

THE PREPARATION OF α,ω -DIBROMOPERMETHYLPOLYSILANES AND CHARACTERIZATION OF THESE AND RELATED CHLOROPERMETHYLPOLYSILANES BY MASS SPECTROMETRY

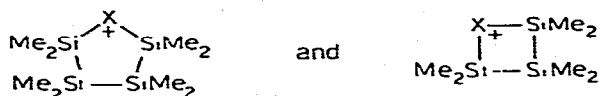
CATHERINE HURT MIDDLECAMP, WIESLAW WOJNOWSKI and ROBERT WEST*

Department of Chemistry, University of Wisconsin, Madison, WI 53706 (U.S.A.)

(Received August 16th, 1976; in expanded form May 2nd, 1977)

Summary

The series of α,ω -dibromopermethyldipolysilanes, $\text{Br}(\text{SiMe}_2)_n\text{Br}$, ($n = 2-6$) has been prepared by the action of bromine on dodecamethylcyclohexasilane. The mass spectra of these compounds, of the corresponding chlorine compounds $\text{Cl}(\text{SiMe}_2)_n\text{Cl}$ ($n = 2-6$), and of the 1-chloropermethyldipolysilanes $\text{Cl}(\text{SiMe}_2)_n\text{Me}$ ($n = 2, 3, 4, 6$) have been recorded at 14 and 70 eV. For compounds with $n > 3$, the formation of the ions $\text{Si}_3\text{Me}_6\text{X}^+$ and $\text{Si}_4\text{Me}_8\text{X}^+$ ($\text{X} = \text{Cl}, \text{Br}$) is strongly favored, with these ions being major or base peaks in the spectra. It is proposed that the stability of these ions is due to cyclization and bridging:



Introduction

In an earlier paper we described the preparation of α,ω -dichloropermethyldipolysilanes by the reaction of cyclopermethyldipolysilanes with chlorine [1]. We have now carried out the analogous reaction with bromine to give α,ω -dibromopermethyldipolysilanes. Of these compounds only 1,2- $\text{Br}_2\text{Si}_2\text{Me}_4$ has been previously reported [2]. In this paper, NMR, IR and mass spectral data are presented for these compounds. Mass spectral data for related chloropermethyldipolysilanes are also presented in order to provide a more complete picture of the unusual manner in which halogen substituents affect the mass spectrum.

Experimental

Preparation of α,ω -dihalopermethyldipolysilanes

To prepare 1, n - $\text{Br}_2\text{Si}_n\text{Me}_{2n}$ ($n = 2-4,6$), a 100 ml three-necked flask fitted

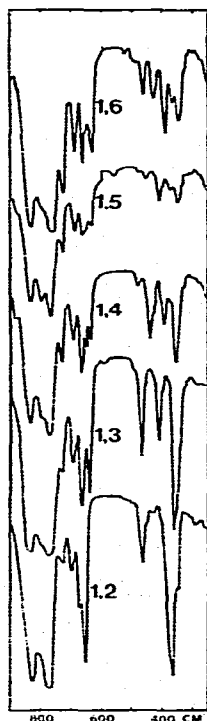


Fig. 1. Infrared spectra for α,ω -dibromopermethypolysilanes (CsI, thin film).

with a gas inlet tube, rubber septum and Vigreux column (leading eventually to water, to trap excess bromine) was charged with 100 ml deoxygenated hexane and 10 g $\text{Si}_6\text{Me}_{12}$ *. A stream of dry nitrogen (approx. 20 ml/min) which passed first over a pool of bromine in another flask served to carry bromine through the gas inlet tube into the reaction flask. When the flow of bromine was initiated in this manner, the reaction immediately turned and remained pale yellow-orange. Throughout the bromination, the reaction mixture was stirred magnetically and kept at 0°C .

The reaction was stopped at the point at which all of the $\text{Si}_6\text{Me}_{12}$ had reacted, as indicated by VPC analysis. The solvent was removed under vacuum by trap-to-trap distillation. From the remaining residue, samples of the desired bromopolysilanes were separated by preparative gas chromatography (VPC).

