

The mechanism of the isomerization of organosilicon cyanates to isocyanates

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Abstract

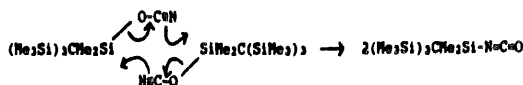
Isomerization of the cyanate $(\text{Me}_3\text{Si})_3\text{CSi}(\text{CD}_3)_2\text{OCN}$ in the molten state at 150°C gives the unrearranged isocyanate $(\text{Me}_3\text{Si})_3\text{CSi}(\text{CD}_3)_2\text{NCO}$ and the rearranged isocyanate $(\text{Me}_3\text{Si})_2[(\text{CD}_3)_2\text{MeSi}]\text{CSiMe}_2\text{NCO}$ in a ratio of ca. 75/25, and isomerization in solution in Ph_2O 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_4 catalyzed by ICl , indicating that ionization is not involved; this conclusion is supported by the observation that the isomerization of $(\text{Me}_3\text{Si})_2(\text{PhMe}_2\text{Si})\text{CSiMe}_2\text{OCN}$, in which the Ph group would provide anchimeric assistance to ionization, proceeds at a similar rate to that of $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{OCN}$.

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 $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{OCN}$, a later kinetic study showed that for a solution in Ph_2O at $150\text{--}200^\circ\text{C}$ the isomerization to the isocyanate $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{NCO}$ 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 $[\text{OCN}]^-$ through its N centre, on a molecule of $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{OCN}$ with displacement of another ion $[\text{OCN}]^-$. (The cyanate $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{OCN}$ is very rapidly isomerized by KOCN in MeCN [3].) If the ionization equilibrium lay far over to the left, then the concentration of $[\text{OCN}]^-$ would be proportional to that of $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{OCN}$ and so the reaction would be of second order. (The implicit assumption that recombina-

tion of **I** and $[\text{OCN}]^-$ always gives cyanate is in line with the fact that reaction of $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{I}$ with AgOCN via **I** gives only the cyanate; furthermore, isomerization to the isocyanate by re-attachment of $[\text{OCN}]^-$ 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 $(\text{PhMe}_2\text{Si})_3\text{CMe}_2\text{OCN}$, in which the Ph groups could provide anchimeric assistance to the leaving of $[\text{OCN}]^-$ [4], undergoes isomerization more readily than $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{OCN}$ [5], and that $(\text{Me}_3\text{Si})_2(\text{MeOMe}_2\text{Si})\text{CSiMe}_2\text{OCN}$ 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 account for the fact that the isomerization in CCl_4 was catalyzed by ICl , since the latter could be expected to assist the leaving of $[\text{OCN}]^-$ by forming complex ions such as $[(\text{OCN})\text{ICl}]^-$ or $[(\text{OCN})(\text{ICl})_2]^-$ [3].



Scheme 1.

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

2.2. Isomerization of $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{OCN}$ catalysed by ICl

As already mentioned, the earlier work showed that isomerization of $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{OCN}$ to the isocyanate in CCl_4 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^3 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 $(\text{Me}_3\text{Si})_2(\text{PhMe}_2\text{Si})\text{CSiMe}_2\text{X}$ 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 $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{OCN}$ in CCl_4 in the presence of ICl proceeded by ionization, then that of $(\text{Me}_3\text{Si})_2(\text{PhMe}_2\text{Si})\text{CSiMe}_2\text{OCN}$ should be markedly faster. In order to monitor the reactions conveniently by ^1H NMR spectroscopy we had to use CDCl_3 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 ± 4 min at 35°C and the other cyanate one of 18 ± 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 $(\text{Me}_3\text{Si})_3\text{CSi}(\text{CD}_3)_2\text{OCN}$, **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 ^1H NMR spectrum of the residue in CDCl_3 , in which the $(\text{Me}_3\text{Si})_3\text{C}$ 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 $(\text{Me}_3\text{Si})_3\text{CSi}(\text{CD}_3)_2\text{I}$ (1.0 g, 2.4 mmol), AgOCN (0.45 g, 3 mmol) (freshly prepared and carefully dried), anhydrous CH_2Cl_2 (20 cm^3) and anhydrous Et_2O (40 cm^3) 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_2OCN 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 ^1H NMR spectrum of the product showed that complete conversion of cyanate to isocyanate had occurred, and from the integral for the SiMe_2NCO peak at $\delta 0.46$ relative to that for the Me_3Si 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^3) 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_3 (0.10 cm^3) the ^1H 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_4 (4 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 ^1H NMR spectrum of the residue in CDCl_3 showed it to be the isocyanate **3** containing less than 5% of the rearranged **4**.

3.4. Reactivities of $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{OCN}$ and $(\text{Me}_3\text{Si})_2(\text{PhMe}_2\text{Si})\text{CSiMe}_2\text{OCN}$ towards $\text{ICl}-\text{CDCl}_3$

A solution of $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{OCN}$ (15 mg) in 0.20 M ICl in CDCl_3 (0.5 cm^3) in an NMR tube was kept at 35°C in the NMR spectrometer (Bruker WM360) and the ^1H 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 $(\text{Me}_3\text{Si})_2(\text{PhMe}_2\text{Si})\text{CSiMe}_2\text{OCN}$ 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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