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OBSERVATION OF A SILANIMINE IN AN INERT MATRIX AND IN SOLUTION AT LOW TEMPERATURE

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Irradiation of Mes_3SiN_3 in 3-methylpentane at 77 K or -140 °C yields the silanimine, $Mes_2Si{=}NMes$. The silanimine is yellow (λ_{max} = 296, 444 nm) and decomposes at temperatures above ca. -120 °C.

Compounds containing silicon-carbon[1)] and silicon-silicon[2)] double bonds have recently been isolated as solids at room temperature. Evidence for the transient existence of Si=N, Si=O, Si=P, and Si=S double bonds has also been published.[3)] The matrix isolation technique has been used in the observation of a Si=O double bond[4)] and also Si=C double bonds prior to their isolation as stable compounds.[5)] Recently, Wiberg has reported the isolation of a stable THF complex of a silanimine.[6)] We report here our results on the generation of Si=N double bonds (silanimines) both in matrix[7)] and in solution at low temperatures.

Irradiation[8)] of trimesitylazidosilane (Mes_3SiN_3)[9)] at 77 K in a 3-methylpentane (3-MP) glass leads to the formation of three new bands in the UV-VIS spectrum (Fig. 1). Two of these bands (296 nm and 444 nm) grow in at the same rate and can most likely be assigned to one species. The third band (257 nm) grows in at a different rate than the first two. All three bands persist on warming until the temperature reaches approximately -120 °C when the 296 nm and 444 nm bands rapidly disappear. The 257 nm band remains even after warming to room temperature and recooling to 77 K. These results indicate that two products are formed in the photolysis of Mes_3SiN_3.

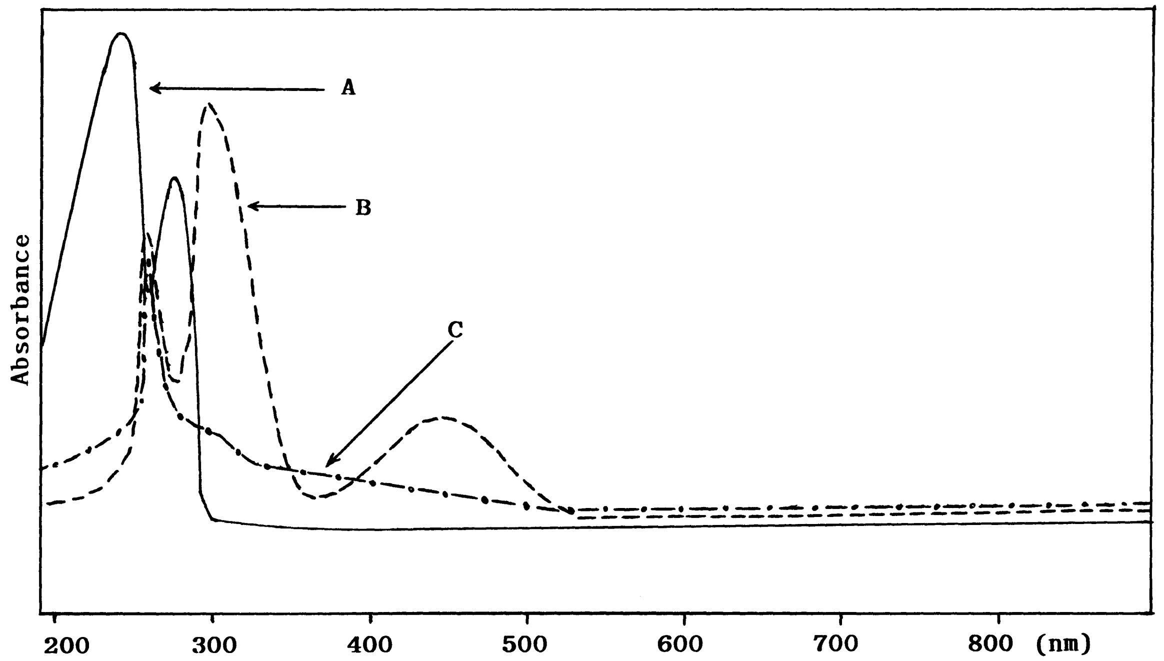
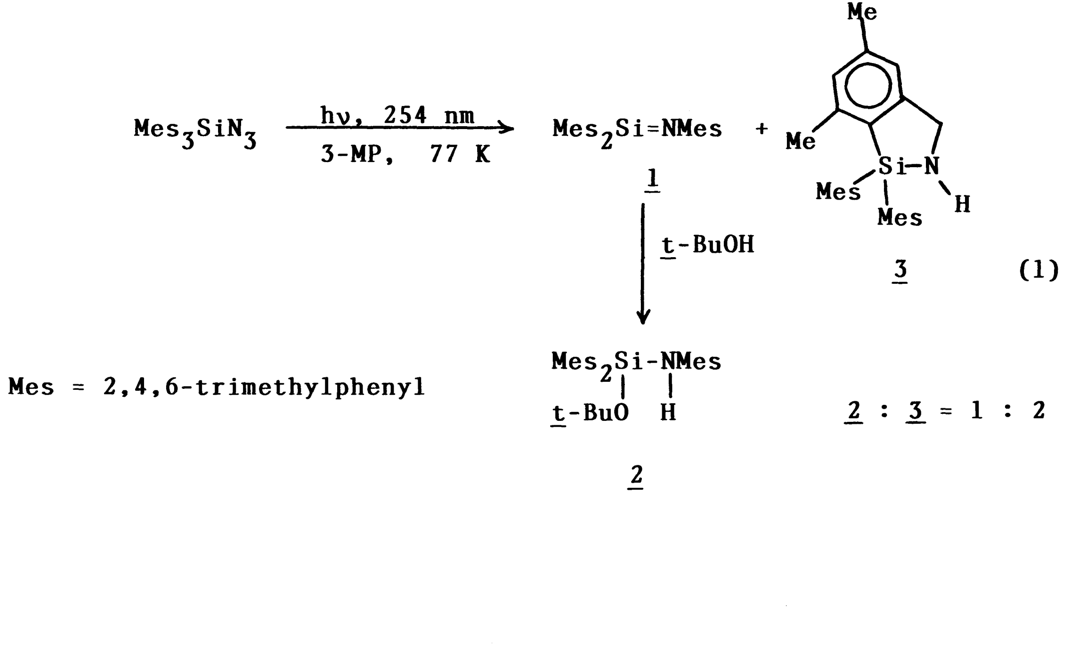


