Journal of Organometallic Chemistry, 113 (1976) 249—256

CHEMISTRY OF ORGANOSILICON COMPOUNDS

LXXXVIII. MASS SPECTROSCOPY OF ORGANOSILICON COMPOUNDS. PART 2. METHOXYMETHYLDISILANES *

YASUHIRO NAKADAIRA, TOSHIAKI KOBAYASHI, MITSUO KIRA, HIDEKI SAKURAI *,
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980 (Japan)
YASUJI YAMADA and YASUO SHIDA
Tokyo College of Pharmacy, Kitashinjuku, Shinjuku-ku, Tokyo 160 (Japan)
(Received January 5th, 1976)

Summary

Mass spectra of various methoxymethyldisilanes were examined in detail. Characteristic features of the spectra of these compounds are: (a) the fission of the Si—C bond occurs more readily than that of the Si—Si bond; (b) the methoxy group is eliminated as formaldehyde; (c) the silicon analog of an acyl cation is formed from the $[M - 15]^+$ ion; (d) the 1,2-shift of the methoxy group is characteristic in the fragmentation process.

Introduction

Reactivities of methoxymethyldisilanes are quite unique; for example, thermolysis of these compounds generates silylenes by α-elimination of the methoxy group [1]. Physicochemical studies of alkoxysilanes (including methoxymethyldisilanes) have shown interesting properties in their possible $p\pi$—$d\pi$ interaction in the silicon—oxygen bond [2]. Interesting reactivity traits of various methoxymethyldisilanes in the oxidation with perbenzoic acid have also been observed in our laboratory [3].

In connection with these studies, we have investigated mass spectra of methoxymethyldisilanes. These investigations complement our previous mass spectroscopic study on methylpolysilanes [4].

Mass spectra of a few methoxymethyldisilanes have been reported to date. Thus 1,2-dimethoxytetramethyldisilane was studied by Hungarian chemists [5] and recently, after our study had been completed, Childs and Weber reported

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* Presented at the 9th Symposium on Mass Spectrometry of Organic Compounds, Sendai, Japan, October 1974; Abstracts, p. 130; for part 1 see ref. 4.

the spectrum of 1,1,2,2-tetramethoxydimethyldisilane [6]. Particularly in these studies, the elimination of methoxy groups as formaldehyde in the fragmentation paths has been noted. We now describe a more systematic study of the mass spectra and fragmentation patterns of various methoxymethyldisilanes including methoxypentamethyldisilane (I), 1,1-dimethoxytetramethyldisilane (II), 1,1,1-trimethoxytrimethyldisilane (III), 1,2-dimethoxytetramethyldisilane (IV), 1,1,2-trimethoxytrimethyldisilane (V), and 1,1,2,2-tetramethoxydimethyldisilane (VI). For comparison, mass spectra of hexamethyldisilane (VII) and trimethoxymethylsilane (VIII) also were measured under the same conditions.

Results and discussion

The molecular ion and base ion peaks

The molecular ions of compounds I—VI are generally much less intense in comparison with that of hexamethyldisilane (VII). In hexamethyldisilane (VII) and arylpentamethyldisilanes (IX) the base ion peaks arise from the metastable-confirmed cleavage of the weaker Si—Si bond, and the positive charge is located on one of the silicon atoms that is stabilized more effectively by substituents as shown in eq. 1 [7].

$$\mathrm{Ph(CH_3)_2Si{-}Si(CH_3)_3}^{+\cdot} \xrightarrow{m^*} \underset{(X)}{\mathrm{Ph(CH_3)_2\overset{+}{Si}}} + \mathrm{\dot{Si}(CH_3)_3} \qquad (1)$$

However, in methoxymethyldisilanes cleavage of the Si—C bonds becomes much more prominent and consequently the metastable peaks occur in these steps, not in the Si—Si bond fissions. This means that in these methoxydisilanes the Si—C bond is broken more readily than the Si—Si bond in mass spectral fragmentation [8]. The fragmentation is ascribable to the stability of the fragment ion produced and/or the relative lability of the Si—C bond. Therefore, in methoxypen-

