Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

THE MASS SPECTRA OF PHENYL-SUBSTITUTED 1,1-DIMETHYLSILACYCLOPENTANES AND -SILACYCLOPENTADIENES AND OF 1,1,4,4-TETRAMETHYL-2,3,5,6-TETRAPHENYL-1,4-DISILACYCLOHEXADIENE*

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(Received August 12th, 1971)

SUMMARY

The mass spectra of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene, 1,1-dimethyl-2,5-diphenyl-1-silacyclopentane, 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene and 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disila-2,5-cyclohexadiene were recorded using a 90° magnetic-sector type instrument. From the observed meta-stable peaks, most of the fragmentations giving rise to the more abundant ions have been assigned. For these compounds, up to 30% of the total intensity is carried by ions formed by some type of rearrangement. Specifically, four types of rearrangements are indicated and they involve the migration of: (1) hydrogen atoms from a phenyl group bonded to either an α- or β-carbon atom to the silicon atom of a siliconium ion; (2) a phenyl group from an α-carbon atom to a silicon atom; (3) a methyl group from one silicon atom to a second silicon atom in the 4-position; and (4) hydrogen atoms from silicon methyl groups to silicon with the simultaneous loss of CH_2 or C_2H_4.

INTRODUCTION

Several studies of mass spectra of silanes, organosilanes and organopolysilanes have been carried out in which the goal was either to determine thermodynamic data[1-8] or to correlate their fragmentation patterns with those of analogous compounds of other Group IV elements[9-16]. Mass spectra of volatile trimethylsilyl ethers and esters of nonvolatile alcohols and acids have been studied extensively to identify and help elucidate the structures of these compounds[17-25]. The application of mass spectrometry to the determination of the structures of highly substituted organosilanes has, however, lagged considerably behind the use of this technique for determining the structures of other hetero-organic compounds. This may have arisen because organosilanes give spectra that are complicated and do not appear to readily correlate with the structure of the compounds.

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* Presented in part at the 3rd Central Regional Meeting of the American Chemical Society, Cincinnati, Ohio, June 7, 1971.

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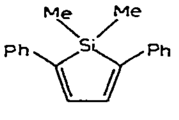
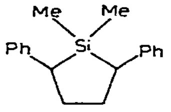
Recent work in this area has, however, shed some light on the reasons for the apparently complicated spectra. It appears that siliconium and silylcarbonium ions formed by electron impact can undergo a variety of fragmentations in which the silicon atom plays an important role$^{17,26-33}$. We report here the results of a study of the mass spectra of some phenyl-substituted organosilacycles. The compounds which have been investigated are: 1,1-dimethyl-2,5-diphenyl-1-sila-2,4-cyclopentadiene (I), 1,1-dimethyl-2,5-diphenyl-1-silacyclopentane (II), 1,1-dimethyl-2,3,4,5-tetraphenyl-1-sila-2,4-cyclopentadiene (III), and 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disila-2,5-cyclohexadiene (IV). Rather independent of the rest of the molecule the mass spectra of these compounds all have peaks in common which are due to ions formed by a variety of fragmentations and rearrangements of the common silicon structural feature.



(I)



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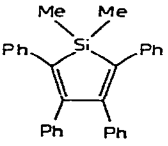

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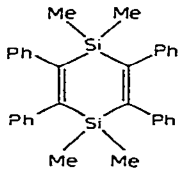


(IV)

RESULTS AND DISCUSSION

The main peaks in the mass spectra of diphenylsilacyclopentadiene (I), silacyclopentane (II), tetraphenylsilacyclopentadiene (III), and disilacyclohexadiene (IV) are given in Tables 1 through 4. The two silacyclopentadienes give spectra that have very few intense peaks and in both the parent ion is the most abundant. Silacyclopentane (II), and disilacyclohexadiene (IV), on the other hand, give spectra with several fairly intense peaks and both have parent ions whose intensity is less than that of some other ions.

Johnson, Gohlke and Nasutavicus^{34} have reported the mass spectrum of disilacyclohexadiene (IV), and those of several other disila- and digermacyclohexadienes. The spectrum they reported for silacyclohexadiene (IV) differs considerably from that obtained in this investigation. After considerable effort on our part to insure that we were working with the same compound, it seems that the most probable explanation for the discrepancies observed are due to differences in the design of the mass spectrometers (90° magnetic-sector *versus* time-of-flight).

