

The First Silicon Thiocyanate

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The first normal thiocyanate of silicon, $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OMe})(\text{SiMe}_2\text{SCN})$ has been prepared from $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OMe})(\text{SiMe}_2\text{Cl})$ and AgSCN ; it is much more readily solvolysed than its isomer $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OMe})(\text{SiMe}_2\text{NCS})$.

Until recently all attempts to make normal cyanates or thiocyanates of silicon had been unsuccessful, and only the iso-isomers were known.¹ Two years ago treatment of some highly sterically hindered iodides with silver cyanate gave the first normal cyanates; *e.g.*, $\text{TsiSiMe}_2\text{OCN}$ [$\text{Tsi} = (\text{Me}_3\text{Si})_3\text{C}$] was obtained from $\text{TsiSiMe}_2\text{I}$, and $(\text{Me}_3\text{Si})_2\text{C}(\text{SiPh}_2\text{Me})(\text{SiMe}_2\text{OCN})$ (by a rearrangement) from $\text{TsiSiPh}_2\text{I}$.² We now report the first preparation of a normal thiocyanate.

The starting point was the compound $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OMe})(\text{SiMe}_2\text{Cl})$, in which the γ -OMe group supplies powerful anchimeric assistance to the leaving of Cl^- .³ When this (0.6 mmol) was treated with AgSCN (0.6 mmol) in anhydrous MeCN (20 cm³) for 30 min at room temperature (*ca.* 21 °C), subsequent filtration followed by evaporation of the filtrate gave a white solid, m.p. 266 °C, which was identified as the normal thiocyanate, $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OMe})(\text{SiMe}_2\text{SCN})$; δ_{H} (CCl_4) 0.28 (18H, s, SiMe_3),

0.33 (6H, s, SiMe_2OMe), 0.61 (6H, s, SiMe_2SCN), and 3.4 (3H, s, OMe); δ_{C} (in CDCl_3) 2.74 (SiMe_2OMe), 4.73 (SiMe_3), 8.57 (SiMe_2SCN), and 49.16 (OMe); $\nu(\text{SCN})$ 2085 cm⁻¹; m/z 348 ($[\text{M} - \text{Me}]^+$).

The isomeric isothiocyanate was obtained by refluxing a solution of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OMe})(\text{SiMe}_2\text{Cl})$ (0.88 mmol) with KSCN (13 mmol) in MeCN (30 cm³) for 1 h; it was isolated by removal of the solvent, extraction of the residue with CCl_4 , filtration and evaporation of the extract, and sublimation (100 °C at 0.2 mmHg) of the residual solid. It had m.p. 269 °C; δ_{H} 0.28 (18H, s, SiMe_3), 0.33 (6H, s, SiMe_2OMe), 0.50 (6H, s, SiMe_2NCS), and 3.40 (3H, s, OMe); δ_{C} 2.44 (SiMe_2OMe), 4.32 (SiMe_3), 5.18 (SiMe_2NCS), and 49.32 (OMe); $\nu(\text{NCS})$ 2085 cm⁻¹; m/z 348 ($[\text{M} - \text{Me}]^+$).

The physical constants listed above for the two isomers are remarkably similar (even the melting points) [in contrast to the situation with the cyanates and isocyanates, the main

$\nu(\text{SiSCN})$ and $\nu(\text{SiNCS})$ bands coincide], though there are small but significant differences in the chemical shifts in both the ^1H and ^{13}C n.m.r. spectra for SiMe_2SCN and SiMe_2NCS . The two isomers differ greatly in chemical reactivity, however; thus the thiocyanate undergoes methanolysis very rapidly in MeOH, with an estimated half-life of 2–3 min at 35 °C, comparable with that for the corresponding chloride;³ in 4:1 v/v MeOH–dioxane at 35 °C the half-life is 8 min. In contrast, the isothiocyanate has a half-life in MeOH of 50 h at 50 °C, *i.e.* it is very roughly 3000–4000 times less reactive. The cyanate $\text{TsiSiMe}_2\text{OCN}$ is correspondingly much more reactive than the isocyanate.⁴

Attempts to make other, related, normal thiocyanates have so far failed. Organosilicon halides are much less reactive towards AgSCN than towards AgOCN (*cf.* ref. 5), and $\text{TsiSiMe}_2\text{I}$ does not react at a detectable rate with AgSCN under the usual conditions. The less hindered compound TsiSiPhHI does react, but product is solely the isothiocyanate.⁶ In the case of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{CH}=\text{CH}_2)(\text{SiMe}_2\text{I})$, in which the vinyl group is thought to supply substantial anchimeric assistance, the isolated product is again solely the isothiocyanate, but monitoring of the reaction by ^1H n.m.r. spectroscopy reveals the appearance of additional peaks which later give way to those of the final product, suggesting

that the thiocyanate is initially formed but isomerizes to the isothiocyanate.⁷ The greater difficulty of isolating normal thiocyanates compared with normal cyanates presumably stems from the slowness of the initial reaction with AgSCN , which affords opportunity for isomerization to the isothiocyanate.

We thank the S.E.R.C. for support, Mr. R. W. Bott for valuable help, and the Dow Corning Co., Ltd., for gifts of organosilicon chemicals.

Received, 31st August 1984; Com. 1245

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