135°) gave a product composition of 74% **2**, 14% **7**, 10% **4**, and 2% **6**.

Competitive Silation of 2 and Trimethylchlorosilane.—To a cooled (−100°), stirred solution of 0.57 g (2.5 mmol) of bis(trimethylsilyl)dichloromethane (**2**) and 0.269 g (2.5 mmol) of trimethylchlorosilane in 40 ml of THF was slowly added 1 ml (2.3 mmol) of 2.3 *M* *n*-butyllithium in hexane. After stirring for 1 hr, the solution was allowed to warm to room temperature. Most of the solvent was then distilled off. The crude sample was then analyzed by vpc (SE-30, programmed from 60° to 135°), showing that most of the starting material, **2**, had reacted and that the ratio of tris(trimethylsilyl)chloromethane (**7**) to trimethylbutylsilane (**3**) was approximately 15:1. In the absence of **2**, the reaction between *n*-butyllithium and trimethylchlorosilane was shown to proceed cleanly at −100° to give **3**.

Vacuum Line Metalation of Methylene Chloride.—Five milliliters (11 mmol) of 2.3 *M* *n*-butyllithium was placed in a 100-ml round-bottom flask and pumped on to remove the hydrocarbon solvent. Methylene chloride (0.46 g, 5.5 mmol) and 20 ml of THF were condensed into the flask, and the solution was warmed to −100 (methanol slush) and allowed to stand for 3 hr in a closed system. Butane is volatile at −100° and was removed by pumping through a −100° bath to liquid nitrogen. After repeated pumping, 0.35 g of butane (1 equiv = 0.32 g) was collected in the liquid nitrogen trap; THF was in the −100° trap. These were both identified by infrared and mass spectral analysis. There was a trace of THF mixed with the butane.

While still cold, 10 ml of trimethylchlorosilane was distilled in the reaction flask. The mixture was allowed to slowly warm to room temperature overnight. Pumping through −78°, −100°, and liquid nitrogen, as before, afforded about 0.15 g (0.5 equiv) of butane. The black reaction mixture was worked up similarly to the other silation reactions. Analysis of the crude product by vpc (SE-30, 100°) showed the same products as previous silations of methylene chloride except that there was a larger amount of monosilated products; *i.e.*, trimethylsilyldichloromethane (**1**) and butyltrimethylsilane (**3**). The changes in product composition may be a result of changes in this particular reaction, namely less solvent, pure THF solvent, no mechanical mixing, and the apparent decomposition. The reaction was repeated to give the same overall results: 1 equiv of butane prior to silane, 0.5 equiv after silation and, relatively, the same product mixture.

The reaction as described was repeated except that 10 ml (23 mmol) of 2.3 *M* *tert*-butyllithium was combined with 0.8 g (10 mmol) of methylene chloride and 25 ml of THF. No silation was performed; however, 0.54 g (0.93 equiv) of isobutane was collected. The isobutane was analyzed by infrared spectroscopy. If the *tert*-butyllithium reaction was done as described except that no methylene chloride was present, isobutane was not observed in the 3-hr reaction time.

Registry No.—**1**, 5926-38-5; **2**, 15951-41-4; **4**, 5926-35-2; **5**, 1068-69-5; **6**, 27484-06-6; **7**, 27484-03-3; **9**, 1066-64-4; methylene chloride, 75-09-2; dichloromethyllithium, 2146-67-0.

Acknowledgment.—We wish to thank Research Corporation for their support of this research.

Mass Spectra of Silanes. Multiple Rearrangements and Bonding to Silicon[1]

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The mass spectra of mono-, bis-, tris-, and tetrakis(trimethylsilyl)methanes and chloromethanes have been compared. All of the major ions in the spectra, except possibly *m/e* 43, appear to be siliconium ions. The spectra of the silanes show little or no molecular ion and a base peak corresponding to loss of a methyl group. The α-chlorinated silanes all exhibit a base peak of the *m/e* 73 (Me_3Si), in addition to fragments which contain Cl–Si bonds. A rearrangement process involving a chlorine migration from carbon to silicon and a methyl migration from silicon to carbon is proposed. Three such rearrangements occur in the fragmentation of trichloro(trimethylsilyl)methane (**11**). Several allyl type siliconium ions appear to be present. Mechanisms are proposed for the various fragmentation reactions.