The preparation of 1,5- $\text{Br}_2\text{Si}_5\text{Me}_{10}$ was carried out in an analogous manner, using $\text{Si}_5\text{Me}_{10}$ this time as a starting material. A flask was charged with 7.0 g of a mixture of $\text{Si}_5\text{Me}_{10}$ (15%) and $\text{Si}_6\text{Me}_{12}$ (85%). Bromination was initiated, and the reaction stopped at the point at which all the $\text{Si}_5\text{Me}_{10}$ had been consumed. At this point, less than 5% of the $\text{Si}_6\text{Me}_{12}$ had reacted, as evidenced by VPC ana-

* See Ref. 1 for the preparation of this and other permethylcyclopolysilanes.

TABLE 1
REACTION OF $\text{Si}_6\text{Me}_{12}$ WITH BROMINE AT 0°C IN HEXANE

	Molar ratios of α,ω -dibromopermethypolysilanes at selected times	
	10 min	20 min
1,2- Br_2	0.15	0.30
1,3- Br_2	0.10	0.20
1,4- Br_2	0.15	0.20
1,5- Br_2	—	—
1,6- Br_2	0.20	0.15
$\text{Si}_6\text{Me}_{12}$	0.40	0.15

TABLE 2
PROTON NMR CHEMICAL SHIFTS FOR DIHALOPERMETHYLPOLYSILANES^a

	$\text{Si}(\text{Me})_2\text{Br}$	$[\text{Si}(\text{Me})_2]_\beta$	$[\text{Si}(\text{Me})_2]_\gamma$	$\text{Si}(\text{Me})_2\text{Cl}$	$[\text{Si}(\text{Me})_2]_\beta$	$[\text{Si}(\text{Me})_2]_\gamma$
1,2- X_2	0.74	—	—	0.56	—	—
1,3- X_2	0.71 (2H)	0.28 (1H)	—	0.54 (2H)	0.26 (1H)	—
1,4- X_2	0.68 (2H)	0.27 (2H)	—	0.51 (2H)	0.25 (2H)	—
1,5- X_2	0.68 (2H)	0.25 (2H)	0.27 (1H)	0.50 (2H)	0.23 (2H)	0.24 (1H)
1,6- X_2	0.66 (2H)	0.24 (2H)	0.25 (2H)	0.48 (2H)	0.21 (2H)	0.22 (2H)

^a Recorded in CCl_4 , ppm from TMS.

lysis. Preparative VPC was used to isolate 1,5- $\text{Br}_2\text{Si}_5\text{Me}_{10}$ after work-up as described above.

The molar ratios of the preparations of $\text{Br}_2\text{Si}_n\text{Me}_{2n}$ compounds after 10 and 20 min are listed in Table 1.

NMR data for both the α,ω -dibromo- and α,ω -dichloro-permethypolysilanes are given in Table 2, as recorded in CCl_4 relative to TMS on a JEOL MH-100 spectrometer. Infrared spectra for the 250–900 cm^{-1} region for the bromopermethypolysilanes are shown in Fig. 1, as recorded on a Perkin–Elmer 457 grating spectrometer using CsI plates.

All chloropermethypolysilanes were prepared as described in a previous paper [1].

Mass spectral studies

Mass spectra were recorded at 70 and 14 eV on an AEI MS-902 instrument with an ion accelerating voltage of 8 kV and ionization chamber temperature of 150°C . The mass spectral data were plotted with the aid of a data acquisition system utilizing a Raytheon 706 computer. Metastable peaks were frequently observed in the normal spectrum at 70 eV, but transitions in the first field-free region were also recorded for chloropolysilanes according to the method of Jennings [3]. For the latter, the magnet was focused on a daughter ion of inter-

(continued on p. 138)

