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CONTRIBUTIONS TO GROUP IV ORGANOMETALLIC CHEMISTRY

X *. ORGANO-1,3,2-DIAZASILACYCLOALKANES

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Summary

The preparation and properties of a series of organo-1,3,2-diazasilacycloalkanes are reported and their mass spectra and ^{1}H, ^{13}C and ^{29}Si NMR spectra discussed in detail.

Introduction

We have for a number of years been interested in the synthesis and properties of silicon heterocycles and have reported our results on organo-1,3,2-dioxasilacycloalkanes [2–5] and organo-1,3,2-dithiasilacycloalkanes [6]. Although there have been a number of reports concerning the synthesis of organo-1,3,2-diazasilacycloalkanes [7–10] their physical properties appear to have been neglected. We now wish to report the results of our investigations concerning the synthesis and physical properties of organo-1,3,2-diazasilacycloalkanes. It is noteworthy that bis-diethylaminosilanes have usually been used as starting materials for transamination [7–10] whereas we found bis(dimethylamino)silanes to be preferable and, indeed, essential in the case of diphenyl-substituted silanes since we were unable to synthesise bis(diethylamino)silane from the interaction of diethylamine and dichlorodiphenylsilane.

Preparation

Attempts at preparing the desired cyclic products by reacting dichlorosilanes with diamines led to the formation of dark coloured, polymeric material. However, the compounds were prepared, in acceptable yield, by transamination reactions involving equimolar amounts of the appropriate bis(dialkylamino)silane and either *N*,*N*′-

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* For part IX see ref. 1.

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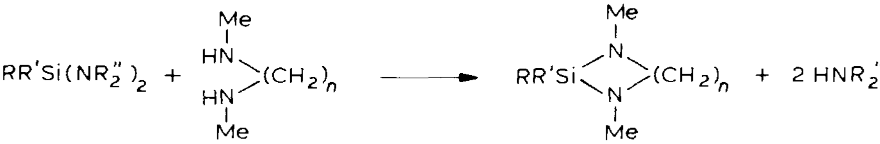
dimethylethane-1,2-diamine or N,N'-dimethylpropane-1,3-diamine [7,9].



(R, R' = Me or Ph ; R'' = Me or Et ; n = 2 or 3)

Heating the reactants alone required relatively high temperatures for prolonged periods of time which, even so, did not always produce complete reaction and tended to encourage polymerization. However, the addition of small quantities (as low as 0.1%) of ammonium sulphate as catalyst [3,10] increased the rate of reaction dramatically. Hence the most obstinate reaction, between bis(dimethylamino)diphenylsilane and N,N'-dimethylpropane-1,3-diamine, was less than 50% complete after 4 d at approximately 140°C but subsequent addition of ammonium sulphate brought about completion in less than 8 h.

After a number of reactions had been carried out it was evident that the best and most convenient general method of preparation was to use the bis(dimethylamino)silane, with catalyst, and to gradually raise the temperature of the reaction vessel, using an oil bath, until dimethylamine was being evolved at a steady rate. Evolution of the gas, which was allowed to escape through a water-cooled reflux condenser and drying tube, usually commenced at well below 100°C. The temperature was increased, as necessary, up to a maximum of about 140°C and reaction was judged to be over when the theoretical mass of amine had been lost (or when there was no further loss in mass). After cooling, the liquid product was either decanted from any solid and purified by distillation or first dissolved in petroleum ether, filtered and distilled after removal of solvent.

Working with the small quantities involved in these preparations (theoretical yields typically in the order of 5 g) it was found difficult to isolate 1,2,2,3-tetramethyl-1,3,2-diazasilacyclopentane in high purity (as indicated by proton NMR) even when both starting materials were freshly distilled. Also, for this reaction, the use of bis(dimethylamino)dimethylsilane appeared to have little advantage over that of bis(diethylamino)dimethylsilane.

Results and discussion

^1H NMR spectra

Shifts for the new heterocycles, together with those of the other compounds for comparison, are given in Table 1. Lack of splitting in the spectra of the five-membered rings is consistent with the existence of either ring planarity or rapid nitrogen inversion [9,10]. In addition it may by noted that the nitrogen-methylene signal appears as a singlet even for the unsymmetrical 1,2,3-trimethyl-2-phenyl-1,3,2-diazasilacyclopentane.

Spectra of the 1,3,2-diazasilacyclohexanes also contained singlets for all silicon-methyl and nitrogen-methyl protons and similar conclusions can be made. However, splitting of methylene signals occurred this time, as expected, reflecting the non-equivalence of adjacent groups.

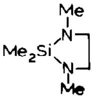
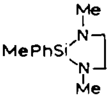
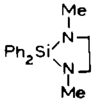
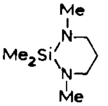
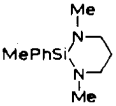
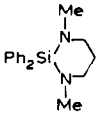
^{13}C NMR spectra

Shifts for all compounds are given in Table 2. The single resonances observed for each nucleus indicate, as do proton and silicon-29 NMR spectra, the absence of isomerism in these compounds and also therefore the actual or time-averaged coplanarity of the two nitrogen–methyl bonds in the heterocycles.