Assignment of ion formulae

Three techniques were used to assign formulae to the major ions observed in

TABLE 1

ION ASSIGNMENTS, INTENSITIES AND "META-STABLE" TRANSITIONS FOR 1,1-DIMETHYL-2,5-DIPHENYL-1-SILACYCLOPENTADIENE (I)

m/e	Formula	Rel. int.[a]	Parent ion	"Meta-stable"	
				Obsd.	calcd.
43	CH_3Si	6.35	C_2H_6Si (58)	31.8	31.9
58	C_2H_6Si	0.43			
59	C_2H_7Si	0.77			
102	C_8H_6	1.00	C_9H_7Si (143)	72.7	72.8
105	C_6H_5Si	6.64	$C_{17}H_{15}Si$ (247)	44.7	44.6
			$C_{15}H_{13}Si$ (221)	49.9	49.9
			[$C_{13}H_{13}Si$ (197)]	55.9	56.0
			C_9H_9Si (145)	76.0	76.0
119	C_7H_7Si	0.85	C_8H_7Si (131)	108.0	108.1
121	C_7H_9Si	7.63	[$C_{18}H_{18}Si$ (262)]	55.9	55.9
129	C_8H_5Si	1.27			
131	C_8H_7Si	1.63			
143	C_9H_7Si	1.46			
145	C_9H_9Si	4.15	$C_{18}H_{18}Si$ (262)	80.2	80.3
			$C_{17}H_{15}Si$ (247)	85.2	85.2
169	$C_{11}H_9Si$	2.05	$C_{17}H_{15}Si$ (247)	115.6	115.7
			[$C_{15}H_{13}Si$ (221)]	129.3	129.3
			$C_{12}H_{12}Si$ (184)	155.2	155.3
171	$C_{11}H_{11}Si$	1.24	$C_{18}H_{18}Si$ (262)	111.6	111.6
184	$C_{12}H_{12}Si$	1.74	[$C_{18}H_{18}Si$ (262)]	129.3	129.3
197	$C_{13}H_{13}Si$	0.85	$C_{18}H_{18}Si$ (262)	148.1	148.2
202	$C_{16}H_{10}$	1.34			
221	$C_{15}H_{13}Si$	1.16	$C_{17}H_{15}Si$ (247)	197.7	197.8
245	$C_{17}H_{13}Si$	1.24	$C_{17}H_{15}Si$ (247)	243.1	243.1
247	$C_{17}H_{15}Si$	6.99	$C_{18}H_{18}Si$ (262)	232.8	232.9
262	$C_{18}H_{18}Si$	21.33			

[a] Total intensity = 1.

the spectra of organosilacycles (I)–(IV). First, all possible combinations of C, H and Si consistent with the molecular formula of the compound under consideration were calculated for all observed m/e values. Then, those combinations which seemed unrealistic were discarded. This simple technique gave single combinations of C, H and Si for about 50% of the ions observed. The decision between possible combinations for the remaining 50% was made by matching the peak under consideration with that of a known composition from a reference compound or by extensive analyses of the meta-stable peaks.

Ions whose formulae could be assigned account for 68 to 81% of the total intensity for the compounds considered and from 71 to 100% of the ion current due to these ions is carried by ions which have at least one silicon atom present. As has been found for other Group IV organometalloids and organometallics[36], 80 to 95% of the ion current carried by these silicon atom fragments is done so by ions containing an even number of electrons.

