*Contribution from the Department of Chemistry,
Iowa State University, Ames, Iowa 50010, U.S.A.*

Mass Spectrometry of Cyclopolysilanes

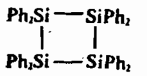
T. H. Kinstle, I. Haiduc* and H. Gilman

Received October 16, 1968

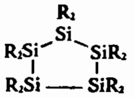
The mass spectra of perphenylated polysilanes containing four-, five-, and six-membered silicon rings and permethylated cyclopolysilanes containing five-, six-, and seven membered rings are presented and discussed. Rearrangement reactions involving methyl or phenyl migration are common features of the mass spectral chemistry of these compounds. The potential of mass spectrometry as a structural tool in this area of organometallic chemistry is evaluated. Mechanisms are suggested for the fragmentation of the title compounds after electron impact.

Introduction

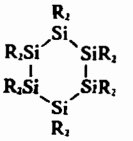
From the reaction of diphenyldichlorosilane with metallic sodium Kipping[1] obtained among several products three individual substances of the general formula $(SiPh_2)_n$ called « Compounds A, B, and C ». The identity of these compounds was a subject of great uncertainty for many years, and only in recent years has the matter been clarified.[2] Thus « Compound A », originally described as a linear biradical, was identified[3] as octaphenylcyclotetrasilane, **1**. « Compound B, » variously described as a four-membered[4] or as a six-membered[5] ring compound is now known as decaphenylcyclopentasilane, **2**.[6] For « Compound C » a six-membered ring structure, **3**, has received some experimental support.[7]



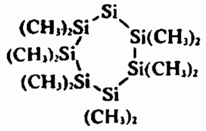
1



2; R = Ph
4; R = CH_3



3; R = Ph
5; R = CH_3



6

We now wish to describe the results of a mass spectrometric investigation of these compounds which provides convincing corroboration of the previous conclusions.[2] We are currently using mass spectrometry to determine not only molecular weights but also to obtain other structural information pertinent to organosilicon compounds.[8] This method has been applied by other authors in their investigations of other inorganic ring systems containing boron-nitrogen,[9,10] boron-oxygen,[11,12] silicon-nitrogen,[13] silicon-oxygen,[14] sulfur,[15] selenium,[16] sulfur-selenium,[17] and phosphorous.[18,19] The only cyclosilane thus far subjected to mass spectrometric scrutiny is decamethylcyclopentasilane (**4**), but this served only to establish its molecular weight and no fragmentation was reported.[20,21] Several other reports describe mass spectra of non-cyclic organosilicon compounds,[23-31] but much

