singlets were replaced by others at δ 0.27 and 0.46, still in 9/2 ratio, and the IR band at

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2240 was replaced by a stronger band at 2280 cm^{-1} and the band at 1160 cm^{-1} had disappeared. The changes in the IR spectrum are very similar to those observed when alkyl cyanates isomerize to isocyanates [5], and we concluded that the initial product was the normal cyanate $TsiSiMe_2OCN$ (**1**) and that it underwent isomerization to the isocyanate $TsiSiMe_2NCO$ (**2**). (The isocyanate Me_3SiNCO gives a very strong ν(NCO) band at 2290 cm^{-1} [6].) Compound **2** had physical properties identical with those of an authentic sample obtained by reaction of $TsiSiMe_2I$ with KOCN in MeCN [7]. The two isomers gave virtually identical mass spectra. The isomers were later found to show substantial differences in their ^{13}C and ^{29}Si spectra (see Table 1).

The related iodides $TsiSi(OMe)_2I$, TsiSiMe(OMe)I and $TsiSiPh_2I$ were found to react with AgOCN to give the cyanates $TsiSi(OMe)_2OCN$, TsiSiMe(OMe)OCN and $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OCN)$, respectively. (The rearrangement involved in the formation of the last compound is of a well-established type for reactions of iodides $TsiSiR_2I$ with silver salts, AgY, the reaction being thought to involve abstraction of I^- by Ag^+ to give the methyl-bridged cation **I**, which can then be attacked by Y^- either at Si(1) to give $TsiSiMe_2Y$, or at Si(2) to give $(Me_3Si)_2(R_2MeSi)CSiMe_2Y$, the proportion of attack at the two centres being determined mainly by the relative degrees of steric hindrance [8].) All three cyanates showed bands in the IR spectrum at 2240 and 1160 cm^{-1}, and all were converted on heating at *c.* 160 °C into the corresponding isocyanates, giving IR bands at 2280 cm^{-1}. (It was noticed during recrystallization of $(Me_3Si)_2(Ph_2MeSi)CSiMe_2OCN$ that it was much less soluble in pentane or hexane than the isomeric isocyanate, and so recrystallization from pentane provides a convenient method of separating the isomers in this case, and possibly in others.)

When the less hindered iodide TsiSiMeHI was treated with AgOCN in CH_2Cl_2 at room temperature, after 20 min the IR spectrum of the solution showed IR bands at both 2240 and 2280 cm^{-1}, pointing to the presence of both the cyanate and the isocyanate, and the ^1H NMR spectrum was consistent with this. When after 1 h the solution was filtered and the solvent removed under vacuum the product was exclusively the isocyanate. Similar initial formation of a mixture of the cyanate and isocyanate, followed by isolation of only the latter, has also been observed in the reactions of the iodides TsiSiPhHI [9] and $[(PhMe_2Si)_3C]SiMe_2I$ [10]. In contrast, treatment of the very reactive chloride $(Me_3Si)_2(MeOMe_2Si)CSiMe_2Cl$ gave no detectable amount of the cyanate [11], perhaps because of rapid isomerization (see below).

TABLE 1. NMR chemical shift data for $TsiSiMe_2(OCN)$ (**1**) and $TsiSiMe_2(NCO)$ (**2**)[a]

Compound	Nucleus	Solvent	Me_3Si	Me_2Si	OCN or NCO
1	^1H	CCl_4	0.29	0.64	
2	^1H	CCl_4	0.27	0.46	
1	^{13}C	$CDCl_3$	4.61	4.27	109.87
2	^{13}C	$CDCl_3$	4.81	6.25	123.12
1	^{29}Si	$CDCl_3$	−1.48	38.11	
2	^{29}Si	$CDCl_3$	−1.31	0.13	

[a] All shifts are in ppm relative to $SiMe_4$. All the signals are singlets.

When the isocyanate TsiSiMeHNCO, obtained as indicated above, was treated with an excess of iodine in CH_2Cl_2 it was converted into the iodide TsiSiMeI(NCO), and reaction of the latter with AgOCN gave a solid whose ^1H and IR spectra (showing a band at 2260, with a shoulder at 2280, and a weaker one at 1170 cm^{-1}) were consistent with its being exclusively the mixed cyanate–isocyanate TsiSiMe(OCN)(NCO), though the presence of a little of the diisocyanate $TsiSiMe(NCO)_2$ could not be ruled out. The product was converted into the latter when heated at 160 °C.

