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Preliminary communication

PYROLYSIS OF SILYL AZIDES. GENERATION AND REACTIONS OF UNSATURATED SILICON—NITROGEN INTERMEDIATES [R_2Si=NR]

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Summary

Thermal, gas phase generation of [R_2Si=NR] (R = Ph, Me) from the corresponding silyl azides and subsequent reactions of the reactive intermediates with aldehydes and ketones in a pseudo-Wittig manner are described. The reactive intermediates also insert into $(Me_2SiO)_3$ and $(Me_2SiNMe)_2$ to form the ring expanded products. The latter reactions are the first reported examples of any unsaturated silicon intermediates inserting into a Si—N σ bond.

Following our demonstration that photolysis of triorganosilyl azides, R_3SiN_3 gives reactive silaimine intermediates [R_2Si=NR]** which can be chemically trapped [2], we undertook an investigation of the possible generation of these intermediates by the high temperature, gas phase pyrolysis of R_3SiN_3 compounds. If the thermolysis was successful, it would be of considerable interest to determine if the chemical behavior of silaimines generated in this new manner would parallel that of those generated photochemically.

Early work on the neat thermal decomposition of triphenylsilyl azide prompted some investigators to tentatively postulate an unsaturated silicon—nitrogen species as an intermediate [3,4]. However, this postulate was based on the isolation of hexaphenylcyclodisilazane, $(Ph_2SiNPh)_2$, and its formation under these conditions could be explained by other mechanisms. It was also observed in previous studies that neat thermal decomposition of trimethylsilyl azide produced about twenty volatile compounds [3]. The following compounds were identified from the complex pyrolysis mixture: hydrogen, nitrogen, methane, ethane, ethylene, acetylene, hydrogen cyanide, hydrazoic acid and

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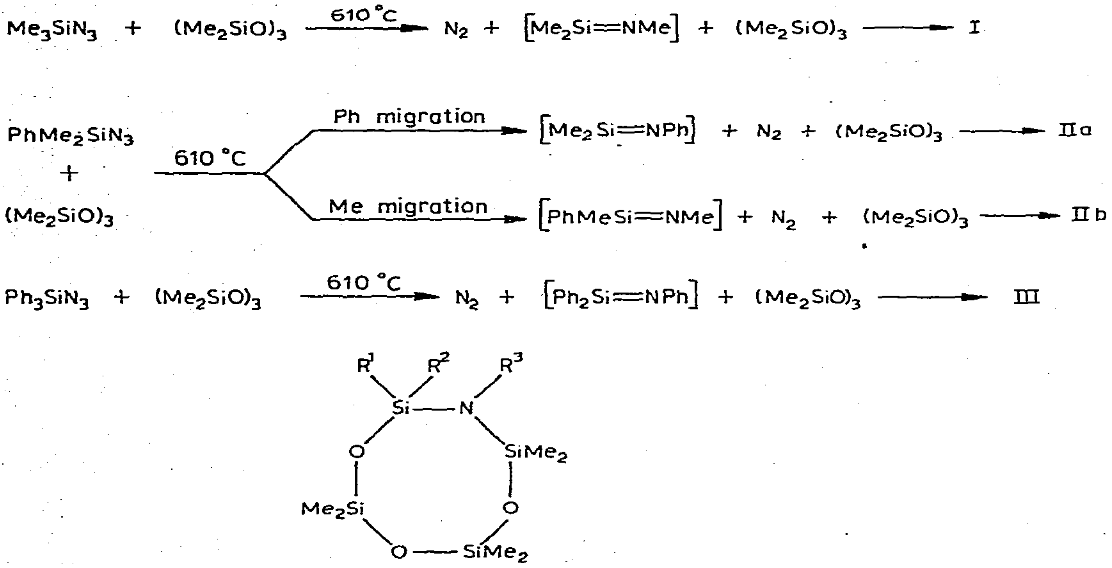
** Chemical behavior indicates (p_π—p_π) double-bond character for [R_2Si=NR]. Theoretical calculations indicate a ground-state triplet structure for [H_2Si=CH_2] [1]. Thus, triplet ground states and singlet reaction states may obtain for unsaturated silicon intermediates.

ammonium azide [5]. Recently, an indirect thermal generation of two unsaturated silicon—nitrogen intermediates was reported [6].