In connection with our studies on the silation of lithiodichloromethane,[2] we have had the opportunity to obtain the mass spectra of a variety of silanes and α-chlorosilanes. Molecular weight determination was our primary interest; however, many of the compounds did not display a molecular ion and, consequently, fragmentation ions had to be relied upon for structural information. Mass spectral studies on methylsilanes,[3] alkylsilanes,[4] bis(trimethylsilyl)methanes,[5] and other di- and trisilanes (alicyclic and cyclic)[5,6] have been reported, but the interpretations in most cases are either brief or ambiguous and, therefore, of little help. This paper reports our observations concerning the mass spectra of some selected silanes. The spectra of tris- and tetrakis(trimethylsilyl)methane and the α-chlorosilanes have not been previously described.

Interpretation of the elemental composition of fragment ions was generally quite simple since the compounds studied were composed of only C, H, Si, and possibly Cl. For example, the *m/e* 73 peak must be C_3H_9Si, since C_5H_{13} is an impossible composition. In some cases, the isotope pattern of chlorine was clearly evident.[7] It should be pointed out, however, that there is a certain element of risk involved with assigning compositions without high-resolution spectra to corroborate the findings. Unfortunately, we did not have a high-resolution instrument at our disposal. All our spectra were obtained with a CEC 21-103 mass spectrometer, at an ionizing voltage of 70 eV, with an inlet temperature of about 180° and a source temperature of 250°.

Compounds.—Most of the compounds studied were

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(1) Taken in part from the Master's Thesis of F. Ramon, Marquette University, 1972.

(2) D. R. Dimmel, C. A. Wilkie, and F. Ramon, *J. Org. Chem.*, **37**, 2662 (1972).

(3) G. P. van der Kelen, O. Volders, H. van Onckelen, and Z. Eeckhaut, *Z. Anorg. Allg. Chem.*, **338**, 106 (1965).

(4) N. Ya. Chernyak, R. A. Khmelńitskii, T. V. Dýakova, and V. M. Vdovin, *Zh. Obshch. Khim.*, **36**, 89 (1966); *J. Gen. Chem. USSR*, **36**, 93 (1966).

(5) (a) G. Fritz, H. Buhl, J. Grobe, F. Aulinger, and W. Reering, *Z. Anorg. Allg. Chem.*, **312**, 201 (1961); (b) F. Aulinger and W. Reering, *Z. Anal. Chem.*, **197**, 24 (1963); (c) F. Aulinger and W. Reering, *Collog. Spectrosc. Int., 9th, 1961*, **3**, 556 (1962); (d) G. Fritz, J. Grobe, and D. Kummer, *Advan. Inorg. Chem. Radiochem.*, **7**, 348 (1965).

(6) N. Ya. Chernyah, R. A. Khmelńitskii, T. V. Dýakova, K. S. Pushchevaya, and V. M. Vdovin, *Zh. Obshch. Khim.*, **37**, 917 (1967); *J. Gen. Chem. USSR*, **37**, 867 (1967).

(7) The normal isotope ratio of ^{35}Cl to ^{37}Cl is 3:1 and, consequently, a monochloro fragment should show a 3:1 pattern, a dichloro fragment a 1:0.67:0.1 pattern, and a trichloro fragment a 1:1:0.33:0.03 pattern.

obtained from the reaction of methylene chloride with varying amounts of *n*-butyllithium (eq 1).[2] (The symbol Σ represents a trimethylsilyl group, Me_3Si–.)

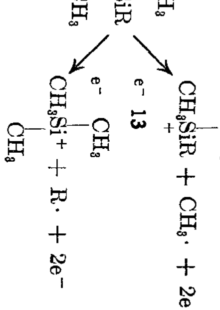
$$\underset{x\,=\,1\text{–}4}{CH_2Cl_2 + x\text{BuLi}} \xrightarrow[-100°]{\text{THF/hexane}} \xrightarrow{Me_3SiCl} \underset{1}{\Sigma CHCl_2} + \underset{2}{\Sigma_2CHCl} + \underset{3}{\Sigma_2CCl_2} + \underset{4}{\Sigma_2CClBu} + \underset{5}{\Sigma_3CH} + \underset{6}{\Sigma_3CCl} + \underset{7}{\Sigma_4C} + \underset{8}{\Sigma Bu} \quad (1)$$