When structures could be assigned to the ions, nearly all were found to have been formed by cleavage of carbon–carbon or carbon–silicon single bonds or by

TABLE 2

ION ASSIGNMENTS, INTENSITIES AND "META-STABLE" TRANSITIONS FOR 1,1-DIMETHYL-2,5-DIPHENYL-1-SILACYCLOPENTANE (II)

m/e	Formula	Rel. int.	Parent ion	"Meta-stable"	
				Obsd.	Calcd.
29	SiH	0.58			
31	SiH_3	0.68	C_2H_7Si (59)	16.3	16.3
43	CH_3Si	4.40	[C_7H_9Si (121)]	15.2	15.3
			[C_2H_6Si (58)]	31.9	31.9
45	CH_5Si	0.67	[C_8H_9Si (133)]	15.2	15.2
58	C_2H_6Si	2.92			
59	C_2H_7Si	4.01			
65	C_5H_5	0.66	[C_8H_9Si (133)]	31.9	31.8
			[C_7H_7 (91)]	46.5	46.5
78	C_6H_6	1.01	[C_8H_8 (104)]	58.5	58.5
			[C_8H_7Si (131)]	46.5	46.5
91	C_7H_7	3.08	[$C_{10}H_{13}Si$ (161)]	51.5	51.5
104	C_8H_8	2.96	$C_9H_{13}Si$ (149)	72.7	72.6
105	C_6H_5Si	1.57	C_8H_7Si (131)	84.2	84.2
107	C_6H_7Si	0.67	$C_8H_{11}Si$ (135)	84.9	84.9
115	C_9H_7	1.22	C_9H_9 (117)	113.1	113.1
117	C_9H_9	10.79	[$C_{18}H_{22}Si$ (266)]	51.5	51.5
121	C_7H_9Si	5.29	[$C_{17}H_{19}Si$ (251)]	58.5	58.4
			$C_9H_{13}Si$ (149)	98.3	98.3
129	C_8H_5Si	0.74			
131	C_8H_7Si	0.98			
133	C_8H_9Si	0.84	$C_9H_{12}Si$ (148)	119.4	119.5
135	$C_8H_{11}Si$	2.23			
145	C_9H_9Si	2.00	$C_9H_{11}Si$ (147)	143.0	143.1
147	$C_9H_{11}Si$	8.09	$C_{10}H_{14}Si$ (162)	133.4	133.4
			$C_{10}H_{13}Si$ (161)	134.3	134.3
148	$C_9H_{12}Si$	2.44	$C_{10}H_{14}Si$ (162)	135.3	135.3
149	$C_9H_{13}Si$	5.35			
161	$C_{10}H_{13}Si$	0.75			
162	$C_{10}H_{14}Si$	5.70			
175	$C_{11}H_{15}Si$	1.54			
251	$C_{17}H_{19}Si$	0.42			
266	$C_{18}H_{22}Si$	9.63			

rearrangements of ions thus formed. Silicon was usually bound to at least one carbon atom which participates in π-bonding with at least one other carbon. This is observed even for silacyclopentane (II) in which silicon is initially bonded to four sp^3 hybridized carbon atoms. The stability of this type of ion has been attributed to d_π–p_π bonding between carbon and silicon[37].

Meta-stable transitions

Meta-stable peaks are quite numerous in the spectra of these compounds. By varying instrumental parameters such as intensity, scan rate, resolution, repeller voltage, accelerating voltage, and ionizing voltage, from 21 to 31 distinct meta-stable transitions were observed for organosilacycles (I) through (IV). About 2/3 of these

TABLE 3

ION ASSIGNMENTS, INTENSITIES AND "META-STABLE" TRANSITIONS FOR 1,1-DIMETHYL-2,3,4,5-TETRAPHENYL-1-SILACYCLOPENTADIENE (III)

