[Tris(trimethylsilyl)methyl](dimethyl)silyl Cyanate. The Cyanate to Isocyanate Isomerization, and the High Activity of Cyanate as a Leaving Group in Solvolysis

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The isomerization of the cyanate $(Me_3Si)_3CSiMe_2(OCN)$, (**1**), to the isocyanate (i) in Ph_2O at 195 °C is second order in (**1**), (ii) in CCl_4 is catalysed by ICl, and (iii), in MeOH is catalysed by NaOMe; in solvolysis in MeOH, (**1**) is comparable in reactivity to the corresponding trifluoromethanesulphonate, and shows an abnormally high selectivity for reaction with the water in slightly aqueous MeOH.

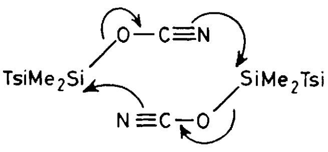
We recently reported the first isolation of organosilicon cyanates, and showed them to undergo isomerization to the isocyanates on heating.[1] We have now studied the isomerization of one of the cyanates, $TsiSiMe_2(OCN)$ [Tsi = $(Me_3Si)_3C$], (**1**), and also its solvolysis, with the results outlined below.

The conversion of (**1**) into the corresponding isocyanate in

$TsiSiMe_2OCN$ (1)

$TsiSiMe_2OH$ (2)

$TsiSiMe_2OMe$ (3)



(A)

diphenyl ether at 195 ± 5 °C was monitored by recording the ^1H n.m.r. spectrum of the solution at various times and noting the relative heights of the signals from the Si*Me*$_2$(OCN) and Si*Me*$_2$(NCO) protons. Second order plots of $1/[(\mathbf{1})]$ against time were satisfactorily linear; for initial concentrations of (**1**) of 9.0×10^{-2} and 4.05×10^{-2} M the derived second order rate constants, k_2, were *ca.* 6.4 and 7.1 l mol^{-1} s^{-1}, respectively. The reaction is thus of second order with respect to (**1**), and the simplest representation of the mechanism is that shown in (A).

The isomerization of (**1**) in CCl_4 was found to be powerfully catalysed by iodine monochloride. In runs at 35 °C involving 0.40 M ICl and initially 0.038 and 0.073 M (**1**), satisfactory second order plots were obtained for the isomerization, with values of 10^2k_2 of 3.0 and 2.7 l mol^{-1} s^{-1}, respectively. With the initial concentration of (**1**) kept constant at 0.11 M, and ICl concentrations of 0.05, 0.10, and 0.20 M, satisfactory second order plots were again obtained, giving rate constants 10^4k_2 of *ca.* 3.7, 15.8, and 90 l mol^{-1} s^{-1} respectively, and these results taken along with those for the 0.40 M ICl solutions indicate that the order with respect to ICl is in the region of 2, and thus that the overall order of the catalysed process is *ca.* 4. [It is quite likely that there are simultaneous processes of first, second, third, and even higher order in ICl, corresponding to involvement of various $(ICl)_n$ species, the observed overall order varying with the ICl concentration.] In the simplest representation of the catalysis each cyanate molecule in a process of type (A) is complexed with an ICl molecule, but there is also the possibility, for example, that one of the cyanate molecules is uncomplexed and the other associated with an $(ICl)_2$ or $(ICl)_3$ species.

Acetyl chloride also catalysed the rearrangement [thus a solution of (**1**) in 2:1 v/v $CDCl_3$–MeCOCl showed *ca.* 25% of isomerization in 2 h at *ca.* 25 °C], as (see below) does NaOMe in MeOH.

In solution of (**1**) in MeOH dried by standard methods a fairly rapid solvolysis occurred at 35 °C, but the product was mainly the hydroxide (**2**) along with some of the methoxide (**3**). When the MeOH was more rigorously dried and the reaction conducted under dry nitrogen the product was solely the methoxide. With a batch of MeOH dry enough to give no detectable hydroxide from the triflate $TsiSiMe_2OSO_2CF_3$ (which, like the perchlorate,[2] is known to select water very effectively from incompletely dried MeOH[3]), a substantial amount of the hydroxide was formed from (**1**). The rate of the methanolysis of (**1**) was comparable with that of the triflate,[4] indicating that cyanate is an exceptionally good leaving group from silicon. Surprisingly the presence of 0.2 M NaOMe led to virtually exclusive isomerization to the isocyanate (which does not undergo solvolysis), and this catalysis poses an interesting mechanistic problem.

The ease of hydrolysis of organosilicon cyanates in these sterically hindered systems can be utilized in the preparation of hydroxides. Thus treatment of $(IMe_2Si)_4C$ with AgOCN in moist ether gives $(HOMe_2Si)_4C$ (presumably as a result of initial formation of Si–OCN bonds), and this represents the simplest method we have found for making this tetrahydroxide.

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