$TsiSiMe_2OCN$ **1** $\qquad$ $TsiSiMe_2NCO$ **2**

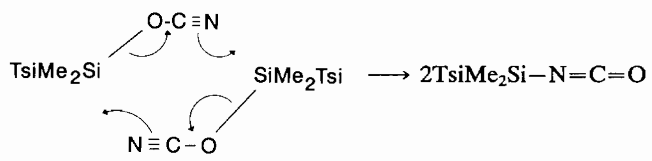
Mechanism of the thermal isomerization of 1

The rate of isomerization of **1** in Ph_2O was determined by measuring at intervals the ratio of the heights of the sharp singlets in the ^1H NMR spectrum from the $SiMe_2OCN$ and $SiMe_2NCO$ groups and taking this as a measure of the relative concentrations of the initial and isomerized species. (This measure is subject to significant error, especially when the concentration of one component is low, and the rate constants could be in error by as much as ±8%, but this does not affect the validity of the discussion below.) Usually the solution was kept in a sealed NMR tube, which was placed in a bath at the chosen temperature and removed briefly at intervals for rapid recording of the spectrum, but for some runs a larger volume of solution was kept in a closed vessel in the bath and samples were removed at intervals for recording of the spectra. The rates determined by the two methods were in satisfactory agreement, and good second order plots were obtained.

The second order rate constants, k_2, determined by the second method for 0.091 and 0.045 M solutions (i.e. one half the concentration of the other) were 7.3×10^{-4} and 7.2×10^{-4} $l\ mol^{-1}\ s^{-1}$ at 200±3 °C and the half-lives were 4.8 and 9.6 h; the doubling of the half-life upon halving of the initial concentration confirms the second order nature of the reaction. The values of k_2 determined by the first method for 0.091 and 0.0405 M solutions were 6.6×10^{-4} and 6.9×10^{-4}

$1\ mol^{-1}\ s^{-1}$, respectively, at 195±3 °C, and 1.02×10^{-4} and $1.08\times10^{-4}\ l\ mol^{-1}\ s^{-1}$ at 155±3 °C. The factor of *c.* 6.4 between the mean rate constants determined by the first method at 195 and 155 °C corresponds to a rough value of the activation energy of 76 kJ mol^{-1} and one of $\log(A/s^{-1})$ of *c.* 5.3.

The simplest interpretation of the second order kinetics is that two molecules of **1** are involved in a cyclic transition state, as shown in eqn. (1). The $\log A$ factor is consistent with (though not diagnostic of) such a process; e.g. the corresponding value of $\log A$ for the dimerization of cyclopentadiene is 5.7–8.1 and that for the combination of benzoquinone and cyclopentadiene is 5.4–7.0 [12], the specific value in each case being dependent upon the solvent used.



(1)

In terms of this mechanism the stabilization of the cyanates associated with the presence of the Tsi or related bulky group could be attributed to steric hindrance, since the silicon atoms are five-coordinate in the transition state. It is not obvious, however, how the mechanism could account for the fairly ready isomerization of $(PhMe_2Si)_3CSiMe_2OCN$ [10] and for the seeming instability of $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2OCN)$ implied by the exclusive formation of the isocyanate in the reaction of $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Cl)$ with AgOCN in CH_2Cl_2 [11].

An alternative mechanism that cannot be ruled out involves reversible ionization as in eqn. (2a), with the equilibrium lying far over to the left, and subsequent attack of the liberated ion $[NCO]^-$ on another molecule of the cyanate, as in eqn. (2b)*. The initial ionization would, of course, give a bridged anion of type **I**, but for convenience this is depicted simply as $[TisiSiMe_2]^+$ in eqn. (2a). The observed rate would be given by $k'_2[TsiSiMeOCN][NCO]^-$, and so by $k_2[TsiSiMe_2OCN]^2$, since for an equilibrium (2a) lying far to the left the concentration of $[NCO]^-$ would be proportional to the concentration of the cyanate.

