Mass Spectroscopy of Organosilicon Compounds. Examples of Interaction of the Silyl Center with Remote Phenyl Groups

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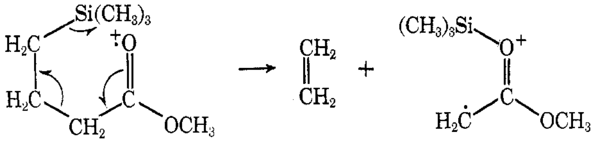
The mass spectra of 1-(trimethylsilyl)-3-phenylpropane and β-(trimethylsilyl)styrene have been studied in detail. The mass spectral rearrangements observed are shown to occur by interaction of the silyl center and the phenyl ring.

Mass spectroscopy is a particularly powerful analytical method of structure determination. The occurrence of molecular rearrangements of ions, often with concurrent fragmentation, in the mass spectrometer complicates the determination of the original structure. Certainly such rearrangements must be recognized if fragment ions are to provide useful structural data. Two major types of rearrangements involving silyl centers have been observed. The first involves the direct transfer of an intact trimethylsilyl group from one part of the ion to another with concurrent fragmentation in a manner similar to certain types of hydrogen migrations frequently observed in mass spectroscopy, such as the McLafferty rearrangement.[1-4] The second involves interaction of a siliconium ion center, formed by loss of a methyl group from silicon in the parent ion, with distant electron-rich centers in the molecule.[4-7] These rearrangements are important for the understanding of the mass spectra of organosilicon compounds. The fact that related rearrangements involving the silyl center sometimes occur in volatile trimethylsilyl ether derivatives makes these rearrangements of more general interest. This is true because these derivatives have been a frequent choice for the separation and structure determination of nonvolatile materials by a combination of gas chromatography and mass spectroscopy.[6-10] We propose to discuss two examples of the interaction of a silyl center with a remote phenyl group in mass spectroscopy.

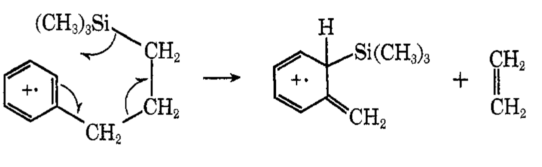
Several examples of the apparent migration of a trimethylsilyl group from an ether oxygen to a positively charged carbonyl oxygen functionality in the mass spectrometer have been reported.[1,2] More recently the probable transfer of a trimethylsilyl group from the γ-carbon of an alkyl chain to a positively charged carbonyl oxygen in a silyl–McLafferty-type rearrangement has been observed (eq 1).[4]



(1)

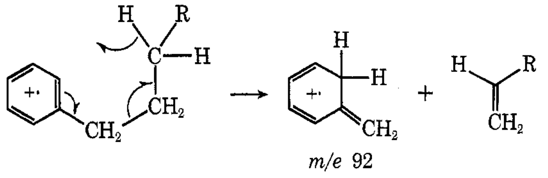
We would now like to report a new example of the high migratory aptitude of a trimethylsilyl group in which this group is transferred from a saturated carbon atom to an unsaturated carbon atom in the mass spectrometer.

The peak at mass 164 in the mass spectrum of 1-(trimethylsilyl)-3-phenylpropane probably results from migration of the trimethylsilyl group from the terminal γ-carbon of the alkyl chain to the positively charged phenyl ring with simultaneous loss of ethylene (eq 2) (see Tables I–III for substantiating data). A metastable peak at mass 140 [calculated $m/e = (164)^2/192 = 140.1$] provides evidence in support of this rearrangement. The mass spectra of both 1-(trimethylsilyl)-1,1-dideuterio-3-phenylpropane and 1-(trimethylsilyl)-3-deuterio-3-phenylpropane were examined and found to support the proposed rearrangement (see Tables I and II).



(2)

This rearrangement is similar to the transfer of a hydrogen from the γ-carbon of an alkylbenzene to the phenyl ring with concurrent β fragmentation.[11] This leads to formation of the mass 92 ion and a neutral olefin molecule. It has been shown that the γ-hydrogen is transferred to the ortho position of the phenyl ring by the observation that the rearrangement does not occur if both ortho positions are blocked (2,4,6-trimethyl-1-octadecylbenzene) (eq 3).[12] While the position on the phenyl ring to which the trimethylsilyl group is transferred has not been determined by our



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[2] G. H. Draffan, R. N. Stillwell, and J. A. McCloskey, *Org. Mass Spectrom.*, **1**, 669 (1968).

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[5] W. P. Weber, R. A. Felix, and A. K. Willard, *ibid.*, **91**, 6544 (1969).

[6] J. Diekman, J. B. Thomson, and C. Djerassi, *J. Org. Chem.*, **34**, 3147 (1969).

[7] J. Diekman, J. B. Thomson, and C. Djerassi, *ibid.*, **33**, 2271 (1968).

[8] K. M. Baker, M. A. Shaw, and D. H. Williams, *Chem. Commun.*, 1108 (1969).

[9] D. C. DeJongh, T. Radford, J. D. Hribar, S. Hanessian, M. Bieber, G. Dawson, and C. C. Sweeley, *J. Amer. Chem. Soc.*, **91**, 1728 (1969).

