

## (Dimethyl)[tris(trimethylsilyl)methyl]silyl Cyanate and Related Species: the First Silicon Cyanates

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Treatment of  $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{I}$ ,  $(\text{Me}_3\text{Si})_3\text{CSiMe}(\text{OMe})\text{I}$ , or  $(\text{Me}_3\text{Si})_3\text{CSiPh}_2\text{I}$  with  $\text{AgOCN}$  in  $\text{CH}_2\text{Cl}_2$  has given  $(\text{Me}_3\text{Si})_3\text{CSiMe}_2(\text{OCN})$ ,  $(\text{Me}_3\text{Si})_3\text{CSiMe}(\text{OMe})(\text{OCN})$ , and  $(\text{Me}_3\text{Si})_2\text{C}(\text{SiPh}_2\text{Me})[\text{SiMe}_2(\text{OCN})]$ , respectively, the first normal cyanates of silicon; on heating these isomerize to the corresponding isocyanates.

Although many silicon and organosilicon isocyanates are known, there is no reported example of a normal cyanate.<sup>1</sup> We have now found that treatment of some iodides  $\text{TsiSiRR}'\text{I}$  [ $\text{Tsi} = (\text{Me}_3\text{Si})_3\text{C}$ ] with  $\text{AgOCN}$  in  $\text{CH}_2\text{Cl}_2$  gives normal cyanates, which can undergo isomerization to the corresponding isocyanates.

A solution of  $\text{TsiSiMe}_2\text{I}$  in  $\text{CH}_2\text{Cl}_2$  was stirred for 15 min with an excess of freshly-prepared  $\text{AgOCN}$ . The solution was filtered and evaporated at room temperature under reduced pressure. The organic component of the residue was extracted into  $\text{CCl}_4$ , and the extract was filtered and evaporated. The recovered solid showed (in  $\text{CCl}_4$ ) moderately strong i.r. bands at 2240 and 1160  $\text{cm}^{-1}$  and  $^1\text{H}$  n.m.r. peaks at  $\delta$  0.29 (27 H,  $\text{SiMe}_3$ ) and 0.64 (6 H,  $\text{SiMe}_2$ ). When the solid was heated in a sealed tube at ca. 150 °C for 2 h the i.r. band at 2240 was replaced by a very strong band at 2280  $\text{cm}^{-1}$  and that at 1160  $\text{cm}^{-1}$  disappeared, while the  $^1\text{H}$  n.m.r. peaks at  $\delta$  0.29 and 0.64 were replaced by peaks at  $\delta$  0.27 and 0.46, respectively.

The changes in the i.r. spectrum correspond closely to those observed when alkyl cyanates isomerize to isocyanates,<sup>2</sup> and there is no reason to doubt that the initial product we obtained was the cyanate,  $\text{TsiSiMe}_2(\text{OCN})$ , and that this isomerizes to the thermodynamically more stable isocyanate,  $\text{TsiSiMe}_2(\text{NCO})$ .† [The isocyanate  $\text{Me}_3\text{SiNCO}$  has a very strong  $\nu_{\text{as}}(\text{NCO})$  band at 2290  $\text{cm}^{-1}$ .<sup>3</sup>]

The iodides  $\text{TsiSiMe}(\text{OMe})\text{I}$  and  $\text{TsiSiPh}_2\text{I}$  on treatment with  $\text{AgOCN}$  likewise gave normal cyanates,  $\text{TsiSiMe}(\text{OMe})(\text{OCN})$  and  $(\text{Me}_3\text{Si})_2\text{C}(\text{SiPh}_2\text{Me})[\text{SiMe}_2(\text{OCN})]$  (giving bands

at 2240 and 1160  $\text{cm}^{-1}$ ). (The rearrangements of the type involved in the formation of the latter are well established.<sup>4</sup>) These changed into the isocyanates (bands at 2280 vs  $\text{cm}^{-1}$ ) on heating. In contrast, when the less sterically hindered  $\text{TsiSiPh}_2\text{I}$  was treated with  $\text{AgOCN}$  in  $\text{CH}_2\text{Cl}_2$  the product solution contained only the isocyanate,  $\text{TsiSiPh}_2\text{H}(\text{NCO})$  [ $\nu(\text{CNO})$  2290 vs  $\text{cm}^{-1}$ ], and the isolated solid underwent no change on heating.<sup>5</sup>

The fact that the cyanates  $\text{TsiSiRR}'(\text{OCN})$  can be isolated can reasonably be attributed to the severe steric hindrance in these compounds, which impedes the isomerization, and their formation raises the possibility that reactions between silicon halides and silver cyanate always initially give cyanates, which normally isomerize very rapidly to the isocyanates.

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† The cyanate and isocyanate gave satisfactory analyses. Both isomers showed the same prominent peaks in the mass spectrum, at  $m/z$  316 ( $M-\text{Me}$ )<sup>+</sup>, 201 ( $M-\text{Me}_3\text{SiX}-\text{Me}$ )<sup>+</sup> ( $X = \text{OCN}$  or  $\text{NCO}$ ), and 73 ( $\text{Me}_3\text{Si}^+$ ).