(i) Substituent effects. Substituent changes for the cyclic compounds are limited to the introduction of a phenyl group at the silicon atom. This has generally little effect on shifts except for those of the silicon-methyl (C(7)) and silicon-phenyl (C(8))

TABLE 1

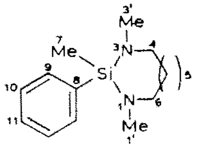
^1H NMR SHIFTS (δ in ppm from TMS)

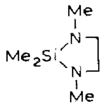
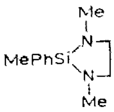
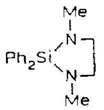
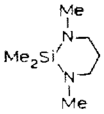
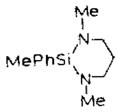
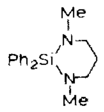
Compound	Phenyl [a]	Si-Me	N-Me	N-CH$_2$	CH$_2$	C-CH$_3$
	–	0.02(s) (0.00) [10]	2.51(s) (2.47) [10]	2.93(s) (2.89) [10]	–	–
	7.33–7.63(m)	0.35(s)	2.48(s)	3.10(s)	–	–
	7.24–7.60(m)	–	2.50(s)	3.11(s)	–	–
	–	−0.04(s)	2.36(s)	2.75(t)	1.75(m)	–
	7.20–7.50(m)	0.33(s)	2.33(s)	2.91(m)	1.90(m)	–
	7.26–7.62(m)	–	2.40(s)	3.02(t)	1.96(m)	–
Me$_2$Si(NMe$_2$)$_2$	–	0.02(s)	2.44(s)	–	–	–
MePhSi(NMe$_2$)$_2$	7.28–7.60(m)	0.27(s)	2.50(s)	–	–	–
Ph$_2$Si(NMe$_2$)$_2$	7.15–7.55(m)	–	2.56(s)	–	–	–
Me$_2$Si(NEt$_2$)$_2$	–	0.02(s)	–	2.80(q)	–	0.94(t)
MePhSi(NEt$_2$)$_2$	7.28–7.66(m)	0.29(s)	–	2.88(q)	–	0.96(t)

[a] Overall ranges. Signal intensities in ratio 2/3 in each case. s = singlet, t = triplet, q = quartet, m = multiplet greater than quartet.

TABLE 2

^{13}C NMR SHIFTS (δ in ppm from TMS)



Compound	1'/3'	4/6	5	7	8	9	10	11
 [a]	34.21	52.17	–	−2.18	–	–	–	–
	34.21	52.29	–	−4.85	137.35	134.32	127.77	129.59
	34.33	52.05	–	–	134.44	135.29	127.65	129.71
	36.74	51.69	29.17	−3.68	–	–	–	–
	37.00	51.69	29.48	−5.09	138.57	134.08	127.65	129.10
	37.37	51.69	29.48	–	135.78	135.29	127.65	129.35
$Me_2Si(NMe_2)_2$	37.61	–	–	−3.88	–	–	–	–
$MePhSi(NMe_2)_2$	37.98	–	–	−4.36	138.07	134.44	127.65	128.98
$Me_2Si(NEt_2)_2$	–	39.31	15.65	−1.09	–	–	–	–
$MePhSi(NEt_2)_2$	–	39.31	15.28	−2.18	139.54	134.56	127.40	128.62
$Ph_2Si(NMe_2)_2$	38.58	–	–	–	135.93	135.53	127.53	129.10

[a] Some minor peaks were attributed to impurity.

carbon atoms which move to higher field by approximately 2 and 3 ppm respectively.

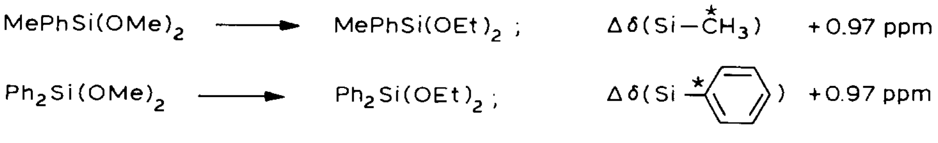
For the acyclic diamines there is the additional effect of a change from *N*-methyl to *N*-ethyl substitution, which results in downfield shifts of the C(7) and C(8) resonances.

$$\mathrm{Me_2Si(NMe_2)_2 \rightarrow Me_2Si(NEt_2)_2;} \quad \Delta\delta(\mathrm{C(7)})\ +2.79\ \mathrm{ppm}$$