[10] J. A. McCloskey, A. M. Lawson, P. M. Kruger, R. N. Stillwell, and K. Tsuboyama, *ibid.*, **90**, 4182 (1968).

[11] J. D. McCollum and S. Meyerson, *ibid.*, **81**, 4116 (1959).

[12] "Catalog of Mass Spectral Data," American Petroleum Institute Research Project 44, Spectra 1573 and 1515.

TABLE I

MASS SPECTRUM OF 1-(TRIMETHYLSILYL)-3-PHENYLPROPANE AND RELATED DEUTERIUM-LABELED COMPOUNDS AT 70 eV

Mass, m/e	Rel intensity $C_6H_5(CH_2)_3$-$Si(CH_3)_3$	 $C_6H_5(CH_2)_2$-$CD_2Si(CH_3)_3$	 C_6H_5CHD-$(CH_2)_2Si(CH_3)_3$
72	7.1	5.2	8.3
73	100.0	100.0	100.0
74	39.2	38.8	42.3
75	33.0	32.8	18.9
76	1.8	2.2	2.8
77	3.6	10.1	5.6
78	1.8	6.6	5.6
79		4.5	2.8
80		1.0	
85	2.7		5.6
86		1.2	
87	1.8	1.2	
88		3.2	
89	1.8	5.4	
90		3.6	
91	22.3	24.2	11.5
92	1.8	16.1	27.8
93		7.2	3.3
94		10.8	
101	80.3		74.5
102	8.9	2.0	8.3
103	4.5	79.6	3.9
104		8.9	2.8
105	1.8	6.6	3.3
106		1.3	
107		1.4	
115	3.6	1.1	3.9
116		3.2	6.7
117	8.9	4.7	8.3
118	2.7	3.5	8.3
119	1.8	12.0	3.3
120		5.1	2.8
121	2.7	3.4	3.5
129	9.8		
130			
131	1.8		
132			
133	1.8	1.4	
134			
135	10.7	5.9	13.9
136	1.8	1.4	1.7
144	2.7		
145	1.8		
146	3.6	1.4	
159	1.8		
160			
161	2.7		
162		1.4	2.8
163		3.0	
164	34.8	21.6	6.7
165	5.4	3.5	31.7
166	1.8		4.4
167	0.9		1.7
177	66.0		8.9
178	11.6		61.2
179	2.7	48.1	9.5
180		5.7	2.9
181		1.3	
192	7.1		2.1
193	1.8		9.5
194	0.9	2.8	1.1
195		0.4	0.6
196		0.06	

TABLE II

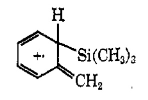
MASS SPECTRUM OF 1-(TRIMETHYLSILYL)-3-PHENYLPROPANE AND RELATED DEUTERIUM-LABELED COMPOUNDS AT 20 eV

Mass m/e	Rel intensity $C_6H_5(CH_2)_3$ $Si(CH_3)_3$	 $C_6H_5(CH_2)_2$-$CD_2Si(CH_3)_3$	 C_6H_5CHD-$(CH_2)_2Si(CH_3)_3$
73	100.0	83.3	65.7
74	8.1	16.1	5.7
75	5.4	6.8	2.1
76		3.1	
101	75.6	1.5	100.0
102	8.1	2.8	10.0
103	2.7	100.0	2.9
104		16.7	
105		5.6	
106		0.6	
161		0.6	
162		3.1	
163		0.9	
164	35.1	80.9	11.4
165	5.4	15.4	43.6
166	1.4	3.7	7.1
167		0.6	1.4
176		0.6	
177	41.9	3.1	11.4
178	6.8	1.8	41.4
179	1.4	72.8	7.9
180		14.2	1.4
181		3.7	
182		0.6	
192	5.4	0.4	1.7
193	1.4	0.3	6.3
194		7.4	0.7
195		1.5	
196		0.6	

TABLE III

HIGH-RESOLUTION MASS SPECTRAL DATA AT 70 eV

$C_6H_5CH_2CH_2CH_2Si(CH_3)_3$

Elemental composition	Calcd mass	Obsd mass	Possible structure of ion
$C_{11}H_{17}Si$	177.1099	177.1097	$C_6H_5(CH_2)_3\overset{+}{Si}(CH_3)_2$
$C_{10}H_{16}Si$	164.1021	164.1054	
$C_8H_{11}Si$	135.0630	135.0645	$C_6H_5\underset{+}{Si}(CH_3)_2$
$C_5H_{13}Si$	101.0786	101.0783	$(CH_3)_3SiCH_2CH_2^+$
C_7H_7	91.0548	91.0542	Tropylium ion
C_3H_9Si	73.0473	73.0473	$(CH_3)_3Si^+$

results, we favor a six-membered ring transition state with transfer of the trimethylsilyl group to the ortho position of the phenyl ring by analogy to the alkylbenzene behavior. This migration of a trimethylsilyl group from a saturated carbon of an alkyl chain to the unsaturated phenyl ring is only an important process when the trimethylsilyl group is on the γ-carbon and hence when a six-membered ring transition state is possible. In the mass spectrum of 1-(trimethylsilyl)-4-phenylbutane, no ion at mass 164 was observed. The usual transfer of a hydrogen from the γ-carbon of the alkyl side chain to the phenyl ring does occur in this compound, leading to a significant ion at mass 92. (see Tables IV and V for substantiating data).