m/e	Formula	Rel. int.	Parent ion	"Meta-stable"	
				Obsd.	Calcd.
41	CHSi	0.72	CH_3Si (43)	39.0	39.1
43	CH_3Si	9.99	[$C_{15}H_{13}Si$ (221)]	8.3	8.4
			$C_{10}H_{11}Si$ (159)	11.7	11.6
			$C_8H_{11}Si$ (135)	13.7	13.7
			C_2H_6Si (58)	31.9	31.9
58	C_2H_6Si	1.14			
59	C_2H_7Si	1.15	[$C_{30}H_{26}Si$ (414)]	8.3	8.4
105	C_6H_5Si	10.51	$C_{15}H_{13}Si$ (221)	49.9	49.9
			$C_{10}H_{11}Si$ (159)	69.3	69.3
119	C_7H_7Si	0.76	[$C_{29}H_{23}Si$ (399)]	35.4	35.5
			[$C_{15}H_{13}Si$ (221)]	64.1	64.1
121	C_7H_9Si	4.70	[$C_{30}H_{26}Si$ (414)]	35.4	35.4
129	C_8H_5Si	1.21	$C_{13}H_{13}Si$ (197)	84.5	84.5
135	$C_8H_{11}Si$	2.16	$C_{30}H_{26}Si$ (414)	44.0	44.0
159	$C_{10}H_{11}Si$	1.05	$C_{16}H_{15}Si$ (235)	107.8	107.6
160	$C_{10}H_{12}Si$	1.33	[$C_{29}H_{23}Si$ (399)]	64.1	64.2
165	$C_{13}H_9$	0.59			
178	$C_{14}H_{10}$	2.83	$C_{17}H_{14}$ (218)	145.6	145.4
183	$C_{12}H_{11}Si$	1.18	$C_{30}H_{26}Si$ (414)	81.0	80.9
197	$C_{13}H_{13}Si$	2.82	$C_{30}H_{26}Si$ (414)	93.8	93.8
218	$C_{17}H_{14}$	0.63			
221	$C_{15}H_{13}Si$	8.92	$C_{29}H_{23}Si$ (399)	122.5	122.4
235	$C_{16}H_{15}Si$	0.95	$C_{23}H_{17}Si$ (321)	172.2	172.1
283	$C_{20}H_{15}Si$	0.97	$C_{22}H_{18}Si$ (310)	258.4	258.4
310	$C_{22}H_{18}Si$	1.10			
321	$C_{23}H_{17}Si$	1.31			
399	$C_{29}H_{23}Si$	1.27	$C_{30}H_{26}Si$ (414)	384.6	384.6
414	$C_{30}H_{26}Si$	17.14			

meta-stable peaks could be assigned to particular fragmentations.

Fragmentations and rearrangements

A detailed examination of the spectra of these compounds and of the neutral fragments which were lost during meta-stable transitions indicates that the similarities in the spectra are determined more by the ion formed than they are by the identity of the neutral fragment lost. Except for the loss of a methyl radical, which gives rise to a total of eleven meta-stable transitions, no other neutral fragment was observed to have taken part in a meta-stable transition in all four compounds. However, certain types of neutral fragments do give rise to a number of meta-stable transitions. For example, the elements of acetylene or a substituted acetylene can account for a total of at least fourteen neutral fragments, while the elements of ethylene, ethylenic radicals and benzene, C_6H_6, account for an additional fourteen.

With one exception, there are nine ions which are common to the fragmentation patterns of all four compounds which carry a total of 56, 30, 67 and 34% of the ion

TABLE 4

ION ASSIGNMENTS, INTENSITIES AND "META-STABLE" TRANSITIONS FOR 1,1,4,4-TETRAMETHYL-2,3,5,6-TETRAPHENYL-1,4-DISILACYCLOHEXADIENE (IV)