Trimethylsilylchloromethane (9)[8] and tetramethylsilane (10) were commercially available. Trimethylsilyltrichloromethane (11) was synthesized by adding trimethylchlorosilane to a mixture of carbon tetrachloride and 1 equiv of *n*-butyllithium at −100°.[9] Bis(trimethylsilyl)methane (12) was obtained by hydride reduction of **3**.[2] All of the compounds gave suitable chemical analysis and were consistent with the properties already recorded in the literature.[2,9,10]

$$\underset{9}{\Sigma CH_2Cl} \qquad \underset{10}{\Sigma CH_3} \qquad \underset{11}{\Sigma CCl_3} \qquad \underset{12}{\Sigma_2CH_2}$$

Results

The Silanes.—The unsubstituted silanes **5**, **7**, **8**, **10**, and **12** are characterized by having no molecular ion, or at best a very weak one, and an intense M − 15 peak (see Table I). The weakness of the molecular ion was not unexpected, since, by analogy, branched hydrocarbons and groups possessing strong ion stabilizing powers, like alcohols, also show very weak molecular ions.[11] The loss of a methyl group results in the most intense peak in the spectra of all the simple silanes, except butyltrimethylsilane (**8**) which loses the butyl group in preference to the methyl by a factor of 5:1 (compare *m/e* 73 to *m/e* 115). In the bis-, tris-, and tetrakis(trimethylsilyl)methanes (**12**, **5**, and **7**), loss of the substituted methane fragment can also occur, producing a trimethylsilyl ion (**14**) (eq 2).



13

14

(2)

The exact origin of *m/e* 59, 45, and 31 (not shown in Table I but a weak peak in all spectra) is not clear. Zemany and Price,[12] in their study of the mass spectrum of tetramethylsilane, assigned the molecular formulas of Me_2SiH, $MeSiH_2$, and SiH_3 for peaks 59, 45, and 31. Metastable studies[3] have indicated that the *m/e* 45 peak arises by loss of ethylene (C_2H_4) by a rearrangement process from ion **14**. The *m/e* 59 fragment must also arise by a rearrangement process. Since the *m/e* 59 peak is virtually absent (<1%) in the spectra of the monosilated compounds **1**, **10**, and **11** and weak in **9**, it would appear that ion **13** is the precursor of *m/e* 59

TABLE I

RELATIVE INTENSITIES[a] OF THE MAJOR PEAKS IN THE MASS SPECTRA OF SELECTED SILANES AND α-CHLOROSILANES

Compd	Mol wt	*m/e* (with proposed structures)										
		43 C_3H_7 or CH_2SiH	45 $MeSiH_2$	59 Me_2SiH	63 MeCHCl	65 H_2SiCl	73 Me_3Si	79 MeSiHCl	85 Me_2Si–CH_2=CH	93 Me_2SiCl	113 $MeSiCl_2$	Others (rel intensity)
10, ΣCH_3	88[b]	15	21				100					
8, ΣBu	130	16	13	46			100					115 (20)
12, Σ_2CH_2	160[b]	14	13	11		c	32		2			129 (5), 145 (100)
5, Σ_3CH	232	9	13	13			33		3			129 (22), 201 (4) 217 (100)
7, Σ_4C	304	11	15	15			74		3			201 (29), 289 (100)
9, ΣCH_2Cl	122[b]	20	15	3	10	7	100	46		2		107 (8, Cl)
1, $\Sigma CHCl_2$	156[b]	20	19		16	10	100	4		14	33	155 (1, Cl_2)
11, ΣCCl_3	190	19	27		15	11	100	3		16	37	133 (2, Cl_3), 155 (1, Cl_2)
2, Σ_2CHCl	194[b]	15	12	23			100		37	6		106 (5, Cl), 129 (2), 179 (7, Cl)
3, Σ_2CCl_2	228[b]	22	16	26	8	10	100	9	42	43	2	105 (25, Cl), 163, 178 (1, Cl)
4, $\Sigma CClBu$	250	28	20	32			100		20	20		99 (17), 127 (70)
6, Σ_3CCl	266[b]	14	20	25			100		29	6		83 (10), 143 (25), 158 (8), 163 (6), 178 (17, Cl), 251 (9, Cl)

[a] Expressed as a percentage of the base peak. [b] Noticeable, but weak, molecular ion. [c] A peak of relative intensity 9% was observed at *m/e* 65; the structure of this ion is believed to be 15.[5b]

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(8) Peninsular ChemResearch (PCR), Inc., P. O. Box 1466, Gainesville, Fla. 32601.