We now report the direct thermal, gas phase generation and reactions of several silaimines from silyl azide precursors*. We have determined that copyrolysis of silyl azides with a suitable trapping agent results in a clean reaction (as monitored by GLPC) and permits isolation of products in reasonable yields (Scheme 1)**.

SCHEME 1



(I) $R^1 = R^2 = R^3 = Me$; 11%
(IIa) $R^1 = R^2 = Me$, $R^3 = Ph$; 17%
(IIb) $R^1 = R^3 = Me$, $R^2 = Ph$; 10%
(III) $R^1 = R^2 = R^3 = Ph$; 25%

(Yields are based on amounts of material isolated by preparative GLPC)

The ring expansion products shown in Scheme 1 were isolated in yields comparable to those obtained from the photolysis of silyl azides in the presence of hexamethylcyclotrisiloxane [2]. This result is compatible with the postulate of a common silaimine intermediate from both the photolysis and pyrolysis of silyl azides.

Thermally generated silaimines also react in a pseudo-Wittig manner when generated in the presence of aldehydes and ketones to produce imines

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*Experimental details of the pyrolysis apparatus and procedure have been previously reported [7].

**New compounds (III, Va, Vb, VI) were characterized by their IR, NMR, and mass spectra. Satisfactory exact mass determinations were obtained either on the parent molecular ion or the $P-15$ m/e (Me) ion.

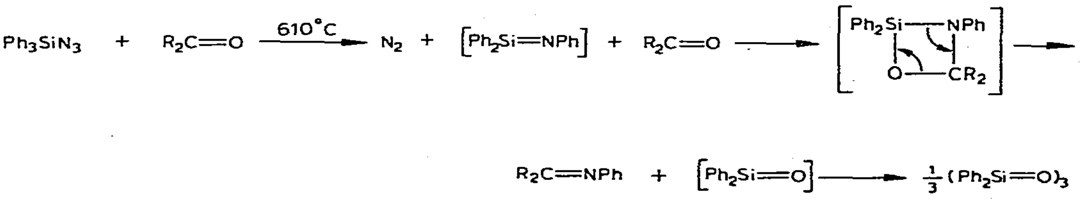
TABLE 1

COPYROLYSIS OF TRIPHENYLSILYL AZIDE WITH ALDEHYDES AND KETONES AT 610°C.

Silyl azide	Trapping Reagent	Yield (%)	
		N-Phenyl imine [a]	$(Ph_2SiO)_3$ [b]
Ph_3SiN_3	$PhMeC{=}O$	62	11
Ph_3SiN_3	$Me_2C{=}O$	34	4
Ph_3SiN_3	$PhHC{=}O$	40	— [c]

[a] Yields are based on amounts of material isolated by preparative GLPC. [b] Hexaphenylcyclotrisiloxane could not be collected by preparative GLPC. Yields are based on the weights of pure material isolated after crystallization. [c] Experimental difficulties precluded the isolation of the hexaphenylcyclotrisiloxane which may have been formed in this reaction.

(Table 1). The reaction is thought to proceed via a four-centered intermediate similar to those proposed for the reaction of aldehydes and ketones with other unsaturated silicon intermediates (eq. 1) [8]. Pyrolysis is at present the only means of generating the silaimines for pseudo-Wittig type reactions.



(1)

Attempts at photochemical generation of silaimines in the presence of carbonyl containing compounds have so far proven unsuccessful.

In addition, we have determined that thermally generated silaimines insert into the Si—N bond of hexamethylcyclodisilazane* to form ring expanded products (Scheme 2).

This is the first reported example of any unsaturated silicon intermediate inserting into a Si—N σ bond. The unusual reactivity of this particular Si—N σ bond is very likely due to ring strain in the four membered ring.

The ability of silaimines to ring expand compounds like hexamethylcyclodisilazane and hexamethylcyclotrisiloxane is of synthetic interest as well. The insertions offer a viable pathway to a large group of novel heterocycles. These compounds would be difficult, at best, to synthesize by other routes.

Formation of organic imines from carbon azides by evolution of nitrogen followed by, or concerted with, rearrangement of the nitrene, have long been known to proceed by photolysis or pyrolysis [10]. From a fundamental standpoint it is interesting to note that of the numerous attempts to form unsaturated silicon species by methods analogous to those employed with carbon compounds, the silyl azide case is one of the few which have yielded positive results.