Several additional ions in the mass spectrum of 1-(trimethylsilyl)-3-phenylpropane deserve comment.

TABLE IV

MASS SPECTRUM OF 1-(TRIMETHYLSILYL)-4-PHENYLBUTANE AT 70 EV

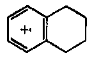
$C_6H_5(CH_2)_4Si(CH_3)_3$

Mass	Rel intensity	Mass	Rel intensity
71		119	2.2
72	3.1	120	
73	100.0	121	1.9
74	8.7		
75	4.1	129	2.8
76		130	
77	3.1	131	2.2
78	1.5	132	18.7
79	1.2	133	2.2
		134	
82	1.5	135	3.1
83	12.5		
84	1.2	189	4.7
		190	
87	5.6	191	34.4
		192	6.6
91	18.7	193	1.6
92	5.9		
		206	7.2
97	2.2	207	1.6
		208	
103	1.6		
104	3.4		
105	1.6		
115	1.2		

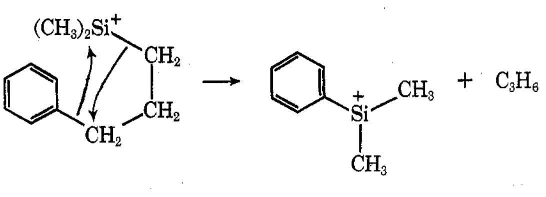
TABLE V

HIGH-RESOLUTION MASS SPECTRAL DATA AT 70 EV

$C_6H_5CH_2CH_2CH_2CH_2Si(CH_3)_3$

Elemental composition	Calcd mass	Obsd mass	Possible structure of ion
$C_{13}H_{22}Si$	206.1491	206.1486	Parent
$C_{12}H_{19}Si$	191.1256	191.1227	$C_6H_5(CH_2)_4\overset{+}{Si}(CH_3)_2$
$C_8H_{11}Si$	135.0630	135.0638	$C_6H_5\overset{+}{Si}(CH_3)_2$
$C_{10}H_{12}$	132.0939	132.0927	
C_7H_7	91.0548	91.0552	Tropylium ion
C_3H_7Si	73.0473	73.0468	$(CH_3)_3Si^+$

The ion at mass 177 results from loss of a methyl group from the parent ion. Fragmentation at such a highly branched center producing this ion is a favored process. Rearrangement of this ion with migration of the electron-rich phenyl group to the siliconium ion center with simultaneous loss of C_3H_6, possibly as cyclopropane, leads to formation of the dimethylphenylsiliconium ion at mass 135. The observation of a metastable ion at mass 103 [calculated $m/e = (135)^2/177 = 103$] provides evidence in support of this rearrangement (eq 4).


(4)

The mass spectra of both 1-(trimethylsilyl)-1,1-dideuterio-3-phenylpropane and 1-(trimethylsilyl)-3-deuterio-3-phenylpropane support this proposed rearrangement (see Tables I, II, and III). A similar rearrangement in the case of 1-(trimethylsilyl)-2-phenylethane has been observed (eq 5) (see Table VI).[13,14]

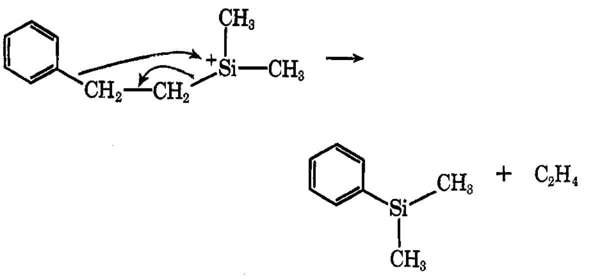

(5)

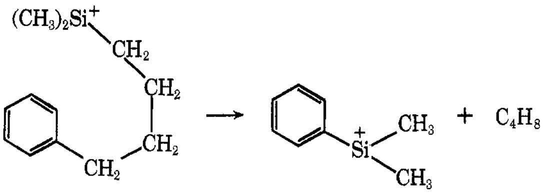
TABLE VI

HIGH-RESOLUTION MASS SPECTRAL DATA AT 70 EV

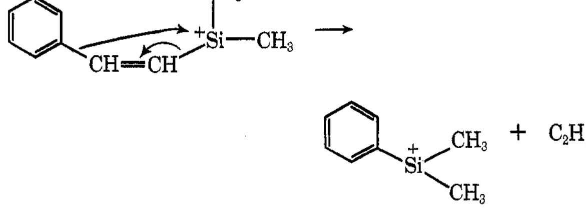
$C_6H_5CH_2CH_2Si(CH_3)_3$

Elemental composition	Calcd mass	Obsd mass	Possible structure of ion
$C_{11}H_{18}Si$	178.1178	178.1184	Parent
$C_{10}H_{15}Si$	163.0943	163.0934	$C_6H_5CH_2CH_2\overset{+}{Si}(CH_3)_2$
$C_8H_{11}Si$	135.0630	135.0633	$C_6H_5\overset{+}{Si}(CH_3)_2$
C_3H_9Si	73.04735	73.0462	$(CH_3)_3Si^+$

Similarly, in the mass spectrum of 1-(trimethylsilyl)-4-phenylbutane a rearrangement of the parent − 15 ion with loss of C_4H_8 leads to the dimethylphenylsiliconium ion at mass 135. It should be noted that this is the only ion in the mass spectrum of 1-(trimethylsilyl)-4-phenylbutane which arises by interaction of the remote phenyl group and the silyl center (eq 6).