---

(*) Postdoctoral Visiting Scholar, 1966-67. Present address: Department of Chemistry, Babes-Bolyai University, Clug, Romania.
(1) F. S. Kipping, *J. Chem. Soc.*, 2291 (1924).
(2) H. Gilman and G. L. Schwekke, *Advan. Organometal. Chem.*, *1*, 89 (1964); See H. Gilman, W. H. Atwell and F. K. Cartledge, *Advan. Organometal. Chem.*, *4*, 1 (1966), for a summary of these developments.
(3) A. W. P. Jarvie, H. J. S. Winkler, D. J. Peterson, and H. Gilman, *J. Am. Chem. Soc.*, *83*, 1921 (1961).
(4) E. Hengge, H. Reuter, and R. Petzgold, *Z. Naturf.*, *18b*, 425 (1963).
(5) H. J. S. Winkler, A. W. P. Jarvie, P. J. Peterson, and H. Gilman, *J. Am. Chem. Soc.*, *83*, 4089 (1961).
(6) H. Gilman and G. L. Schwebke, *J. Am. Chem. Soc.*, *86*, 2693 (1964).
(7) H. Gilman and G. L. Schwebke, *J. Organometal. Chem.*, *3*, 382 (1965).
(8) I. Haiduc and H. Gilman, *J. Organomet. Chem.*, *11*, 55 (1968). These authors are particularly grateful to Dr. T. H. Kinstle for his special assistance in our early applications of this technique to organometallic chemistry.
(9) M. F. Lappert and M. K. Majumdar, *Advan. Chem. Ser.*, *42*, 208 (1964).
(10) E. F. H. Britain, J. B. Leach and J. H. Morris, *J. Chem. Soc.*, (A), 340 (1968).
(11) D. L. Hildenbrand, L. P. Theard, and A. M. Saul, *J. Chem. Phys.*, *39*, 1973 (1963).
(12) R. F. Porter and S. K. Gupta, *J. Phys. Chem.*, *68*, 280 (1964).
(13) J. Silbiger, C. Lifshitz, J. Fuchs, and A. Mandelbaum, *J. Am. Chem. Soc.*, *89*, 4308 (1967).
(14) V. Yu. Orlov, *Zhur. Obshch. Khim.*, *37*, 2300 (1967).
(15) J. Buchler, *Angew. Chem.*, *78*, 1021 (1966).
(16) E. Fujisaki, J. B. Westmore, and A. W. Tickner, Abstr. of Papers, 152nd Meeting American Chemical Society, New York, September, 1966, 155-0.
(17) R. Copper and J. V. Culka, *J. Inorg. Nucl. Chem.*, *29*, 1217 (1967).
(18) M. Baudler, K. Kipker, and H. W. Valpertz, *Naturwiss.*, *53*, 612 (1966).
(19) C. E. Brion and N. L. Paddock, *J. Chem. Soc.* (A), 388, 393 (1968).
(20) E. Carberry and R. West, *J. Organometal. Chem.*, *6*, 582 (1966).
(21) Note added in proof: After acceptance of this manuscript, a paper describing a study similar to the present one appeared.[22] We acknowledge the kind correspondence of Professor Neumann describing his research results prior to publication.
(22) K. Kulhlein and W. P. Neumann, *J. Organometal. Chem.*, *14*, 317 (1968).
(23) G. Fritz, H. Buhl, J. Grove, F. Aulinger, and W. Reering, *Z. Anorg. Alleg. Chem.*, *312*, 201 (1961).
(24) A. G. Sharkey, R. A. Friedel, and S. H. Langer, *Anal. Chem.*, *29*, 770 (1957).
(25) G. G. Hess, F. W. Lampe, and L. H. Sommer, *J. Am. Chem. Soc.*, *87*, 5327 (1965) and references cited therein.
(26) V. H. Dibeler, F. L. Mohler, and R. M. Reese, *J. Chem. Phys.*, *21*, 180 (1953).
(27) N. Ya. Chernyak, R. A. Khmel'nitskii, T. V. D'yakova, and V. M. Vdovin, *Zh. Obshch. Khim.*, *36*, 89 (1966).
(28) D. R. Weyenberg and W. A. Atwell, Abstr. of Papers, 3rd International Symposium on Organometallic Chemistry, Munich, September, 1967, p. 260.
(29) T. H. Kinstle and P. J. Ihrig, Abstr. of Papers, 155 th Meeting of the American Chem. Soc., San Francisco, April, 1968, M 112.
(30) D. B. Clambers and F. Glocking, *J. Chem. Soc.*, *A*, 735 (1968).

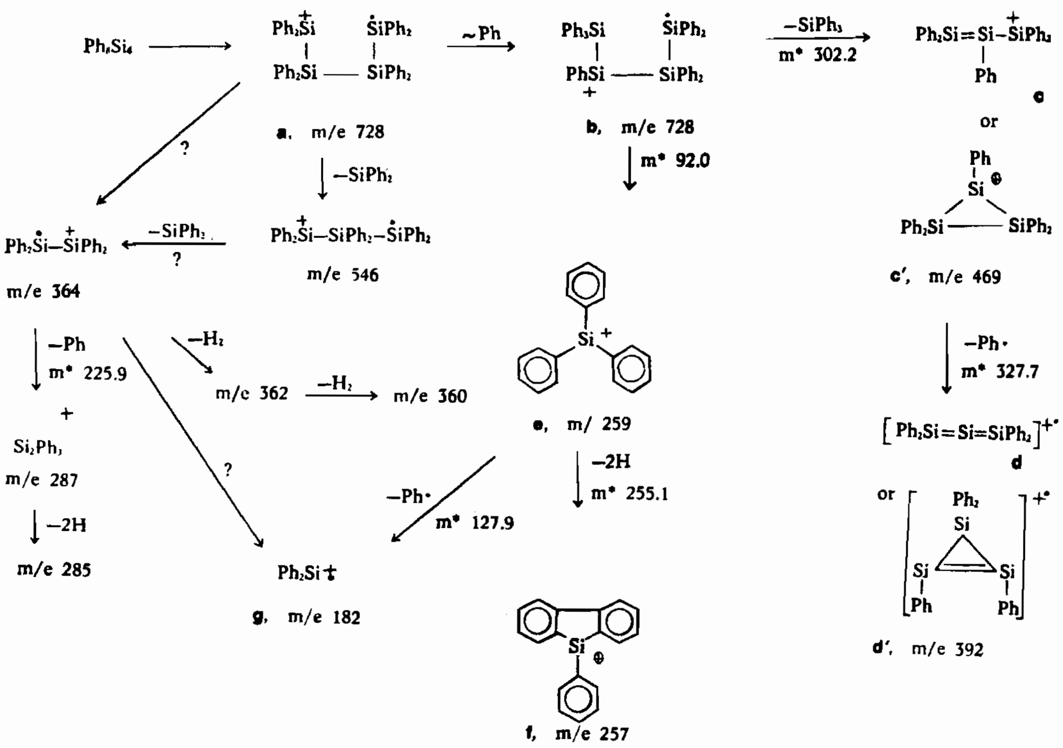
work remains to be done to understand the mechanisms of the mass spectral reactions of these materials. Of particular interest in the present work, as well as in much of the organometallic mass spectral work reported in the recent literature,[30,31] is the relatively common occurrence of structural rearrangements.

