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THE PHOTOLYSIS OF SILYL AZIDES

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SUMMARY

The photolysis of several trialkylsilyl azides has been studied in detail. The first observable product of the photolysis was found to be a silazane azide which was shown to undergo subsequent photolysis to cyclodisilazanes and higher molecular weight materials. Migratory aptitude ratios are discussed in the context of conformational analysis.

Since the first preparation of silyl azide by Wiberg[1] in 1954, a variety of silyl azides have been prepared[2] and some of the descriptive chemistry of this functional group has been examined[3]. Quantitative work on the decomposition of silyl azides has been restricted to thermal reactions as studied by Ettenhuber and Rühlmann[4]. The only work reported thus far on the photolysis of silyl azides was of an exploratory nature, and the products were not characterized[5].

In this work the photolysis of trimethylsilyl azide, n-propyldimethylsilyl azide and pentamethyldisilanyl azide has been monitored from the first 2% to completion.

TABLE 1

PHOTOLYSIS OF TRIMETHYLSILYL AZIDE

The numbers in parentheses are for the neat photolysis; the rest of the data are for the 10% (benzene) solution photolysis.

Reaction (%)	Yield (% of starting material accounted for)			
	$Me_3SiNMeSiMe_2N_3$ (I)	$(Me_2SiNMe)_2$ (II)	$Me_3Si(NMeSiMe_2)_2N_3$ (III)	$(Me_2SiNMe)_3$ (IV)
2	97			
5	64 (68)		trace	
15	26	9	9	
20	(30)	(8)	(17)	(7)
30	15 (15)	10 (10)	14 (15)	6 (6)
50	11 (14)	10 (10)	12 (16)	5 (5)
70	10 (10)	11 (12)	9 (10)	5 (4)
90	8 (9)	9 (12)	9 (9)	4 (4)

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TABLE 2

PHOTOLYSIS OF n-PROPYLDIMETHYLSILYL AZIDE

The numbers in parentheses are for the neat photolysis; the rest of the data are for the 10% solution photolysis.

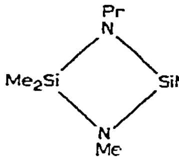
Starting material reacted (%)	Yield (% starting material accounted for)				
	$PrMe_2SiNPrSiMe_2N_3$ (V)	$PrMe_2SiNMeSiPrMeN_3$ (VI)	$(PrMeSiNMe)_2$ (VII)	$(Me_2SiNPr)_2$ (VIII)	 (IX)
2	61	39			
3	(44)	(29)			
5	39 (42)	27 (26)	25 (trace)		
12	24	18	18	8	
20	20 (21)	12 (13)	16 (14)	9 (6)	
30	18	11	19	10	4
47	15	11	20	10	3
90	11 (11)	8 (8)	19 (19)	9 (9)	3 (3)

TABLE 2a

PHOTOLYSIS OF (V) AND (VI)

Photolysis (%)		Product, yield (%)
(V)	68	(VIII) 18, (IX) 7
(VI)	68	(VII) 24, (IX) 6

A summary of our observations is found in Tables 1–3. The reaction sequence outlined in eqns. (1a), (1b) and (1c) is consistent with our observations.

$$R(CH_3)_2SiN_3 \xrightarrow{h\nu} [R(CH_3)_2SiN^*]^\star \qquad (1a)$$

$$[R(CH_3)_2SiN^*]^\star + R(CH_3)_2SiN_3 \rightarrow R(CH_3)_2SiN(R)Si(CH_3)_2N_3 \qquad (1b)$$

$$R(CH_3)_2SiN(R)Si(CH_3)_2N_3 \xrightarrow{h\nu} [(CH_3)_2SiNR]_2 + N_2 \qquad (1c)$$

(or isomer)

Thus the first product of photolysis of all the silyl azides studied here was the silazane azide indicated in eqn. (1b). Cyclodisilazanes were observed only after the presence of the silazane azides was detected. We therefore assume that the cyclodisilazane products were formed by photolysis of the silazane azide (eqn. 1c). This was demonstrated to be a moderate yield reaction in a separate experiment, the results of which are tabulated in Table 2a. Aside from the cyclization reaction depicted by eqn. (1c), it is possible for the intermolecular insertion process to continue, in which case

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⋆ The chemical nature of the intermediate is as yet unknown.