TABLE 3
MASS SPECTRAL DATA ^a FOR CHLOROPOLYSILANES

	73	93	116	131	151	174	209	267	325
	SiMe ₃ ⁺	(SiMe ₂)Cl ⁺	(SiMe ₂) ₂ ⁺	Si ₂ Me ₅ ⁺	(SiMe ₂) ₂ Cl ⁺	(SiMe ₂) ₃ ⁺	(SiMe ₂) ₃ Cl ⁺	(SiMe ₂) ₄ Cl ⁺	(SiMe ₂) ₅ Cl ⁺
(I) at 70 eV									
1,6-Cl ₂ Si ₆ Me ₁₂	98	13	20	0	6	8	49	100	5
1-ClSi ₆ Me ₁₃	100	1	10	0	0	1	28	99	7
1,5-Cl ₂ Si ₅ Me ₁₀	77	6	33	0	4	0	100	70	4
1,4-Cl ₂ Si ₄ Me ₈	99	15	24	0	6	0	100	3	—
1-ClSi ₄ Me ₉	100	6	22	2	2	21	45	1	—
1,3-Cl ₂ Si ₃ Me ₆	100	16	42	0	80	0	8	—	—
1-ClSi ₃ Me ₇	100	14	70	2	5	0	8	—	—
1,2-Cl ₂ Si ₂ Me ₄ ^b	73	100	0	0	27	—	—	—	—
1-ClSi ₂ Me ₅	100	11	0	2	15	—	—	—	—
(II) at 14 eV									
1,6-Cl ₂ Si ₆ Me ₁₂	0	0	2	46	0	10	26	100	4
1-ClSi ₆ Me ₁₃	0	0	2	25	0	7	10	100	7
1,5-Cl ₂ Si ₅ Me ₁₀	0	0	10	40	0	2	70	100	0
1,4-Cl ₂ Si ₄ Me ₈	0	0	3	49	0	0	100	0	—
1-ClSi ₄ Me ₉	0	0	0	24	0	2	100	0	—
1,3-Cl ₂ Si ₃ Me ₆	0	0	100	11	25	0	0	—	—
1-ClSi ₃ Me ₇	6	0	100	40	0	0	0	—	—
1,2-Cl ₂ Si ₂ Me ₄ ^b	9	56	0	0	0	—	—	—	—
1-ClSi ₂ Me ₅	100	0	0	13	5	—	—	—	—

^a Relative peak heights, reduced to monoisotopic values. ^b Base peak at 14 eV is molecular ion.

TABLE 4
MASS SPECTRAL DATA^a FOR BROMOPOLYSILANES

	73	110	131	137	174	195	253	311	369
	SiMe ₃ ⁺	(SiMe ₂) ₂ ⁺	Si ₂ Me ₅ ⁺	(SiMe ₂)Br ⁺	(SiMe ₂) ₃ ⁺	(SiMe ₂) ₂ Br ⁺	(SiMe ₂) ₃ Br ⁺	(SiMe ₂) ₄ Br ⁺	(SiMe ₂) ₅ Br ⁺
(I) and 70 eV									
1,6-Br ₂ Si ₆ Me ₁₂	55	13	20	2	12	3	63	100	3
1,6-Br ₂ Si ₅ Me ₁₀	77	24	25	3	3	4	100	62	—
1,4-Br ₂ Si ₄ Me ₈	57	20	27	8	0	8	100	4	—
1,3-Br ₂ Si ₃ Me ₆	97	39	8	12	0	100	5	0	—
1,2-Br ₂ Si ₂ Me ₄	59	1	0	100	0	11	—	—	—
(II) at 14 eV ^b									
1,6-Br ₂ Si ₆ Me ₁₂	0	2	0	0	11	0	45	100	2
1,6-Br ₂ Si ₅ Me ₁₀	1	8	0	0	2	0	77	100	—
1,4-Br ₂ Si ₄ Me ₈	1	10	0	0	0	2	100	0	—
1,3-Br ₂ Si ₃ Me ₆	0	100	0	0	0	86	0	—	—
1,2-Br ₂ Si ₂ Me ₄ ^c	26	0	0	60	0	14	—	—	—

^a Relative peak heights, reduced to monoisotopic values. ^b 1,6-Br₂Si₅Me₁₀ recorded at 15 eV, 1,6-Br₂Si₆Me₁₂ at 16 eV. ^c Base peak at 14 eV is molecular ion.

