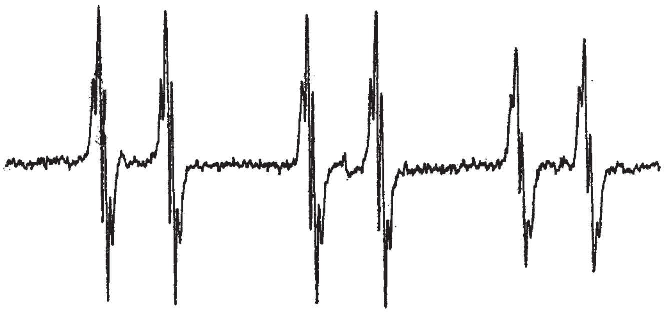

Fig. 2. ESR spectrum of the nitroxide radicals formed on dissolving a γ-irradiated solid sample of DL-α-alanine in a water solution of *t*-nitrosobutane. The secondary splitting is a doublet further split into a quartet (1 : 3 : 3 : 1) indicating trapping of the radical $CH_3—\dot{C}H—COO(H)$.

cysteine, cystine and methionine, which very probably contain radicals with the odd electron localized chiefly on the sulphur atom. These findings seem to conform with the fact that in our experience the most stable nitroxide radicals are those formed by the trapping of radicals in which the odd electron is localized on a carbon atom, and which have structures such as $\dot{C}H_3$, $R—\dot{C}H_2$, $R_2\dot{C}H$ and $R_3\dot{C}$ (R = alkyl, aryl or COOH).

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Photodecomposition of Trimethylsilyl Azide in Solid Argon

WHEN some group IV azide derivatives have been subjected to photodecomposition in argon matrices at cryogenic temperatures, isocyanides have been produced. In the case of methyl azide H_3CNNN, hydrogen isocyanide $HN{\equiv}C$ was proved to result from a secondary photolysis of methylenimine $H_2C{=}NH$ (ref. 1). From silyl azide, H_3SiNNN, iminosilicon HNSi has been detected[2], but the mechanism of formation was uncertain; the vibrational absorptions of other products were not then assigned. From germyl azide H_3GeNNN, HNGe has been tentatively identified (unpublished work with S. Cradock). The force constants of the heavy-atom valence-stretching vibrations of HNSi and HNGe are probably appropriate to what might effectively constitute "double bonds" rather than to a "triple bond" as in the case of HNC. Because π-type bonds of atoms beyond the first row are decreasingly stable because of the reduced overlap of the p-orbitals of the larger atoms, it is interesting to know the results of a situation in which there might be unsaturation either in a chemical bond between only first row atoms or alternatively, in a bond involving a second row atom. Such a case has been discovered following the photolysis of trimethylsilyl azide isolated in solid argon at 17° K.

Deposition of less than 30 μmoles of $(H_3C)_3SiNNN$ in argon at matrix ratios of 195 or >300 during 6 h was followed by spectroscopic scanning from 370 to 4,200 cm^{-1} using a modified 'Unicam' *SP*100 spectrophotometer[3]. The temperature of 17° K was maintained by an Air Products Cryotip refrigerator[4], model *AC*-3*L*-110, by pumping on hydrogen gas from the second Joule–Thomson expansion nozzle with a mechanical pump (450 l. min^{-1}). After the recording of the vibrational absorption, irradiation was effected by focusing the emission from an *HPK* 125 W (Philips) mercury lamp onto the sample. No temperature increase ($<0{\cdot}2°$) was noticed during either photolysis or scanning operations. The repeated scanning of the irradiated sample indicated the extent of decomposition of the $(H_3C)_3SiNNN$ and the formation of products. The figures illustrate the spectra recorded before and after 1·5 h of photolysis. The bands due to hexamethyldisiloxane impurity ($\sim$2 per cent of the sample before deposition) are unchanged, but bands of HNNN are greatly reduced although remaining extremely narrow. Bands tentatively assigned (vide infra) to a specified product are labelled *A* in Fig. 1.