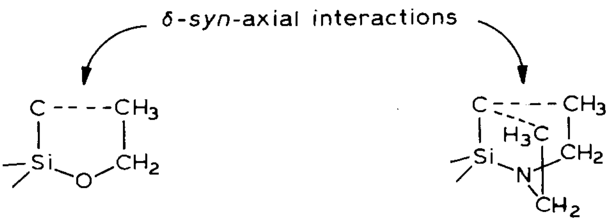
$$\mathrm{MePhSi(NMe_2)_2 \rightarrow MePhSi(NEt_2)_2;} \Delta\delta(\mathrm{C(7)})\ +2.18\ \mathrm{ppm}$$

$$\Delta\delta(\mathrm{C(8)})\ +1.47\ \mathrm{ppm}$$

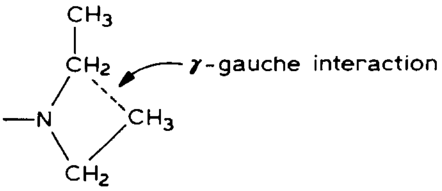
A similar but smaller effect is observable for the dialkoxysilanes and has been attributed to a δ-*syn*-axial steric interaction [11] e.g.



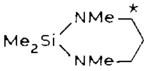
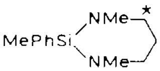
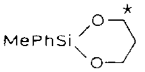
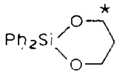
It is therefore tempting to rationalize the results for diamines in the same way since there are two methyl groups δ- to each silicon-carbon atom, per nitrogen atom.



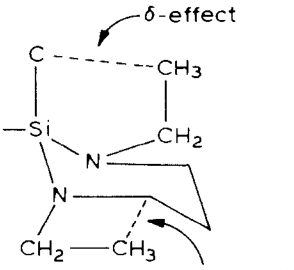
Taken at face value the shifts for methylene carbons (C(4)) in the bis(diethylamino) compounds (39 ppm) are much higher field than might be expected by comparison with those of equivalent carbons in either sized ring (52 ppm). Although this could be interpreted as implying a considerable amount of ring strain in the cyclic structures, with a resultant deshielding of the C(4) nuclei, a more likely explanation would be that at least some of the difference might be accounted for by this time assuming a γ-gauche steric interaction between methyl and methylene groups in the diethylamino moieties, leading to 'higher-than-expected' shifts for these carbons.

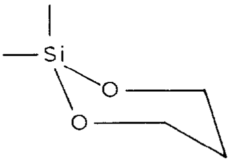


The situation is different for the acyclic dialkoxysilanes since in these each oxygen atom is bonded to only one alkyl group and a steric interaction involving the oxygen-methylene carbons as suggested above for amines is therefore impossible. Accordingly, shifts for these carbons in cyclic and acyclic dioxa compounds are relatively much closer, except for those of the highly strained five-membered rings.

	$\overset{\star}{\delta}(C)$		$\overset{\star}{\delta}(C)$	Δδ(ppm)
$Me_2Si[N(\overset{\star}{C}H_2CH_3)_2]_2$	39.31		51.69	12.38
$MePhSi[N(\overset{\star}{C}H_2CH_3)_2]_2$	39.31		51.69	12.38
$MePhSi(O\overset{\star}{C}H_2CH_3)_2$	58.48		64.18	5.70
$Ph_2Si(O\overset{\star}{C}H_2CH_3)_2$	58.85		64.43	5.58

In the absence of further data the assumption might therefore be made that steric interactions involving *N*-ethyl (and other) substituents could play a significant part in determining the shifts of nitrogen-carbon and silicon-carbon resonances in other 1,3,2-diazasilacycloalkanes. There can be no counterpart for the analogous dioxa compounds.





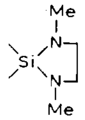
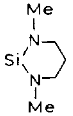
(ii) Ring size. Shifts for the nitrogen-carbon atoms (C(4/6)) of both ring sizes are much closer than might be expected (a range of 51.69 to 52.29 ppm for all six compounds). This could be taken as indicating a lack of any significant ring strain in the 1,3,2-diazasilacyclopentanes and contrasts with the case of five- and six-membered 1,3,2-dioxasilacycloalkanes where ^{13}C (and ^{29}Si) NMR shifts for ring atoms are significantly lower field for the five-membered rings.

A comparison of chemical properties is interesting on this point. Monomeric heterocyclic silicon derivatives of *N*,*N*′-dimethylethane-1,2-diamine are prepared as readily as those of *N*,*N*′-dimethylpropane-1,3-diamine and neither show any obvious tendency for the purified product to polymerize. In contrast, monomeric derivatives of α-diols are difficult to obtain pure and have a marked tendency to dimerize or form higher polymers: 2,2-dimethyl-1,3,2-dioxasilacyclopentane, the dioxa analogue of compound Ia, cannot be prepared.

Support for this interpretation could be expected to come from the shifts of nitrogen-carbon atoms in comparable open-chain, strain-free compounds. However, because of the possible steric interactions already discussed, a comparison with shifts for the bis(diethylamino)silanes ($N-\overset{\star}{C}H_2$, 39.31 ppm) may not be valid. Those for the ethyl-methylene carbons in di(methylethylamino)silanes would be of more interest and relevance but are not available at the present time. The evidence of ^{29}Si NMR spectra with respect to ring strain is discussed in the following section.