$$TsiSiMe_2OCN \rightleftharpoons [TsiSiMe_2]^+ + [OCN]^- \qquad (2a)$$

$$[OCN]^- + TsiSiMe_2OCN \longrightarrow TsiSiMe_2NCO + [OCN]^- \qquad (2b)$$

Both steps are reasonable in the sense that: (i) the return of the $[OCN]^-$ to the cation $[TsiSiMe_2]^+$ would be expected to regenerate the normal cyanate, since the reaction of $TsiSiMe_2I$ with AgOCN is thought to involve attack of $[OCN]^-$ on the cation formed by abstraction of I^- by Ag^+; (ii) reaction of $TsiSiMe_2I$ with KOCN in MeCN gives only the isocyanate [5]; (iii) isomerization of **1** occurs rapidly in solution in MeCN containing KOCN. This mechanism would account for the relative ease of isomerization of $(PhMe_2Si)_3CSiMe_2OCN$ and the (seeming) instability of $(Me_3Si)_2(MeOMe_2Si)CSiMe_2OCN$, since γ-Ph and γ-OMe groups can provide anchimeric assistance (mild in the first case and very powerful in the latter) to the formation of the cation. (The fact that $(Me_3Si)_2(Ph_2MeSi)CSiMe_2OCN$ is apparently more stable than $(PhMe_2Si)_3CSiMe_2OCN$ could indicate that anchimeric assistance arising from three $PhMe_2Si$ groups is more effective than that from one Ph_2MeSi group.) There is, however, a problem with this mechanism, namely that if ionization takes place at the required rate in diphenyl ether at high temperature it would be expected to occur readily in a good ionizing solvent such as MeCN and CF_3CH_2OH, whereas no isomerization was observed in the former solvent in 7 days at 60 °C or in the latter in 48 h at 35 °C. We thus cannot decide between the two mechanisms considered, and it is possible, of course, that neither is correct.

Isomerization catalysed by electrophiles

During studies of the reactions of the cyanates with a range of reagents it was found that addition of a little ICl or IBr to a solution of **1** in CCl_4 caused rapid isomerization, and this was studied in the case of ICl. A solution of **1** in CCl_4 containing ICl was kept at 35 °C in an NMR tube (in the spectrometer) and the ratio of cyanate to isocyanate determined at intervals in the usual way. In runs involving 0.40 M ICl and initial concentrations of **1** of 0.045 and 0.90 M, good second order plots were obtained up to *c.* 70% completion of reaction and gave second order rate constants, k_2, of 3.7×10^{-4} and $3.9\times10^{-4}\ l\ mol^{-1}\ s^{-1}$, respectively, with half-lives of 9.5 and 5.0 min. When the initial concentration of **1** was kept constant at 0.090 M and the concentration of ICl varied from 0.050 to 0.100 to 0.200 to 0.40 M, again good second order plots were obtained in all cases, and the derived values of $10^4\times k_2$ were 4.8, 20, 90, and 370 s^{-1}, respectively. Thus for each doubling of the concentration of ICl there was an approximate four-fold increase in the rate, indicating second order dependence on the ICl concentration. (Overall, on going from 0.050 to 0.40 M ICl the value of k_2 rose by a factor of 77, compared with one of 64 expected for exact second order dependence.) We note that the available data do not rule out the possibility

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*The isomerization of EtOCN is considered to proceed via an ion-pair (D. Martin, H.-J. Niclas and D. Habisch, *Justus Liebigs Ann. Chem.*, *727* (1969) 10).

that processes of first, second, and third order with respect to ICl are operating (giving rise by chance to apparent second order dependence in the range examined), perhaps involving the species $(ICl)_n$ with $n = 1–3$. (High orders with respect to halogens and interhalogens are often observed for reactions in nonpolar media and may be attributable to the presence of, for example, the species $(I_2)_n$, $(ICl)_n$, etc. (see ref. 13). However, the simplest interpretation of the results is that complexes **1**·ICl are involved, either in the cyclic process analogous to that depicted in eqn. (1) or in the ionization process shown in eqn. (3) (with equilibria (3a) and (3b) both lying well over to the left.

$$\mathrm{TsiSiMe_2OCN + ICl \rightleftharpoons TsiSiMe_2OCN \cdot ICl} \qquad (3a)$$

$$\mathrm{TsiSiMe_2OCN \cdot ICl \rightleftharpoons [TsiSiMe_2]^+ + [OCN \cdot ICl]^-} \qquad (3b)$$

$$\mathrm{[OCN \cdot ICl]^- + TsiSiMe_2OCN \cdot ICl \longrightarrow TsiSiMe_2NCO + ICl + [OCN \cdot ICl]^-} \qquad (3c)$$

Alternatively, the steps could be as in eqn. (2) but with $(ICl)_2$ assisting the initial ionization.

$$\mathrm{TsiSiMe_2OCN + (ICl)_2 \rightleftharpoons [TsiSiMe_2]^+ + [OCN(ICl)_2]^-} \qquad (4)$$

In both cases the function of the ICl is to stabilize the leaving $[OCN]^-$ anion, either as $[OCN \cdot ICl]^-$ (analogous to I_3^-) or $[OCN(ICl)_2]^-$ (analogous to I_5^-).