The complicated overlapped nature of the spectrum after photolysis almost precludes complete analysis, even if many isotopically substituted trimethylsilyl azides had been available to provide further data. A tentative assignment is therefore now being attempted. It is presumed that photolysis leads in the primary process to formation of molecular nitrogen which plays no further part in the chemical processes. Neither molecular nitrogen nor hydrogen could be detected spectrometrically in these experiments, but ethane, analogous to hydrogen from the secondary photolysis of $H_2C{=}NH$, could have been and was not. The intense absorption at 1,671 cm^{-1}, the most notable spectral feature appearing after photolysis, provides a valuable clue to the nature of the products. The following bands have similar intensity behaviour relative to 1,671 cm^{-1} in different experiments, and might be assigned to a species $(H_3C)_2SiH—N{=}CH_2$ as follows: 2,815 and 2,860 cm^{-1} to the methylene valence-stretching vibrations, 1,489 and 916 cm^{-1} to CH_2 deformation and wag, 2,087 and 794 cm^{-1} to the SiH stretching and bending vibrations, 613 cm^{-1} to the Si—N stretching mode, and 1,671 cm^{-1} to the CN double bond stretching vibration. The latter frequency is most appropriate to a double bond of first row atoms. The comparatively small frequency and intensity of the 2,087 cm^{-1} feature are unusual for a SiH mode, but no overtone nor combination can be found to describe this value. The structure appearing in the 2,150 cm^{-1} band after photolysis in Fig. 2 is absent before photolysis only because of complete absorption in this particular experiment. Other characteristic absorptions of the $Si(CH_3)_2$ group would probably be of very similar frequency to those of the $Si(CH_3)_3$ group of the parent substance; other observed absorptions can at present not be assigned.

Milligan suggested that in his experiments methylenimine was formed by the rearrangement of a "hot" methylimino radical $H_3C—N$ (ref. 5). The 1,671 cm^{-1} frequency is not reasonable for any vibrations of the trimethylsilylimino radical, and would be anomalously large for the SiN stretching vibration of a species $(H_3C)_2Si{=}NCH_3$, particularly in view of the fact that even in iminosilicon, in which the opportunity for a "triple bond" exists, the NSi vibration frequency is only 1,198 cm^{-1} (ref. 2). The proposed *N*-(dimethylsilyl)methylenimine product might therefore be envisaged to result from what would effectively be a methyl migration and a hydrogen atom back-migration, all presumably occurring in the interval between the absorption by a $(H_3C)_3SiNNN$ molecule of an energetic