m/e	Formula	Rel. int.	Parent ion	"Meta-stable"	
				Obsd.	Calcd.
31	SiH_3	1.05	C_2H_7Si (59)	16.3	16.3
43	CH_3Si	2.99	$C_{15}H_{13}Si$ (221)	8.4	8.4
			[$C_{10}H_{11}Si$ (159)]	11.6	11.6
45	CH_5Si	0.93	C_3H_9Si (73)	27.8	27.8
59	C_2H_7Si	2.31	$C_{24}H_{20}Si$ (336)	10.4	10.4
73	C_3H_9Si	13.37	[$C_{31}H_{29}Si$ (457)]	11.6	11.7
105	C_6H_5Si	3.55	[$C_{15}H_{13}Si$ (221)]	49.9	49.9
			C_8H_7Si (131)	84.2	84.2
107	C_6H_7Si	0.56	[$C_8H_{11}Si$ (135)]	84.9	84.8
121	C_7H_9Si	0.74	[$C_{25}H_{23}Si_2$ (379)]	38.7	38.7
			[$C_{18}H_{22}Si_2$ (294)]	49.9	49.8
129	C_8H_5Si	1.05			
131	C_8H_7Si	0.64	$C_{10}H_{11}Si$ (159)	107.9	107.9
135	$C_8H_{11}Si$	7.48	[$C_{32}H_{32}Si_2$ (472)]	38.7	38.6
			[$C_{26}H_{26}Si_2$ (394)]	46.4	46.3
148	$C_9H_{12}Si$	0.69	[$C_{32}H_{32}Si_2$ (472)]	46.4	46.4
159	$C_{10}H_{11}Si$	3.82			
197	$C_{13}H_{13}Si$	0.96	[$C_{31}H_{29}Si_2$ (457)]	84.9	85.0
221	$C_{15}H_{13}Si$	5.14	$C_{25}H_{23}Si_2$ (379)	128.9	128.9
			$C_{17}H_{19}Si_2$ (279)	175.1	175.1
279	$C_{17}H_{19}Si_2$	5.88	$C_{18}H_{22}Si_2$ (294)	264.8	264.8
280	$C_{17}H_{20}Si_2$	0.20	$C_{25}H_{23}Si_2$ (379)	206.9	206.9
292	$C_{18}H_{20}Si_2$	0.76	$C_{32}H_{32}Si_2$ (472)	180.8	180.7
294	$C_{18}H_{22}Si_2$	0.71			
336	$C_{24}H_{20}Si$	1.29			
379	$C_{25}H_{23}Si_2$	4.22	$C_{31}H_{29}Si_2$ (457)	314.4	314.4
			$C_{26}H_{26}Si_2$ (394)	364.7	364.7
394	$C_{26}H_{26}Si_2$	0.86	$C_{32}H_{32}Si_2$ (472)	329.1	329.0
457	$C_{31}H_{29}Si_2$	3.57	$C_{32}H_{32}Si_2$ (472)	442.6	442.6
472	$C_{32}H_{32}Si_2$	6.46			

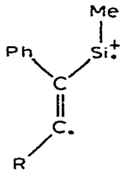
current for (I) through (IV) respectively. These ions and their contribution to the spectra of silacycles (I) through (IV) are given in Table 5. A close examination of the formulae and proposed structures for some of these ions shows that rearrangements play a large role in their formation. The peaks at *m/e* 221 and 145, are considered as one ion since they probably contain the same basic carbon and silicon structure. When the substituent on carbon atom three in the parent compound is hydrogen, the peak at *m/e* 145 is quite large and when it is phenyl, the peak at *m/e* 221 is large. Except for diphenylsilacyclopentadiene (I), where both are present, the structure of the parent molecule determines which peak is present and which is absent. Two structures have been proposed for the ion of *m/e* 221 in the spectrum of disilacyclohexadiene (IV)^{34} and are given by (V) and (VI). A third structure, (VII), must also be considered and should be the most stable since it has neither a highly strained three-membered ring as does (VI) nor two unpaired electrons as does (V). In addition, meta-

TABLE 5

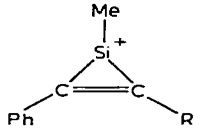
RELATIVE INTENSITIES[a] FOR COMMON IONS IN THE SPECTRA OF ORGANOSILACYCLES (I) THROUGH (IV)

Ion	Silacyclopentadiene (I)	Silacyclopentane (II)	Silacyclopentadiene (III)	Disilacyclohexadiene (IV)
Parent (P^+)	21.3	9.6	17.1	6.5
$(P-Me)^+$	7.0	0.4	1.3	3.6
$C_{15}H_{13}Si^+$ (221)	1.2		8.9	5.2
$C_9H_9Si^+$ (145)	4.2	2.0		
$C_8H_{11}Si^+$ (135)		2.2	2.2	7.5
$C_8H_5Si^+$ (129)	1.3	0.7	1.2	1.1
$C_7H_9Si^+$ (121)	7.6	5.3	4.7	0.7
$C_6H_5Si^+$ (105)	6.6	1.6	10.5	3.6
$C_2H_7Si^+$ (59)	0.8	4.0	1.2	2.3
CH_3Si^+ (43)	6.4	4.4	10.0	3.0
Total	56.4	30.2	57.1	33.5

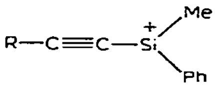
[a] Total intensity = 100.