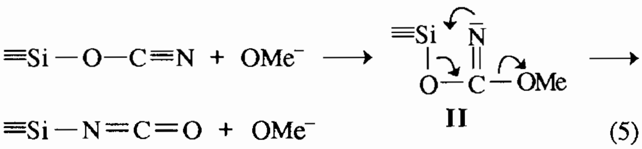
The isomerization of **1** was also found to be catalysed by acetyl chloride. Thus when **1** (0.30 mmol) was dissolved in a 1/2 vol./vol. mixture (1 cm^3) of MeCOCl and $CDCl_3$ in an NMR tube, by the time the ^{1}H NMR spectrum could be recorded about 30% of **1** had been converted into the isocyanate. Work-up after 1 h at 35 °C gave a solid which from analysis by linked GLC-MS appeared to be a 30/70 mixture of the isocyanate and the hydroxide $TsiSiMe_2OH$. The latter could have come from hydrolysis of **1** during work-up, but this would imply that after the initial rapid formation of 30% of the isocyanate there was no further isomerization. It is possible that the MeCOCl was not the real catalyst (hydrogen chloride, for example, could have been formed from traces of water present), but we did not consider the system worthy of further study.

Reactions with nucleophiles

The results of a detailed study of the solvolysis of **1** in MeOH or MeCN containing water will be presented elsewhere. For the present purposes it suffices to say that in both MeOH and MeCN dried by conventional methods, at the low initial concentrations of **1** used there was enough water present to cause some hydrolysis. In the MeOH used the half-life for the (overall) solvolysis at 35 °C was *c*. 42 min, and the product a 9/1 mixture of $TsiSiMe_2OMe$ and $TsiSiMe_2OH$ [14].

When NaOMe was present in the MeOH the isocyanate was the greatly predominant product. With 0.060 M **1** and 0.10 or 0.25 M NaOMe the overall disappearance of **1** showed good first order kinetics up to 70% completion of reaction (in the later stages significant amounts of the NaOMe are neutralized by the HOCN generated by the solvolyses), and the observed overall first order rate constants were 1.3×10^{-2} and 3.2×10^{-2} s^{-1}, respectively. The final product mixture consisted of $TsiSiMe_2NCO$, $TsiSiMe_2OMe$, and $TsiSiMe_2OH$ in approximate ratios of 7/2/1 and 8/1/1 in 0.10 and 0.25 M NaOMe respectively, and thus the isomerization contributes a value of *c*. 0.91×10^{-2} and 2.56×10^{-2} s^{-1}, respectively, in the two media. The rate of isomerization is thus increased by a factor of *c*. 2.8 for a 2.5-fold increase in the NaOMe concentration, satisfactorily consistent with first order dependence on the latter. The overall rates of disappearance of **1** in the 0.10 and 0.25 M NaOMe solutions are *c*. 4.7 and 11.5 times that in MeOH alone. The base evidently very effectively diverts the reaction from solvolysis to isomerization.

We suggest that the catalysis of the isomerization by NaOMe involves initial nucleophilic attack of MeO^- on the carbon atom of the OCN group to give the intermediate anion **II**, which then gives the isocyanate with loss of MeO^- (eqn. 5). The rate-determining step could either be the initial attachment of the MeO^- anion, with subsequent rapid isomerization by breakdown of the intermediate, or as we think more likely, in the latter process after formation of the intermediate in rapid reversible ionization in an equilibrium lying far over to the left.



II

(5)

When a sample of **1** (0.30 mmol) was treated with a solution of NaN_3 (15 mmol) or KOCN (25 mmol) in MeOH (10 cm^3), or with KSCN (41 mmol) in MeCN (1 cm^3) reaction was complete within 5 min at room temperature as judged from the ^{1}H NMR spectrum, and the products were exclusively $TsiSiMe_2N_3$, $TsiSiMe_2NCO$ and $TsiSiMe_2NCS$, respectively. These substitutions took place very much more rapidly than those of $TsiSiMe_2I$ under comparable conditions [7] (the reactivity difference involves a factor of at least 300 in the case of KSCN), illustrating the very high lability of the Si–OCN bond, which is, indeed, comparable with that of the $Si–OClO_3$ bond. (In methanolysis **1** is approximately as reactive as the triflate $TsiSiMe_2OSO_2CF_3$ [14].)

The outcomes of the reactions of **1** with various salts in MeOH or MeCN (both dried by standard methods but evidently still containing significant amounts of water) during 1 h at room temperature were investigated. (In at least some cases the primary reactions were probably complete in a much shorter time.) The compositions of the product mixtures, as determined by linked analysis by GLC-MS, supplemented by ^1H NMR data, are indicated in Table 2. (The siloxane $(Me_3Si)_2CHSiMe_2OSiMe_3$, shown in Table 2 as A, is produced by base-catalysed rearrangement of initially-formed $TsiSiMe_2OH$ [15].)