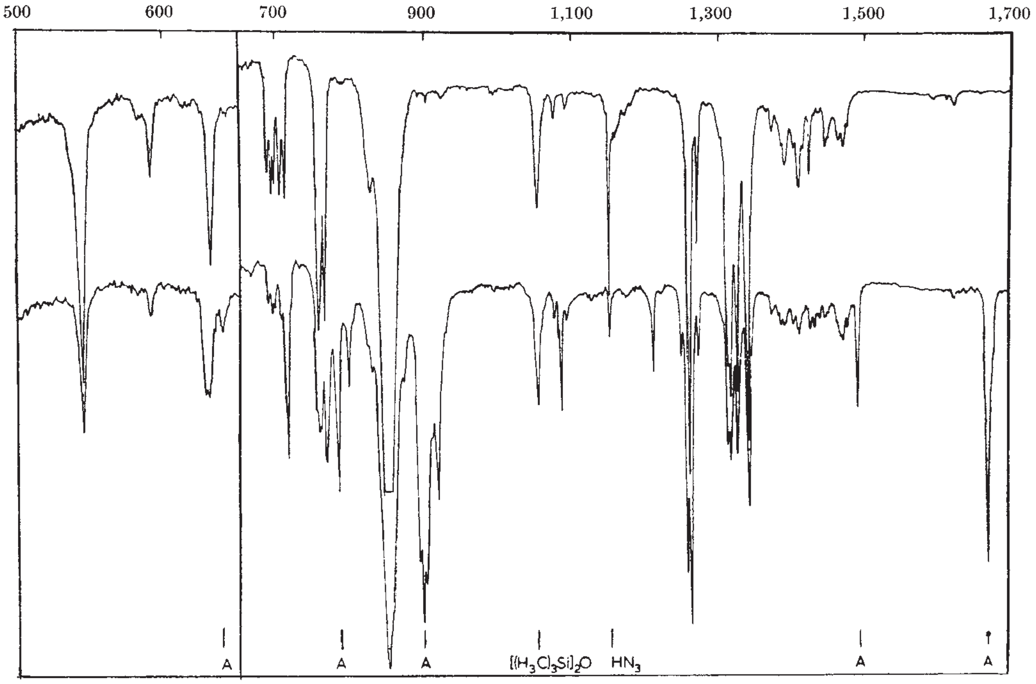

Fig. 1. Infrared transmittance of $(H_3C)_3SiNNN$ and decomposition products in an argon matrix at 17° K., matrix ratio 195. Upper curve, before, and lower curve, after 1·5 h of photolysis. Note change of scale at 650 cm^{-1}; curves have been displaced for clarity.

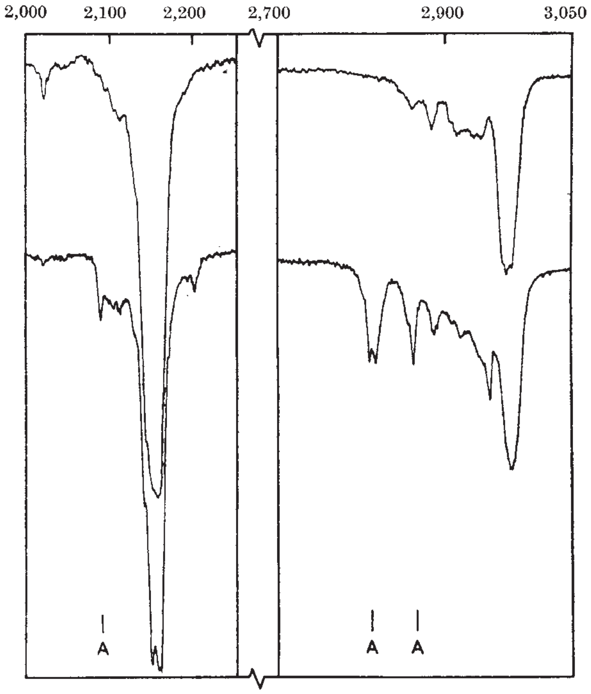

Fig. 2. Same as Fig. 1, but different spectral range.

photon (wavenumber greater than 40,000 cm^{-1} in the region of significant electronic absorption of this molecule) and the degradation of excess energy to the argon lattice. Notwithstanding the speculative nature of the proposed assignment of the specified absorptions to $(H_3C)_2SiH—N=CH_2$* the conclusion is that these frequencies are not appropriate for the species $(H_3C)_2Si=NCH_3$, the most simply rearranged isomer of the $(H_3C)_3SiN$ product of the presumed primary photochemical process. Whether the 1,671 cm^{-1} band belongs to the $C=N$ vibration of either the proposed structure or to a $C=C$ or $C=N$ bond of a different structure, the rearrangement necessary to accomplish this structure would seem to be more complex. Thus the final structure would almost certainly represent greater thermodynamic stability than that of $(H_3C)_2Si=NCH_3$. The essential difference between the latter structure and any other reasonable one is the position of the π-bond. These experiments have therefore provided some evidence for the comparative weakness of the π-bonding effect for atoms beyond the first row.

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* Comparison with a vapour-phase spectrum of $(H_3C)_2SiH-CH=CH_2$, provided by Drs P. W. Owen and P. S. Skell of the Pennsylvania State University, indicates frequency similarities in the 700 to 1,300 cm^{-1} region but no counterpart of their intense SiH vibration at 2,130 cm^{-1}; however, the latter might still be hidden under the azide band.

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BIOLOGICAL SCIENCES

Altered Gene Expression during Differentiation : Population Changes in Hybridizable RNA after Stimulation of the Chick Oviduct with Oestrogen

THE molecular control mechanisms regulating embryogenesis are not fully defined. The appearance of morphological differentiation must reflect prior biochemical differentiation and changes in patterns of protein synthesis. In spite of the well documented evidence that *m*RNA is present before the eggs are fertilized[1], it seems plausible