Fig. 1. (———) Mes_3SiN_3 prior to photolysis (A). (– – –) After photolysis [5 min , 77 K, 3-MP, starting material subtracted (B)]. (—•—•—) After warming to room temperature and recooling to 77 K (C).

In order to determine the structure of these products, Mes_3SiN_3 was irradiated in a 3-MP matrix containing t-BuOH as a trapping agent. In these experiments, the same three bands appear, but those at 296 nm and 444 nm immediately disappear on annealing the matrix. Again, the 257 nm band is not affected by increasing temperature. Analysis[10)] of the photolysate shows that the trapping product 2 and the C-H insertion compound 3 are formed in a ratio of about 1 : 2 (Eq. 1).



(1)

Mes = 2,4,6-trimethylphenyl

2 : 3 = 1 : 2

The silazane 2 must result from the addition of t-BuOH to the silanimine 1.[11]

Based on the above evidence, we assign the silanimine 1 as the species responsible for the 296 nm and 444 nm bands. It is probable that the 296 nm band is due to a π-π^* transition while that at 444 nm is an n-π^* transition. The 257 nm band is due to the C-H insertion compound 3. This assignment is confirmed by the following control experiment: the UV-VIS spectrum of a mixture of Mes_3SiN_3 and 3 was taken at 77 K in 3-MP. After subtracting out the spectrum due to Mes_3SiN_3, a spectrum is obtained which is identical to curve C in Fig. 1.

A yellow solution of 1, admixed with 3, can be made by the photolysis of a 3-MP solution of Mes_3SiN_3 at -140 °C. The solution is stable for at least one hour at this temperature. Addition of t-BuOH immediately discharges the yellow color with the formation of trapping product 2. Warming the yellow solution above ca. -120 °C leads to loss of color and the production of as yet unidentified products. Thus 1 appears to be stable at low temperature in solution, as well as in 3-MP matrix at 77 K.

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8) All photolyses were carried out on degassed samples in quartz vessels with a Rayonet RPR-100 photochemical reactor equipped with 16 RPR-2537 Å lamps.

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