TABLE 3

PHOTOLYSIS OF PENTAMETHYLDISILANYL AZIDE

Starting material reacted (%)	Yield (% starting material accounted for)	
	$Me_5Si_2N(SiMe_3)SiMe_2N_3$ (X)	$[Me_2SiNSiMe_3]_2$ (XI)
3	87	
7	45	44
14	33	64
25	18	62
50	19	53
75	19	54
90	18	53

polysilazane azides result. With the exception of the disilazane azide (III) we were unable to detect such products by gas chromatography.

Recently Abramowitz and Kyba have reported the results of their study of the photolysis of tertiary aliphatic azides[6]. Eqn. (2) describes the first step of their photolysis.

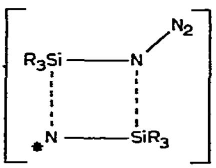
$$R_2R'CN_3 \rightarrow R_2C{=}NR' + RR'C{=}NR \qquad (2)$$

At low temperature they found the migratory aptitudes of R and R' to be non-statistical with the smaller group migrating preferentially. Their interpretation is based on conformational analysis of the ground state azide which requires the smaller group to be in the position most suited to migration to the azide orbital which is vacated during photoexcitation. Since the steric requirement of the azide group is vital to their argument, Abramowitz and Kyba conclude that the reacting species is the photoexcited azide and not the nitrene.

Our data can be interpreted on the basis of conformational analysis also, but we can draw no conclusion about the chemical nature of the reactive intermediate.

From the (V)/(VI) ratio in Table 2 it can be seen that for reaction (1b) where R = Pr the Pr/Me migratory aptitude ratio is approximately 3 throughout the photolysis. The data in Table 2a shows that in the photolysis of (V) (reaction 1c) this ratio is approximately 5; and in the photolysis of (VI) (reaction 1c) this ratio is 1/2. Our explanation of this apparent anomaly is as follows:

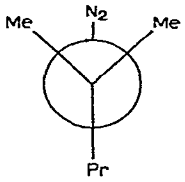
Since reaction (1b) is a bimolecular reaction, we assume that formation of an intermediate such as (XII) precedes product formation. (The asterisk implies only a reactive nitrogen atom, be it nitrene or photoexcited azide.) This complex might appear to be formed by either: (*a*) prior association of two ground state azides; or (*b*) formation of photoexcited azide followed by association; or (*c*) formation of nitrene followed by association. However, process (*a*) seems less likely than (*b*) or (*c*) since:



(XII)

(*i*) cryoscopic data gives no evidence for association of silyl azides[7]; and (*ii*) within the context of the argument below it is necessary for the azide in the complex to either have the same preferred conformation as the unassociated azide or for reaction to occur before a new conformation is achieved. This last condition could be achieved by either (*b*) or (*c*). The extinction coefficients for all the azides studied here are from 10 to 20 so the lifetime of the excited state should be long enough for (*b*) to be a feasible reaction.

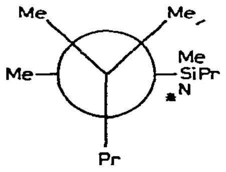
In any case, given the non-linear structure of silyl azides[8] and the assumption that the N_2 group has a larger steric requirement than the nitrogen lone pair, the preferred conformation of the unassociated azide would be as shown in (XIII).



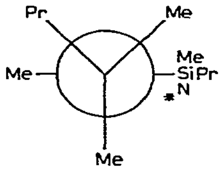
(XIII)

Given the conformation (XIII) of the ground state half of (XII) the active nitrogen will be immediately adjacent to the n-propyl group, thus requiring the migration of this group to nitrogen.