(6)

An analogous rearrangement is found in the case of β-(trimethylsilyl)styrene in which acetylene is eliminated as the neutral fragment in the rearrangement of the P − 15 ion to the dimethylphenylsiliconium ion (eq 7) (see Tables VII–IX for substantiating data).


(7)

However, in this case loss of acetylene is not so important as is loss of methane from the P − 15 ion. A metastable ion at mass 130.9 [calculated, $(145)^2/161 = 130.6$] provides evidence in support of this pathway. A tempting possibility was the formation of an aromatic (2-π electron) substituted silacyclopropenium cation by

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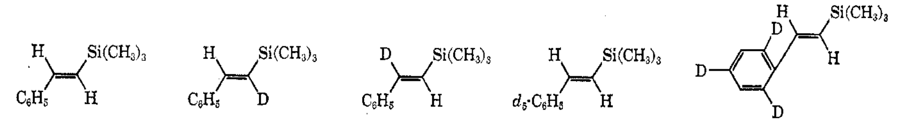
(13) T. H. Kinstle, P. J. Ihrig, and E. J. Goettert, *J. Amer. Chem. Soc.*, **92**, 1780 (1970).

(14) W. P. Weber, R. A. Felix, and A. K. Willard, *Tetrahedron Lett.*, 907 (1970).

Table VII

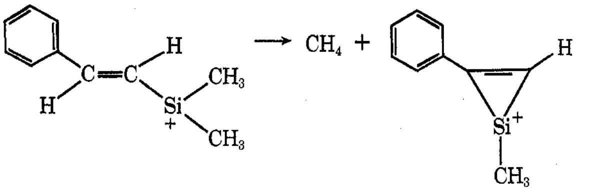
Mass Spectrum of β-(Trimethylsilyl)styrene and Related Deuterium-Labeled Compounds at 70 eV



A B C D E

Mass, m/e	A	B	C	D	E
71	1.9				
72	1.3	1.9			
73	12.8	20.3	5.5	4.9	6.1
74	3.4	4.8	1.4		
75	2.4	2.7			0.6
76	3.3	3.8	1.4		
77	7.6	9.7	2.8		
78	3.4	6.8	2.1		
79	3.4	4.3	1.6	0.5	0.9
80		1.1		0.5	1.0
81	2.4	4.8	1.8	0.5	
82				2.4	2.0
83	2.1	2.1			
89	2.1	1.6			
90		1.2			
91	4.9	4.8	1.8		
92	1.3	3.2	1.6		
93	3.4	4.1	1.8		
94	1.1	1.4			0.7
95	1.3	1.1		0.6	
96				1.6	
102	2.2	2.7	1.0		
103	3.4	7.5	2.5		
104	2.1	4.4	1.6		
105	12.6	17.7	8.7		1.1
106	2.1	4.8	2.5		1.1
107	4.3	5.4	2.7	1.1	3.1
108				0.8	3.6
109	1.9			2.6	
110				3.5	0.6
115	6.9	5.6	2.3		
116	2.1	6.6	3.7		
117	4.1	5.1	2.2		0.7
118	1.7	5.4	2.3		1.3
119	5.6	6.6	3.7	1.2	
120	1.4	3.8	2.3	1.0	0.8
121	6.9	7.0	4.8	0.5	0.9
122	1.3	4.8	2.3	1.6	0.6
123			0.5	1.4	0.6
124					3.5
125					
126					
127					
128	1.7				
129	4.7	2.2	1.5		
130	2.1	1.6	1.0		
131	6.9	4.8	2.8		
132	1.4	4.8	3.7		0.7
133	10.0	8.6	5.5		1.0
134	1.7	7.5	6.4	0.7	1.9
135	37.0	56.5	38.5	0.5	2.1
136	5.6	9.7	8.0	1.2	4.7
137	1.9	2.4	2.0	2.0	6.2
138				3.2	31.5
139				3.8	3.4
140				33.6	0.9
141	1.9			3.6	
142	5.0			0.2	
143	5.0	2.7	2.0		
144	1.5	3.2	3.2		
145	85.7	34.9	18.3		0.7
146	13.9	76.3	68.3		2.9
147	4.9	11.8	10.6	1.2	23.9
148	1.1	3.8	3.2	2.5	32.8
149	1.7			33.8	5.2
150				13.9	0.8
151				1.9	2.1
157	1.4				
158	2.1				
159	11.3		4.1		
160	2.9	8.0	8.4		
161	100.0	35.5	18.3		2.1
162	16.1	100.0	100.0		7.5
163	5.1	16.9	17.2	2.3	17.8
164		4.3	4.8	4.8	100.0
165				9.0	15.4
166				100.0	4.4
167				14.8	
168				3.1	
175	1.7				
176	28.9	10.2	4.8		
177	6.0	30.0	28.4		
178	2.1	5.7	5.0		4.2
179		1.3	1.4		28.5
180				1.6	4.0
181				27.8	0.8
182				3.7	
183					

loss of the α-hydrogen and a methyl group from silicon (eq 8).