(V)



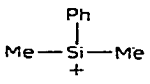
(VI)



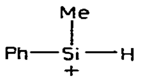
(VII)

stable peaks are observed in the spectra of (I), (II) and (IV) for the fragmentation of either m/e 221 and 145 to both m/e 105, $PhSi^+$, and m/e 43, $MeSi^+$. Structure (VII) is obtained by the rearrangement of a phenyl group from an α-carbon atom to the silicon atom of the siliconium ion given in (V). This is consistent with the types of rearrangements that are observed in the mass spectral fragmentation patterns of these organosilacycles. In fact m/e 135, 121, and 105 must be formed, at least in part, by this very type of rearrangement.

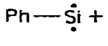
The structures proposed for these last three ions are given by (VIII), (IX), and (X). Since silacyclopentadiene (I) and silacyclopentane (II) have phenyl groups bonded only to the α-carbon atoms, it must be one of these phenyl groups that becomes bonded to the silicon atom of siliconium ions (VIII), (IX), and (X).


$\mathrm{Me{-}\overset{Ph}{\underset{+}{Si}}{-}Me}$

(VIII)

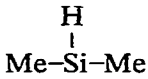

$\mathrm{Ph{-}\overset{Me}{\underset{+}{Si}}{-}H}$

(IX)


$\mathrm{Ph{-}\underset{\cdot}{\dot{Si}}\,+}$

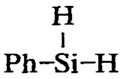
(X)

The structure, (IX), proposed for the ion of m/e 121 requires a second type of rearrangement that is very common in the mass spectra of organosilacycles and that is the rearrangement of hydrogen atom from carbon to silicon. This type of rearrangement has been reported for organosilanes but is noteworthy because of the specific types of hydrogen atoms which migrate. In addition to the abundant ions $C_7H_9Si^+$, (IX) (m/e 121) and $C_2H_7Si^+$, (XI) (m/e 59) there are several less abundant ions formed by hydrogen atom rearrangements. Four such ions which contribute to the spectra of some but not all of these compounds are $C_6H_7Si^+$ (XII) (*m/e* 107), CH_5Si^+ (XIII) (*m/e* 45), SiH_3^+ (*m/e* 31), and SiH^+ (*m/e* 29). Most of these rearrangements can occur



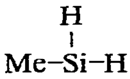
$$\overset{\displaystyle H}{\underset{+}{\text{Me–Si–Me}}}$$

(XI)



$$\overset{\displaystyle H}{\underset{+}{\text{Ph–Si–H}}}$$

(XII)



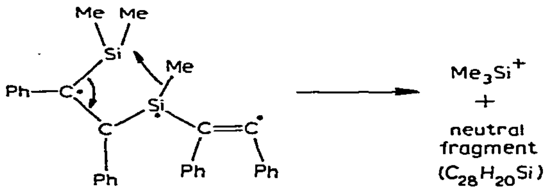
$$\overset{\displaystyle H}{\underset{+}{\text{Me–Si–H}}}$$

(XIII)

by migration of methyl or alkyl type hydrogen atoms[3,11,13,15]. However, the formation of $C_2H_7Si^+$, (XI) during the fragmentation of tetraphenylsilacyclopentadiene (III) gives rise to a different type of hydrogen atom rearrangement since the hydrogen atom which becomes bonded to the silicon atom must be one of the original phenyl hydrogen atoms. The rearrangement of aryl hydrogen atoms to non-aryl centers is not surprising; however, to the best of our knowledge, this is the first example where this type of rearrangement has been observed to occur and give rise to a fairly intense peak.

The methylsiliconium ion, CH_3Si^+, is quite abundant in all the spectra and several meta-stable transitions are observed for its formation from a variety of ions. Its large abundance probably arises because it is the final product of several fragmentation pathways and, with one minor exception, does not appear to undergo further fragmentation. This behavior is also observed for $C_7H_9Si^+$, (IX) and $C_6H_5Si^+$, (X), which along with CH_3Si^+ are the most abundant of the common ions reported in Table 5.