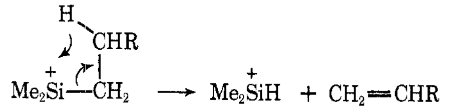
(9) W. R. Bamford and B. C. Pant, *J. Chem. Soc. C*, 1470 (1967).

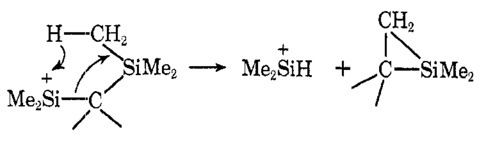
(10) R. L. Merker and M. J. Scott, *J. Organometal. Chem.*, **4**, 98 (1965).

(11) K. Biemann, "Mass Spectrometry: Organic Chemical Applications," McGraw-Hill, New York, N. Y., 1962, pp 51–52.

(12) P. D. Zemany and F. P. Price, *J. Amer. Chem. Soc.*, **70**, 4222 (1948).

and that R must be greater that one carbon in length. The strength of the m/e 59 ion in the spectra of butyltrimethylsilane (**8**) and ethyltrimethylsilane[4] suggests a process indicated by eq 3. The fact that bis and other higher silanes also display moderately intense m/e 59 peaks would seem to indicate that δ hydrogens can be transferred in the rearrangement which gives rise to this fragment (eq 4).


(3)

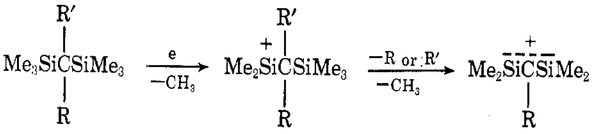

(4)

The m/e 43 peak, which could be C_3H_7 or CH_3Si or both, is present in all spectra. The appearance of a metastable peak at m/e 41.1 (45 → 43) indicates that at least some of the m/e 43 peak is due to a silicon fragment.[13]

The m/e 65 peak of bis(trimethylsilyl)methane (**12**) is probably due to the doubly charged species **15**.[5b] The mass spectrum of hexamethyldisiloxane (**16**) also shows a strong doubly charged ion at m/e 66, **17**.[14]

$\mathrm{Me_2\overset{+}{Si}CH_2\overset{+}{Si}Me_2}$ **15** $\mathrm{Me_3SiOSiMe_3}$ **16** $\mathrm{Me_2\overset{+}{Si}O\overset{+}{Si}Me_2}$ **17**

Both bis- and tris(trimethylsilyl)methane (**12** and **5**) show a peak at m/e 129, which is attributed to the allyl ion **18**. Similarly, the allyl ion **19** is probably responsible for the peak at m/e 201 in the spectra of **5** and **7**. Equation 5 indicates a way in which these allyl ions might arise. Another allyl ion, m/e 85, is present in the spectra of the unsubstituted silanes and will be discussed later. The mass spectrum of tris(trimethylsilyl)methane is shown in Figure 1.[15a]

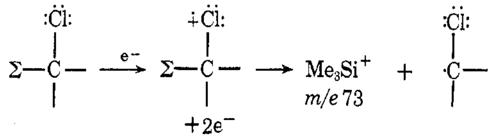

(5)

$$\mathrm{Me_3Si\underset{R}{\overset{R'}{C}}SiMe_3 \xrightarrow[-CH_3]{e} Me_2Si\underset{R}{\overset{+\,R'}{C}}SiMe_3 \xrightarrow[-CH_3]{-R\ or\ R'} Me_2\overset{+}{\overline{Si\underset{R}{C}Si}}Me_2}$$

12, R = R′ = H
5, R = H; R′ = Σ
7, R = R′ = Σ

18, m/e 129, R = H
19, m/e 201, R = Σ

The α-Chlorosilanes. –The base peak in the spectra of all the α-chlorosilanes is at m/e 73. Assuming that the initial ionization is predominantly the removal of a nonbonded electron of chlorine, then the strong production of the trimethylsiliconium ion can be explained by an α-cleavage mechanism (eq 6). The fact that