(8)

However, the mass spectra of 1-phenyl-1-deuterio-2-(trimethylsilyl)ethylene, 1-phenyl-2-deuterio-2-(trimethylsilyl)ethylene, 1-(2′,4′,6′-trideuteriophenyl)-2-(trimethylsilyl)ethylene, and, finally, 1-pentadeuteriophenyl-2-(trimethylsilyl)ethylene conclusively ruled out this possibility. In all of these four cases deuterium was completely retained in the P − 15 ion. However, the subsequent loss of methane from this ion is a complicated process. Evidence from the labeled compounds indicates that it involves loss of CH$_3$ from the siliconium ion center and one hydrogen of the styryl portion of the molecule. However, the hydrogen lost does not come from any specific site in the styryl portion of the molecule. Rather, the mass spectra clearly demonstrate that all seven hydrogens of the styryl portion extensively scramble prior to loss of one together

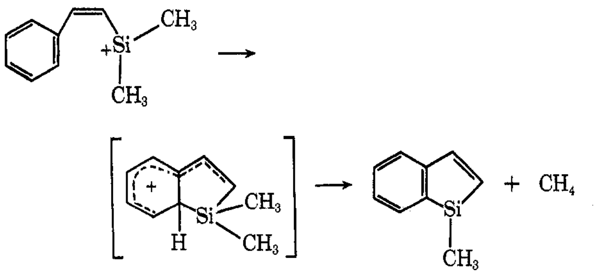
TABLE VIII

MASS SPECTRUM OF β-(TRIMETHYLSILYL)STYRENE AND RELATED DEUTERIUM-LABELED COMPOUNDS AT 20 EV[a]

Mass, *m/e*	A	B	C	D	E
133	1.3	1.8			
134		1.8	0.5		
135	0.3	9.2	1.0		
136		1.8			
137					
138					0.6
145	3.8	10.0	1.5		
146	0.6	22.0	6.0		
147		3.5	1.0		1.3
148		1.4			2.4
149				1.4	
159		2.1			
160		2.1	1.0		
161	100.0	3.2	16.9		
162	15.9	100.0	100.0		0.6
163	4.4	16.3	17.2		16.6
164		4.2	4.5		100.0
165					15.3
166				8.0	4.1
167				100.0	
168				15.2	
169				2.7	
176	77.5	17.0	11.6		
177	13.3	51.1	74.2		
178	3.8	9.2	12.6		11.6
179		2.5	3.5		72.7
180				5.1	11.4
181				73.7	2.6
182				11.1	
183				1.6	

[a] See structures for A–E in Table VII.

with the methyl group from silicon as methane. A possible mechanism for this scrambling process involves initial electrophilic attack by the siliconium ion center on the phenyl ring. Scrambling of the seven hydrogens of the styryl systems occurs by rapid proton shifts in this intermediate, prior to loss of methane, possibly to form an indenylsiliconium ion (eq 9) (see Tables VII and VIII).



(9)

The mass spectrum of 1-(trimethylsilyl)-2-phenylacetylene has only two major ions, the parent at mass 174 and the P − 15 due to loss of a methyl group from the quaternary silyl center, at mass 159. A doubly charged ion at mass = 159/2 = 79.5 is significant. In this case the linear nature of the acetylenic linkage, as well as the impossibility of losing a stable neutral species, probably prevents interaction between the silyl center and the phenyl ring (see Tables X and XI).

TABLE IX

HIGH-RESOLUTION MASS SPECTRAL DATA AT 70 EV

$C_6H_5CH{=}CHSi(CH_3)_3$

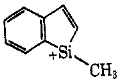
Elemental composition	Calcd mass	Obsd mass	Possible structure of ion
$C_{11}H_{16}Si$	176.1021	176.1021	Parent
$C_{10}H_{13}Si$	161.07865	161.0798	$C_6H_5CH{=}CH\overset{+}{Si}(CH_3)_2$
$C_{10}H_{11}Si$	159.0630	159.0632	$C_6H_5C{\equiv}C\overset{+}{Si}(CH_3)_2$
C_9H_9Si	145.04735	145.0472	
$C_8H_{11}Si$	135.0630	135.0620	$C_6H_5\underset{+}{Si}(CH_3)_2$
C_8H_8	104.0626	104.0618	
C_8H_7	103.0548	103.0548	
$C_5H_{13}Si$	101.07865	101.0781	$(CH_3)_3SiCH_2CH_2{}^+$
C_7H_7	91.05477	91.0555	Tropylium ion
C_6H_5	77.0391	77.0415	$C_6H_5{}^+$
C_3H_9Si	73.04735	73.0475	$(CH_3)_3Si^+$

