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# The mechanism of the isomerization of organosilicon cyanates to isocyanates

Abdulrahman I. Almansour<sup>a,\*</sup>, G. Adefikayo Ayoko<sup>b</sup>, Colin Eaborn<sup>b,\*</sup>

<sup>a</sup> Department of Chemistry, King Saud University, PO Box 2455, Riyadh-11451, Saudi Arabia
<sup>b</sup> School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

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### Abstract

Isomerization of the cyanate  $(Me_3Si)_3CSi(CD_3)_2OCN$  in the molten state at 150°C gives the unrearranged isocyanate  $(Me_3Si)_3CSi(CD_3)_2NCO$  and the rearranged isocyanate  $(Me_3Si)_2[(CD_3)_2MeSi]CSiMe_2NCO$  in a ratio of ca. 75/25, and isomerization in solution in Ph<sub>2</sub>O at 220°C gives the same products in a ratio of ca. 85/15. The occurrence of a significant amount of rearrangement is consistent with a mechanism involving initial ionization of the cyanate. In contrast, no rearrangement accompanies the isomerization in CCl<sub>4</sub> catalyzed by ICl, indicating that ionization is not involved; this conclusion is supported by the observation that the isomerization of  $(Me_3Si)_2(PhMe_2Si)CSiMe_2OCN$ , in which the Ph group would provide anchimeric assistance to ionization, proceeds at a similar rate to that of  $(Me_3Si)_3CSiMe_2OCN$ .

Keywords: Silicon; Cyanate; Isomerization, Mechanism

# **1. Introduction**

When the first silicon cyanates were made, in 1982, it was observed that when heated they underwent isomerization to the corresponding isocyanates [1]. In the case of the compound (Mc<sub>3</sub>Si)<sub>3</sub>CSiMe<sub>2</sub>OCN, a later kinetic study showed that for a solution in Ph<sub>2</sub>O at 150–200°C the isomerization to the isocyanate (Me<sub>1</sub>Si)<sub>1</sub>CSiMe<sub>2</sub>NCO was of second order, and two possible mechanisms were considered [2,3]. The first of these, shown in Scheme 1, involved a cyclic bimolecular transition state. The second, shown in Scheme 2, involved reversible ionization to an Me-bridged cation I, followed by nucleophilic attack of the ion [OCN]<sup>-</sup> through its N centre, on a molecule of (Me<sub>3</sub>Si)<sub>3</sub>CSiMe<sub>2</sub>-OCN with displacement of another ion [OCN]<sup>-</sup>. (The cyanate (Me<sub>3</sub>Si)<sub>3</sub>CSiMe<sub>2</sub>OCN is very rapidly isomerized by KOCN in MeCN [3].) If the ionization equilibrium lay far over to the left, then the concentration of [OCN]<sup>-</sup> would be proportional to that of (Me<sub>3</sub>Si)<sub>3</sub>CSiMe<sub>2</sub>OCN and so the reaction would be of second order. (The implicit assumption that recombina-

tion of I and [OCN]<sup>-</sup> always gives cyanate is in line with the fact that reaction of (Me<sub>1</sub>Si)<sub>1</sub>CSiMe<sub>2</sub>I with AgOCN via I gives only the cyanate; furthermore, isomerization to the isocyanate by re-attachment of [OCN]<sup>-</sup> to I through its N centre would be a first order process.) This mechanism had the advantage that it could account for the fact that the cyanate (PhMe<sub>2</sub>Si)<sub>3</sub>CMe<sub>2</sub>OCN, in which the Ph groups could provide anchimeric assistance to the leaving of [OCN]<sup>~</sup> [4], undergoes isomerization more readily than (Me<sub>3</sub> Si)<sub>1</sub>CSiMe<sub>2</sub>OCN [5], and that (Me<sub>1</sub>Si)<sub>2</sub>(MeOMe<sub>2</sub>Si) CSiMe<sub>2</sub>OCN could not be obtained by the method used for other cyanates, presumably because of the powerful assistance to ionization by the OMe group [6]. Furthermore, this mechanism could be adapted to acccount for the fact that the isomerization in CCl<sub>4</sub> was catalyzed by ICl, since the latter could be expected to assist the leaving of [OCN]<sup>-</sup> by forming complex ions such as  $[(OCN)ICI]^{-}$  or  $[(OCN)(ICI)_{2}]^{-}$  [3].