Results and Discussion

The 70 ev mass spectra of the cyclopolysilanes were recorded on an Atlas CH4 Mass Spectrometer using a direct solid insertion sample inlet and ambient (at least initially) source temperatures. Under these conditions, minimal sample heating was required and thermal reactions were no problem. Electron currents of 2-6 μA were employed. A constant total ion current was maintained throughout each individual measurement. The spectra of the perphenylated cyclosilanes contain a relatively large number of peaks corresponding to species of general formula Si_mPh_n, as well as peaks corresponding to loss of hydrogen therefrom. The mass spectra of the methylated cyclosilanes contain larger numbers of peaks but only relatively few of these are of major intensity.

Perphenyl Cyclopolysilanes. Si_4Ph_8. The mass spectrum of **1** is rather simple and contains a very intense (25% relative intensity) peak corresponding to the parent molecular ion at m/e 728 (Si_4Ph_8) accompanied by the ^{29}Si, ^{30}Si, and ^{13}C isotope peaks of the expected intensity at m/e 729, 730, 731, and 732. Simple cleavage of a Si–Ph bond is not an important fragmentation of the molecular ion, since the ions at m/e 651 (M–Ph) and 574 (M–2Ph) have only 2% and 1% relative intensity, respectively. Consideration of bond strengths suggests that this result is not surprising. The dissociation energy of an Si-aromatic carbon bond is approximately 77 kcal/mole and the dissociation energy of an H-aromatic carbon bond is an even higher 102 kcal/mole. In contrast, the Si–Si bond dissociation energy is only about 53 kcal/mole.[32] Thus, cleavage of one of the Si–Si bonds in the molecule ion leads to all the major fragment ions. Ejection of one $SiPh_2$ unit, possibly as the diphenylsilene, from ion **a**,[33] Scheme I, leads to an m/e 546 ion of 5% relative intensity The consecutive cleavages of additional $SiPh_2$ units from the m/e 546 ion to produce the ions at m/e 364 (6% relative intensity) and m/e 182 (ion **g**, Scheme I, 8% relative intensity) are possible fragment modes, although no metastable ions were observable for these processes. Very reasonable alternative pathways, with some metastable ion corroboration,[34] are shown in Scheme I.

A very intense peak in the spectrum of **1** appears at m/e 469 (70% relative intensity) and is due to the loss of $SiPh_3$. This cleavage is accompanied by an intense metastable at m/e 302.2.[34] The genera-



Scheme I

---

(31) D. B. Chambers, J. R. C. Light, and F. Glocking, *Quart. Rev. Soc.*, *22*, 317 (1968).

(32) J. A. Connor, R. N. Haszeldine, G. J. Leigh, and R. D. Sedgwick, *J. Chem. Soc.* (*A*), 768 (1967).

(33) It is obvious that definitive structural assignments of the ions cannot be made, and the drawings in the Schemes are meant to be only suggestive and used as atomic bookkeeping aids.