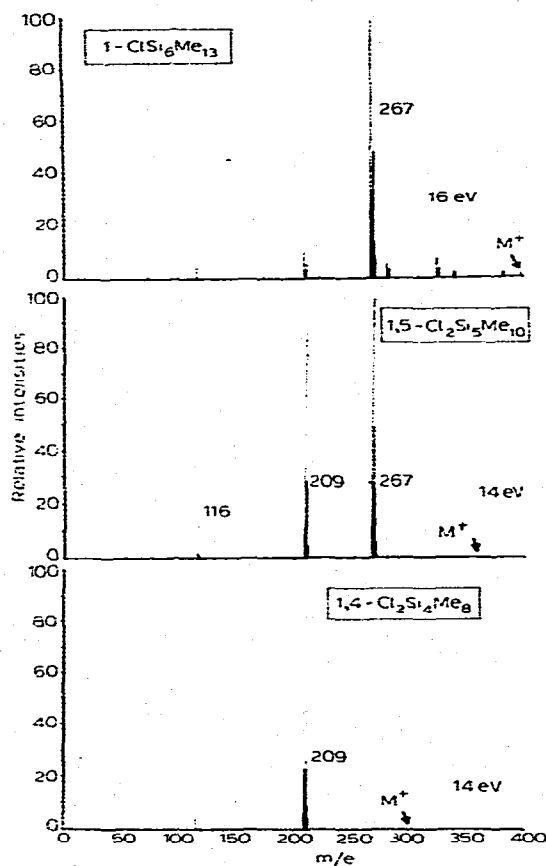


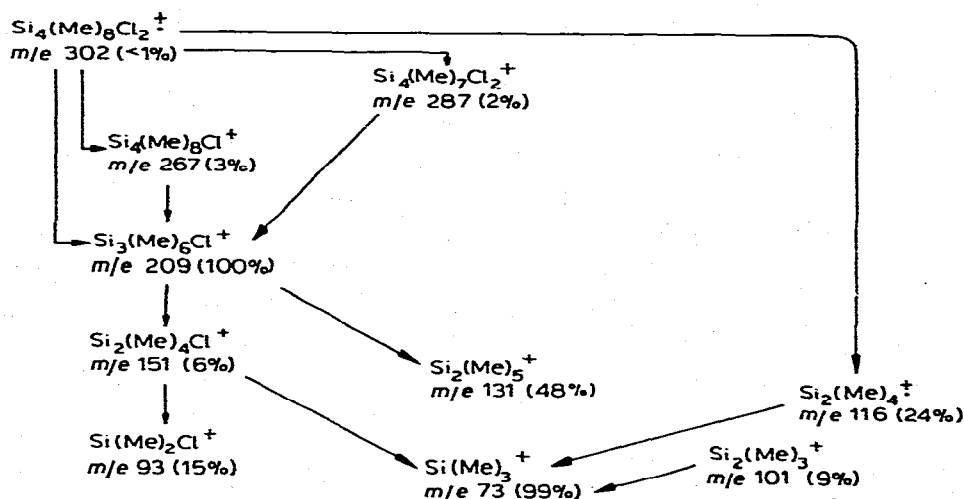
Fig. 2. Mass spectra for selected chlorosilanes at low ionizing voltages.

est at 2 or 4 kV and the accelerating voltage was then scanned to locate precursor ions.

The fragments $\text{Si}_3\text{Me}_6\text{X}^+$ and $\text{Si}_4\text{Me}_8\text{X}^+$ ($\text{X} = \text{Cl}, \text{Br}$) were identified in the spectra of $1,5\text{-X}_2\text{Si}_5\text{Me}_{10}$ by peak matching to 6 ppm. Subsequently, these and other halogen-containing ions were identified in other spectra by their characteristic isotopic envelopes, arising from the approximate 3/1 and 1/1 natural abundances of $^{35,37}\text{Cl}$ and $^{79,81}\text{Br}$ respectively. Results of mass spectral studies are shown in Tables 3 and 4 and in Fig. 2. Fragmentation pathways for $1,4\text{-Cl}_2\text{Si}_4\text{Me}_8$ and $1,6\text{-Cl}_2\text{Si}_6\text{Me}_{12}$ are shown in Schemes 1 and 2.

