Matrix Photolysis of Trimethylazidosilane: Silicon–Hydrogen Bond Formation

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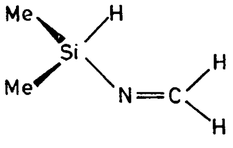
Summary The major product of u.v. photolysis of Me_3SiN_3 in Ar, N_2, and CO matrices at 10 K is shown to be either $Me_2Si(H)N{=}CH_2$ or $Me_2Si(H)CH{=}NH$; no evidence for π-bonded Si=N species is obtained.

CHEMICAL trapping experiments have suggested that the photolysis of substituted azidosilanes results in formation of compounds containing Si=N π-bonded groups as short-lived intermediates.[1] Matrix isolation, which has been applied to some related systems, should be the most suitable technique for the direct detection of such species. Photolysis of $Me_3SiC(H)N_2$ in matrices resulted in production of Me_3SiCH and $Me_2Si{=}C(H)Me$.[2] While matrix photolysis of MeN_3 gave rise to CH_2NH, followed by HNC as a secondary product,[3,4] HNSi was the only product detected on photolysis of SiH_3N_3.[5]

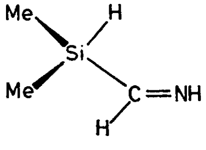
In this communication I report the results of photolysing Me_3SiN_3 in N_2, Ar, and CO matrices at 10 K; the reaction was followed by i.r. spectroscopy. Experiments with $(CD_3)_3SiN_3$ and ^{15}N enriched azide were used as an aid in assignment.‡ The major observations and deductions are set out below.

(i) In all three matrices a new set of i.r. bands grows on u.v. irradiation with very similar wavenumbers and relative intensities. Such behaviour is characteristic of a single product; this product is generated almost quantitatively and is stable to annealing to 40 K.

(ii) The strongest product band is observed at 1668 cm^{-1} (Figure, band a_1). In experiments with mixtures containing equal proportions of $Me_3Si^{15}N^{14}N_2$ and $Me_3Si^{14}N_2{}^{15}N$, this band is replaced by two bands of approximately equal intensity. One is coincident with band a_1, the other is 21 cm^{-1} to lower wavenumber (Figure, bands c_1 and c_2), behaviour indicative of a C=N stretching vibration.



(1)



(2)

(iii) A group of intense product bands unaffected by ^{15}N substitution is centred at 2134 and 2118 cm^{-1} (Figure, bands b_1 and b_2).§ Deuteriated samples show bands at 1631, 1627, and 1566 cm^{-1} (Figure, bands d_1, d_2, and d_3), corresponding collectively to the group of bands a_1, b_1, and

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‡ $Me_3Si(^{15}N^{14}N_2)$ was synthesised by reaction of Me_3SiCl with $Na(^{15}N^{14}N_2)$ in diglyme; similarly, reaction of $(CD_3)_3SiBr$ and NaN_3 generated $(CD_3)_3SiN_3$.

§ The complex structure between 2110 and 2150 cm^{-1} was significantly different in Ar and N_2 matrices and may be attributed to the presence of different conformers or to trapping in a variety of matrix sites. All frequencies are quoted for N_2 matrices except for those of deuteriated species (Ar matrices).

b$_2$. These observations strongly suggest the presence of a Si–H bond in the product (*cf.* Me$_3$SiH[6]). The presence of Si–H and C=N bonds leads to two possible structures for the photoproduct, (**1**) and (**2**). Strong support for these conclusions is obtained from two further groups of i.r. absorptions.

(iv) Product bands at 2947, 2805, 1668, 1487, 1204, and 1083 cm^{-1} may be assigned to the vibrations of a H$_2$C=N– or HN=C(H)– group by comparison with the matrix spectra of H$_2$C=O[7] and H$_2$C=NH,[4] which they resemble both in wavenumber and in their shifts on isotopic substitution (see Figure, bands c$_1$–c$_4$, c$_6$, and c$_7$).