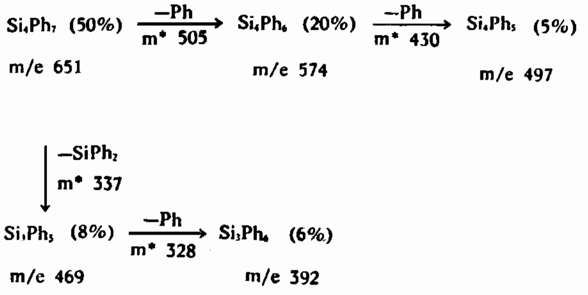
(34) Extensive use of the many observed metastable ions observed in the spectra of all these compounds permitted us to assign fragmentation pathways with some degree of confidence. Otherwise, only a more crude and undoubtedly much less correct interpretation could have been made.

lity of this phenyl migration process will be discussed below with regard to the other compounds studied. This rearrangement is depicted as a 1,2-phenyl shift in Scheme I, although other rearrangement modes cannot be ruled out.

All the other prominent ions in the spectrum are derived from the species mentioned above. Loss of a phenyl group from the m/e 469 ion produces the m/e 392 ion (Si_3Ph_4) of 10% relative intensity. Since the m/e 469 ion might exist in either of two forms **c** or **c'**, the m/e 392 ion could conceivably exist in either the allenic form **d** or the cyclic form **d'**. Cleavage of an interior Si–Si bond in ion **a** could produce the m/e 364 ion (6% relative intensity). This ion undergoes two further modes of fragmentation. Loss of a phenyl group leads to the m/e 287 ion of 5% relative intensity. Ions at m/e 362 and 360 (and to a much smaller extent 361 and 359) are derived from hydrogen loss from the m/e 364 ion. This hydrogen loss process will be discussed in more detail below.

A final sequence of ions is derived from cleavage of the rearrangement ion **b** with charge retention on the $SiPh_3$ fragment ion **e**, to produce the base peak m/e 259. This ion could, of course, also be derived in part from other fragment ions. Ion **e** suffers a pronounced loss of molecular hydrogen to form the m/e 257 ion **f** (20% relative intensity). Similar hydrogen loss processes have been clearly documented for mass spectrally produced triarylmethyl cations.[35] Similar structures can be drawn for the hydrogen loss processes described above for the m/e 364 ion. The m/e 259 ion alternatively loses a phenyl radical to produce the ionized diphenylsilene species **g** at m/e 182 of 8% relative intensity.

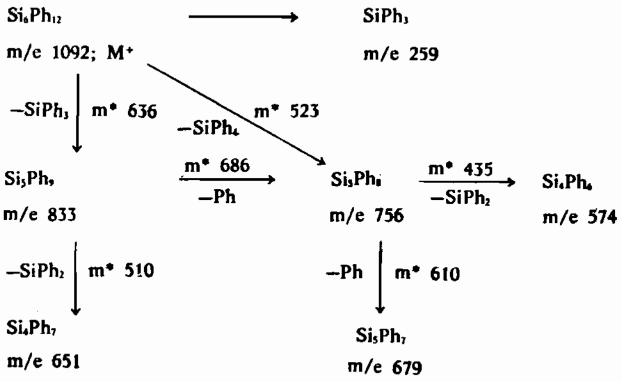
Si_5Ph_{10} and Si_6Ph_{12}. The mass spectra of **2** and **3** are in many respects similar to that of the simpler compound. The proposed constitution of **2** is substantiated by the presence of a molecular ion at m/e 910 (Si_5Ph_{10}). The relative intensity of this molecular ion is much lower (12%) than that found for **1**. The most important fragment ions are again rearrangement ions. The base peak is again at m/e 259 ($SiPh_3$) and the second most intense ion (50% relative intensity) is at m/e 651 (M–$SiPh_3$) formed from the molecule ion with an accompanying metastable at m/e 466. These ions presumably arise *via* pathways similar to those shown in Scheme I for **1**. The subsequent fate of the m/e 651 ion is depicted in Scheme II.



Scheme II

The major difference in the behavior of the m/e 651 ion from that of the similarly formed m/e 469 ion of **1** is that it loses an $SiPh_2$ group to produce an m/e 469 ion, conceivably of similar structure to the m/e 469 ion derived from **1**. Another difference is the sequential loss of two phenyl groups from m/e 651 to produce a very highly unsaturated species at m/e 497. The structures of these highly unsaturated silicon species would be of considerable interest, particularly the m/e 392 ion which corresponds formally to a silicon analog of cyclopropene, but these structures remain undetermined at present. One other difference in the fragmentation of **1** and **2** is the possible loss of $SiPh_4$ from the molecule ion of **2**, substantiated by a weak metastable centered at m/e 362.