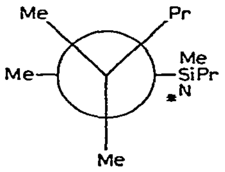
In reaction (1c), considering the photolysis of (VI), structures (XIVa), (XIVb), and (XIVc) are the possible rotational isomers about the R_3Si–N bond.



(XIVa)



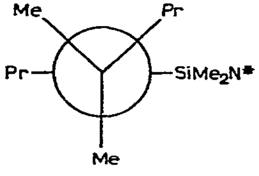
(XIVb)



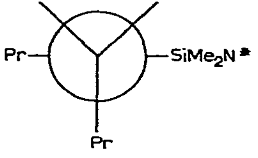
(XIVc)

Conformer (XIVb) would appear to be the preferred one, which would explain the preference for methyl migration in this case.

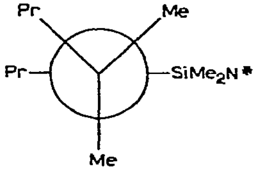
Considering the photolysis of (V), structures (XVa), (XVb), and (XVc) are the possible conformers.



(XVa)



(XVb)



(XVc)

The choise is less obvious here since both the n-propyl and the dimethylazidosilyl groups are bulky. The Pr/Me migratory aptitude ratio observed requires that (XVa) be the preferred structure.

Formally both reaction (1b) and (1c) involve the insertion of monovalent nitrogen into a silicon–carbon bond. The existence of an intermediate such as (XII) is supported by the fact that when trimethylsilyl azide is photolyzed in tetramethylsilane, the tetramethylsilane proved to be completely inert. This is presumably due to the inability of the tetramethylsilane to complex with the reactive intermediate.

The data in Table 3 shows that in the photolysis of pentamethyldisilanyl azide the trimethylsilyl group migrates exclusively compared to the methyl group. This is consistent with the above conformational arguments plus the inherently greater susceptibility of the Si–Si bond to cleavage due to its lower bond energy. The rather high yield of the single cyclodisilazane (XI) suggests that the bond energy factor is the more important.

The data in Table 1 shows that the formation of hexamethylcyclodisilazane (II) from trimethylsilyl azide is a relatively unimportant process. This again can be understood in terms of intermediates like (XII). In this case the trimethylsilyl azide has a small enough steric requirement that it can readily complex the photoexcited species from $Me_3SiN(Me)SiMe_2N_3$ (I) to give $Me_3SiN(Me)SiMe_2N(Me)SiMe_2N_3$ (III). This greater complexing ability would give a higher yield of high molecular weight silazane azides as the data indicate.

In summary, although the formation of the silazane azides (I), (V), (VI), and (X) was not expected at the outset of this work, an internally consistent mechanistic scheme for this reaction can be obtained assuming the existence of (XII) and using the principles of conformational analysis.

EXPERIMENTAL

The starting azides were prepared by refluxing lithium azide and the corresponding chlorosilane in THF. Yields were 70–80%. The boiling point of trimethylsilyl

TABLE 4

ELEMENTAL ANALYSIS

Compound	Calculated (%)				Found (%)			
	C	H	N	Si	C	N	N	Si
$PrMe_2SiN_3$	41.92	9.15	29.33	19.60	41.69	9.10	29.30	19.71
(I)	35.60	8.96	27.68	27.76	36.37	9.26	27.70	27.86
(III)	37.33	9.40	24.18	29.09	37.02	9.35	24.00	29.92
(V)	46.46	10.14	21.67	21.73	46.10	10.96	21.09	21.92
(VI)	46.46	10.14	21.67	21.73	46.17	10.71	21.76	21.91
(VII)	52.11	11.37	12.15	24.37	52.18	11.38	11.90	24.20
(VIII)	52.11	11.37	12.15	24.37	52.22	11.44	11.96	24.11
(IX)	52.11	11.37	12.15	24.37	52.21	11.13	11.96	23.99
(X)	37.68	9.14	17.58	35.25	37.41	9.12	17.57	34.89
(XVI)	55.11	12.72	16.06	16.11	54.84	12.38	16.21	16.22
(XVII)	49.25	12.40	19.15	19.20	50.00	12.67	19.21	19.76
(XVIII)	49.25	12.40	19.15	19.20	49.85	12.47	19.93	20.00