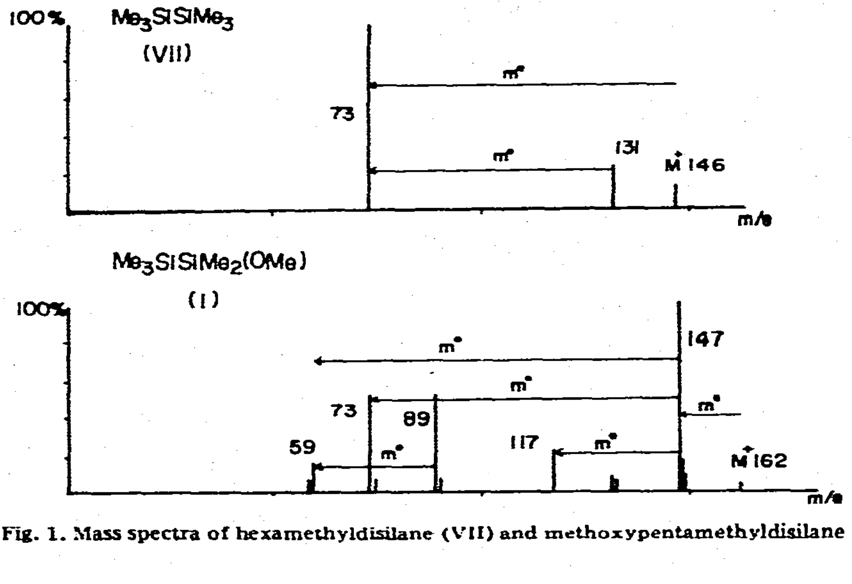


Fig. 1. Mass spectra of hexamethyldisilane (VII) and methoxypentamethyldisilane (I) at 25 eV.

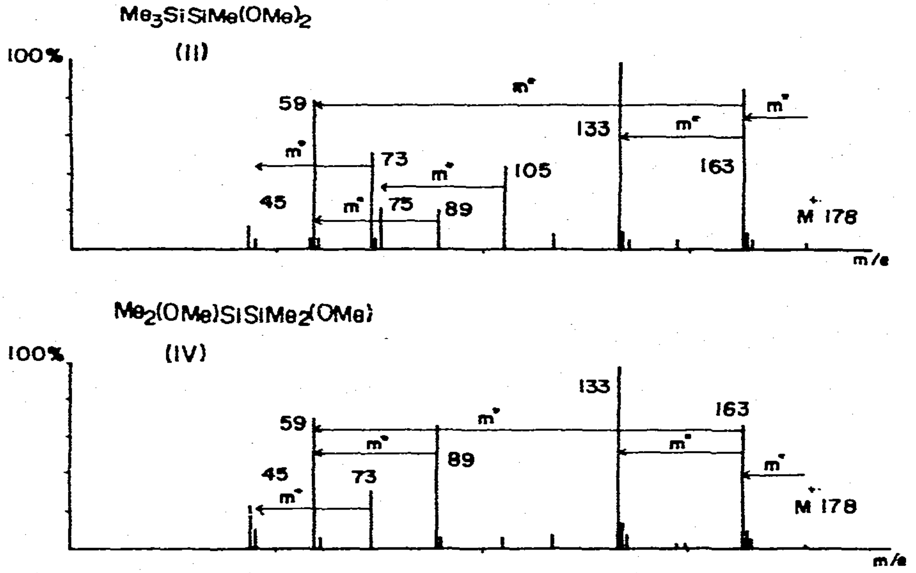
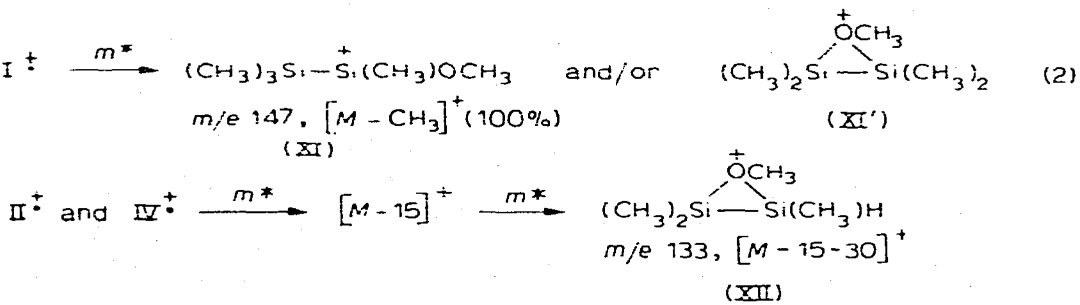