We (with others) recently made the deuteriumlabelled iodide  $(Me_3Si)_3CSi(CD_3)_2I$ , and showed that in its reactions with silver salts AgY some of the rearranged product (Me<sub>3</sub>Si)<sub>2</sub>[(CD<sub>3</sub>)<sub>2</sub>MeSi]CSiMe<sub>2</sub>Y was produced along with unrearranged (Me<sub>3</sub>Si)<sub>3</sub>CSi- $(CD_3)_2 Y$  [7], in accord with the view that such reactions for iodides of the type (Me<sub>3</sub>Si)<sub>3</sub>CSiR<sub>2</sub>I involve formation of the methyl-bridged cations similar to I, which can be attacked by  $Y^-$  at either the (original)  $\alpha$ -Si or the  $\gamma$ -Si centre [8,9]. If the bridged ion were fully formed and free from association with an anion then equal amounts of the unrearranged  $(Me_3Si)_3CSi(CD_3)_2Y$ and rearranged (Me<sub>3</sub>Si)<sub>2</sub>[(CD<sub>3</sub>)<sub>2</sub>MeSi]CSiMe<sub>2</sub>Y would be expected; however, in practice, in most cases the unrearranged product was found to predominate, and possible reasons for this were discussed [7]. The proportion of rearrangement was especially low for reactions in  $Et_2O$ , and this meant that the labelled cyanate (Me<sub>3</sub>- $Si_3CSi(CD_3)_2OCN$ , 1, containing only a small percentage of the rearranged isomer  $(Me_1Si)_2[(CD_1)_2MeSi]$ -CSiMe<sub>2</sub>OCN, 2, could be obtained by treatment of  $(Me_1Si)_1CSi(CD_1)_1$  with AgOCN in ether. We have now used the cyanate 1 thus made available to investigate further the thermal and ICI-catalyzed isomerization of the cyanates. For convenience, we subsequently use the term isomerization for the conversion of cyanate into isocyanate and the term rearrangement for the migration of an Me group.

# 2. Results and discussion

#### 2.1. Thermal isomerization

If the thermal isomerization of 1 proceeded by the mechanism shown in Scheme 1 for the unlabelled cyanate, then (unless there were an incidental rearrangement of 1 to the cyanate not on the main reaction path, which seems unlikely) the isocyanate would be wholly unrearranged  $(Me_3Si)_3CSi(CD_3)_2NCO, 3$ . In contrast, if the ionization mechanism shown in Scheme 3 operated, then return of cyanate ion to the cation II would give both unrearranged cyanate 1 and rearranged cyanate 2, and depending on the balance between such return and the attack of the  $[OCN]^-$  ion on another molecule of 1 to give unrearranged isocyanate 5 there would be more or less rearranged isocyanate formed. In fact we

found that when a sample of 1 (containing 4% of the rearranged 2) in a sealed tube was kept at 150°C for 2 h, all the cyanate was converted into an approximate 75/25 mixture of the isocyanates 3 and 4; a little of the 4 would have come from the 2 initially present, but it appears that the isomerization is accompanied by ca.  $21 \pm 5\%$  of rearrangement. When the reaction was carried out in Ph<sub>2</sub>O at 220°C the ratio of 3 to 4 was ca. 85/15, implying ca. 11% of rearrangement.