azide was 95° (lit.[9] 96°); for pentamethyldisilanyl azide 47–49/10 mm (lit.[5] 158–160); ν_{asym}(NNN) 2129 cm^{-1} (s) [lit.[5] 2128 cm^{-1} (s)]. n-Propyldimethylsilyl azide was previously unreported. Its boiling point is 143°. The elemental analytical data for this compound are found in Table 4.

The photolyses were carried out using degassed neat samples or 10% by weight solutions in benzene. The photolyses done in tetramethylsilane also had 10% concentration of solute. The photolyses ware carried out in a Rayonet Reactor using Rayonet RPR-2537 lamps for periods ranging from 30 min. to 65 h.

Yield data were obtained gas chromatographically by reference to peak areas of internal standards of appropriate hexaalkyldisiloxanes which were shown to remain invariant in concentration in separate experiments. Total nitrogen production was monitored also.

Product identification was done by elemental analysis and comparison of physical properties with literature values in the more straightforward cases and by comparison of GLC retention times and IR and NMR spectra with independently synthesized samples in the more complicated cases. The elemental analytical data are listed in Table 4, selected IR data in Table 5, NMR data in Table 6.

TABLE 5

SELECTED IR ABSORPTION BANDS FOR PREVIOUSLY UNREPORTED COMPOUNDS

Compound	ν_{asym}(SiNSi) (cm^{-1})	ν_{asym}(NNN) (cm^{-1})
$PrMe_2SiN_3$		2133
(I)	908	2133
(III)	901	2135
(V)	952	2132
(VI)	908	2143
(VII)	897	
(VIII)	921	
(IX)	920, 986	
(X)	901	2150

TABLE 6

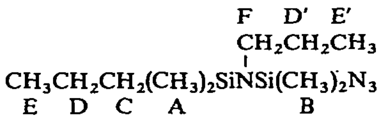
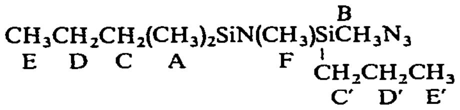
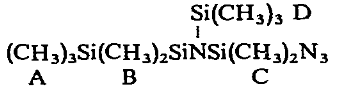
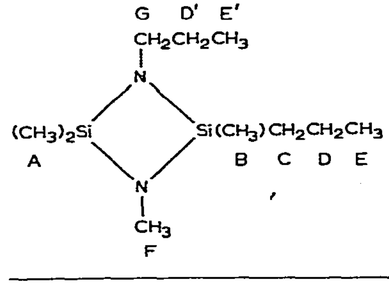
NMR DATA

The numbers in parentheses are the number of lines observed, m stands for many.

Compound		Signal (τ)	Assignment
$CH_3CH_2CH_2(CH_3)_2SiN_3$		9.92 (1)	A
D C B A		9.45 (3)	B
		8.73 (m)	C
		9.00 (3)	D
$(CH_3)_3SiN(CH_3)Si(CH_3)_2N_3$	(I)	9.87 (1)	A
A C B		9.71 (1)	B
		7.44 (1)	C
$(CH_3)_3Si(NCH_3)_2Si(CH_3)_2N_3$	(III)	9.89 (1)	A
A C B		9.70 (1)	B
		7.46 (1)	C

(Continued)

TABLE 6 (*continued*)