Fig. 2. Mass spectra of 1,1-dimethoxytetramethyldisilane (II) and 1,2-dimethoxytetramethyldisilane (IV) at 25 eV.

tamethyldisilane (I), the $[M - CH_3]^+$ ion constitutes the base peak (Fig. 1), while in cases of other methoxymethyldisilanes having more than one methoxy group, the $[M - CH_3]^+$ ion is intense but ejects a further CH_2O unit to yield the $[M - 15 - 30]^+$ ion which is more intense and constitutes the base peak (Fig. 2, 3, and 4). This behaviour of methoxydisilanes on fragmentation may be accounted for by stabilization of the resulting siliconium ions due to the methoxy group. Such stabilization by the methoxy group may be described by means of direct conjugation (XI) and/or bridging forms (XI′ and XII).



If such stabilization of the siliconium ion is attributed only to the methoxy group bonded to the cationic center, both Si—C and Si—Si bonds should be expected to be enhanced toward mass spectral fragmentation to almost the same extent. The preference for Si—C bond fission could be accounted for by assuming that the stabilization of the cation is caused by bridging of the methoxy group as shown in XI′ and XII. In the case of I, the mass 147 ion may be composed of XI and XI′, which possibly are equilibrated with each other (eq. 2). In this

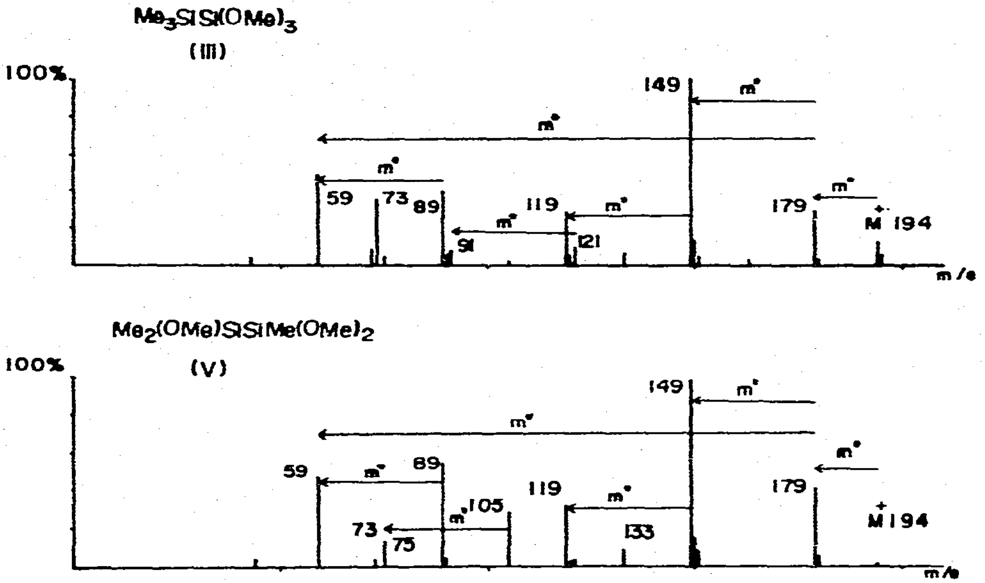


Fig. 3. Mass spectra of 1,1,1-trimethoxytrimethyldisilane (III) and 1,1,2-trimethoxytrimethyldisilane (V) at 25 eV.

paper, the structure of the fragment ion is described as the bridged form, if it is possible. However, this does not necessarily mean that the ion exists only as the bridged form. It should be taken as one of the possible structures of the ion.