TABLE 3

^{29}Si NMR SHIFTS (All values relative to internal TMS, in ppm)

	Silicon atom substituents		
	Me_2	MePh	Ph_2
	−1.07 (lit. −1.75) [a]	−9.06	−17.04
	−5.52	−11.32	-
	+9.82	−2.45	−13.05
	−1.38	−13.05	−22.73

[a] Mean value from ref. 12.

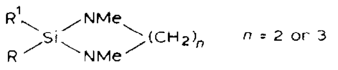
^{29}Si NMR spectra

Although there are numerous reported shift data for compounds containing a silicon–nitrogen bond [12], diamines have received virtually no attention and the only direct relevant reported shift appears to be that for bisdimethylaminodimethylsilane (−1.75 ppm. mean value from 12), and silazanes [13]. Those values reported here therefore constitute a novel set of data and are of additional specific interest in relation to shifts of analogous 1,3,2-dioxasilacycloalkanes and dioxysilanes.

The shifts are, coincidentally, of much the same order as those for the dioxa compounds though spanning a narrower range. The approximate overall range of bis(dialkylamino)silanes and 1,3,2-diazasilacycloalkanes (Table 3) is +10 to −23 ppm and of dialkoxysilanes and comparable 1,3,2-dioxasilacycloalkanes [11] is +22 to −33 ppm.

(i) Substituent effects

Of direct comparison with that for the cyclic and acyclic dioxa compounds is the methyl → phenyl substituent effect. An apparent relationship between this and the electronegativities of the heteroatoms has been demonstrated [14] and, accordingly, values are somewhat less for the diazo compounds. However, there is also greater variation in this case, with substituent shifts for the heterocycles considerably greater than for the acyclic diamines (Table 4). Hence, whilst the size of the effect for all the dialkoxysilanes and 1,3,2-dioxasilacyclo-pentanes and -hexanes varies by less than 3 ppm (range −12.18 to −14.92 ppm;) there is here a variation of almost 7 ppm for far fewer compounds. Furthermore the magnitudes of these substituent shifts clearly



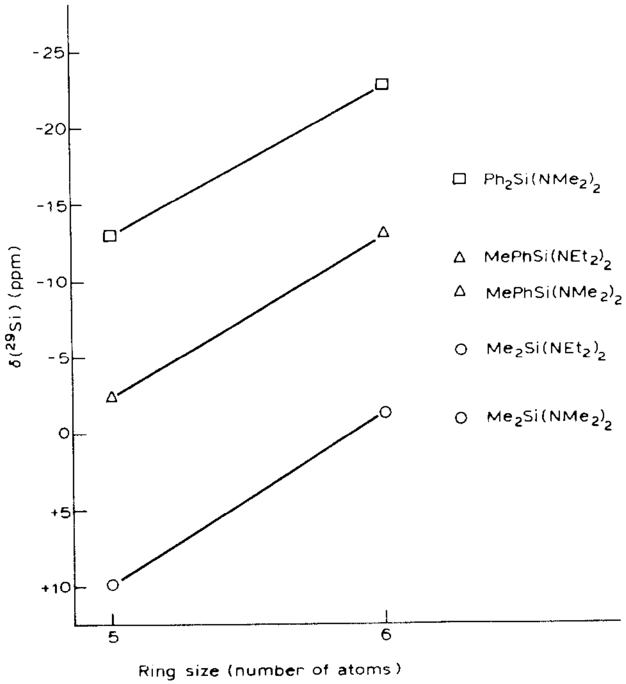
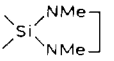
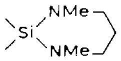


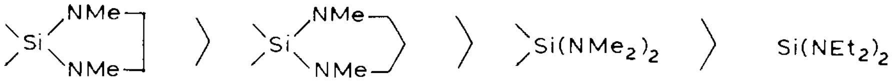
Fig. 1. ^{29}Si NMR shifts.

TABLE 4

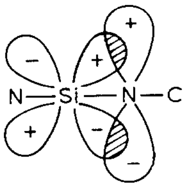
SUBSTITUENT SHIFTS ($\Delta\delta(^{29}Si)$ (ppm)) FOR PHENYL SUBSTITUTION AT THE SILICON ATOM

Silicon substituents			$>Si(NMe_2)_2$	$>Si(NEt_2)_2$
$Me_2 \rightarrow MePh$	−12.27	−11.67	−7.99	−5.80
$MePh \rightarrow Ph_2$	−10.60	−9.68	−7.98	–
Mean	−11.44	−10.68	−7.99	–

decrease in the order

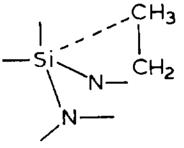


The wide range of values and their apparent dependence on molecular structure invites some speculation as to a possible rationalization of these findings. It seems reasonable to propose that in the case of the 1,3,2-diazasilacycloalkanes the presence of a silicon-phenyl group may result in an enhancement of back-donation from nitrogen to silicon due to the favourable orientation of nitrogen-*p* and silicon-*d* orbitals in the planar or near-planar molecules. (Though if this is so it must be considered as an additional factor to those discussed concerning the methyl → phenyl substituent effect in general.