In MeOH, CsF, NaN_3, and KSCN give high yields of the direct substitution products $TsiSiMe_2X$, the azide being especially effective. Sodium iodide gives no substitution product (I^- is very weakly nucleophilic towards silicon) but does induce a little isomerization, whereas LiCl gives substantial amounts of substitution and isomerization products along with solvolysis products. The formation of the isocyanate $TsiSiMe_2NCO$ in the presence of KOCN can reasonably be assumed to come partly from direct substitution and partly from base-induced isomerization of **1**, the presence of base (generated from a salt formed from a strong base and weak acid) being reflected in the base-catalysed formation of a substantial amount of the siloxane $(Me_3Si)_2CHSiMe_2OSiMe_3$.

In MeCN, NaI again gives no substitution product but *c.* 12% of the isocyanate, though hydrolysis greatly predominates. Again LiCl gives substantial amounts of substitution and isomerization products, but in this case, there is only 5% of the hydroxide and some 32% of an unidentified component. The high proportion of isomerization induced by CsF and NaN_3 is probably due to formation of hydroxide ion from the very small amount of the salts that dissolve, and the presence of the rearranged $(Me_3Si)_2CHSiMe_2OSiMe_3$ along with the hydroxide is consistent with this. In contrast, KSCN which is much more soluble, gives exclusively the substitution product, as does KOCN, though in this case it is possible that some of the isocyanate comes from the base-catalysed isomerization.

TABLE 2. Approximate percentage compositions of the product mixtures formed in reactions of $TsiSiMe_2I$ (RI) with salts MX in MeOH or MeCN

MX	RX	RNCO	ROH	ROMe	A[a]
In MeOH					
LiCl	43	27	15	15	0
NaI	0	2	55	43	0
CsF	86	0	7	7	0
NaN_3	100	0	0	0	0
KOCN	40	[b]	11	8	22
KSCN	82	0	7	0	11
In MeCN					
LiCl[c]	32	31	5	0	0
NaI	0	12	88	0	0
CsF	2	80	12	0	6
NaN_3	0	94	6	0	0
KOCN	(100)[b]	[b]	0	0	0
KSCN	100	0	0	0	0

[a] $(Me_3Si)_2CH(SiMe_2OSiMe_3)$. [b] Some of the RNCO could have been formed by catalysed isomerization rather than substitution. [c] An additional product (32%) was unidentified.

Presumably all the anions catalyse the isomerization in the way suggested above for the methoxide ion (eqn. (7)). The relative amounts of substitution and isomerization products will then be related to the relative ease of nucleophilic attack on the silicon and on the carbon atom of the OCN group. Towards silicon, I^- is exceptionally weakly nucleophilic whereas F^-, N_3^-, and to a lesser extent $[SCN]^-$, are very strongly nucleophilic, and so in solutions in which these ions are present in substantial concentration (as in MeOH, and in the case of $[SCN]^-$ in MeCN) substitution greatly predominates and there is no detectable isomerization. In contrast methoxide ion, in this system at least, is, as we have seen above, much less effective in bringing about substitution, and this is consistent with the earlier (still puzzling) observation that NaOMe does not significantly accelerate the methanolysis of other compounds $TsiSiMe_2X$ in which X is an exceptionally good leaving group, viz. ClO_4, SO_2CF_3, and I [16].

Finally it should be mentioned that the isocyanate **2** is inert under the conditions used for all the reactions of **1** described above.

Experimental

Starting materials and solvents

The following were prepared by published methods: $TsiSiPh_2I$ [17], $TsiSiMe_2I$ [18], TsiSiMe(OMe)I [18], $TsiSi(OMe)_2I$ [18], TsiSiMeHI [18]. The salts LiCl, NaI, NaN_3, KOCN, KSCN and CsF were of analytical grade and were dried at 110° for 2 h followed by 6 h at 60 °C under vacuum (0.1 mm Hg). Because we had sometimes found commercially supplied AgOCN to be ineffective in reactions with sterically hindered organosilicon iodides we routinely used freshly prepared samples made from aqueous $AgNO_3$ and KOCN and carefully dried, but we observed that the material made in this way did not significantly lose its effectiveness when kept away from light in a closed vessel for several months.

Methanol was dried by refluxing over and distillation from $Mg(OMe)_2$; it was usually distilled in this way immediately before use, but sometimes stored over 3

Å molecular sieves. Acetonitrile was boiled with CaH_2 for 2 h, distilled out, and either used immediately or stored over 4 Å molecular sieves. (In one experiment Aldrich Gold Label anhydrous MeCN was used, and clearly contained less water than that we had treated in this way.) Methylene chloride was refluxed with $CaCl_2$ then distilled and kept over 4 Å molecular sieves.

Spectra

The ^1H NMR spectra were recorded either at 60 MHz on a Perkin-Elmer R12 spectrometer or at 90 MHz on a Perkin-Elmer R32 spectrometer; for isolated compounds solutions in CCl_4 containing $CHCl_3$ or CH_2Cl_2 as lock and internal standard were used. The ^{13}C NMR spectra were recorded as solutions in $CDCl_3$ at 90.5 MHz on a WM 360 spectrometer, and ^{29}Si spectra with solutions in $CDCl_3$ at 71.5 MHz on a Bruker WM 360 spectrometer.