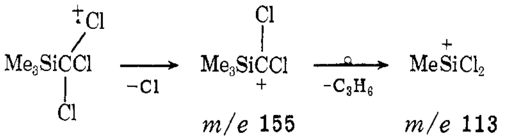

(6)

$$\Sigma{-}\overset{:\ddot{Cl}:}{C}{-} \xrightarrow{e^-} \Sigma{-}\underset{+2e^-}{\overset{+\ddot{Cl}:}{C}}{-} \longrightarrow \underset{m/e\ 73}{\mathrm{Me_3Si^+}} + \cdot\overset{:\ddot{Cl}:}{C}{-}$$

the M − 15 peak is relatively weak in the chlorosilanes spectra also supports the initial ionization being at chlorine and not at the C–Si bond.

Another characteristic feature of the chlorosilane spectra is the appearance of silicon–chlorine containing fragments that can be best explained as arising *via* a rearrangement process producing Si-Cl units. For example, dichloro(trimethylsilyl)methane[15a] exhibits a substantial peak at m/e 113, which on the basis of the accompanying peaks at m/e 115 and 117 (approximate rates of 1:0.67:0.1) is assigned the elemental composition and structure of CH_3SiCl_2. There are also significant peaks at m/e 93, 79, 65, and 63, which all contain one chlorine atom.[16] The rationale by which these chlorinated fragments arise is presented in Schemes I and II.

Two pathways are proposed in Scheme I to account for the formation of the m/e 113 ion. To decide which of the two pathways was correct, trichloro(trimethylsilyl)methane (**11**) was synthesized and its spectrum recorded. Examination of Table I shows that the spectrum of **11** is practically identical with that of **1**. Path A can accommodate these similarities, if it is assumed that **1** loses a hydrogen atom to give the m/e 155 fragment and **11** loses a chlorine atom to give the same fragment (eq 7). Both compounds exhibit a weak m/e 155 peak. The appearance of metastable peaks at m/e 82.4 (155 → 113) and 84.2 (157 → 115) in the spectrum of **11** further supports the proposed fragmentation given in eq 7.


(7)

$$\mathrm{Me_3Si\underset{Cl}{\overset{\dot{+}Cl}{C}}Cl \xrightarrow[-Cl]{} \underset{m/e\ 155}{Me_3Si\underset{+}{\overset{Cl}{C}}Cl} \xrightarrow[-C_3H_6]{a} \underset{m/e\ 113}{Me\overset{+}{Si}Cl_2}}$$

In addition to the above evidence for pathway A, the ionic intermediates **20** and **21** would seem to be adequate presursors of the other chloro fragments (Scheme II). It is difficult to rationalize a reasonable process by which the m/e 93, 79, and 63 fragments could form from the ionic intermediates of path B, namely, **22** and **23**. In fact, a pathway similar to B may not even be responsible for the small amount of m/e 133 ion observed for compound **11**. Metastable ions in the regions of m/e 119.5 and 121.5 suggest that the precursor of the $SiCl_3$ fragment is CH_3SiCl_3 (m/e 148, 150, 152, and 154).

It is interesting that the spectrum of bis(trimethylsilyl)dichloromethane (**3**) is quite different from that of **1** and **11**. The primary fragmentation of **3** must not