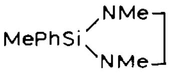
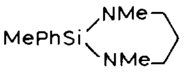
Conversely, the orientation required for such $(p \rightarrow d)\pi$ overlap would be least likely in the sterically crowded bis(diethylamino)silanes. (It may be noted that bis(diethylamino)diphenylsilane could not be prepared from dichlorodiphenylsilane, reaction being incomplete.) The observed trend could therefore be seen as resulting from a difference in the enhancement of $(p \rightarrow d)\pi$ back-donation, this being at a maximum for the most nearly planar heterocycle (arguably the five-membered ring) and at a minimum for the most sterically crowded acyclic diamine. This interpretation of the results could not be defended unless absolute shift values were also seen to be increased (upfield, −ve) for the cyclic compounds. It is therefore relevant that these shifts (Table 3) are highest for the 1,3,2-diazasilacyclohexanes, and not the acyclic diamines, where a silicon-phenyl substituent exists. For dioxa analogues the reverse is true, with shifts of dialkoxysilanes representing limiting values. Further discussion is given subsequently when the effect of ring size is considered.

Substitution of *N*-methyl by *N*-ethyl groups in the acyclic diamines causes higher field shifts and this is consistent with the γ-gauche steric effect, of the methyl groups, which appears to operate in dialkoxysilanes.

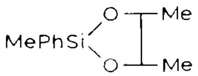
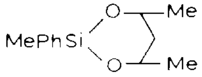


(ii) The effect of cyclization and ring size. In these respects, the shifts are compared most easily by reference to Fig 1.

Whilst the lowest field shifts are, as expected, for the five-membered rings they are not greatly lower than those of either the six-membered rings (a difference of 9.68 to 11.20 ppm) or of the acyclic compounds (a difference of 3.99 to 10.89 ppm for the bis(dimethylamino)silanes).

		$MePhSi(NMe_2)_2$	$MePhSi(NEt_2)_2$	
− 2.45	− 13.05	− 9.06	− 11.32	(ppm)

The situation may therefore be contrasted with that which is found for the analogous 1,3,2-dioxasilacyclopentanes where the shifts are lower by about 22 ppm than those of the 1,3,2-dioxasilacyclohexanes and by some 25 ppm compared to those of comparable dialkoxysilanes [11].

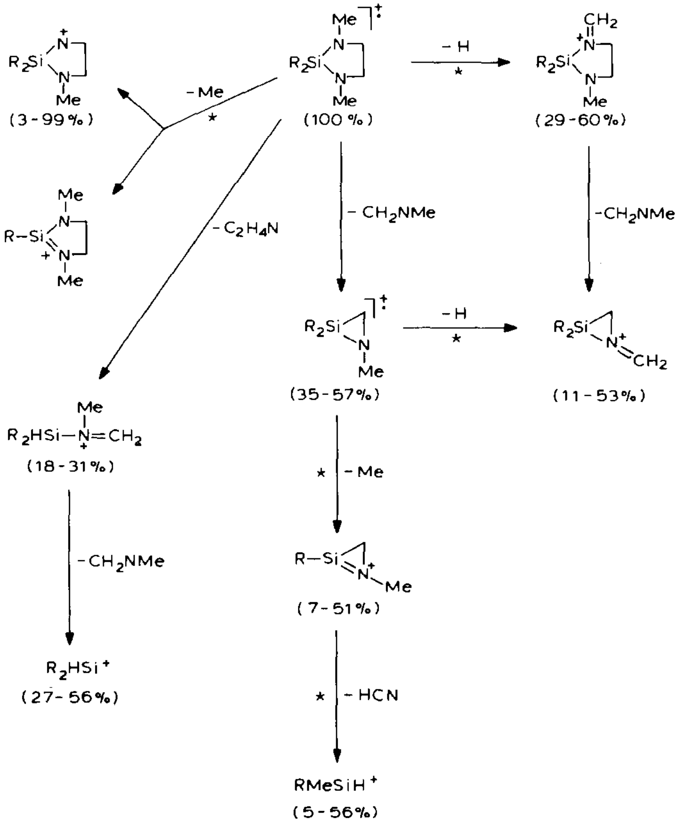
		MePhSi(OEt)$_2$	MePhSi(O-i-Pr)$_2$	
+ 7.06	− 14.82 (mean)	− 18.43	− 21.96	(ppm)

The narrower range of shifts in general for the diaza compounds cannot alone account for these significant differences in trends and it is proposed that two, possibly complementary, additional factors may be important.