The IR spectra were recorded as Nujol mulls between NaCl plates on a Perkin–Elmer 157G spectrophotometer. Mass spectra were recorded by electron impact at 70 eV.

Gas-liquid chromatography: a column of 3% OVIOI on Chromasorb G at 180 or 200 °C was used with a Pye Unicam GCD chromatograph.

Syntheses and isomerizations

$TsiSiMe_2OCN$ (1)

A mixture of $TsiSiMe_2I$ (0.50 g, 1.2 mmol) and AgOCN (0.225 g, 1.50 mmol) in CH_2Cl_2 (25 cm^3) was stirred vigorously under nitrogen, with protection from light, for 1 h. The solution was filtered and evaporated under reduced pressure to leave the cyanate $TsiSiMe_2OCN$ (0.37 g, 93%) as a white solid. *Anal.* Found: C, 47.2; H, 10.2. Calc. for $C_{13}H_{33}ONSi_4$: C, 47.1; H, 10.0%. δ(H) 0.29 (s, 27H) and 0.64 (6H); ν(OCN) 2240 and 1160 cm^{-1}; *m/z* 316 (100%, $[M-Me]^+$), 289 ($[M-OCN]^+$), 275, 228, 201, 100 ($[Me_2SiOCN]^+$), 73, 59.

When a sample (50 mg) of the above material was kept in a sealed tube at 150 °C for 2 h it was converted quantitatively into the isocyanate $TsiSiMe_2NCO$, m.p. > 300 °C. *Anal.* Found: C, 47.3; H, 10.1. δ(H) 0.27 (s, 27H) and 0.46 (s, 6H); ν(NCO) 2280 cm^{-1}; the mass spectrum showed the same peaks as that for the cyanate, with slightly different relative intensities.

$(Me_3Si)_2C(SiMePh_2)(SiMe_2OCN)$

A mixture of $TsiSiPh_2I$ (1.0 g, 1.90 mmol) and AgOCN (0.30 g, 2.0 mmol) in CH_2Cl_2 (30 cm^3) was stirred for 1 h at room temperature. The solution was dried and then evaporated under vacuum to leave a white solid, which was recrystallized from n-pentane and shown to be the cyanate $(Me_3Si)_2C(SiMePh_2)(SiMe_2OCN)$ (0.59 g, 68%). δ(H) 0.19 (s, 18H, $SiMe_3$), 0.34 (s, 6H, $SiMe_2OCN$), 0.97 (s, 3H, $SiMe_2Ph$), 7.2–8.0 (m, 10H, Ph); ν(OCN) 2240 and 1160 cm^{-1}.

A sample of the cyanate (0.4 g) was kept under N_2 in a sealed tube at 160 °C for 2 h and the solid then recrystallized from EtOH to give the isocyanate $(Me_3Si)_2C(SiMePh_2)(SiMe_2NCO)$ (85%). δ(H) 0.29 (s, 18H), 0.38 (s, 6H), 1.00 (s, 3H), 7.2–8.0 (m, 10H); ν(NCO) 2280 cm^{-1}.

TsiSiMe(OMe)(OCN)

A solution of TsiSiMe(OMe)I (25 mg) in CH_2Cl_2 (2.5 cm^3) was stirred with AgOCN (25 mg) for 1 h at room temperature. The solution was filtered and the solvent evaporated under reduced pressure to leave exclusively the cyanate TsiSiMe(OMe)(OCN). δ(H) 0.23 (s, 27H), 0.61 (s, 3H, SiMe), 3.65 (s, 3H, OMe); ν(OCN) 2240 and 1160 cm^{-1}.

A sample of the cyanate (15 mg) was kept at 160 °C in a Schlenk tube for 3 h (from time to time sublimed material was scraped down to the bottom of the tube). The product was judged to be exclusively the isocyanate TsiSiMe(OMe)(NCO). δ(H) 0.22 (s, 27H), 0.42 (s, 3H), 3.47 (s, 3H); ν(NCO) 2280 cm^{-1}.

$TsiSi(OMe)_2OCN$

A mixture of $TsiSi(OMe)_2I$ (50 mg) and AgOCN (50 mg) in CH_2Cl_2 (2.5 cm^3) was stirred for 1 h at room temperature. The solution was filtered and the solvent evaporated to leave a white solid, which was judged to be exclusively the cyanate $TsiSi(OMe)_2(OCN)$. δ(H) 0.24 (s, 27H), 3.80 (s, 6H); ν(OCN) 2240 and 1160 cm^{-1}.