TABLE X

MASS SPECTRUM OF 1-(TRIMETHYLSILYL)PHENYLACETYLENE AT 70 EV

$C_6H_5C{\equiv}CSi(CH_3)_3$

Mass	Rel intensity	Mass	Rel intensity
75	1.4	128	1.4
76	1.0	129	12.8
77	7.1	130	1.8
78	1.4	131	7.8
79	2.8	132	
[79.5]	5.7	133	1.4
80	1.0		
		142	1.4
89	2.8	143	5.3
90	1.4	144	1.4
91	3.5	145	2.1
93	1.4	159	100.0
		160	14.9
101	1.8	161	4.3
102	3.5		
103	6.3	174	17.7
104	1.0	175	2.8
105	12.8	176	0.7
106	1.6		
107	2.6		
115	8.5		
116	2.1		
117	3.9		
118			
119	1.4		

TABLE XI

HIGH-RESOLUTION MASS SPECTRAL DATA AT 70 EV

$C_6H_5C{\equiv}CSi(CH_3)_3$

Elemental composition	Calcd mass	Obsd mass	Possible structure of ion
$C_{11}H_{14}Si$	174.08647	174.0861	Parent
$C_{10}H_{11}Si$	159.0630	159.0677	$C_6H_5C{\equiv}C\overset{+}{Si}(CH_3)_2$

Obviously, the interaction of a silyl center with a phenyl group plays a dominant role in the mass spectra of the compounds discussed.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. All compounds described were purified for mass spectral study by preparative gas chromatography on a 10 ft × 0.25 in. SE-30 column. Ir spectra were determined as neat liquids on a Perkin-Elmer 337 ir spectrometer. Nmr spectra were run on a Varian A-60 nmr spectrometer using 10% solutions in carbon tetrachloride. Either chloroform or methylene chloride was used as internal standard.

Conditions used in determining low-resolution mass spectra on the Hitachi RMU-6E instrument were as follows: source temperature, 200°; all-glass inlet temperature, 200°; ionizing voltage, 70 and 20 eV; filament emission, 70 μA; and target current, 50 μA. Comparisons were made between unlabeled compounds at 20 eV and labeled compounds at 20 eV under identical conditions.

Conditions used in determining high-resolution spectra on the AEI MS-902 instrument were as follows. The exact mass determination of the composition of important ions was carried out at a resolution of at least 10,000. Exact mass was determined by peak matching with peaks of known mass of perfluorokerosene. The ionizing voltage was 70 eV; filament emission was 480 μA; and source temperature was 150°.

1-(Trimethylsilyl)-3-phenylpropane[15] was prepared by a coupling reaction between the Grignard reagent formed from 1-bromo-3-phenylpropane (Aldrich) and trimethylchlorosilane (Alfa Inorganics). The reaction was carried out in a three-necked, 200-ml, round-bottomed flask equipped with a reflux condenser, a pressure equalizing addition funnel, a nitrogen inlet, and a magnetic stirring bar. The flask was charged with 1.5 g (0.06 g-atom) of magnesium turnings (Mallinckrodt). The apparatus was flamed to dryness under a stream of nitrogen. Trimethylchlorosilane (7.6 g, 0.07 mol) in 100 ml of tetrahydrofuran was added to the flask, and 10.0 g (0.05 mol) of 1-bromo-3-phenylpropane was added dropwise. The reaction started immediately. The bromide was added at such a rate that a gentle reflux was maintained, and the reaction mixture was stirred for an additional hour. The reaction was then hydrolyzed by the addition of 50 ml of water. Ether (100 ml) was added and the organic and aqueous layers were separated. The organic layer was washed twice with 50-ml portions of water, dried over anhydrous magnesium sulfate, and filtered; the solvent was removed by evaporation under reduced pressure. The residue was distilled through a 15-cm vacuum-jacketed Vigreux column yielding 8.5 g (89% yield) of 1-(trimethylsilyl)-3-phenylpropane, bp 112° (35 mm). The physical properties of the compound thus prepared were in complete accord with literature values.

1,1-Dideuterio-1-(trimethylsilyl)-3-phenylpropane (98% d_2) was prepared by coupling the Grignard reagent prepared from 1-bromo-1,1-dideuterio-3-phenylpropane with trimethylchlorosilane in THF. The necessary bromide was synthesized as follows. 3-Phenylpropionic acid (Eastman) was converted to the corresponding methyl ester by treatment with 100 ml of methanolic HCl. The product, methyl 3-phenylpropionate, was purified by distillation, bp 236° (760 mm). 1,1-Dideuterio-3-phenylpropan-1-ol was prepared by reduction of this methyl ester with lithium aluminum deuteride (98% deuterium) in ether solvent in 95% yield. This alcohol was converted to the corresponding tosylate by reaction with recrystallized (ligroin) *p*-toluenesulfonyl chloride in ether in the presence of 1.1 equiv of pyridine. The desired bromide was prepared from the tosylate by reaction with anhydrous lithium bromide in acetone. This bromide contained 98% d_2 by 20-eV mass spectral analysis.