Elimination of the methoxy group

The principal degradation path of the methoxy group bonded to a silicon atom involves the loss of formaldehyde. The composition of the *m/e* 30 ion in VI is proven to correspond to that of formaldehyde by high resolution mass measurements. Thus, the mass 165 ion peak, $[M-15-30]^+$, was observed at *m/e* 165.0373. Since the $[M-15]^+$ ion peak is at *m/e* 195.0509 ($C_5H_{15}O_4Si_2$), the mass difference between these two peaks is calculated to be 30.0136, which corresponds to CH_2O (30.0105) but not to C_2H_6 (30.0469). Although in anisole derivatives the methyl ether moiety is known to be lost as formaldehyde, this type of fragmentation cannot be an important process in aliphatic methyl ethers

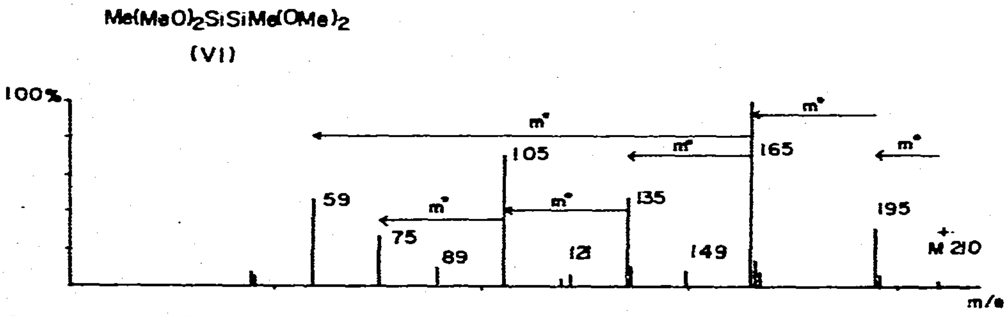
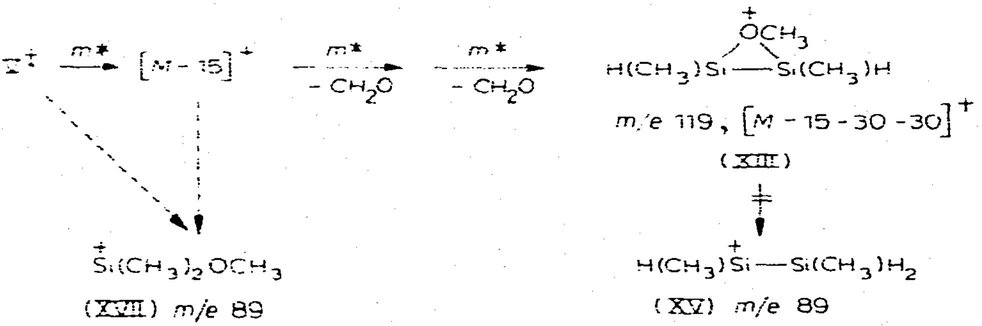


Fig. 4. Mass spectrum of 1,1,2,2-tetramethoxydimethyldisilane (VI) at 25 eV.

[9]. In this sense, mass spectroscopically the methoxysilanes resemble the silicon analog of an aryl methyl ether.

The general pattern of fragmentation can be described as follows. After elimination of a methyl radical by Si—C bond fission, the molecular ion loses methoxy groups as formaldehyde, one by one successively, which is evidenced by the presence of the corresponding metastable peak. Direct elimination of the methoxy group as a methoxy radical from the M^+ ion is negligible but becomes more evident at higher ionization voltage. Seemingly, removal of formaldehyde does not occur from the molecular ion directly, but occurs only after formation of the trivalent siliconium ion.