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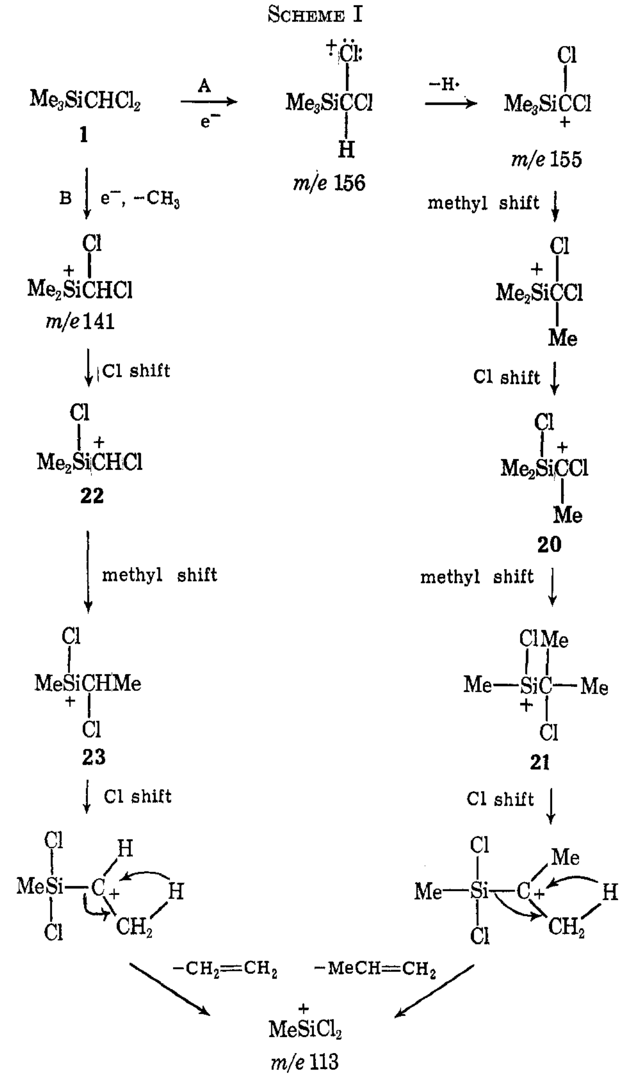
[13] In general there were few metastables in the various spectra to aid in the interpretation. The most frequent metastables were m/e 27.8 (73 → 45) and 41.1 (45 → 43).[3]

[14] V. H. Dibeler, F. L. Mohler, and R. M. Reese, *J. Chem. Phys.*, **21**, 180 (1953).

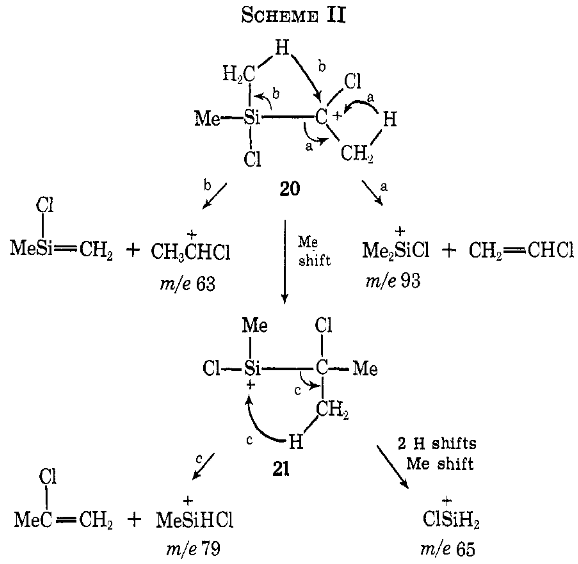
[15] (a) The bar graph representation of the mass spectrum of this compound will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JOC-72-2665. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche. (b) In the supplementary data, available in the microfilm of this paper, a postulated breakdown of bis(trimethylsilyl)dichloromethane (**3**) is presented which tries to rationalize the formation of the allyl ions m/e 85 and 105. (c) In the supplementary data, available in the microfilm of this paper, a scheme is presented which attempts to depict reasonable structures for the fragments of **6**.

[16] The 3:1 pattern indicative of one chlorine atom is quite evident for the m/e 93/95 and 79/81 peaks. The m/e 63 and 65 fragments were assumed to be monochloro because (a) other elemental compositions do not make sense and (b) if $^1/_3$ of the m/e 63 intensity is subtracted from the m/e 65 intensity, the remaining m/e 65 to 67 ratio is exactly 3:1. Other spectra containing m/e 63, 65, and 67 peaks also showed a similar pattern.

SCHEME I



SCHEME II

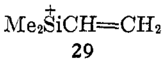


be loss of a trimethylsilyl group to give the *m/e* 155 fragment, but rather loss of a chlorine atom and eventual production of a monochloro fragment, *m/e* 93. Similarly, the differences in the spectra of **2** and **3** mean that they do not initially fragment to a common intermediate.

Allyl ions are also present in the α-chlorosilane spectra. The *m/e* 85 fragment would seem to be such an ion. Inspection of Table I reveals that the *m/e* 85 peak is absent in the spectra of the monosilated compounds, but present in all others. The fragment does not contain chlorine, as indicated by the lack of a substantial peak at *m/e* 87. Fritz, *et al.*,[5a] have proposed several structures to account for the *m/e* 85 peak. For example, they suggested structures **27** or **28** in the breakdown of **24**, **27** coming from **25** and **29** arising by loss of a methyl from **26**. Of these suggested structures, the last one seems the most reasonable (*m/e* 85 is the dominant peak in the spectrum of **26**). We are of the opinion that, regardless of the structures of the silanes, the *m/e* 85 fragment is best represented as **29**, even though several rearrangements may have to be proposed to achieve this structure.