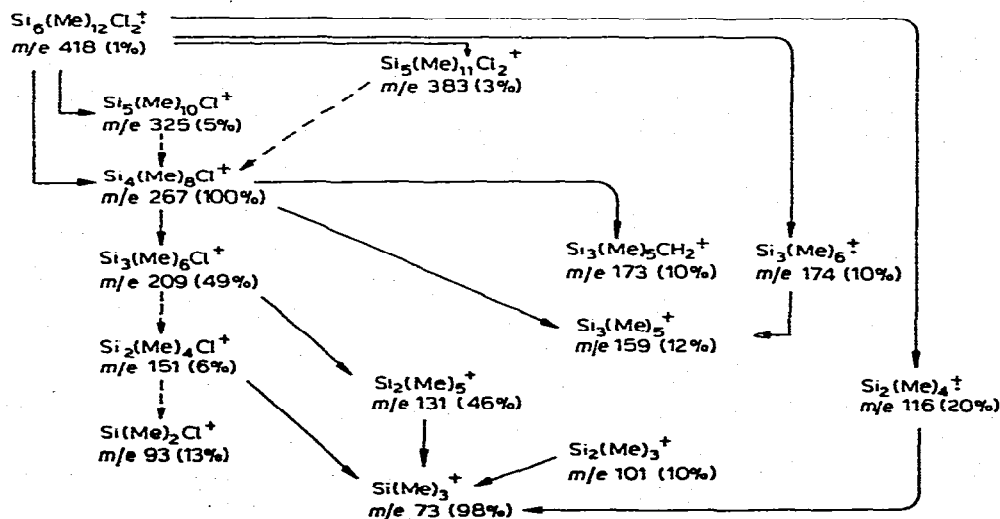
Results and discussion

The reaction of cyclopermethylpolysilanes with bromine to give α,ω -dibromopermethypolysilanes closely parallels the analogous reaction with chlorine [2]. In Table 1, the results for a typical reaction of bromine with $\text{Si}_6\text{Me}_{12}$ are given. From these and additional preparative runs, it can be seen that, similar to the



SCHEME 1. Fragmentation scheme for 1,4- $\text{Cl}_2\text{Si}_4(\text{Me})_8$ at 70 eV. Solid arrows show pathways which are supported by metastable peaks. Relative intensities (monoisotopic values) are given in parentheses.

chlorine case, the initial reaction is the cleavage of the polysilane ring to form 1,6- $\text{Br}_2\text{Si}_6\text{Me}_{12}$ (1,6- Br_2) with subsequent cleavage of the silicon-silicon bonds in this compound to form smaller dibromosilanes: 1,4- $\text{Br}_2\text{Si}_4\text{Me}_8$ (1,4- Br_2), 1,3- $\text{Br}_2\text{Si}_3\text{Me}_6$ (1,3- Br_2) and 1,2- $\text{Br}_2\text{Si}_2\text{Me}_4$ (1,2- Br_2). There is little bromination of the silicon-silicon bond adjacent to the SiMe_2Br group, consistent with earlier observations [1]. This resistance to cleavage is evidenced by the fact that less than 5% of 1,5- $\text{Br}_2\text{Si}_5\text{Me}_{10}$ (1,5- Br_2) is formed during the course of the reaction.



SCHEME 2. Fragmentation scheme for 1,6- $\text{Cl}_2\text{Si}_6(\text{Me})_{12}$ at 70 eV. Solid arrows show pathways which are supported by metastable peaks. Relative intensities (monoisotopic values) are given in parentheses.

When a mixture of $\text{Si}_5\text{Me}_{10}$ and $\text{Si}_6\text{Me}_{12}$ is brominated, the initial reaction is the formation of $1,5\text{-Br}_2$, with corresponding decrease of $\text{Si}_5\text{Me}_{10}$ but with no decrease of $\text{Si}_6\text{Me}_{12}$. Evidently $\text{Si}_5\text{Me}_{10}$ reacts with bromine much more rapidly than does $\text{Si}_6\text{Me}_{12}$, as is also true for the reaction of these compounds with chlorine [1]. Also analogous to the chlorination reaction, the reaction of bromine with cyclopolysilanes is quite rapid, with bromine never accumulating in sufficient concentration to turn the reaction observably dark.