1-Deuterio-1-phenyl-3-(trimethylsilyl)propane (78% d_1).—1-Bromo-1-phenyl-3-(trimethylsilyl)propane was treated with 4 equiv of lithium aluminum deuteride in ether solution for 18 hr. A 50% yield of 1-deuterio-1-phenyl-3-(trimethylsilyl)propane was obtained (78% d_1). The required bromide was prepared from 1-phenyl-3-(trimethylsilyl)propane by treatment with 1.1 equiv of *N*-bromosuccinimide in carbon tetrachloride solution. The reaction was initiated by irradiation with a sun lamp. Succinimide was removed by suction filtration. The solvent was removed by evaporation under reduced pressure. The residue was distilled under vacuum to give a 71% yield of 1-bromo-1-phenyl-3-(trimethylsilyl)propane, bp 60° (0.2 mm). 1-Bromo-1-phenyl-3-(trimethylsilyl)propane was characterized by its nmr spectrum (CH_2Cl_2, δ 5.35, as internal standard): δ 0.14 (9 H), 0.71 t (2 H), 2.26 m (2 H), 4.96 t (1 H), 7.46 s (5 H).

1-Phenyl-4-(trimethylsilyl)butane[15] was prepared by coupling the Grignard reagent formed from 1-bromo-4-phenylbutane with trimethylchlorosilane as above in 91% yield. The required bromide was synthesized from 4-phenylbutyric acid (Aldrich). The acid was converted to methyl 4-phenylbutyrate [bp 90° (0.3 mm)] by treatment with methanolic HCl. Reduction of the methyl ester with lithium aluminum hydride in ether gave 4-phenyl-1-butanol (yield 90%). The alcohol was converted to the tosylate by treatment with recrystallized *p*-toluenesulfonyl chloride in ether, in the presence of 1.1 equiv of pyridine. Displacement of the tosylate by lithium bromide in acetone solution gave 1-bromo-4-phenylbutane in 90% yield.

β-(Trimethylsilyl)styrene[16] was prepared by coupling the Grignard reagent prepared from β-bromostyrene (Eastman) with trimethylchlorosilane. The reaction was carried out as described above. The yield of product, bp 81° (3 mm), was 64%.

1-Phenyl-1-deuterio-2-(trimethylsilyl)ethylene.—α-Deuteriobenzaldehyde was prepared by reaction of *tert*-butyl isocyanide[17] and phenyllithium, followed by quenching with D_2O (40% yield).[18] A Perkin condensation between α-deuteriobenzaldehyde and malonic acid (Eastman) employing α-picoline as base gave β-deuteriocinnamic acid (50% yield).[19] Treatment of β-deuteriocinnamic acid with bromine in chloroform gave the expected dibromocinnamic acid. This was converted to α-deuterio-β-bromostyrene by refluxing the dibromocinnamic acid in aqueous base (40% yield).[20] The product contained 86% d_1. Coupling of the Grignard reagent prepared from α-deuterio-β-bromostyrene with trimethylchlorosilane yielded (89%) the desired product which contained 86% d_1. The per cent deuterium content was determined by mass spectrometry.

1-Phenyl-2-deuterio-2-(trimethylsilyl)ethylene.—A Perkin condensation between benzaldehyde and perdeuteriomalonic acid (Merck) using α-picoline as base yielded α-deuteriocinnamic acid in 55% yield.[19] This was converted to β-deuterio-β-bromostyrene as above in 25% overall yield.[20] The product contained 78% deuterium. Coupling of the Grignard reagent prepared from β-deuterio-β-bromostyrene with trimethylcholorosilane yielded the desired product containing 74% deuterium in 70% yield. The per cent deuterium content was determined by mass spectrometry.

2-(Trimethylsilyl)phenylacetylene.[16]—Phenylacetylene (Aldrich) was treated with 1.1 equiv of butyllithium in hexane solution in the presence of 1.1 equiv of *N,N,N′,N′*-tetramethylethylenediamine. The anion which formed almost immediately was quenched with trimethylchlorosilane. The desired product was obtained in 93% yield, bp 110° (25 mm).

1-Pentadeuteriophenyl-2-(trimethylsilyl)ethylene.—To perdeuteriobenzene (99% d_6) (Merck) in the presence of 1.5 equiv of aluminum chloride in *sym*-tetrachloroethane solvent (purified by treatment with concentrated sulfuric acid) was added 1.5 equiv of acetyl chloride at 0°. The reaction was then heated at 60° for 2 hr. An 85% yield of pentadeuterioacetophenone was obtained. Reaction of pentadeuterioacetophenone with phosphorus pentachloride converted it to the corresponding 1,1-dichloro-1-phenyl-d_5-ethane. This was treated with sodium amide in liquid ammonia to yield phenyl-d_5-acetylene in 20% overall yield.[21] Treatment of phenyl-d_5-acetylene in the presence of *N,N,N′,N′*-tetramethylethylenediamine with *n*-butyllithium followed by quenching of the anion with trimethylchlorosilane gave 1-(trimethylsilyl)-2-phenyl-d_5-acetylene in 85% yield. Hydrogenation of 1-(trimethylsilyl)-2-phenyl-d_5-acetylene over Raney nickel catalyst in methanol at 1-atm pressure yielded a mixture of unreacted acetylene, the desired ethylene, and the completely hydrogenated ethane. These were separated on a 10 ft × 0.25 in. TCEP column. The desired 1-(trimethylsilyl)-2-phenyl-d_5-ethylene was obtained in 40% yield. This compound was found to be 94% d_5.