The last methoxy group remaining bonded to the disilane moiety in the ions XII, XIII, and XIV appears scarcely removable as formaldehyde. This is consistent with the fact that the corresponding metastable peaks were not observed. For example in V, if the last methoxy group is lost from the ion XIII, it should yield the mass 89 ion XV. Since the Si—Si bond fission of the molecular ion or $[M-15]^+$ should give the mass 89 ion XVII, there should be two kinds of the mass 89 ions; i.e. XV ($Si_2C_2H_9$; 89.02424) and XVII (SiC_3OH_9; 89.04222). However, no splitting of the peak at m/e 89 was detected in the high resolution mass spectrum. This means that the mass 89 ion observed should correspond only to XVII and elimination of the last methoxy group does not occur, at least in V. These features of the methoxy groups may give another indication of the bridged structure.



The methoxy group of a monosilane fragment is also eliminated as formaldehyde and the corresponding metastable peak can be observed (Fig. 1, 2, 3 and 4). In accord with this fact, trimethoxymethylsilane shows a similar fragmentation pattern. The methoxy part is lost as formaldehyde successively after Si—C bond fission of the molecular ion.

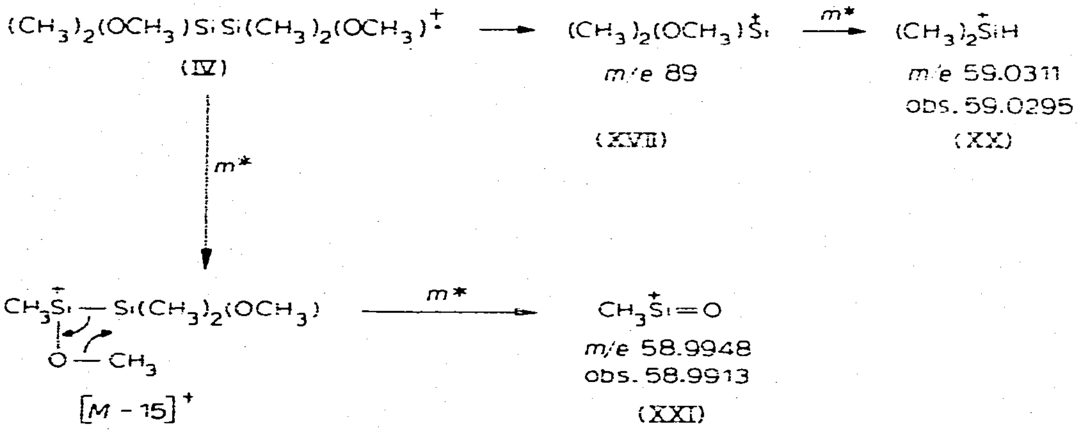
$$[(CH_3O)_3SiCH_3]^+ \xrightarrow[-CH_3]{m*} \overset{+}{Si}(OCH_3)_3 \xrightarrow[-CH_2O]{m*} H\overset{+}{Si}(OCH_3)_2$$

m/e 121 m/e 91 (22)
base peak

The $[M-15]^+$ ion

The $[M-15]^+$ ion is fragmented in two paths as are methoxydisilanes. One gives $[M-15-30]^+$ ions by loss of formaldehyde and the other produces the mass 59 ion. On the other hand, for the mass 59 ion, there are two precursors indicated by the presence of two kinds of metastable peaks, the mass 89 ion (the methoxydimethylsiliconium ion, XVII) and $[M-15]^+$ ion, respectively. As a typical example, the fragmentation pattern of IV is shown in Scheme 1. This path is confirmed by high resolution measurements, which reveal the mass 59 ion as being composed of two peaks, the dimethylsiliconium ion (XX) and the silicon analog of the acyl cation XXI. Similarly, the mass 59 ion peaks from II and III are shown to be split into two peaks and the intensity ratio of these peaks is dependent on the structure of methoxymethyldisilanes.

SCHEME 1



Rearrangement of methyl and methoxy groups

Relative intensities of fragments derived from the Si—Si bond fission of the corresponding molecular ion are summarized in Table 1. Some of the peaks are obtainable only after rearrangements of methyl and/or methoxy groups. Such kinds of rearrangements have been reported in $A_3MM'B_3$ type compounds (where A, B: alkyl or aryl, M, M′; IVB metals) [10]. Since Si—O bond fission is not likely to be efficient, at least some of these rearranged ions, for example XVII from II, conceivably arise from a 1,2-shift of the methoxy group.

