

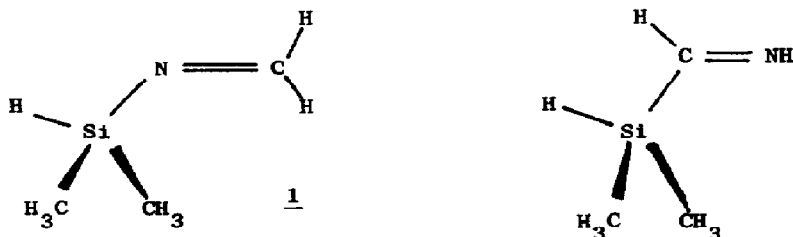
PHOTOLYSIS OF TRIMETHYLAZIDOSILANE IN INERT MATRICES: REARRANGEMENT TO A DIMETHYLSILYL IMINE

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When azidomethane ( $\text{CH}_3\text{N}_3$ ) is photolysed in inert matrices at low temperature, the initial product is methyleneimine ( $\text{CH}_2\text{NH}$ ) which readily undergoes further photolysis to HNC. Analogous experiments with  $\text{SiH}_3\text{N}_3$  lead direct to  $\text{HNSi}$  without detection of  $\text{SiH}_2\text{NH}$ .<sup>2</sup> In an attempt to observe the primary photoproducts of azidosilanes, I have photolysed  $(\text{CH}_3)_3\text{SiN}_3$  in  $\text{N}_2$ , Ar and CO matrices at 10K. The products were identified by i.r. spectroscopy, using  $^2\text{H}$  and  $^{15}\text{N}$  substitution as an aid in assignment.

The spectra of the photolysis product and its analogue 50%  $^{15}\text{N}$  enriched are illustrated in the figure. Characteristic product bands at  $1668\text{cm}^{-1}$  (shifted  $21\text{cm}^{-1}$  on  $^{15}\text{N}$  substitution) and  $2134\text{cm}^{-1}$  (shifted about  $500\text{cm}^{-1}$  on deuteration) indicate the presence of C=N and SiH groups respectively. On the basis of these observations and comparisons with spectra of related compounds, the photoproduct is identified as either 1 or 2 (the conformations shown are arbitrary):



The rearrangement to a compound containing C=N and Si-H units may be contrasted with the evidence for Si=N units obtained by chemical trapping of the products of photolysis of substituted azidosilanes in solution.<sup>3</sup> These experiments underline the importance of direct detection of unstable intermediates by spectroscopic methods.

### References

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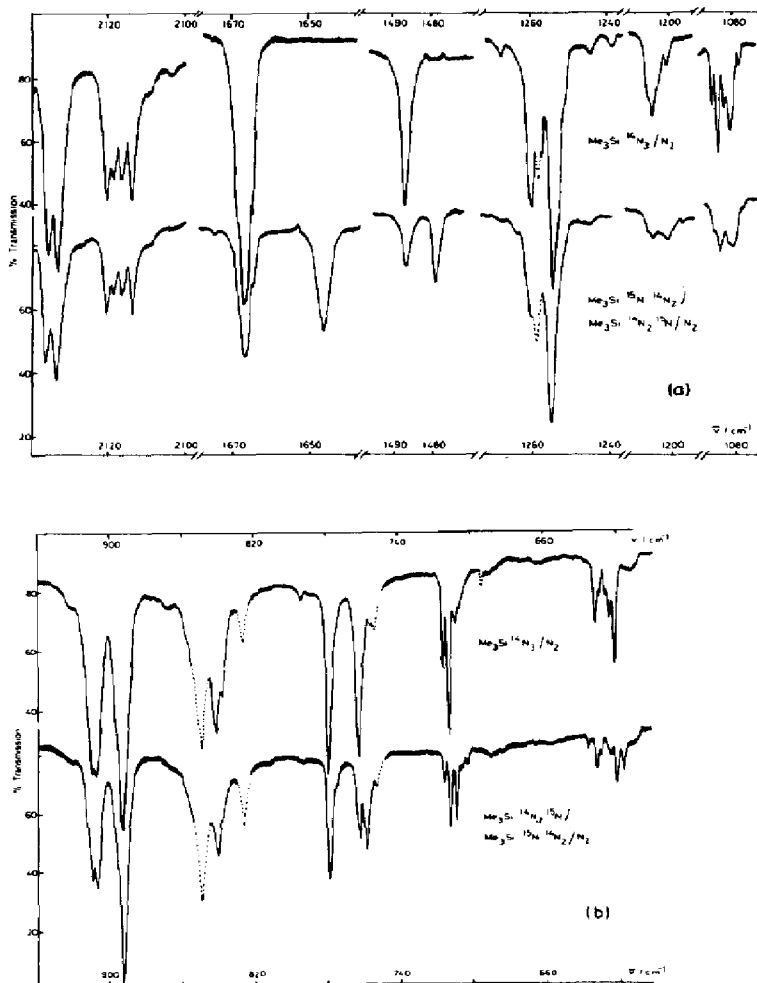


Figure: I.r. spectra taken after 12h. u.v. photolysis of  $\text{Me}_3\text{SiN}_3$  in  $\text{N}_2$  at 10K: (a)  $2200\text{--}1000\text{ cm}^{-1}$  (b)  $1000\text{--}500\text{ cm}^{-1}$ . Each pair of spectra shows results using  $\text{Me}_3\text{Si}^{14}\text{N}_3/\text{N}_2$  (1:2500) above and  $\text{Me}_3\text{Si}^{15}\text{N}^{14}\text{N}_2/\text{Me}_3\text{Si}^{14}\text{N}_2^{15}\text{N}/\text{N}_2$  (1:1:5000) below. Full line : photoproduct, broken line : starting material.