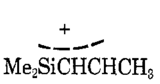
$(Me_3Si\text{-})_2CHCH_3$ **24** $(Me_3Si)_2C(CH_3)_2$ **25** $Me_3SiCH{=}CH_2$ **26**

Me_2SiCCH_3 **27** Me_3SiC **28**

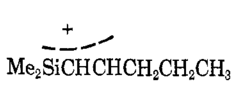


$Me_2\overset{+}{Si}CH{=}CH_2$ **29**

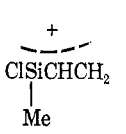
Besides the *m/e* 85 ion, there are other apparent allyl ions in the spectra. The butylated derivative **4** shows a pair of strong peaks, *m/e* 99 and 127, which appear to be homologs of *m/e* 85. Possible structures of these ions are **30** and **31**. Bis(trimethylsilyl)dichloromethane shows as a relatively strong peak at *m/e* 105, containing chlorine, which is probably due to the allyl ion **32**.[15b]



30, *m/e* **99**



31, *m/e* **127**



32, *m/e* **105**

Finally, contrary to most of the spectra, tris(trimethylsilyl)chloromethane (**6**)[15a] shows several relatively abundant high molecular weight fragments, some of even mass, which lend support to the conclusion that carbon-silicon double bonds are present.[15c]

Conclusions

The major fragmentation site of the nonchlorinated silanes is at a C-Si bond, resulting in the formation of a tertiary siliconium ion. The direction of fragmentation by silicon can be explained by the low electronegativity of silicon; thus, silicon can accommodate a positive charge much better than carbon.[17] The presence of a trimethylsilyl group in a hydrocarbon is indicated by the homologous series of *m/e* 73, 59, 45, and 31 peaks in its mass spectrum.[4-6,14,18] The *m/e* 59 peak may, however, be very weak if there are no β, γ, ... hydrogens available for back donation to the siliconium ion as is the case for the four-carbon silanes **1** and **9–11**.

Both the polysilated hydrocarbons and alkyl chlo-

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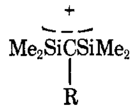
[17] J. Kleinberg, W. J. Argersinger, Jr., and E. Griswold, "Inorganic Chemistry," D. C. Heath, Boston, Mass., 1960, pp 104–105.

[18] R. A. Khmel'nitzkii, A. A. Polyakova, and A. A. Petro, *Akad. Nauk Kirg. SSR*, 236 (1962); *Chem. Abstr.*, **62**, 2348*b* (1965).

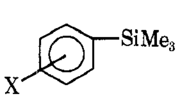
rides showed several peaks indicative of allyl ions of the following type.



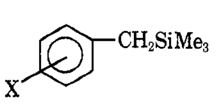
R = Me; R′ = H *m/e* 85
R = R′ = Me *m/e* 99
R = Me; R′ = Pr *m/e* 127
R = Cl; R′ = H *m/e* 105, 103

R = H *m/e* 129
R = Σ *m/e* 201
R = Cl *m/e* 163, 161

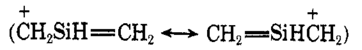
Production of allyl ions was unexpected, since multiple bonding between carbon and silicon is rare.[19] Recently, Freeburger, *et al.*,[20] reported that the mass spectra of arylsilanes (**33**) and substituted benzylsilanes (**34**) displayed fragmentation patterns that were characteristic by lacking in the generation of carbon–silicon double bonds, like the one represented by structure **35**.



33



34

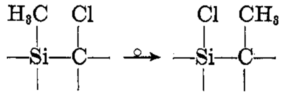


$(\overset{+}{C}H_2SiH{=}CH_2 \longleftrightarrow CH_2{=}SiH\overset{+}{C}H_2)$

35

If it is assumed that the intensities of certain ions in a mass spectrum are related to their stabilities (and steric factors to formation), then it may be possible to explain the differences observed by Freeburger and ourselves. The aryl-substituted silanes may be able to fragment in such a way as to avoid -C=Si- situations and still give stable ions. However, allyl ions containing silicon may be moderately stable ions and reasonable postulates in the fragmentations of aliphatic silanes which have no strong cation-stabilizing groups other than silicon. Based on our results, these simple silanes are apparently good models for observing carbon–silicon multiple bonding.