Compound		Signal (τ)	Assignment
 $\underset{E}{CH_3}\underset{D}{CH_2}\underset{C}{CH_2}\underset{A}{(CH_3)_2}Si\overset{\overset{F\ D'\ E'}{CH_2CH_2CH_3}}{N}\underset{B}{Si(CH_3)_2}N_3$	(V)	9.70 (1)	A
		9.65 (1)	B
		9.40 (3)	C
		8.75 (m)	D,D'
		9.00 (m)	E,E'
		7.22 (3)	F
 $\underset{E}{CH_3}\underset{D}{CH_2}\underset{C}{CH_2}\underset{A}{(CH_3)_2}SiN\underset{F}{(CH_3)}\underset{\underset{C'\ D'\ E'}{CH_2CH_2CH_3}}{\overset{B}{Si}}CH_3N_3$	(VI)	9.68 (1)	A
		9.65 (1)	B
		9.40 (m)	C,C'
		8.75 (m)	D,D'
		9.08 (m)	E,E'
		7.45 (1)	F
 $\underset{A}{(CH_3)_3Si}\underset{B}{(CH_3)_2Si}\overset{Si(CH_3)_3\ D}{N}\underset{C}{Si(CH_3)_2}N_3$	(X)	9.95 (1)	A
		9.85 (1)	B
		9.75 (1)	C
		10.00 (1)	D
$[\underset{A}{(CH_3)_2}Si\underset{B}{NCH_3}]_2$	(II)	9.89 (1)	A
		7.55 (1)	B
$[\underset{A}{(CH_3)_2}Si\underset{B}{NCH_3}]_3$	(IV)	9.95 (1)	A
		7.55 (1)	B
$[\underset{D}{CH_3}\underset{C}{CH_2}\underset{B}{CH_2}\underset{A}{(CH_3)}Si\underset{E}{NCH_3}]_2$	(VII)	9.76 (1)	A
		9.40 (3)	B
		8.68 (m)	C
		9.05 (3)	D
		7.48 (1)	E
$[\underset{A}{(CH_3)_2}SiN\underset{D}{CH_2}\underset{B}{CH_2}\underset{C}{CH_3}]_2$	(VIII)	9.72 (1)	A
		8.70 (m)	B
		9.06 (3)	C
		7.16 (3)	D
	(IX)	9.76 (1)	A
		9.69 (3)	B
		9.35 (3)	C
		8.70 (m)	D,D'
		9.00 (m)	E,E'
		7.43 (1)	F
		7.21 (3)	G

Hexamethylcyclodisilazane (II) was identified on the basis of its ν_{asym}(SiNSi) (s) at 910 cm^{-1} (lit.[10] 910 cm^{-1}); and its NMR spectrum (Table 6).

N,N-Bis(trimethylsilyl)tetramethylcyclodisilazane (XI) was identified on the basis of its ν_{asym}(SiNSi) (s) at 885 cm^{-1} (lit.[11] 880–890 cm^{-1}), and its NMR spectrum. Nonamethylcyclotrisilazane (IV) was identified by its melting point, 34° (lit.[11] 36°), its ν_{asym}(SiNSi) (s) at 940 cm^{-1} (lit.[11] 935–940 cm^{-1}), and its NMR spectrum.

The remaining cyclodisilazanes were identified by independent synthesis by the method of Lienhard and Rochow[12]. Compounds (V), (VI) and (IX) are new compounds. The following detailed account of the preparation of (VIII) is typical of the preparation of all three. The reaction sequence is shown in eqn. (3).

$$Me_2SiCl_2 + 2\ PrNH_2 \rightarrow Me_2Si(NHPr)_2 \qquad (XVI) \qquad (3a)$$

$$Me_2Si(NHPr)_2 + 2\ BuLi \rightarrow Me_2Si(NLiPr)_2 \qquad (3b)$$

$$Me_2Si(NLiPr)_2 + Me_2SiCl_2 \rightarrow (Me_2SiNPr)_2 \qquad (VIII) \qquad (3c)$$

One mole (129 g) of dimethyldichlorosilane was dissolved in 1.5 liter of petroleum ether. The solution was cooled to 0°, and 120 g (2 moles) of n-propylamine was added slowly with stirring. After warming and filtration, a reduced pressure distillation was done. Bis(n-propylamino)dimethylsilane (XVI) was collected at 92–93°/45 mm in 77% yield. Its elemental analytical data is found in Table 2.