Firstly there is the clear implication that, since shifts for the annular silicon atoms appear to be related to ring strain, the 1,3,2-diazasilacyclopentanes are considerably less strained than the 1,3,2-dioxasilacyclopentanes. This would appear to be supported by both ^{13}C NMR shifts and chemical properties, as already discussed. Since the two types of rings differ only in the identity of the 1,3-heteroatoms (and of 1,3-substituents) any significant difference in ring strain is most reasonably attributed to the different bond angle requirements of the Si–N–C and Si–O–C moieties (and, to a lesser extent N–Si–N and O–Si–O). Known bond angle data for compounds containing these fragments indicate that there is a difference and that angles are greatest for the latter. Hence Si–N–C bond angles appear to have the approximately sp^2 values of about 120° (e.g. 123 and 120° in Cl_3SiNMe_2 and F_3SiNMe_2 respectively [15]; 117° [16] in $(SiH_3)_2NMe$) whereas those of Si–O–C are found to exceed this value even in cyclic structures (e.g. 128° in α-naphthylphenylfluoromenthoxysilane [17] 126–133° in a series of 2,2-dimethyl- and 2,2-diphenyl-1,3-dioxa-6-aza-2-silacyclooctanes [18].

Secondly, the relatively high-field shifts of cyclic, compared to acyclic, compounds suggests that some additional shielding mechanism is effective. Whilst shifts for acyclic dialkoxysilanes are found to represent limiting values those of the bis(dialkylamino)silanes are approximately the same as (compound IIa), or lower-field than (compounds IIb and IIc), those of the 1,3,2-diazasilacyclohexanes (Fig. 1).

Observed phenyl substituent shifts have already been tentatively explained in terms of the enhanced $(p \rightarrow d)\pi$ back-donation from nitrogen to silicon which might result as a consequence of the ease of overlap of nitrogen-p and silicon-d orbitals in a planar or nearly planar ring. On this basis alone, of course, the highest-field shifts of all might be expected for the five-membered rings if these are assumed to have the most planar conformation. However, any ring strain (which has the effect of lowering shift values) is also greatest for these compounds and therefore tends to nullify the effect of increased back-donation. It can be seen that the two effects would be optimized for the 1,3,2-diazasilacyclohexanes, to give highest field shifts of all, if these are regarded as nearly-strain-free molecules with silicon–nitrogen and nitrogen–carbon bonds coplanar. The non-coplanarity of atom C(5), which would be required in order to accommodate the three sp^3 carbon atoms in a strainfree structure, need not affect the planarity of the rest of the molecule or the extent of any nitrogen to silicon $(p \rightarrow d)\pi$ bonding.



* Metastable ions for at least 2 compounds

R = Me or Ph

SCHEME 1. Suggested fragmentation pattern for 1,3,2-diazasilacyclopentanes.

There is clearly scope for further work, on a greater range of compounds, with regard to the effect on ^{29}Si NMR shifts of (i) different nitrogen atom substituents, (ii) ring carbon atom substituents, (iii) larger ring sizes.

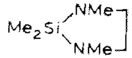
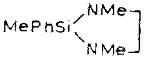
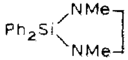
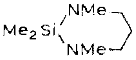
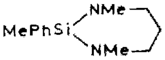
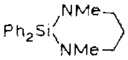
Mass spectra

Relative intensities of the common ions in these spectra are given in Table 5. The silicon atom is retained in almost all ions and the principal fragmentation patterns arise from the initial loss of a proton or methyl group followed by fragmentation of the ring [20]. Possible fragmentation Schemes are given (Schemes 1 and 2).