It is not clear whether the Si—Si bond fission occurs in the molecular ion or in the $[M-15]^+$ ion, although from considerations of fragmentations observed in hexamethyl- and phenylpentamethyl-disilanes, the Si—Si bond cleavage is thought to occur both in the molecular and in $[M-15]^+$ ions [4,7]. For the case

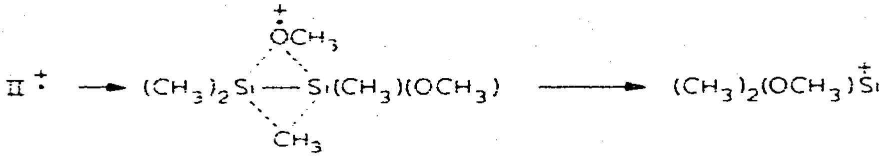
TABLE 1

SILICONIUM IONS PRODUCED FROM THE Si—Si FISSION OF THE MOLECULE

(Figures are relative intensities of the corresponding peaks and italic figures indicate the rearranged ion.)

Fragment ion		m/e	Dimethoxy		Trimethoxy		Tetramethoxy
			II	IV	III	V	VI
$\overset{+}{\mathrm{Si}}\mathrm{Me}_3$	(XVI)	73	57	*26*	37	*4*	
$\overset{+}{\mathrm{Si}}\mathrm{Me}_2\mathrm{OMe}$	(XVII)	89	*21*	66	*41*	56	*10*
$\overset{+}{\mathrm{Si}}\mathrm{Me(OMe)}_2$	(XVIII)	105	44	*6*	*5*	27	70
$\overset{+}{\mathrm{Si}}\mathrm{(OMe)}_3$	(XIX)	121			10	*4*	*7*

of the molecular ion, the rearrangement may be described to proceed through a bridged transition state such as XXII which is quite similar to that assumed in thermal elimination of a silylene from the corresponding methoxymethyldisilane [1]. However in the mass spectra of these methoxymethyldisilanes, no peak related to such silylene ejection from the disilane unit is detected in appreciable intensitity.



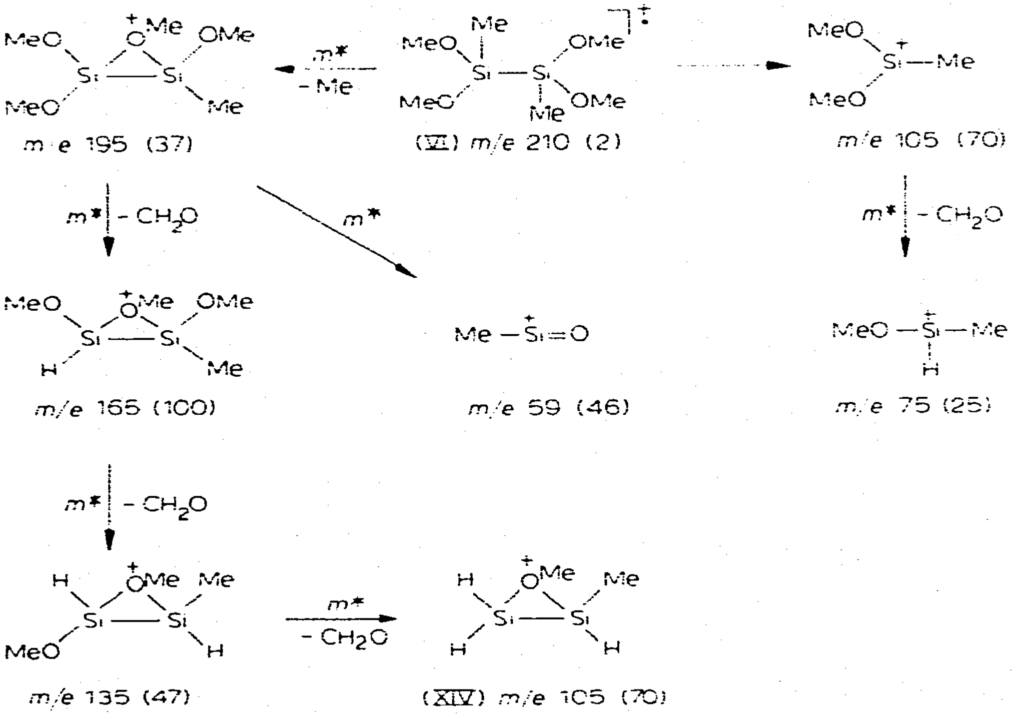
(XXII) (XVII)