The last ion to be considered in detail is the most abundant one in the spectrum of disilacyclohexadiene (IV). The peak at *m/e* 73 (rel. int. 100) has been assigned to the trimethylsiliconium ion, $C_3H_9Si^+$. A meta-stable peak at 11.6 in the spectrum of (IV) indicates that $C_3H_9Si^+$ may be formed from the $(P-Me)^+$ ion (M^* calcd. 11.7). An acceptable five-membered ring transition state can be written for the rearrangement of a silicon methyl to the second silicon atom in the 4-position of this compound (eqn. 1).



(1)

In all, at least four distinct types of rearrangements were observed during fragmentation of these organosilicycles. These are the migration of: (1) hydrogen atoms from a phenyl group bonded to either an α- or β-carbon atom to the silicon atom of a siliconium ion; (2) a phenyl group from an α-carbon atom to a silicon atom; (3) a methyl group from one silicon atom to a second silicon atom in the 4-position; and (4) hydrogen atoms from silicon methyl groups to silicon with the loss of CH_2 or C_2H_4. A total of 5, 8, 8 and 11 ions in the spectra of (I) through (IV), respectively, are certainly formed by some type of rearrangement and these ions carry

16, 16, 23, and 30% of the total ion current for the respective compounds. It is very likely that if the structure of all the ions formed during the fragmentation of these compounds were known, that a much larger number would be found to be due to rearrangements.

From this work and work reported previously, it appears that rearrangement of atoms and groups to the silicon atom of siliconium ions is a very favorable process particularly when silicon is bonded to one or more carbon atoms which have sp^2 type hybridization. This probably arises from a variety of factors most of which involve, in some way, the ability of the $3d$ orbitals on silicon to participate in bonding both of the σ and π types.

EXPERIMENTAL

Instrumentation

The mass spectra reported in this investigation were recorded on a Hitachi RMU-6-H mass spectrometer. The ionizing voltage was 70 V and the temperature of all heated parts of the system was maintained at 250° unless otherwise specified. Samples were introduced both by direct inlet and through the heated reservoir, non-volatile, liquid-solid inlet system. The method of sample introduction had no effect on the spectrum of these compounds. Depending on the sample and the information desired, the accelerating voltage was either 3.6, 2.4, or 1.8 kV.

Materials

The preparations of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene, (I) and 1,1-dimethyl-2,5-diphenyl-1-silacyclopentane (II) were carried out during another investigation and have been published elsewhere[35].

In addition to the preparation of 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexadiene (IV), by the co-pyrolysis of diphenylacetylene and the 1/1 adduct of diphenylacetylene with 1,1-dimethyl-2,5-diphenylsilacyclopentadiene[35], it was also prepared for this investigation by the co-pyrolysis of diphenylacetylene with 7,7-dimethyl-1,2,3,4,5-pentaphenyl-7-silanorbornadiene[38] and by the reaction of sodium with dichlorodimethylsilane in the presence of diphenylacetylene[39]. Samples of disilacyclohexadiene (IV) prepared by these three methods were purified by recrystallization from n-hexane, 60–90° petroleum ether, acetone, benzene, and benzene/60–90° petroleum ether mixtures. In addition, some samples were isolated and purified on a neutral alumina column using 60–90° petroleum ether as the solvent and were further purified by sublimation under high vacuum (10^{-5} mm). All samples, shown to be pure by IR and NMR, gave the mass spectrum reported in Table 4. (Found: C, 81.2; 81.5; H, 7.00, 6.78; Si, 11.6, 11.7; mol. wt., 496. $C_{32}H_{32}Si_2$ calcd.: C, 81.3; H, 6.78; Si, 11.9%; mol. wt., 472.)

1,1-Dimethyl-2,3,4,5,-tetraphenyl-1-silacyclopentadiene (III) was prepared by a procedure given in the literature[40] and purified by recrystallization from n-hexane. (Found: C, 86.7; H, 6.40; Si, 6.88. $C_{30}H_{26}Si$ calcd.: C, 86.9; H, 6.29; Si, 6.78%.)

ACKNOWLEDGEMENT

We thank the Research Corporation, New York, N.Y., for partial financial support and Drs. J. Grunwell and J. Hayes for many helpful suggestions.

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