NMR spectra. The chemical shifts for proton resonances (relative to TMS) are presented in Table 2. The terminal SiMe_2Br resonances appear at lowest field, being deshielded by the electronegative bromine substituent. This deshielding is rapidly attenuated along the chain, but all of the proton resonances are at lower field than those of the corresponding permethylpolysilanes [4]. As the chain becomes longer the proton resonances of SiMe_2Br appear at higher field; this same phenomenon has previously been reported for the terminal groups of both halo- [5] and methyl-polysilanes [4].

It is interesting to note that the innermost (γ) SiMe_2 groups in $1,5\text{-Br}_2$ and $1,5\text{-Cl}_2$ are slightly more deshielded (0.01–0.02 ppm) than the $\beta\text{-SiMe}_2$ groups. From the spectra of these two compounds (which clearly show that the inner methyl groups (1H) are at lower field than the outer ones (2H)), one can similarly assign the SiMe_2 groups which appear at lower field in $1,6\text{-Br}_2$ and $1,6\text{-Cl}_2$ to the innermost positions in the chain. This deshielding is actually consistent with previous reports that chemical shifts for methyl groups appear at lower field as the distance from the end of the polysilane chain increases [4,5]. For example, in the linear permethylpolysilane $\text{Si}_5\text{Me}_{12}$, the $\gamma\text{-SiMe}_2$ protons are 0.031 ppm more deshielded than the β -protons. However, the difference is much smaller, about 0.01 ppm, between the γ and β -protons in $1,5\text{-X}_2$ and $1,6\text{-X}_2$ ($\text{X} = \text{Cl}, \text{Br}$). It appears, then, that the halogen substituent deshields the β -protons by about 0.02 ppm relative to the γ -protons.

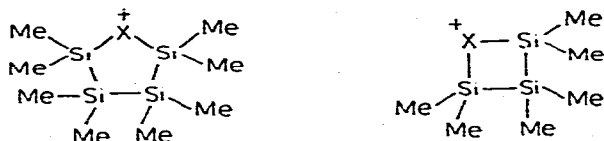
The proton resonances of the bromo compounds appear consistently at lower field than those for the same positions in the chloro analogs. This is unusual, for it would be expected that chlorine, being more electronegative, would more effectively deshield the methyl protons. A possible explanation for the reversal is that $d_\pi\text{-}p_\pi$ interaction from halogen atoms to the silane chain may be more pronounced for chlorine than for bromine. This would increase the electron density at silicon (and in turn at carbon) in the chlorine compounds. Similar trends have been reported for the proton resonances in the series Me_3SiX ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) [6].

Mass spectra. The mass spectra of linear chloro- and bromo-polysilanes are strikingly different from their permethyl analogs, but by examining the spectra of linear permethylpolysilanes one can gain useful insights into the behavior of halopolysilanes. At 25 eV, linear permethylpolysilanes show a fairly abundant molecular ion together with a series of fragments differing in the number of SiMe_2 and/or Me groups [7]. Fragmentation leads to the formation of SiMe_3^+ , a very stable even electron ion [8] which is characteristically the base peak. However, an interesting feature of the halopolysilane spectra is that they often contain fragments with intensities greater than SiMe_3^+ , suggesting the presence of other highly stabilized ions. These fragments, $\text{Si}_3\text{Me}_6\text{Cl}^+$ (m/e 209), $\text{Si}_4\text{Me}_8\text{Cl}^+$ (m/e 267), $\text{Si}_3\text{Me}_6\text{Br}^+$ (m/e 252) and $\text{Si}_4\text{Me}_8\text{Br}^+$ (m/e 311) are major or base

peaks in the spectra of the longer chain compounds at 70 eV, and completely dominate the spectra with low-ionizing voltages (Fig. 2). Furthermore, it is interesting that these fragments contain chlorine or bromine, for halogens, being electronegative, tend to appear with low abundances in the mass spectra of positive ions.

