CHEMISTRY LETTERS, pp. 1029-1032, 1986.

MATRIX ISOLATION OF A SILICON-NITROGEN DOUBLE BONDED SILAIMINE

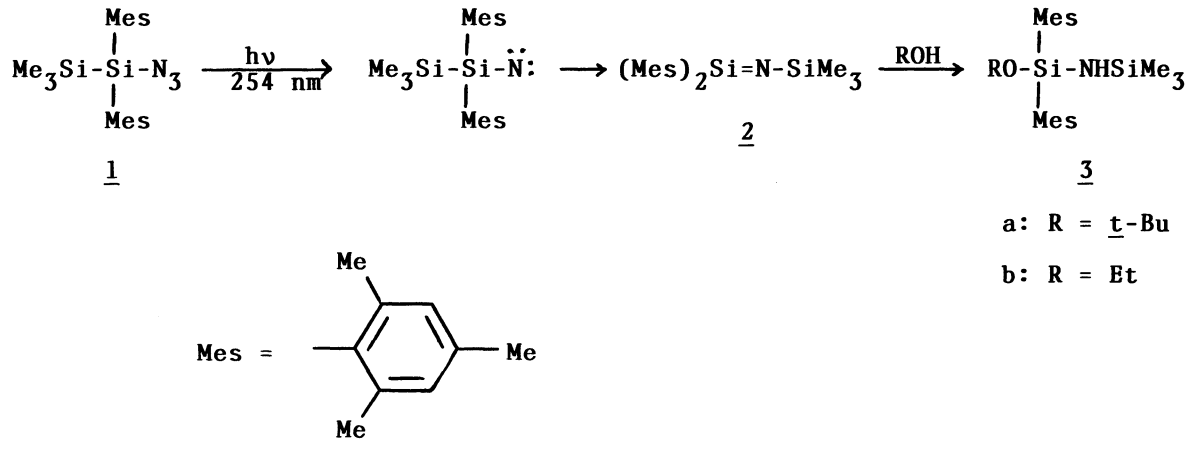
Akira SEKIGUCHI, Wataru ANDO,* and Koichi HONDA†
Department of Chemistry, The University of Tsukuba,
Niihari-gun, Ibaraki 305
†National Chemical Laboratory for Industry,
Yatabe, Ibaraki 305

A silicon-nitrogen double-bonded silaimine was isolated in the matrix at low temperature by the photolysis of (dimesityl)-(trimethylsilyl)silylazide. The silaimine has an intense orange color, and shows electronic absorption bands at 272 and 474 nm assigned to π-π^* and n-π^* transitions respectively.

Much interest has been expressed recently in multiply-bonded silicon compounds, and silenes and disilenes have been isolated as stable compounds at room temperature.1) The exsistence of compounds with Si=O2) and Si=P3) double bonds has been confirmed by chemical and spectroscopic means. However, there is little precedent for the isolation of Si=N double-bonded compounds (silaimines) since evidence for their transient exsistence was first presented in 1974 by Sommer.4) A recent report of Wiberg et al.,5) which describes the isolation of a silaimine at room temperature, prompts us to communicate our results so far. We wish to report here the matrix isolation of a silaimine by photolysis of (dimesityl)(trimethylsilyl)silylazide 1.6)

When a cyclohexane solution of 17) was irradiated with a low pressure mercury lamp (254 nm) at room temperature, an unidentified polymeric substance was formed. However, photolysis of a cyclohexane/t-butanol solution of 1 gave disilazane 3a in almost quantitative yield (92%). Similarly, disilazane 3b was obtained in 81% yield in cyclohexane/ethanol (Scheme 1).8)

The formation of silazanes 3a and 3b can be rationalized by the reaction of silaimine 2 with alcohols. It should be noted that exclusive migration of trimethylsilyl group to the nitrene center was observed; neither mesityl migration nor C-H insertion of the nitrene into the ortho methyl groups occurred.



Scheme 1.

Similar effective and selective migration of trimethylsilyl group has been shown for polysilylated carbenes.[9)]

When an isopentane/methylcyclohexane (3 : 1) solution of 1 ($\approx 10^{-3}$ to $\approx 10^{-4}$ M) was irradiated at room temperature, the absorption band (237 nm) of 1 decreased regularly with irradiation time. However, when the solution was cooled to 77 K, photolysis of the resulting matrix led to the appearance of a new band with a maximum of 272 nm which grew on irradiation. At higher concentration (≈ 0.1 to ≈ 0.01 M), an additional band with a maximum of 474 nm was also observed, and indeed the matrix turned intensely orange after photolysis. These bands gradually decreased on prolonged irradiation, and immediately disappeared on melting of the matrix. The same absorption bands were observed in an EPA (5 : 5 : 2) matrix at 77 K, and melting of the matrix resulted in an immediate discoloration with the concurrent formation of trapping product 3b. On the basis of these results, it is reasonable to assume that the absorption band at 272 nm is due to the π-π^* transition and that at 474 nm is the n-π^* transition of silaimine 2.