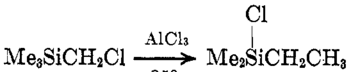
Besides displaying fragments similar to the hydrocarbon silanes, the α-chlorinated silanes show multiple rearrangements which eventually bring the silicon and chlorine together (*i.e.*, *m/e* 133, 113, 93, 79, and 65). The driving force of these rearrangements would appear to be the gain (approximately 18 kcal) in bond energies associated mainly with the strong Si–Cl bond (eq 8).[17] It is well known that chlorine can stabilize



$$-\underset{|}{\overset{\overset{H_3C}{|}}{Si}}-\underset{|}{\overset{\overset{Cl}{|}}{C}}- \xrightarrow{\circ} -\underset{|}{\overset{\overset{Cl}{|}}{Si}}-\underset{|}{\overset{\overset{CH_3}{|}}{C}}- \qquad (8)$$

carbonium ions by 3p–2p orbital resonance; however, a chlorine should be able to stabilize a siliconium ion to even greater extent because of the more favorable 3p–3p orbital overlap. This latter fact may also account for the tendency to form chlorosiliconium ions.

Our proposal of chloro-methyl interchanges in the mass spectra of α-chlorosilanes is analogous to the ground state reaction of **9** with aluminum chloride as reported by Whitmore, Sommer, and Gould (eq 9).[21]



$$\underset{\mathbf{9}}{Me_3SiCH_2Cl} \xrightarrow[85°]{AlCl_3} Me_2\overset{\overset{Cl}{|}}{Si}CH_2CH_3 \qquad (9)$$

There have also been some recent reports of halogen rearrangements in the mass spectra of related silanes. Silicon–halogen fragments have been observed in the mass spectra of **33** and **34** (X = halogen),[20] halomethylsilanes (**36**) and disilanes (**37**),[22] and silated alcohols (**38**) and acids (**39**).[23] Besides halogen, phenyl[24] and

$\underset{\mathbf{36}}{XCH_2SiH_3}$ $\underset{\mathbf{37}}{XCH_2SiH_2SiH_3}$ $\underset{\mathbf{38}}{X(CH_2)_nOSiMe_3}$ $\underset{\mathbf{39}}{X(CH_2)_nCO_2SiMe_3}$

oxygen[21] rearrangements to silicon are known. It appears, however, that nitrogen and sulfur show little tendency to rearrange to silicon.[25] Our spectra are the first to show multiple rearrangements to silicon.

Registry No. –**1**, 5926-38-5; **2**, 5926-35-2; **3**, 15951-41-4; **4**, 27484-06-6; **5**, 1068-69-5; **6**, 27484-03-3; **7**, 1066-64-4; **8**, 1000-49-3; **9**, 2344-80-1; **10**, 75-76-3; **11**, 5936-98-1; **12**, 2117-28-4.

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[19] V. G. Fritz and J. Grobe [*Z. Anorg. Allg. Chem.*, **311**, 325 (1961)] have reported the formation of $Me_2Si{=}CHSiMe_3$ in the pyrolysis of tetramethylsilane. The base peak in the mass spectrum of this compound is at *m/e* 129, which probably is best represented by the allyl ion **18**, although Fritz, *et al.*,[5a] propose the structure $MeSi{=}CHSiMe_3$.

[20] M. E. Freeburger, B. M. Hughes, G. R. Buell, T. O. Tiernan, and L. Spialter, *J. Org. Chem.*, **36**, 933 (1971).

[21] F. C. Whitmore, L. H. Sommer, and J. J. Gould, *J. Amer. Chem. Soc.*, **69**, 1976 (1947).

[22] J. M. Bellama and J. A. Morrison, Organosilicon Symposium, Carnegie-Mellon University, March 27, 1971.

[23] E. White, V, and J. A. McCloskey, *J. Org. Chem.*, **35**, 4241 (1970).

[24] W. P. Weber, A. K. Willard, and H. G. Boettger, *ibid.*, **36**, 1620 (1971).

[25] (a) J. Diekman, J. B. Thomson, and C. Djerassi, *ibid.*, **34**, 3147 (1969); **33**, 2271 (1968).