The spectrum of $1\text{-ClSi}_6\text{Me}_{13}$ illustrates the preferential formation of these halogen-containing ions. Initial fragmentation of this compound might occur with silicon-silicon bond rupture at either end of the chain, thus producing ions both with and without chlorine. However, fragmentation occurs almost exclusively to give $\text{Si}_4\text{Me}_8\text{Cl}^+$ (99% rel. abund) with less than 1% of Si_4Me_8^+ or $\text{Si}_5\text{Me}_{11}^+$ (m/e 247, 305).

The unusual stabilities observed for $\text{Si}_4\text{Me}_8\text{X}^+$ and $\text{Si}_3\text{Me}_6\text{X}^+$ leads us to postulate cyclic structures for these ions:



$\text{X} = \text{Cl}, \text{Br}$

Several factors argue in favor of these structures. In a cyclic ion, there is stabilization from the additional silicon-halogen bond which is formed, and the cyclic structure allows for better delocalization of the positive charge. There is precedent in the literature for such ions, for cyclic structures have been proposed for the ions $\text{C}_4\text{H}_8\text{X}^+$ ($\text{X} = \text{Cl}, \text{Br}$) to account for their high abundances in the spectra of linear haloalkanes [9].

It is interesting to compare the abundances of the fragments $\text{C}_3\text{H}_6\text{X}^+$, $\text{C}_4\text{H}_8\text{X}^+$ and $\text{C}_5\text{H}_{10}\text{X}^+$ in the spectra of haloalkanes with the corresponding fragments for halosilanes. In the carbon case, the ion corresponding to the five-membered ring, $\text{C}_4\text{H}_8\text{X}^+$, is very prominent, with $\text{C}_5\text{H}_{10}\text{X}^+$ being much less abundant and $\text{C}_3\text{H}_6\text{X}^+$ nearly negligible. The stabilities of these ions are clearly not determined by ring strain alone. On steric grounds, the six-membered ring should be roughly equivalent to the five, with both of these being less strained than the four.

McLafferty [9] has proposed that the four and six-membered rings can decompose by concerted pathways which provide a driving force for further fragmentation. The five-membered ring shows apparent extra stability because no concerted pathway for decomposition is possible; hence the barrier to cleavage and further fragmentation is higher than the excess energy remaining in the ion.

In contrast to the mass spectra of haloalkanes, in the spectra of halopoly-silanes both the fragments $\text{Si}_3\text{Me}_6\text{X}^+$ and $\text{Si}_4\text{Me}_8\text{X}^+$ are abundant and so must lack sufficient energy to undergo further fragmentation. However, the stabilities of these ions cannot be explained using the previous arguments of McLafferty, for both ions should easily fragment by loss of $:\text{SiMe}_2$ or $:\text{SiMeCl}$. This suggests that these silicon-containing fragments may be generally more stable than their carbon analogs. A comparison of the chemical properties of carbon and silicon also supports this. For example, since silicon is less electronegative than carbon, it may better be able to accommodate a nearby positive charge. In addition, silicon is closer in size to the halogen, allowing better overlap to form the new bond

and requiring less distortion of the ring. Finally, the β -silicon atoms may play a role in delocalizing the positive charge over the orbital framework of the ring*.

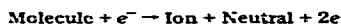
The major fragmentation pathways for 1,4- Cl_2 and 1,6- Cl_2 have been constructed from metastable analyses, and are illustrated in Schemes 1 and 2. Although similar analyses were not carried out for the corresponding bromopolysilanes, it is probable that these compounds undergo analogous fragmentation. From these schemes, two types of fragmentation pathways can be seen which closely parallel those reported for linear permethylpolysilanes [7]. The first type occurs with the loss of a dimethylchlorosilyl radical from the molecular ion. This is followed by successive losses of either dimethyl or chloromethyl silylene units, leading to the eventual formation of SiMe_3^+ . This ion, which at some prior step requires the migration of a methyl group, is a major peak in all our spectra, and is typical for methylpolysilanes in general. In addition, we observed the loss of a disilyl radical, $\cdot\text{SiMe}_2\text{SiMe}_2\text{X}$ from the molecular ion.