A sample (30 mg) of the cyanate was kept in a Schlenk tube at 160 °C for 2 h (sublimed material being scraped down to the bottom of the tube from time to time). The product was judged to be exclusively the isocyanate $TsiSi(OMe)_2(NCO)$. δ(H) 0.21 (s, 27H), 3.66 (s, 6H); ν(NCO) 2280 cm^{-1}.

Reaction of TsiSiMeHI and AgOCN

A mixture of TsiSiMeHI (50 mg) and AgOCN (50 mg) in CH_2Cl_2 (2.5 cm^3) was stirred at room temperature. After 20 min a sample was removed and its ^1H and IR spectra were recorded; the ^1NMR spectra showed, along with the peaks attributable to the isocyanate (see below), peaks at δ(H) 0.36 (s) and 0.79 (d) attributable to the cyanate TsiSiMeH(OCN), and the IR spectrum correspondingly showed, alongside the band at 2280 cm^{-1} from the isocyanate, a band at 2240 cm^{-1} attributable to the cyanate (the weaker band expected at 1160 cm^{-1} was not observable). The solution was stirred for a further 40 min and then filtered and evaporated to leave a white solid that was judged to be exclusively the isocyanate TsiSiMeH(NCO). δ(H)

0.35 (s, 27H), 0.53 (d, 6H), 4.22 (m 1H); ν(NCO) 2280 cm^{-1}, ν(SiH) 2140 cm^{-1}.

TsiSiMeI(NCO), TsiSiMe(OCN)(NCO) and TsiSiMe(NCO)$_2$

A mixture of the isocyanate TsiSiMeH(NCO) obtained as described in the preceding experiment and an excess of iodine in CH_2Cl_2 (5 cm^3) was stirred at room temperature for 4 h. The solution was subsequently shaken with aqueous sodium bisulfite to remove the residual iodine then dried ($MgSO_4$) and evaporated to leave a white solid that was judged to be TsiSiMeI(NCO). δ(H) 0.47 (s, 27H), 1.22 (s, 3H); ν(NCO) 2275 cm^{-1}.

The product was stirred with an excess of AgOCN for 2 h at room temperature and the solution then filtered and evaporated under reduced pressure to leave a white solid that was judged to be the cyanate–isocyanate TsiSiMe(OCN)(NCO). δ(H) 0.39 (s, 27H), 0.68 (s, 3H); ν(OCN) 2260 and 1170 cm^{-1}, with a shoulder at 2280 cm^{-1} due to ν(NCO).

When the cyanate–isocyanate was kept in a Schlenk tube at 160 °C for 3 h (with sublimate scraped back at intervals as usual) the product was judged to be the di-isocyanate TsiSiMe$(NCO)_2$. δ(H) 0.29 (s, 27H), 0.51 (s, 3H); ν(NCO) 2280 cm^{-1}.

Kinetics of thermal isomerization

Solutions of **1** in diphenyl ether (0.5 cm^3) were kept in a closed NMR tube in a silicone oil bath maintained (±3 °C) at the chosen temperature. The tube was transferred at intervals to the probe of the NMR spectrometer for recording of the ^1H NMR spectrum then returned as quickly as possible to the oil bath. The ratio of the heights of the singlets at δ 0.29 and 0.27 was taken as a measure of the ratio of the concentrations of the cyanate and isocyanate, and the concentration [**1**] of the remaining cyanate thus calculated. Plots of $[\mathbf{1}]^{-1}$ against time were very satisfactorily linear upto at least 70% completion of the reaction. The values of the rate constants at various initial concentrations of **1** and three temperatures are given in 'Discussion'.

Following the reaction involving initially 0.91 M **1** at 200 °C, after *c*. 40 h examination of the solution by linked GLC-MS showed that $TsiSiMe_2NCO$ and the hydroxide $TsiSiMe_2OH$ were present in *c*. 95/5 ratio, the hydroxide coming from hydrolysis of unchanged cyanate.

Kinetics of the isomerization catalysed by ICl

A weighed sample of the cyanate in an NMR tube was dissolved in CCl_4 (0.50 ml) containing ICl and the tube was then closed and placed in the probe of the NMR spectrometer at 35±1 °C. The variation of concentration of the cyanate with time was monitored by recording the ^1H NMR spectrum at intervals, as described for the thermal isomerization. Very satisfactory plots of $[\mathbf{1}]^{-1}$ against time were obtained up to 75% completion of the reaction. (There were complications at longer times with the higher concentrations of ICl, probably because of some cleavage of Si–Me bonds (cf. ref. 19).) The results are presented in 'Discussion'.