Compound (XVII), bis(methylamino)-n-propylmethylsilane, was prepared in an analogous manner. Yield 76%, b.p. 57–58°/25 mm.

Seventeen grams (0.1 mole) of (XVI) was then dissolved in 100 ml of petroleum ether, and 100 ml of 2 *M* n-butyllithium was added slowly under nitrogen. The mixture was then refluxed for several hours. To this mixture was added 13 g (0.1 mole) of dimethyldichlorosilane followed by 6 h reflux. After filtration, reduced pressure distillation, gave (VIII) at 90°/25 mm in 72% yield.

In the preparation of (IX), (n-propylamino)(methylamino)dimethylsilane (XVIII) was prepared by adding n-propylamine and subsequently methylamine to dimethyldichlorosilane; yield 53%; b.p. 60–65°/25 mm. The preparation of (IX) then proceeded in 31% yield; b.p. 91–95°/19 mm.

The silazane azides reported in this paper were identified by independent synthesis with the exception of (pentamethyldisilanyl)(trimethylsilyl)(dimethylazidosilyl)amine (X). This last compound was identified by its chemical analysis (Table 4), its NMR spectrum (Table 6), and the presence of strong IR bands at 2150 cm^{-1} [ν_{asym}(NNN)] and 901 cm^{-1} [ν_{asym}(SiNSi)].

The permethylsilazane azide (I) has been reported[13], but the details of the synthesis were not presented. We give the detailed account here as being typical of the preparation of (I), (V), and (VI). The reaction sequence is shown in eqns. (4a)–(4c).

$$R_2R'SiNHR'' + BuLi \rightarrow R_2R'SiNLiR'' \qquad (4a)$$

$$R_2R'SiNLiR'' + R_2SiCl_2 \rightarrow R_2R'SiNR''SiR_2Cl \qquad (4b)$$

$$R_2R'SiNR''SiR_2Cl + LiN_3 \rightarrow R_2R'SiNR''SiR_2N_3 \qquad (4c)$$

In 250 ml of anhydrous ether, 15.5 g (0.15 mole) of (trimethylsilyl)methylamine was dissolved and to this solution 65 ml of 2.29 *M* n-butyllithium (0.15 mole) was added under nitrogen. After 2 h reflux, 19.4 g (0.15 mole) of dimethyldichlorosilane was added. This mixture was refluxed for 3 h and filtered. The yield of condensation product was estimated to be 52% by analytical GLC. To the solution containing the condensation product, 4.9 g (0.10 mole) of lithium azide was added. After a 4 h reflux period and filtration, the ether was removed by vacuum evaporation. Small portions of the final product were isolated by preparative GLC. The yield of step (4c) was estimated to be 35% by analytical GLC.

The elemental analytical data for compounds (I), (V), and (VI) are found in Table 4, and the NMR data are found in Table 6.

The preparation of permethyl-trisilazane (III) was carried out according to reaction sequence (5a)–(5c).

$$\mathrm{Me_3SiN(Me)SiMe_2Cl + MeNH_2 \rightarrow Me_3SiN(Me)SiMe_2NHMe} \tag{5a}$$

$$\mathrm{Me_3SiN(Me)SiMe_2NHMe \xrightarrow[(2)\ Me_2SiCl_2]{(1)\ BuLi} Me_3SiN(Me)SiMe_2N(Me)SiMe_2Cl}$$

$$\mathrm{Me_3SiN(Me)SiMe_2N(Me)SiMe_2Cl + LiN_3 \rightarrow Me_3SiN(Me)SiMe_2N(Me)SiMe_2N_3} \tag{5c}$$

As in the previous preparations, the intermediates were not isolated and the final product was isolated by preparative GLC.

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