The second type of fragmentation occurs with the elimination of a neutral fragment to form a "disilene" or "trisilene" radical cation, $[\text{SiMe}_2]_2^+$ (m/e 116) or $[\text{SiMe}_2]_3^+$ (m/e 174). In the mass spectra of the smaller chloropolysilanes, this type of fragmentation appears to be especially favorable. For example, for 1,3- $\text{Cl}_2\text{Si}_3\text{Me}_6$ ** and 1- ClSi_3Me_7 , the fragment $[\text{SiMe}_2]_2^+$ forms the base peak of 14 eV. As noted earlier, it is likely that this type fragmentation is favorable here because there is no means of stabilizing the chlorine-containing fragments, as there is for the higher polysilanes.

References

- 1 W. Wojnowski, C.J. Hurt and R. West, *J. Organometal. Chem.*, **124** (1977) 271.
- 2 E. Hengge and S. Waldhör, *M. Chem.*, **105** (1974) 671.
- 3 K.R. Jennings, in R. Bonnet and J.G. Davis (Eds.), *Some Newer Physical Methods in Structural Chemistry*, United Trade Press, London, 1967, p. 105.

* An additional factor to consider in electron impact reactions is that the course of fragmentation is determined by the stability of both the ion and neutral species formed:



Consistent with this, in a recent work Schwarz et al. [10] report that the presence of five- or six-membered bromonium ions from ω -phenylalkyl bromides is determined in part by the stability of the accompanying neutral radical. For example, the postulated six-membered fragment, $\text{C}_5\text{H}_{10}\text{Br}^+$, would be expected to be produced in preference to $\text{C}_4\text{H}_8\text{Br}^+$ when this is accompanied by formation of a radical with significantly lower ΔH_f , such as benzyl compared to phenyl. For linear halopolysilanes, the stability of the neutral radical probably does not play as great a role. Here, the neutral fragments differ only in the number of SiMe_2 groups, so the energy differences between them should be small.

** Although the ion $\text{Si}_2\text{Me}_4\text{Cl}^+$ is very abundant (80%) in the mass spectrum of 1,3- $\text{Cl}_2\text{Si}_3\text{Me}_6$ there is no evidence to support the postulate that this ion (or its bromo analog) is in some manner stabilized by cyclization, as was the case for $\text{Si}_4\text{Me}_8\text{Cl}^+$ and $\text{Si}_3\text{Me}_6\text{Cl}^+$. If the formation of this ion were favorable, it should also be abundant in the spectra of 1- ClSi_3Me_7 and 1- ClSi_2Me_5 . It can be seen from Table 3, however, that non-chlorine containing ions predominate in the spectra of these compounds. This is to be expected, for unless there is some way to stabilize chlorine-containing ions, chlorine being electronegative, will tend not to appear in the mass spectrum of positive ions. However, 1,3- Cl_2 is a special case, for no matter which silicon-silicon bond is ruptured in the molecular ion (to eliminate a neutral radical), the resulting cation will contain chlorine. Only by a rearrangement or by the formation of radical cations such as $[\text{SiMe}_2]_2^+$ can non-chlorine containing fragments be formed.

- 4 R. West, F.A. Kramer, E. Carberry, M. Kumada and M. Ishikawa, *J. Organometal. Chem.*, 8 (1967) 79.
- 5 W.G. Boberski and A.L. Allred, *J. Organometal. Chem.*, 74 (1974) 205.
- 6 H. Schmidbaur, *J. Amer. Chem. Soc.*, 85 (1963) 2336.
- 7 Y. Nakadaira, Y. Kobayashi and H. Sakurai, *J. Organometal. Chem.*, 63 (1973) 79.
- 8 M.F. Lappert, J.B. Pedley, J. Simpson and T.R. Spalding, *J. Organometal. Chem.*, 29 (1971) 195.
- 9 F.W. McLafferty, *Anal. Chem.*, 34 (1962) 2.
- 10 H. Schwarz, F. Bohlmann, G. Hillenbrand and G. Altanau, *Org. Mass Spec.*, 9 (1974) 707.