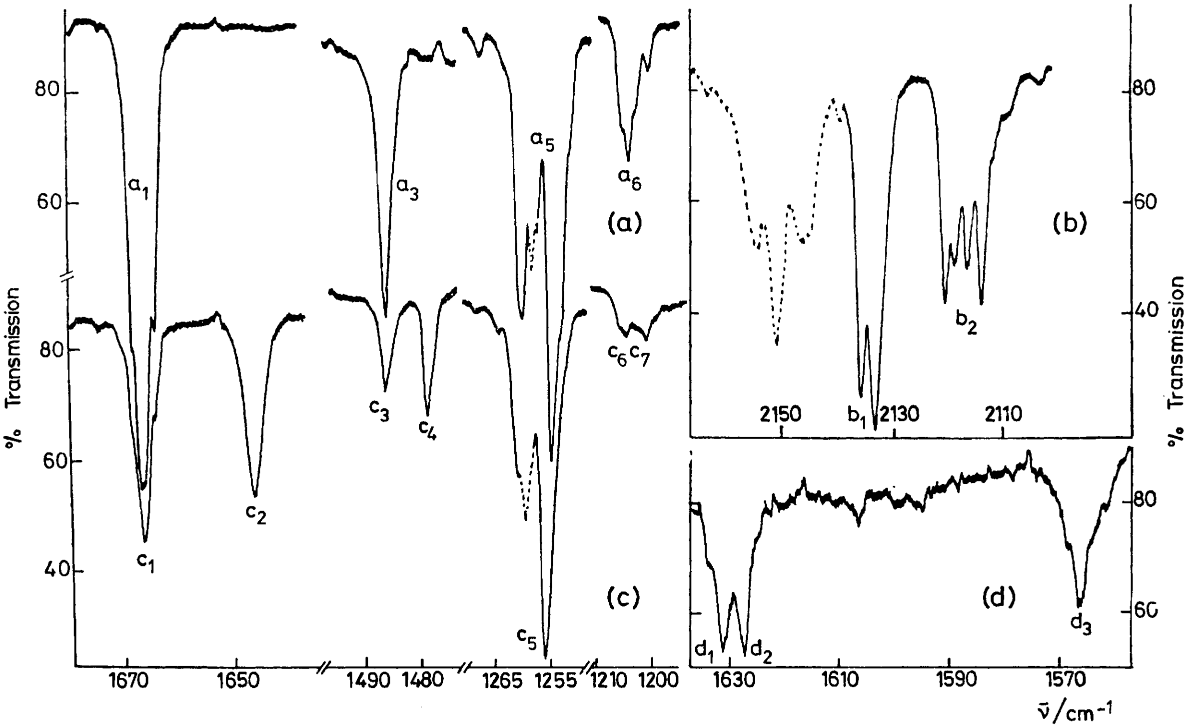

FIGURE. (a) and (b): I.r. spectra of a matrix of Me$_3$Si^{14}N$_3$:N$_2$ (1:2500) at 12 K after 735 min irradiation with a water-filtered Hg arc. (c): I.r. spectrum of Me$_3$Si^{15}N^{14}N$_2$:Me$_3$Si^{14}N$_2$^{15}N:N$_2$ (1:1:6200) after 570 min u.v. photolysis. (d): I.r. spectrum of (CD$_3$)$_3$SiN$_3$:Ar (1:5100) after 700 min u.v. photolysis. Bands shown in broken line (- - - -) are due to starting material. For numbering of bands, see text.

(v) An intense product bands at 1255 cm^{-1} (band a$_5$) and further bands below 1000 cm^{-1}, hardly affected by ^{15}N substitution, indicate methyl groups bound to silicon. The presence of an Me$_2$Si(H)– group was tested by a matrix isolation experiment on Me$_2$Si(H)Cl which revealed a strikingly similar spectrum to that of the photoproduct in this region. [The presence of a H$_2$Si(Me)– group is considered unlikely on mechanistic grounds and because of poor correlation with the spectra of model compounds.[8]]

Distinction between (**1**) and (**2**) is not yet possible from the i.r. spectra although (**1**) is more plausible on chemical grounds. The problems of distinction arise from the absence of an assigned NH stretching vibration in CH$_2$NH,[4] the mixing of vibrations in this low symmetry molecule, and the possibility of combination bands in Fermi resonance with fundamentals in the 2800–3000 cm^{-1} region. Consequently, the isotopic shifts cannot be interpreted unambiguously.

The production of (**1**) [or (**2**)] containing Si–H and C=N bonds is in sharp contrast to the production of Me$_3$SiCH and Me$_2$Si=C(H)Me on photolysis of Me$_3$SiC(H)N$_2$ in matrices.[2] The lack of Si=N π-bonded species on photolysis of Me$_3$SiN$_3$ may be the result of secondary photolysis as in the experiments with SiH$_3$N$_3$.[5] While Me$_2$Si=NMe has remained elusive, these experiments give a striking example of the observation by matrix isolation of an unusual photochemical rearrangement not detected in solution.

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