For simplicity we confine discussion to the early stages of the reaction; in later stages there will be the complication that rearranged cyanate 2 will also be a reactant, and indeed, perhaps even a little of the further-rearranged cyanate (Me<sub>3</sub>Si)<sub>2</sub>[(CD<sub>3</sub>)Me<sub>2</sub>Si]CSi- $(CD_3)$ MeOCN). If a liberated ion  $[OCN]^-$  reacts much more often with a cation II than with a molecule of 1 then isocyanate subsequently formed should be ca. 50% rearranged. In contrast, if the ion [OCN]<sup>-</sup> reacts much more readily with 1 than with the cation II (which is present in very much lower concentration), the chain process thus set up will result in virtually no rearranged isocyanate formation. If the [NCO]<sup>-</sup> reacts as often with the cation as with 1 then (but again only in the early stages) 25% of the formed isocyanate would be rearranged (though this figure would rise later as rearranged cyanate played a larger part). Thus the observed extents of rearrangement are compatible with Scheme 3.

There is a difficulty with this mechanism in that it does not obviously account for the apparently low value of the pre-exponential, log A, factor observed for the isomerization of  $(Me_3Si)_3CSiMe_2OCN$  [2] in Ph<sub>2</sub>O, though that value was only very roughly determined and could be misleading. It is possible to envisage a combination of aspects of Schemes 1 and 2 that could account for both the appearance of a significant proportion of rearranged isocyanate and the low log A factor. For example, if a cyclic process closely similar to that in Scheme 1 involved attack of an ion pair [II ··· (OCN<sup>-</sup>)] on a molecule of 1, then some return of cyanate ion to the  $\gamma$ -position within the ion pair prior to such attack could ultimately give rise to some rearranged isocyanate, and there would also be a low value of log A.



However, for the present, we favour the simpler mechanism shown in Scheme 3 as the working hypothesis.

# 2.2. Isomerization of $(Me_3Si)_3CSiMe_2OCN$ catalysed by ICl

As already mentioned, the earlier work showed that isomerization of (Me<sub>3</sub>Si)<sub>3</sub>CSiMe<sub>2</sub>OCN to the isocyanate in CCl<sub>4</sub> is very effectively catalysed by ICl, the reaction being of approximately second order with respect to both the cyanate and the ICl [3], and the seemingly obvious explanation of the catalysis appeared to be that the ICl assisted the leaving of cyanate ion. However, we found that when a solution of 0.30 mmol of the labelled 1 in 4 cm<sup>3</sup> of  $CCl_4$  containing 0.74 mmol of ICl was kept at room temperature for 1 h there was complete conversion into the unrearranged isocyanate 3. It thus seems very likely that the ICl-catalyzed process is of a wholly different type from the thermal one, and does not involve ionization. This result was so surprising that we thought it appropriate to seek confirmation by an independent method, as described below.

This second method was based on the observation that the ease of ionization of compounds of the type (Me<sub>3</sub>Si)<sub>2</sub>(PhMe<sub>3</sub>Si)CSiMe<sub>2</sub>X is greatly increased by anchimeric assistance by the Ph group to the leaving of  $X^-$  (to give a cation of type I but with a bridging Ph group) [4]. 'Thus if the isomerization of  $(Me_3-Si)_3$ -CSiMe<sub>2</sub>-OCN in CCl<sub>4</sub> in the presence of ICl proceeded by ionization, then that of (Me<sub>3</sub>Si)<sub>2</sub>(PhMe<sub>2</sub>Si)CSiMe<sub>2</sub>-OCN should be markedly faster. In order to monitor the reactions conveniently by 'H NMR spectroscopy we had to use CDCl<sub>3</sub> as solvent. We found that there was no significant difference between the rates for the two compounds in 0.091 M solution in 0.20 M ICl in this solvent (the Ph-containing cyanate having a half-life of  $23 \pm 4$  min at 35°C and the other cyanate one of  $18 \pm 4$ min), confirming that the reaction does not involve ionization. Initial formation of a complex between the cyanate and the ICl seems likely, but further speculation about the mechanism must await a more detailed study.

