Photolysis of Diazidosilanes. Generation and Reactions of Digonal Silicon Intermediates such as Silacarbodi-imides

By Wataru Ando,* Hidetoshi Tsumaki, and Masayuki Ikeno

(Department of Chemistry, University of Tsukuba, Niiharigun, Ibaraki 305, *Japan)*

Summary Photolysis of diazidosilanes affords novel digonal silicon intermediates such as silacarbodi-imides which are trapped with t-butyl alcohol.

Considerable attention has been focused in recent years on the chemical behaviour of reactive silaimine species, and several papers that deal with the generation and chemical trapping of these intermediates have been published.[1]

Although theoretical studies[2] and thermal generation[3] of digonal silicon intermediates such as 2-sila-allene $CH_2{=}Si{=}CH_2$ and the silaketen $CH_2{=}Si{=}O$ have already been reported, we report in this communication the first example of the formation of silacarbodi-imide intermediates by the photolysis of dialkyldiazidosilanes.

A cyclohexane solution of diazidodimethylsilane and a five-fold excess of t-butyl alcohol was irradiated in a quartz tube with a low-pressure mercury lamp for 12 h. Evaporation followed by g.l.c. analysis gave two main products, methyl-*N*-methylaminodi-t-butoxysilane (**1**) and *N*-methylaminotri-t-butoxysilane (**2**) in 27 and 42% yield, respectively. Similarly, the photolysis of diazidomethylphenylsilane gave (**3**) in 30% yield, and that of diazidodiphenylsilane in ether afforded the two photoproducts (**4**) and (**5**) in 6 and 15% yield, respectively.

$$\mathrm{Me_2Si(N_3)_2 + Bu^tOH \xrightarrow[c\text{-}C_6H_{12},\ 12\ h]{h\nu} \underset{(\mathbf{1})}{MeSi(NHMe)(OBu^t)_2} + \underset{(\mathbf{2})}{(Bu^tO)_3SiNHMe}}$$

$$\mathrm{PhMeSi(N_3)_2 + Bu^tOH \xrightarrow[c\text{-}C_6H_{12},\ 12\ h]{h\nu} \underset{(\mathbf{3})}{MeSi(NHPh)(N_3)OBu^t}}$$

$$\mathrm{Ph_2Si(N_3)_2 + Bu^tOH \xrightarrow[Et_2O,\ 9\ h]{h\nu} \underset{(\mathbf{4})}{PhSi(NHPh)(OBu^t)_2} + \underset{(\mathbf{5})}{(PhNH)_2Si(OBu^t)_2}}$$

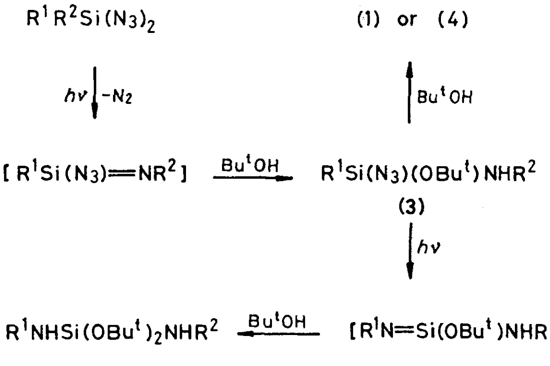
$$\begin{tikzcd}
\mathrm{R^1R^2Si(N_3)_2} \arrow[r, "h\nu", "-2N_2"'] & {[\mathrm{R^1-N=Si=N-R^2}]} \arrow[d, "\mathrm{Bu^tOH}"] \\
\mathrm{R^1NHSi(OBu^t)_3} & \mathrm{R^1NHSi(OBu^t)_2NHR^2} \arrow[l, "\mathrm{Bu^tOH}"']
\end{tikzcd}$$

(**2**) $R^1 = R^2 = Me$ (**5**) $R^1 = R^2 = Ph$

Scheme 1.

The formation of (**2**) and (**5**) strongly suggests the intermediacy of highly reactive unsaturated silicon–nitrogen species, namely *NN'*-dialkylsilacarbodi-imides; product (**5**) may arise from the addition of two molecules of t-butyl alcohol to this intermediate, and the formation of (**2**) can also be explained by a similar addition of t-butyl alcohol to yield bis-*N*-methylaminodi-t-butoxysilane, which subsequently undergoes monobutanolysis to afford compound (**2**) (Scheme 1).

However, the observed product (**3**) indicates another possibility: that the diaminodi-t-butoxysilane $(RNH)_2Si$-



Scheme 2

$(OBu^t)_2$ arises from photolysis of an aminoazido-(t-butoxy)-alkylsilane (Scheme 2). The formation of compounds (**1**) and (**4**) is attributed to monobutanolysis of compounds of type (**3**). The available evidence does not allow us to make a definitive choice between these two mechanisms.

(*Received*, 23*rd March* 1981; *Com.* 330.)

[1] K. C. Patirand and C. N. R. Rao, *Indian J. Chem.*, 1968, **6**, 220; D. W. Klein and J. W. Connolly, *J. Organomet. Chem.*, 1971, **33**, 311; D. R. Paeker and L. H. Sommer, *J. Am. Chem. Soc.*, 1976, **98**, 618; *J. Organomet. Chem.*, 1976, **110**, C1; U. Klingebiel and A. Meller, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 312; U. Klingebiel, D. Bentman, and A. Meller, *J. Organomet. Chem.*, 1978, **144**, 381; U. Klingebiel, *J. Organomet. Chem.*, 1978, **152**, 33; M. Elsheikh, N. R. Pearsos, and L. H. Sommer, *J. Am. Chem. Soc.*, 1979, **101**, 2491; M. Elsheikh and L. H. Sommer, *J. Organomet. Chem.*, 1980, **186**, 301.

[2] M. J. S. Dewar, D. H. Lo, and C. A. Ramsden, *J. Am. Chem. Soc.*, 1975, **97**, 1311.

[3] Bertrand *et al.* reported that the thermal decomposition of the adduct of 3,9-dichloro-4,10-dimethyl-6-sila[5,5]spiroundeca-1,3,7,9-tetraene with dimethyl acetylenedicarboxylate afforded 2-sila-allene or silaketen intermediates: G. Bertrand, G. Manuel, and P. Mazerolles, *Tetrahedron*, 1978, **34**, 1951.