The spectrum of the very non-volatile « Compound C » (**3**), exhibits a molecular ion at m/e 1092, thus providing corroboration of its previous molecular formulation. The base peak in this spectrum is again m/e 259 ($SiPh_3$). Although instrumental problems encountered in measuring this spectrum do not allow us to conclusively state relative intensities of the ions, it is apparent that the molecular ion intensity is very weak (less than 5%). The M–$SiPh_3$ ion at m/e 833 (metastable at m/e 636) is only the 4th largest ion in this spectrum instead of second largest as in the spectra of **1** and **2**. The ions at m/e 756 and 574 are the second and third largest ions, respectively, and all major ions are accounted for in Scheme III.



Scheme III

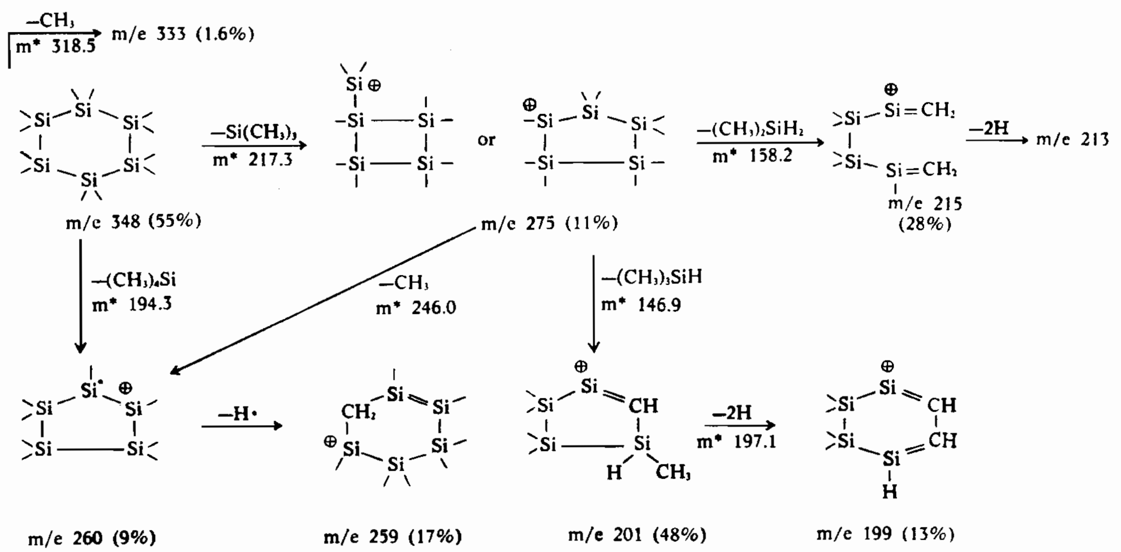
It is obvious that the tendency for consecutive loss of $SiPh_2$ groups increases in going from **1** to **3**. The new mode of $SiPh_2$ loss in the spectrum of **3** occurs from the Si_5Ph_8 ion. Loss of $SiPh_4$ from the molecule ion to produce the m/e 756 ion presumably occurred (strong metastable at m/e 523).[36] Likewise, although it is not indicated in Schemes II and III, there is an increasing tendency in going from **1** to **3** for the elimination of hydrogen to produce silafluorene type species. The intensity of these ions relative to those shown in the Schemes is, nevertheless, weak.

---

(35) T. A. Bryce, P. Wszolek, and F. W. McLafferty, Abstracts of ASTM Committee E-14 Meeting, Denver, Colorado, May 14-19, 1967, page 128. See also P. C. Wszolek, F. W. McLafferty, and J. H. Brewster, *J. Org. Mass Spect.*, *1*, 127 (1968).

(36) J. Seibl, *Helv. Chim. Acta*, *50*, 263 (1967).