# 3. Experimental

# 3.1. Preparation of (Me<sub>3</sub>Si)<sub>3</sub>CSi(CD<sub>3</sub>)<sub>2</sub>OCN, 1

The reactivity of AgOCN, even freshly prepared, varies from batch to batch, probably because of variations in the degree of aggregation. The progress of the reaction can be monitored by removal and evaporation of small samples of the solution and determination of the <sup>1</sup>H NMR spectrum of the residue in CDCl<sub>3</sub>, in which the (Me<sub>3</sub>Si)<sub>3</sub>C peak for the iodide is at  $\delta 1.08$ 

and that for 1 at  $\delta 0.29$ ). The sample of 1 used for the present study was made by the following procedure.

A mixture of  $(Me_3Si)_3CSi(CD_3)_2I(1.0 \text{ g}, 2.4 \text{ mmol})$ , AgOCN (0.45 g, 3 mmol) (freshly prepared and carefully dried), anhydrous  $CH_2Cl_2$  (20 cm<sup>3</sup>) and anhydrous  $Et_2O$  (40 cm<sup>3</sup>) under dry nitrogen was stirred vigorously with protection from light for 5 h at room temperature then filtered. Fresh AgOCN (0.45 g) was added to the filtrate and the stirring was continued for a further 10 h. This filtration and addition of fresh AgOCN was repeated after a further 24 h, and after an additional 8 h the solution was again filtered and the solvent was evaporated to leave 1 containing ca. 4% of 2 (as indicated by the integral for the SiMe<sub>2</sub>OCN peak at  $\delta 0.64$ ).

### 3.2. Thermal isomerization

(i) A sample (0.3 g) of 1 (containing ca. 4% of 2) was heated in a small sealed tube at 150°C for 2 h. The <sup>1</sup>H NMR spectrum of the product showed that complete conversion of cyanate to isocyanate had occurred, and from the integral for the SiMe<sub>2</sub>NCO peak at  $\delta 0.46$  relative to that for the Me<sub>3</sub>Si peak at  $\delta 0.27$  the ratio of 3 to 4 was found to be ca. 75/25.

(ii) A solution of 1 (0.05 g) in  $Ph_2O$  (2 cm<sup>3</sup>) was sealed in an NMR tube under nitrogen. The tube was kept in a bath at ca. 220°C for 72 h then cooled and opened. After addition of CDCl<sub>3</sub> (0.10 cm<sup>3</sup>) the <sup>1</sup>H NMR spectrum of the solution showed that 3 and 4 were present in a ratio of ca. 85/15.

# 3.3. Isomerization in the presence of ICl

A solution of ICl (0.12 g; 0.71 mmol) in CCl<sub>4</sub> (4  $\rm cm^3$ ) was added to 1 (0.10 g, 0.3 mmol) (containing ca. 4% of 2) and the mixture was stirred at room temperature for 1 h. The solvent was then evaporated off under vacuum and the <sup>1</sup>H NMR spectrum of the residue in CDCl<sub>3</sub> showed it to be the isocyanate 3 containing less than 5% of the rearranged 4.

# 3.4. Reactivities of (Me<sub>3</sub>Si)<sub>3</sub>CSiMe<sub>2</sub>OCN and (Me<sub>3</sub>Si)<sub>2</sub>-(PhMe<sub>2</sub>Si)CSiMe<sub>2</sub>OCN towards ICl-CDCl<sub>3</sub>

A solution of  $(Me_3Si)_3CSiMe_2OCN$  (15 mg) in 0.20 M ICl in CDCl<sub>3</sub> (0.5 cm<sup>3</sup>) in an NMR tube was kept at 35°C in the NMR spectrometer (Bruker WM360) and the <sup>1</sup>H NMR spectrum was recorded at intervals. After 10 and 18 min respectively, ca. 37 and 49% of isomerization to 3 had occurred, indicating a half-life of ca. 18 ± 4 min. For  $(Me_3Si)_2(PhMe_2Si)CSiMe_2OCN$  after 5 and 30 min, respectively, there had been ca. 22 and 57% isomerization to 3, indicating a half-life of ca. 23 ± 4 min.

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