The substitution pattern of the methoxy group on a disilane skeleton does not affect its fragmentation appreciably, and the difference in the structure may be recognized only from careful inspections of their mass spectra. Finally the general fragmentation pattern of methoxymethyldisilane is illustrated by that of 1,1,2,2-tetramethoxydimethyldisilane (VI) in Scheme 2.

There are some differences in relative intensities between the spectrum shown in Fig. 4 and that reported before [6]. This is due to the difference in the ionization voltage employed in these two measurements. However, some comments on

SCHEME 2

FRAGMENTATION OF 1,1,2,2-TETRAMETHOXYDIMETHYLDISILANE (VI) AT 25 eV (FIGURES IN PARENTHESES ARE RELATIVE INTENSITIES OF THE CORRESPONDING PEAKS).



the fragmentations shown in Scheme 2 are required. (i) In the mass 59 ion derived from VI the peak at *m/e* 58.994 corresponding to the $CH_3\dot{Si}{=}O$ is much more intense than that corresponding to the $H\overset{+}{Si}(CH_3)_2$. This fact indicates that the 59 ion arises mainly from the $[M-15]^+$ ion but not from the 89 ion as suggested before [6]. (ii) The mass 105 ion peak also splits into two peaks. The major peak is observed at *m/e* 105.034 corresponding to the ion $\dot{Si}CH_3(OCH_3)_2$ (calcd. *m/e* 105.037). The other peak is weak but can be observed clearly at lower mass side of the major peak. This is ascribable to the ion XIV (calcd. *m/e* 105.019). Along with other fragmentations concerning the methoxy group, the mass 135 ion certainly ejects a formaldehyde unit to give the mass 105 ion. However the possible elimination of a silylene unit from the mass 135 ion [6] is not ruled out.

Experimental

Materials were prepared from corresponding chlorodisilanes by methanolysis in the presence of ammonia in ether. Samples were purified by means of preparative VPC before measurement. Mass spectra were recorded on a Hitachi RMU-6 mass spectrometer at 25 eV and high resolution measurements were carried out by using a Hitachi RMU-7 mass spectrometer.

Acknowledgment

We thank Mr. T. Sato for taking some of the mass spectra. We are also indebted to Toshiba Silicone Co., Ltd. for a gift of chlorosilanes.

References

1 W.H. Atwell and D.R. Weyenberg, J. Amer. Chem. Soc., 90 (1968) 3438.
2 F. Hofler and E. Henge, Monatsh. Chem., 103 (1972) 1513; H. Bock, P. Mollere, G. Becker and G. Fritz, J. Organometal. Chem., 61 (1973) 113.
3 M. Kira, PhD. Dissertation, Tohoku University, Sendai Japan 1973.
4 Y. Nakadaira, Y. Kobayashi and H. Sakurai, J. Organometal. Chem., 63 (1973) 79.
5 J. Tamas, K. Ujszaszy and G. Bujtas, Acta Chim. (Budapest), 64 (1970) 305.
6 M.E. Childs and W.P. Weber, J. Organometal. Chem., 86 (1975) 169.
7 H. Sakurai, M. Kira and T. Sato, J. Organometal. Chem., 42 (1972) C24.
8 F.W. McLafferty, T. Wachs, C. Lifshits, G. Innorta and P. Irving, J. Amer. Chem. Soc., 92 (1970) 6867.
9 H. Budzikiewicz, C. Djerassi and D.H. Williams, Interpretation of Mass Spectra of Organic Compounds, Holden-Day, Inc., San Francisco, 1964.
10 D.B. Chamber and F. Glockling, J. Chem. Soc. (A), (1968) 735.