Irradiation of 1 in argon matrix at 20 K also gave the same results. The absorption bands assignable to silaimine 2 also gradually decreased on prolonged irradiation probably due to the secondary photochemical reaction of 2. Evidence for the chemical identity of 2 is provided by the reaction with ethanol. Silyl azide 1 was irradiated at 20 K in argon matrix containing ethanol (Ar/EtOH; 730/30). The matrix was warmed slowly to room temperature, and the substances remaining on the CsI window were collected and shown by GC mass spectroscopy to be a mixture of two components, A and B (Ratio 54/46). Component A had an identical retention time and mass spectrum to that of 3b. This is consistent with the isolation of π-bonded silaimine 2 in argon matrix. The structure of component B cannot be determined at this time, but it may be either a secondary photochemical product of 2 or a C-H insertion product of the nitrene.10)

The infrared spectra of 1 and the photochemical products in argon matrix at 20 K were investigated. During irradiation of 1 in argon matrix at 20 K with a high pressure mercury lamp ($\lambda > 240$ nm), intensity of bands due to 1 in the infrared spectrum decreased and the new bands appeared. The most notable of these are at 1190 (m), 1155 (m), 1080 (m), 930 (s), 835 (s), and 635 cm^{-1} (w). The infrared spectrum after photolysis in the presence of ethanol was identical except for the bands due to ethanol. We cannot determine the infrared bands assignable to 2 because, as mentioned above, a mixture of two components is found upon photolysis. At this time, we are not able to distinguish between the bands which result from 2 and component B. While the infrared spectrum of 2 has remained elusive, the present experiments give a striking example of the isolation of π-bonded silaimine in a matrix.

We thank Professor R. West and Mr. S. S. Zigler for helpful discussions.

References

1) For silenes: A. G. Brook, F. Abdesaken, B. Gutekunst, G. Gutekunst, and R. K. Kallury, Chem. Commun., 1981, 191; A. G. Brook, S. C. Nyburg, F. Abdesaken, B. Gutekunst, G. Gutekunst, R. K. Kallury, Y. C. Poon, Y. M. Chang, and W. Wong-Ng, J. Am. Chem. Soc., 104, 5667 (1982); N. Wiberg and G. Wagner, Angew. Chem., Int. Ed. Engl., 22, 1005 (1983); N. Wiberg and G. Wagner, J. Organomet. Chem., 271, 381 (1984). For disilenes: R. West, M. J. Fink, and J. Michl, Science (Washington, D. C.), 214, 1343 (1981); S. Masamune, Y. Hanzawa, S. Murakami, T. Bally, and J. Blount, J. Am. Chem. Soc., 104, 1150 (1982); H. Watanabe, T. Okawa, M. Kato, and Y. Nagai, Chem. Commun., 1983, 781.

2) C. A. Arrington, R. West, and J. Michl, J. Am. Chem. Soc., 105, 6176 (1983); R. Withnall and L. Andrews, ibid., 107, 2567 (1985).

3) C. N. Smit, F. M. Lock, and F. Bickelhaupt, Tetrahedron Lett., 25, 3011 (1984).

4) C. M. Golino, R. D. Bush, and L. H. Sommer, J. Am. Chem. Soc., 96, 614 (1974).

5) N. Wiberg, K. Schurz, and G. Fischer, Angew. Chem., 97, 1058 (1985).

6) Photolysis of silyl azides in an inert matrix at low temperature has been studied previously, but no evidence for the generation of silaimines was obtained. See: J. F. Ogilvie and S. Cradock, Chem. Commun., 1966, 364; J. F. Ogilvie, Nature, 218, 1248 (1968); R. N. Perutz, J. Photochem., 9, 195 (1978); R. N. Perutz, Chem. Commun., 1978, 762.

7) Silyl azide 1 was prepared in 46% yield from (dimesityl)(trimethylsilyl)-chlorosilane and sodium azide in THF. NMR (CCl_4, δ) 0.23 (s, 9H), 2.25 (s, 6H), 2.32 (s, 12 H), 6.78 (br.s, 4H); IR (KBr) 2130 cm^{-1} (N_3); high resolution mass spectrum, 353.1986 (M^+-N_2) (calcd for $C_{21}H_{31}NSi_2$: 353.1987).

8) Spectral data of products 3a and 3b: 3a: NMR (CCl_4,δ) -0.13 (s, 9H), 1.23 (s,9H), 2.22 (s,6H), 2.32 (s,12H), 6.67 (br.s, 4H); IR (NaCl) 3400 (NH) and 1030 cm^{-1} (Si-O-C); high resolution mass spectrum 427.2726 (calcd for $C_{25}H_{41}NOSi_2$: 427.2716). 3b: NMR (CCl_4,δ) -0.10 (s, 9H), 1.15 (t, 3H), 2.22 (s, 6H), 2.33 (s, 12H), 3.60 (q, 2H), 6.73 (br.s, 4H); IR (NaCl) 3400 (NH) and 1070 cm^{-1} (Si-O-C); high resolution mass spectrum, 399.2412 (calcd for $C_{23}H_{37}NOSi_2$: 399.2404).

9) W. Ando, A. Sekiguchi, and T. Sato, J. Am. Chem. Soc., 103, 5573 (1981); A. Sekiguchi and W. Ando, Chem. Lett., 1983, 871; A. Sekiguchi, W. Ando, and K. Honda, Tetrahedron Lett., 26, 2337 (1985).

10) Mass spectrum of component B: 353 (M^+), 338 (M^+-Me), 234 (M^+-Mes).

(Received March 29, 1986)