Permethyl Cyclopolysilanes. *$Si_6(CH_3)_{12}$* (**5**). In order to compare certain of the spectral features described above with a non-phenylated example, the mass spectrum of the well-known dodecamethylcyclohexasilane (**5**) was measured. As with the phenylated species, the base peak was due to a rearrangement ion, in this instance the $Si(CH_3)_3$ ion at m/e 73. Loss of hydrogen molecule from this species was unimportant, since in contrast to the phenylated species no stable ion such as the silafluorene ion, would result. The intensity of dimethylsilene, $Si(CH_3)_2$, or its dimer was miniscule. This is of interest as a comparison to recent reports of thermal generation of dimethylsilene from permethylated polysilanes.[26]

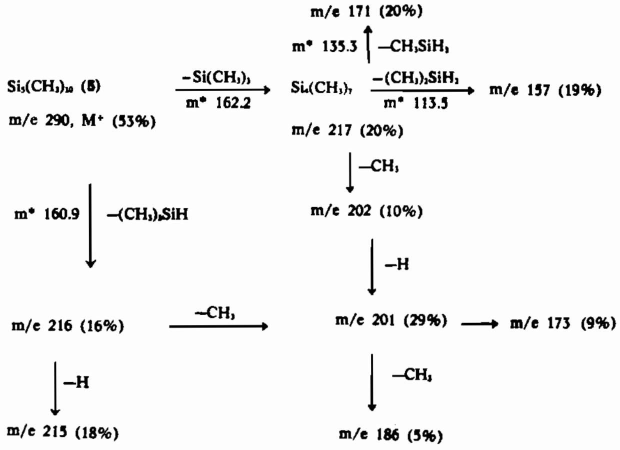


Scheme IV

The molecular ion of **5** appears as an intense peak at m/e 348 (55% relative intensity) with the expected isotope peaks at higher masses. Loss of a single methyl group results in a very weak ion at m/e 333, but the fragment of the highest m/e with significant intensity appears at m/e 275 [M–$Si(CH_3)_3$, 11% relative intensity]. This ion suffers minor hydrogen atom loss to produce the ions at m/e 274 and 273 as well as the other fragmentations shown in Scheme IV. Note that in this peralkylated species, a metastable loss of $Si(CH_3)_4$ from the molecular ion produces an ion at m/e 260. Although reasonable mechanisms can be drawn for their formation and some stability would be expected of such species, the structures of the ions postulated in Scheme IV must be recognized as highly speculative and more in the nature of a pictorial reminder of the amount of unsaturation that must be present in these fragment ions. Note that the processes which form m/e 215 and m/e 201 from the m/e 275 ion by loss of $(CH_3)_2SiH_2$ and $(CH_3)_3SiH$, respectively, had no analogy in the phenylated compounds **1**-**3**. Scheme IV includes all the prominent ions in the spectrum of **5**, with the exception of the base peak m/e 73 ($Si(CH_3)_3$). At mass values lower than 201, a series of very low intensity ions appeared and these were all of the general type $(SiHCH_3)_n$ and $[Si(CH_3)_2]_n$.

At this point we were very fortunate to obtain as gifts samples of the homologous five-membered (**4**) and seven-membered (**7**) permethylated cyclopolysilanes from Professor Robert West and Dr. Edward Carberry. We have studied the mass spectra of these materials and compared the results with those obtained for 5.

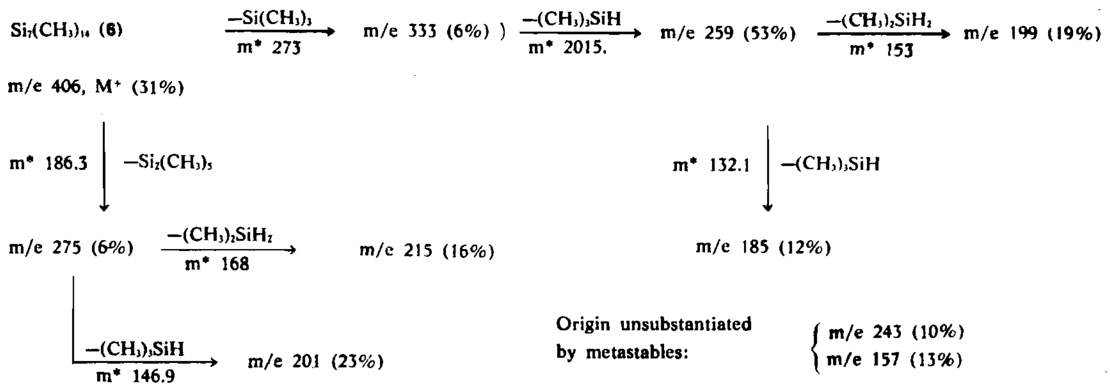
$Si_5(CH_3)_{10}$ (**4**). The spectrum of **4** is relatively simple and all the major ions are listed in Scheme V with the exception of the base peak m/e 73 [$Si(CH_3)_3$]. Ion structures are not postulated in this Scheme since nothing can be documented in this respect.



