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Preliminary communication

Novel thermal rearrangements of type Si–C–O–N→N–C–O–Si in 1-[bis(trifluoromethyl)aminoxyl]alkyl-trichlorosilanes and -trimethylsilanes

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SUMMARY

The silanes $\mathrm{Me_2SiR\underset{\substack{|\\ CH_2ON(CF_3)_2}}{C}HON(CF_3)_2}$ (R = Me or $\mathrm{ON(CF_3)_2}$) and $\mathrm{Cl_3SiCMe_2ON(CF_3)_2}$ rearrange thermally in the range 50–150° to afford near-quantitative yields of the compounds $\mathrm{(CF_3)_2N\underset{\substack{|\\ CH_2ON(CF_3)_2}}{C}HOSiMe_2R}$ and $\mathrm{(CF_3)_2NCMe_2OSiCl_3}$, respectively.

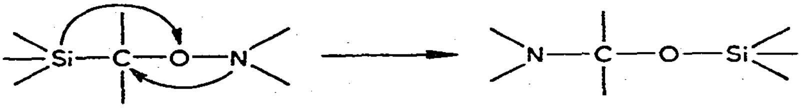
Thermal isomerisations involving insertion of oxygen into an Si–C bond are not common; examples are restricted to the rearrangement of β-silyl ketones[1]:

$$\mathrm{R_3SiCH_2COR'} \xrightarrow{80-175^\circ} \mathrm{R_3SiOCR'{=}CH_2}$$

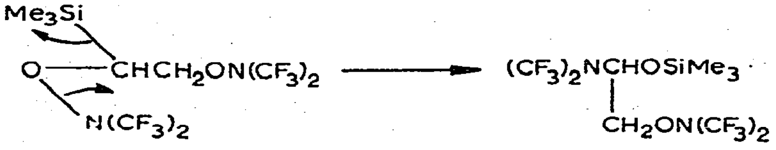
A related but more complex thermal rearrangement involving oxygen insertion into an Si–N bond occurs with tris-organosilylhydroxylamines[2]:

$$\mathrm{(R_3Si)_2NOSiR_3} \xrightarrow{200^\circ} \mathrm{R_3SiNRSiR_2OSiR_3}$$

During the course of an investigation into the reactions of the bis(trifluoromethyl)aminoxy radical, $\mathrm{(CF_3)_2NO^\bullet}$ [3], with vinylsilanes and alkylsilanes, certain of the products isomerised during GLC separation (50–100°). Those which rearranged contained a bis(trifluoromethyl)aminoxyl group on the α-carbon to silicon, and study of additional compounds showed that the rearrangement was of the type

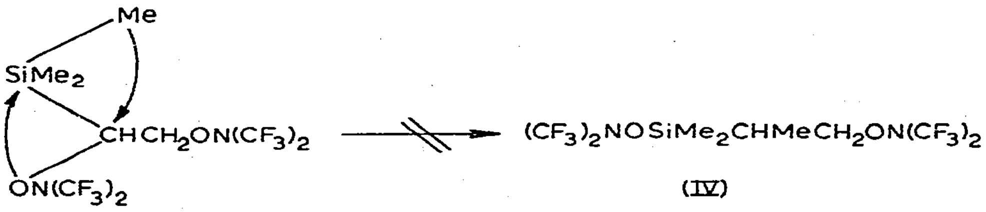


The trimethylsilyl compound (I) when heated *in vacuo* at 50° (12h) gave the rearranged silane (III) (100%). The product was shown not to have the alternative structure (IV) (which would be formed by direct interchange[4] of a methyl group on silicon for the $(CF_3)_2NO$ group on the α-carbon) by the presence in the ^{19}F NMR spectrum of the product of two absorption bands of equal intensity at −22.0 and −8.0 ppm relative to external CF_3CO_2H, in the regions expected for $(CF_3)_2N{-}C$ and $(CF_3)_2NO{-}C$ groups, respectively.



(I)

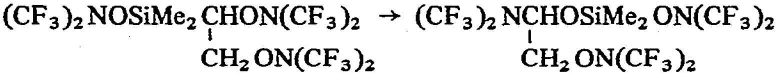
(III)



(IV)

The progress of the reactions at 60 and 80° were determined at various intervals of time by NMR analysis. Plots of time t against $\log_{10}$ (initial concentration of (I)/concentration of (I) after time t) gave straight lines (first-order reactions) from the gradients of which the rate constants were calculated to be ca. $9 \cdot 10^{-5}$ and ca. $6.5 \cdot 10^{-4}$ s^{-1}, respectively; the activation energy for the rearrangement is thus ca. 95 $kJ \cdot mol^{-1}$.

The silane (II) underwent a corresponding rearrangement when heated at 150° (1h) to give the silane (V) (100%), but the silane $Me_3SiCH_2ON(CF_3)_2$ did not.



$$\underset{CH_2ON(CF_3)_2}{(CF_3)_2NOSiMe_2CHON(CF_3)_2} \rightarrow \underset{CH_2ON(CF_3)_2}{(CF_3)_2NCHOSiMe_2ON(CF_3)_2}$$

(II) (V)

Of the trichlorosilyl compounds studied $Cl_3SiCH[ON(CF_3)_2CH_2ON(CF_3)_2$ was stable at 200°, compound $Cl_3SiCHMeON(CF_3)_2$ did not isomerise below 150°, and compound $Cl_3SiCMe_2ON(CF_3)_2$ rearranged readily at 100° (2h) to afford isomer $(CF_3)_2NCMe_2OSiCl_3$ (98%).

The ease of the rearrangement, which involves cleavage of relatively weak N—O and C—Si and formation of stronger Si—O and C—N, is $X_3SiCRR'ON(CF_3)_2 > X_3SiCHRON(CF_3)_2 > X_3SiCH_2ON(CF_3)_2$. Steric factors may play a role since silanes which contain the groups Me_3Si or $(CF_3)_2NOSiMe_2$ rearranged when the α-methylene group was mono-substituted, but silanes containing the less bulky $SiCl_3$ group only underwent rearrangement when the α-methylene group was disubstituted.

All compounds gave satisfactory spectral and elemental analyses.

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