Catalysis of the isomerization by MeCOCl

A sample (10 mg) of **1** was dissolved in a 2/1 vol./vol. mixture of $CDCl_3$/MeCOCl in an NMR tube, which was then closed and kept at 35 °C in the probe of the spectrometer. After 1 h the ^1H spectrum indicated that the cyanate and isocyanate were present in *c*. 7/3 ratio. The solvent was removed under reduced pressure and the residue examined by linked GLC-MS, which revealed that $TsiSiMe_2OH$ and $TsiSiMe_2NCO$ were present in *c*. 7/3 ratio (the silanol presumably coming from hydrolysis of residual **1**).

Catalysis of the isomerization by NaOMe in MeOH

(i) A sample of **1** (0.30 g) was dissolved in a small drop of CCl_4 and 0.10 M NaOMe–MeOH (5 cm^3) was added. The mixture was stirred then kept at room temperature (*c*. 21 °C) for 3 h. Hexane was then added followed by water, and the organic layer was separated, shaken several times with water, dried ($MgSO_4$) and evaporated under vacuum to leave a white solid, the NMR spectrum (CCl_4) of which included a large peak at δ 0.27 and a smaller one at δ 0.23. Analysis by linked GLC-MS indicated that the solid contained $TsiSiMe_2NCO$, $TsiSiMe_2OMe$, and $TsiSiMe_2OH$ in ratio of *c*. 7/2/1.

(ii) When the preceding experiment was repeated but with 0.25 M NaOMe–MeOH, the same products were formed in a ratio of *c*. 8/1/1.

(iii) A sample of **1** (10 mg, 0.030 mmol) was dissolved in a small drop of CCl_4 in an NMR tube and 0.10 or 0.25 M NaOMe in MeOH (0.50 cm^3) was added. The tube was closed, shaken, and placed in the probe of the NMR spectrometer at 35 °C. The progress of the reaction was monitored by determining the relative heights of the signals from the protons of the $SiMe_2OCN$, $SiMe_2NCO$, $Si\mathit{Me}_2OMe$ and $Si\mathit{Me}_2OH$ groups, and calculating the proportion of **1** remaining. A good first order plot was obtained up to 75% disappearance of **1**. The results are presented in 'Discussion'.

Reactions of 1 with alkali metal salts

For all these experiments authentic samples of the products were available.

(i) A mixture of **1** (0.30 mmol) and NaN_3 (15 mmol) in MeOH (10 cm^3) was stirred at room temperature for 5 min, and the ^1H NMR spectrum was then recorded.

It showed the presence of exclusively $TsiSiMe_2N_3$ (with no detectable signals from $TsiSiMe_2OMe$, $TsiSiMe_2OH$ or $TsiSiMe_2NCO$).

(ii) A sample of **1** (0.30 mmol) was stirred for 5 min at room temperature with MeCN (10 cm^3) containing either KOCN (25 mmol, only a small part of which dissolved) or KSCN (41 mmol). The ^1H NMR spectrum revealed that $TsiSiMe_2NCO$ or $TsiSiMe_2NCS$ was the sole product.

(iii) A mixture of an excess of the relevant salt MX, LiCl, 5.0 g; NaI, 12 g; CsF, 5 g; NaN_3, 1.0 g; KOCN, 2.0 g; KSCN, 4.0 g) with MeOH (10 cm^3) or MeCN (10 cm^3) was boiled for 0.5 h under reflux (with exclusion of moisture) to give a saturated solution. The solution was cooled to room temperature then added to **1** (0.10 g) dissolved in a drop of CCl_4. The mixture was stirred at room temperature for 1 h then diluted with water. Extraction three times with pentane was followed by drying ($MgSO_4$) and filtration of the extract and removal of the solvent under vacuum. The white solid left was subjected to analysis by GLC-MS; the products were identified from their retention times and mass spectra, authentic samples being available in all cases. It was assumed that the peak areas were proportional to the molar amounts of the products. The results are set out in Table 2.

Stability of 1 in MeCN and CF_3CH_2OH

(i) A relatively large sample (100 mg, 0.30 mmol) of **1** was dissolved in an NMR tube in 0.50 cm^3 of MeCN that had been dried in the usual way. The tube was sealed then kept in a bath at 60 °C for 1 h, after which the ^1H NMR spectrum indicated that only $TsiSiMe_2OH$ was present.

(ii) The procedure described under (i) was repeated but with Aldrich Gold Label anhydrous MeCN and recording of the ^1H NMR spectrum at intervals. There was no detectable change during 7 days.

(iii) Trifluoroethanol (0.5 cm^3) was added to a sample of **1** (10 mg) in an NMR tube and sufficient CH_2Cl_2 was added to bring all the solid into solution. There was no change in the ^1H NMR spectrum during 48 h at room temperature.

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