Scheme V

Those suggested fragmentations which are not accompanied by an appropriate metastable are very speculative, *albeit* reasonable. The major similarity that exists in the spectra of **5** and **4** is the loss of $Si(CH_3)_3$ from the molecular ion. A major difference between the two is found in the structural nature of the silicon containing fragments lost from these M–$Si(CH_3)_3$ ions. These fragments from **5** are $(CH_3)_3SiH$ and $(CH_3)_2SiH$ while from the smaller ion m/e 217 in **4** the silicon atoms are more highly hydrogen substituted [$(CH_3)_2SiH_2$ and CH_3SiH_3]. Apparently a minimum total of 8 (and preferably 9) silicon and carbon atoms is necessary to accommodate the positive charge in the required state of unsaturation (2 degrees minus one hydrogen atom) in a reasonable way, and since loss of $Si(CH_3)_3H$ from m/e 217 in **4** would result in the formation of $(Si_3C_4H_{11})^+$, the observed process takes place instead.

mentation pattern for these polymethyl derivatives is initial ionization and fragmentation to produce even-electron ions, with all major subsequent reactions being even-electron→even-electron transitions by loss of neutral silane molecules. The nature of the rearrangement reactions which leads to this observed fragmentation is of much intrinsic interest and is being studied by means of deuterium labeling in simpler systems. There is no evidence from the many available metastable transitions that neutral silene fragments are lost. This stands in contrast to the elimination of $SiPh_2$ units from **1**-**3**.



Scheme VI

It is interesting to extend these ideas to **6** whose spectrum is depicted in Scheme VI. Again the m/e 73 ion is the base peak. Note that in accord with expectations based on previously discussed results, the loss of $(CH_3)_3SiH$ from the m/e 333 [M–$Si(CH_3)_3$] ion greatly outweighs both of the alternate processes observed in the smaller compounds, *i.e.* loss of $(CH_3)_2SiH_2$ to produce m/e 273 or loss of CH_3SiH_3 to produce m/e 287, neither of which is an intense ion. The increased number of atoms in **6** allows two new fragmentation pathways to become important. The loss of a unit containing *two* silicon atoms from the molecule ion leads to the intense m/e 275 ion, and loss of another monosilicon species from the m/e 259 ion extends the sequence fragmentation of the molecule through one more step than that observed in **5**. Again, it is apparent that after degradation to a species containing fewer numbers of Group IV atoms, for example m/e 259 and m/e 275, an increasing tendency to observe silicon-hydride type fragments is noted. The m/e 201 ion is very intense in the spectra of each of the materials **4**-**6**, with only rather weak intensity ions at lower m/e values, indicative of a peculiarly stabilized ion.

It is important to note that the generalized fragmentation pattern for these polymethyl derivatives is initial ionization and fragmentation to produce even-electron ions, with all major subsequent reactions being even-electron→even-electron transitions by loss of neutral silane molecules.

An insight to understanding these rather complex fragmentation processes was gained by studying the low energy electron impact spectra of **4**-**6**. The lowest energy fragmentation in **4** is the m/e 217 [M–$Si(CH_3)_3$] ion. In spectra of **5** measured at energies less than 15 ev, it becomes obvious that formation of the m/e 275 ion has the least demanding energy requirements and that the m/e 275→m/e 201 fragmentation (loss of $(CH_3)_3SiH$) is of lower energy than the m/e 275→m/e 215 process (loss of $(CH_3)_2SiH_2$). In the spectrum of **6**, the lowest energy sequence is the loss of $Si(CH_3)_3$ from the molecule ion to give m/e 333, followed by the subsequent loss of $(CH_3)_3SiH$ to give m/e 259. Of only slightly higher energy requirement is the metastable loss of $Si_2(CH_3)_5$ to produce m/e 275.

Acknowledgments. We are grateful to the National Science Foundation for a Scientific Instruments Grant GP 1715 which provided funds for the purchase of the mass spectrometer used in this work.

We are particularly grateful to Professor Robert West and Dr. Edward Carberry for the gift of samples of **4** and **6** and for very profitable discussions.