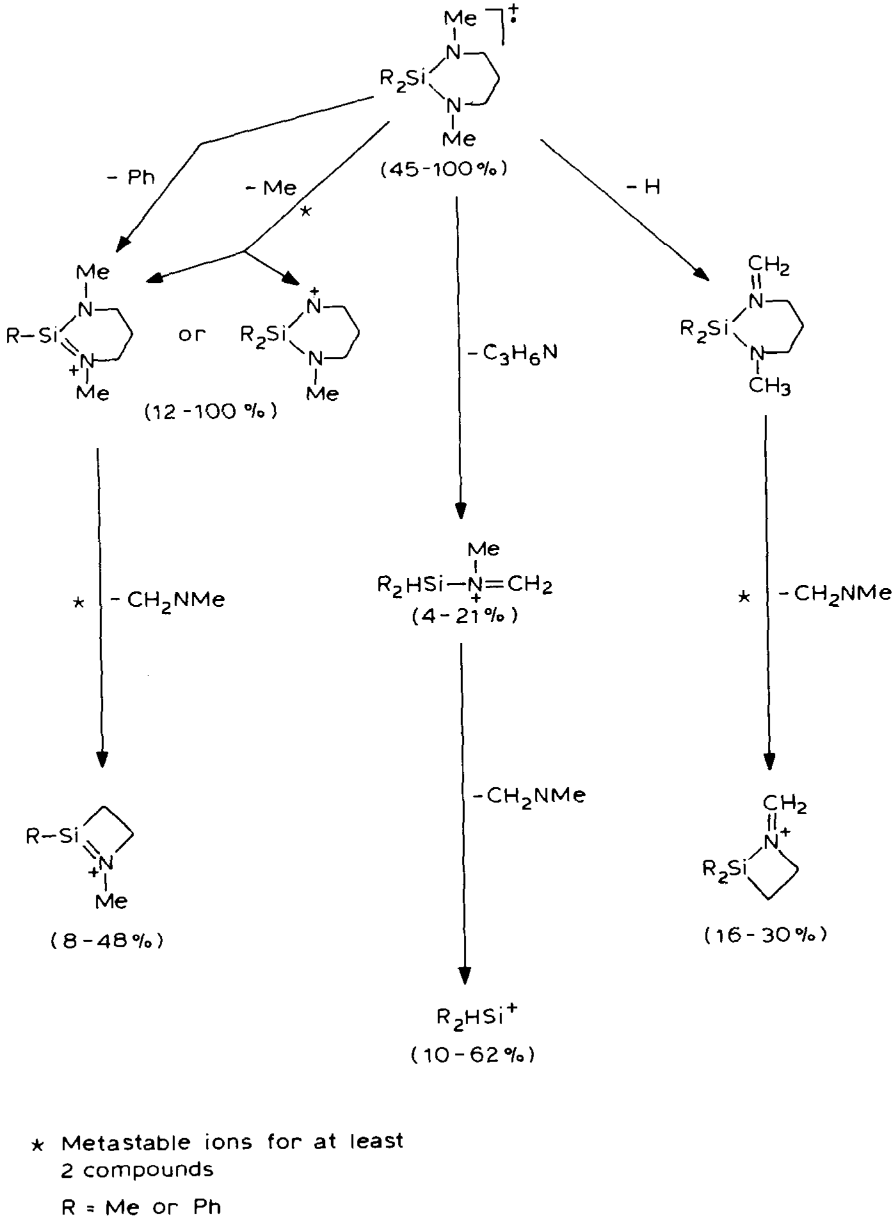
There appears to be a greater tendency for a tetrahedral silicon atom to be retained in the fragmentation of the smaller rings. Hence, loss of a proton from, and ring contraction of, the molecular ion is of more importance for the five- than for the six-membered rings or the acyclic compounds. This may be a consequence of the effect on ring strain of changing the silicon bond angles. Loss of one substituent from the silicon atom would lead to a large increase in the N–Si–N bond angle, due

TABLE 5

MASS SPECTRAL DATA

Compound	m/e														
	M	$M-1$	$M-15$	$M-77$	$M-42$	$M-43$	$M-44$	$M-(43+15)$	$M-(43+77)$	59,121,183 (R_2SiH)[a]	107 ($PhSiH_2$)[a]	105 ($PhSi$)[b]	44	43	42
	100	29	99	–	31	57	11	51	–	40(59)	–	–	31	11	10
	100	49	73	–	24	48	53	20	–	56(121)	7	27	70	16	10
	100	60	3	10	18	35	51	7	–	27(183)	5	25	7	–	4
	49	3	100	–	2	3	16	32	–	10(59)	–	–	10	–	–
	45	5	100	12	4	7	29	48	13	62(121)	14	29	13	23	18
	100	23	21	38	4	8	30	13	8	36(183)	6	17	11	–	–
$MePhSi(NMe_2)_2$	100	6	43	5	8	35	69	31	7	63(121)	10	13	9	13	7
$Ph_2Si(NMe_2)_2$	93	9	–	7	8	40	100	9	6	72(183)	13	28	–	10	–
$Me_2Si(NEt_2)_2$	30	–	26 ($M-29;5$)	–	–	–	($M-72;100$)	–	–	25(59)	–	–	–	–	–
$MePhSi(NEt_2)_2$	30	–	23 ($M-29;8$)	–	–	–	($M-72;100$)	–	–	59(121)	4	5	–	7	–

[a] Probable identity. [b] Confirmed by precise mass.



SCHEME 2. Suggested fragmentation pattern for 1,3,2-diazacyclohexanes.

to changed hybridization, and therefore to increased ring strain. Assuming that the nitrogen lone-pair is already involved to some extent in nitrogen to silicon $(p \rightarrow d)\pi$ bonding, loss of a proton from the *N*-methyl group and the subsequent formation of a nitrogen to carbon $(p \rightarrow p)\pi$ bond would not affect the hybridization or bond angle requirements of nitrogen so markedly. Alternatively, loss of a proton from the parent ion may be accompanied by ring-opening and this again would be more likely for the more strained system. For the 1,3,2-diazasilacyclohexanes, loss of a methyl or phenyl radical from the silicon atom in the molecular ion appears to be the most important fragmentation whilst base peak ions for three of the four acyclic diamines are produced by initial loss of a dimethyl- or diethyl-amino radical.

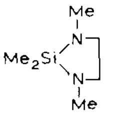
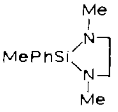
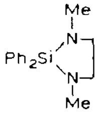
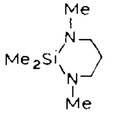
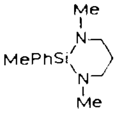
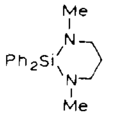
A comparison of these spectra with those of corresponding dioxa-heterocycles reveals similarities in the initial stages of fragmentation though they are necessarily different with respect to the involvement of a nitrogen-methyl group in the fragmentation of the diaza compounds, for which there is no counterpart in the 1,3,2-dioxasilaheterocycles.

