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Photolysis of an Azidogermane. Observation of a Germanimine (Ge=N) in Hydrocarbon Matrices

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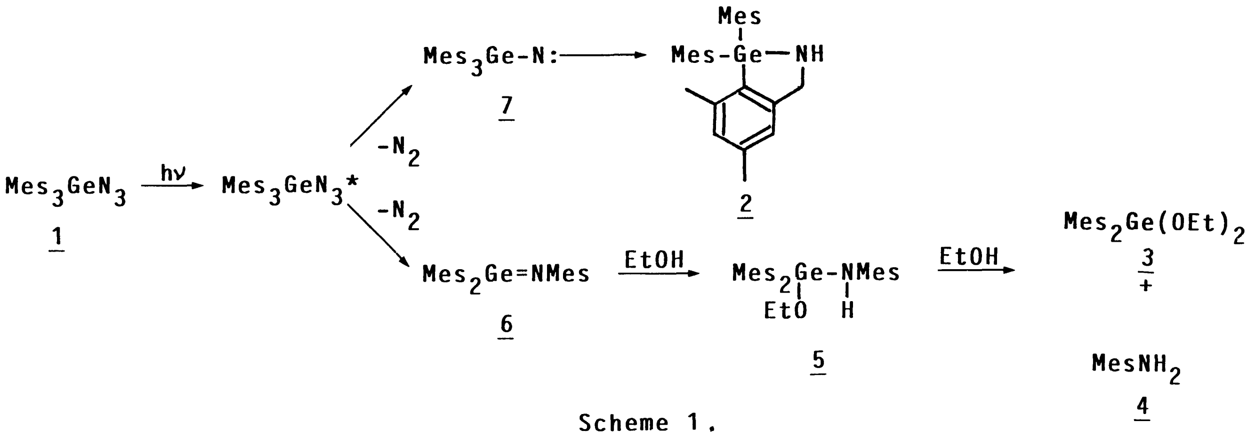
Irradiation of Mes_3GeN_3 in a 3-methylpentane matrix at 77 K yields the germanimine, $Mes_2Ge=NMes$, which is intensely yellow in color with maxima at 309 nm and 459 nm.

Compounds of group 14 with lower coordination numbers are of current interest because of their unusual structure and reactivity.[1)] Although the decomposition of azidosilanes through Curtius type rearrangements are well known to be one of the useful method for generating silanimine (Si=N),[2-4)] the decomposition of azidogermanes remains rather limited so far.[5,6)] Very recently, Glidewell et al. reported the first isolation of a stable germanimine by the reaction of a germylene with a diazo compound.[7)] We report here the matrix isolation of a germanimine by photolysis of azidotrimesitylgermane (1) (mesityl(Mes)=2,4,6-trimethylphenyl).[8)]

When a cyclohexane solution of 1 was irradiated with a low pressure mercury lamp (254 nm) at room temperature, azagermacyclopentene (2)[9)] was obtained in about 50 % yield along with unidentified polymeric products. In the presence of ethanol in addition to 50 % yield of 2, diethoxydimesitylgermane (3)[10)] and 2,4,6-trimethylaniline (4) were obtained in 14 % and 11 % yields, respectively (Scheme 1).

The formation of 3 and 4 can be rationalized by ethanolysis of aminoethoxygermane (5) which is formed by the reaction of germanimine (6) and ethanol. As reported earlier the preliminary addition product (5) was not observed because of the lability of Ge-N bond.[5)] Compound 2 evidently arises from insertion of an intermediate germylnitrene (7) into the C-H bond of an ortho methyl group. Similarly to alkylazides[11)] and azidosilanes[12)] germanimine and germylnitrene may be formed independently from the excited state of azidogermane, and germylnitrene (7) may not undergo rearrangement to germanimine (6)



Scheme 1.

Irradiation of 1 in a 3-methylpentane (3-MP) matrix at 77 K for 10 min led to intense yellow coloration of the glass, and two new absorptions were produced at 309 nm and 459 nm (Fig. 1). These two bands grew in at the same rate and can most likely be assigned to one species. When the matrix was allowed to stand at 77 K in the dark for 3 h, the 309 nm and 459 nm absorptions shifted to 302 nm and 447 nm, respectively. On annealing of the matrix these bands immediately disappeared, and analysis of the photolysate showed the formation of 2. Similar photolysis of 1 in an isopentane (IP)/3-MP (97/3) matrix, which is a relatively soft matrix compared to 3-MP matrix,[13)] the yellow species was formed and UV-vis spectroscopy showed that two absorptions were produced at 302 nm and 447 nm. In this case no remarkable change was observed on standing in the dark. The same absorptions 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 3 and 4.

On the basis of above results it is reasonable to assume that the species responsible for the 309 nm and 459 nm in 3-MP is due to germanimine (6). It is probable that the 309 nm band is due to a π-π^* transition and that at 459 nm is an n-π^* transition. The hypsochromic shift observed in a 3-MP matrix on standing in the dark is tentatively attributed to the change of the conformation of germanimine (6). The germanimine could be generated in a twisted form in a rigid matrix, that relax to the more stable geometry on standing. In a soft matrix the most stable conformation will be readily achieved. Recently, West et al. reported a matrix isolated silanimine, Mes$_2$Si=NMes showed electronic absorptions with λ_{max} at 296 nm and 444 nm.3) Our assignment agrees with that of West et al. While the generation of germylnitrene (6) is the major reaction in the photolysis of azidogermane (1), the present experiments give a striking example of the isolation of a germanimine in matrices.