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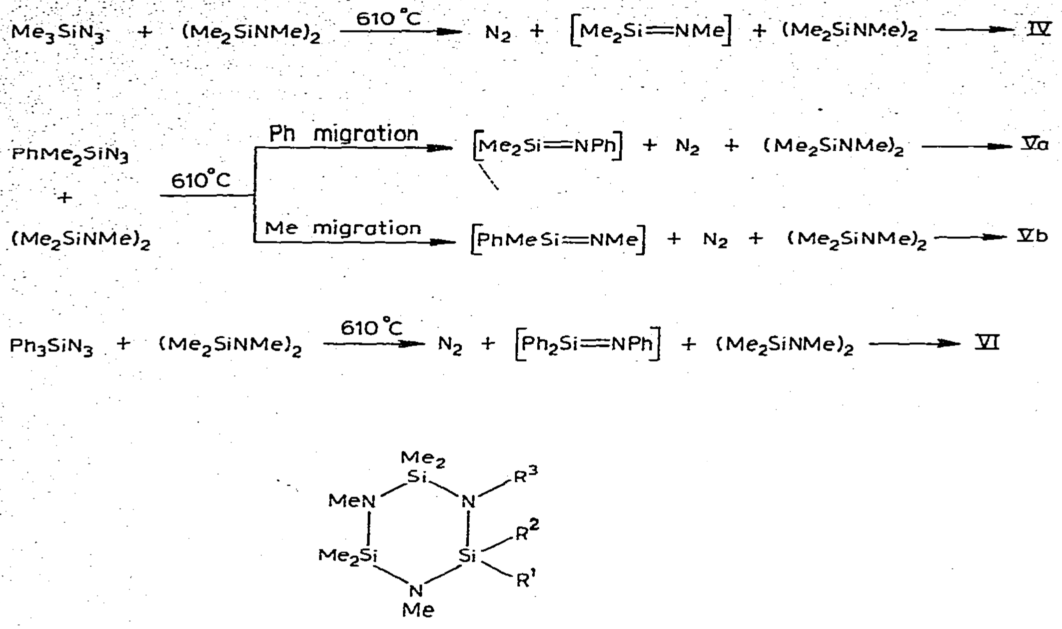
*Neat hexamethylcyclodisilazane was thermally stable under our reaction conditions. Although it has been demonstrated that hexamethylcyclodisilazane may be converted to nonamethylcyclotrisilazane by heating in the presence of catalytic quantities of ammonium bromide [9] no nonamethylcyclotrisilazane was detected after pyrolysis of hexamethylcyclodisilazane with either $PhMe_2SiN_3$ or Ph_3SiN_3.

SCHEME 2



(IV) $R^1 = R^2 = R^3 = Me$; 48%
(Va) $R^1 = R^2 = Me, R^3 = Ph$; 33%
(Vb) $R^1 = R^3 = Me, R^2 = Ph$; 25%
(VI) $R^1 = R^2 = R^3 = Ph$; 31%

Further studies concerning the scope and limitations of the reactions of this interesting class of reactive intermediates are underway.

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References

1 C.M. Golino, W.H. Fink, R.D. Bush and L.H. Sommer, unpublished results.
2 D.R. Parker and L.H. Sommer, J. Amer. Chem. Soc., 98 (1976) 618.
3 W.T. Reichle, Inorg. Chem., 25 (1963) 402.
4 K.C. Patil and C.N.R. Rao, Indian J. Chem., 6 (1968) 220.
5 J.W. Connolly and G. Urry, Inorg. Chem., 1 (1962) 718.
6 C.M. Golino, R.D. Bush and L.H. Sommer, J. Amer. Chem. Soc., 96 (1974) 614.
7 C.M. Golino, R.D. Bush, D.N. Roark and L.H. Sommer, J. Organometal. Chem., 66 (1974) 29.
8 C.M. Golino, R.D. Bush, D.N. Roark and L.H. Sommer, J. Organometal. Chem., 66 (1974) 29;
9 K. Lienhard and E.G. Rochow, Z. Anorg. Allg. Chem., 331 (1964) 316.
10 T.L. Gilchrist and C.W. Rees, Carbenes, Nitrenes, and Arynes, Appleton-Century-Crofts, New York, 1969, p. 94-95.