Hydrocarbon rearrangements involving the phenyl group appear to be unimportant. Hence, fragmentations involving the loss of a benzene molecule, either from the molecular ion or in subsequent stages, are missing even though this is a major feature in the spectra of 2-phenyl-1,3,2-dioxasilacycloalkanes [19].

Likewise the tropylium ion ($C_7H_7^+$; *m/e* 91) is significant on only three spectra

TABLE 6

HETEROCYCLIC DIAMINE DERIVATIVES

Compound	Yield (%)	B.p. (°C/mmHg) (m.p.)	Analysis (found (calcd.)(%))			Ref. b.p.
			C	H	N	
	30	128–132/atm	50.4 (49.9)	11.5 (11.2)	19.8 (19.4)	131/740 [9]
	40	52/0.2	63.8 (64.0)	8.9 (8.8)	13.5 (13.6)	110/11 [9]
	45	120/0.1	72.2 (71.6)	7.7 (7.5)	10.4 (10.4)	175/10 [9]
	46	140–146/atm	53.2 (53.1)	11.7 (11.5)	18.3 (17.7)	
	65	65–67/0.03	65.0 (65.4)	8.7 (9.2)	12.8 (12.7)	
	20	108/0.01	72.2 (72.3)	7.2 (7.9)	9.5 (9.9)	

(rel. int. 5–8%) and the ion of mass 105 was shown by a precise mass determination to be predominantly $C_6H_5Si^+$ and not the alternative hydrocarbon ion $C_8H_9{}^+$. A rationalization may be proposed in terms of the greater strength of the silicon–oxygen, compared to the silicon–nitrogen, bond. Fragmentation by initial fission of an Si–X bond would be more likely when X = nitrogen than when X = oxygen. Loss of a benzene molecule or tropylium ion requires the retention of Si–X bonds, which is more favoured when X = oxygen. It is noticeable that base peak ions in the spectra of bis(dialkylamino)silanes correspond to the loss of a dialkylamino radical from the molecular ion, in three out of four spectra, whereas loss of an alkoxy radical from the analogous dialkoxysilanes is not of major importance. Equally, the ions which can only reasonably be R_2HSi^+ (R = Me or Ph; *m/e* 59, 121 or 183) require the fission of both silicon–nitrogen bonds for their formation and have high relative intensities in all the spectra (10–72%).

Experimental

The mass spectra were recorded using an AEl MS902 mass spectrometer at 70 eV. The source was maintained at 170°C and the compounds were introduced using a variable-temperature, direct-insertion probe. In general only those peaks of relative intensity greater than 5% were considered.

NMR spectra were recorded on a JEOL-PS-100 NMR spectrometer with the instrument in the Continuous-wave mode for proton spectra and in the Fourier transform mode for ^{13}C and ^{29}Si spectra. Samples used were as solutions in either $CDCl_3$ or CCl_4 with internal TMS as standard. For some ^{29}Si spectra it was found necessary to add a trace of chromium acetylacetonate as a relaxing agent. As the experimental procedure was the same in all cases only two examples are discussed in detail and all analytical and physical data are given in Table 6.

Preparation of 1,2,2,3-tetramethyl-1,3,2-diazasilacyclohexane

Dimethylbis(dimethylamino)silane (4.00 g, 0.0274 mol) and *N,N'*-dimethylpropane-1,3-diamine (2.7 g, 0.0274 mol) together with ammonium sulphate (0.5 g) as catalyst, were heated slowly to 120°C for 2 h under reflux, dimethylamine being allowed to escape through a drying tube. There being no further loss in mass, the cooled residue was decanted and distilled at atmosphere pressure to yield 1,2,2,3-tetramethyl-1,3,2-diazasilacyclohexane as a colourless liquid (2.0 g, 46%), b.p. 140–146°C (Found: C, 53.2; H, 11.7; N, 18.3. $C_7H_{18}N_2Si$ calcd.: C, 53.1; H, 11.5; N, 17.7%).

Preparation of 2-phenyl-1,2,3-trimethyl-1,3,2-diazasilacyclohexane

Bis(dimethylamino)methylphenylsilane (8.16 g, 0.0392 mol) and *N,N'*-dimethylpropane-1,3-diamine (4.00 g, 0.0392 mol) were maintained at 120°C under reflux, and with catalyst, for 2 d, dimethylamine being allowed to escape through a drying tube. The residue on distillation afforded 2-phenyl-1,2,3-trimethyl-1,3,2-diazasilacyclohexane as a colourless liquid (5.6 g, 65%), b.p. 65–67°C/0.03 mmHg. (Found: C, 65.0; H, 8.7; N, 12.8. $C_{12}H_{20}N_2Si$ calcd.: C, 65.4; H, 9.2; N, 12.7%).

Acknowledgements

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