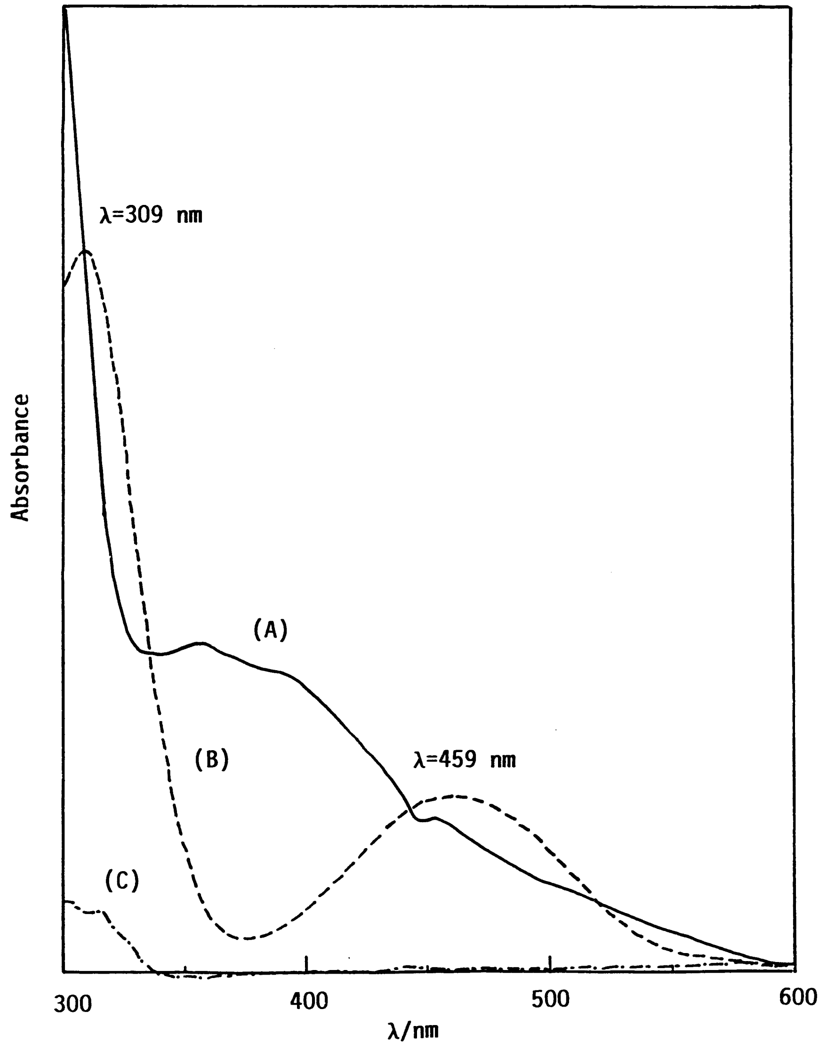


Fig. 1. Photolysis of azidotrimesitylgermane (1) in a 3-MP matrix at 77 K: (A)1 prior to photolysis (———); (B)after photolysis of 1 with a low pressure mercury lamp for 10 min, starting material subtracted (-----); (C)after annealing and recooling to 77 K, starting material subtracted (-·-·-).

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8) The azidogermane (1) was prepared in a quantitative yield from chlorotrimesitylgermane and sodium azide in THF. In the absence of UV light 1 did not react with ethanol at room temperature. 1: mp 170-171 °C; ^{1}H NMR (CDCl$_3$)δ2.20(s,18H), 2.30(s,9H), 6.93(s,6H); IR (KBr) 2090 cm^{-1} (N$_3$); MS, m/e (relative intensity) 445(1,M$^+$-N$_2$), 431(100,Mes$_3$Ge), 354(31,M$^+$-Mes), 326(13,Mes$_2$GeN), 312(58,Mes$_2$Ge).

9) 2: mp 232-235 °C; ^{1}H NMR (CDCl$_3$)δ 2.22(s,18H), 2.29(s,3H), 2.30(s,3H), 4.48(s,2H), 6.77(s,4H), 6.84(s,1H), 6.89(s,1H); ^{13}C NMR(CDCl$_3$)δ 21.0(q), 21.3(q), 23.3(q), 23.8(q), 51.7(t), 121.8(d), 128.9(d), 129.0(d), 130.6(s), 137.5(s), 138.4(s), 139.0(s), 141.1(s), 142.4(s), 150.4(s); IR(KBr) 3360 cm^{-1} (NH); MS, m/e (relative intensity) 445 (41,M$^+$), 430(100,M$^+$-Me), 320(14,M$^+$-Mes).

10) 3: mp 88-89 °C; ^{1}H NMR (CDCl$_3$)δ1.20(t,J=7 Hz,6H), 2.29(s,6H), 2.50(s,12H), 3.70(q,J=7 Hz,4H), 6.85(s,4H); MS, m/e (relative intensity) 357(58,M$^+$-OEt), 312(55,M$^+$-2OEt), 193(100,MesGe).

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