1-(2′,4′,6′-Trideuteriophenyl)-2-(trimethylsilyl)ethylene was prepared from bromobenzene-2,4,6-d_3. Bromobenzene-2,4,6-d_3

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was prepared by the method of Scarbourgh.[22] Its purity by mass spectroscopy was 86% d_3 and 14% d_2. The corresponding hexadeuterated diphenylmercurial was prepared by the reaction of the Grignard reagent made from the bromide with anhydrous mercuric chloride. Reaction of the deuterated diphenylmercury with a slight excess of trimethylvinylsilane in methanol solvent in the presence of a catalytic amount of anhydrous palladium chloride and a stoichiometric amount of cupric chloride to affect the reoxidation of the palladium overnight at room temperature led to a 10% yield of the desired compound. This procedure is basically that of Heck, applied to trimethylvinylsilane.[23,24] Surprisingly only the trans olefin was obtained. The compound was purified for mass spectral study by gc on a 3 m × 0.25 in. SE-30 column at 160°. The deuterated β-(trimthylsilyl)styrene obtained had the following isotopic purity: 86% d_3 and 14% d_2 by mass spectroscopy.

Registry No.—1-(Trimethylsilyl)-3-phenylpropane, 775-24-6; 1,1-dideuterio-1-(trimethylsilyl)-3-phenylpropane, 28901-25-9; 1-deuterio-1-phenyl-3-(trimethylsilyl)propane, 28901-26-0; 1-phenyl-4-(trimethylsilyl)butane, 777-82-2; 1-(trimethylsilyl)-2-phenylethane, 772-64-5; β-(trimethylsilyl)styrene, 18001-47-3; 1-phenyl-2-deuterio-2-(trimethylsilyl)ethylene, 28901-30-6; 1-phenyl-1-deuterio-2-(trimethylsilyl)ethylene, 28901-31-7; 1-pentadeuteriophenyl-2-(trimethylsilyl)ethylene, 28901-32-8; 1-(2′,4′,6′-trideuteriophenyl)-2-(trimethylsilyl)ethylene, 28901-33-9; 2-(trimethylsilyl)phenylacetylene, 2170-06-1; 1-bromo-1-phenyl-3-(trimethylsilyl)propane, 28841-13-6.

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The Reaction of 1,1-Dimethyl-2,5-diphenyl-1-silacyclopentadiene with Diphenylacetylene, 2,3-Dimethyl-1,3-butadiene, and Benzyne[1]

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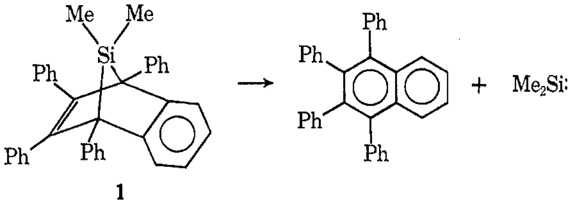
Diphenylacetylene reacts with 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (**4**) to give an isolable 1:1 adduct. Upon pyrolysis in a sealed tube, the adduct not only undergoes dimethylsilylene elimination as has been reported for 7-silanorbornadienes but also disassociates to reactants. When heated under high vacuum or when placed in solution, the adduct again disassociates to reactants. The title silacyclopentadiene reacts with 2,3-dimethyl-1,3-butadiene to give 1,8-diphenyl-3,4,9,9-tetramethyl-9-silabicyclo[4.3.0]nona-3,7-diene (**6**). In this reaction silacyclopentadiene **4** reacts as the dienophile and butadiene as the diene.

Recently, considerable work has been reported on the generation and reaction of several analogs of carbenes.[2-6] As a follow-up of some of this work, an investigation of the reaction of organosilylenes, R_2Si:, with a number of compounds was undertaken. This is not only an effort to help characterize these reactive intermediates but is also an effort to prepare compounds which have eluded preparation by other means.

There appears in the literature three distinctly different ways of generating organosilylenes.[2] The first reported was the reaction of an active metal with a dihalodiorganosilane. The other two methods involve the pyrolysis of either a peralkylated polysilane[2] or methoxypolysilanes[5] or the pyrolysis of a 7-silanorbornadiene.[3] The last method has been adopted for this study because it appears to give the silylene intermediate employing the least drastic conditions and also has the least reactive by-products being formed. This last consideration is very important as the coreactants under consideration in the above mentioned investigation are quite reactive with a number of compounds.

Rather than use 2:3-benzo-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silanorbornadiene (**1**)[3] or 7,7-dimethyl-1,2,3,4,5-pentaphenyl-7-silanorbornadiene (**2**)[3] as the precursor to dimethylsilylene (eq 1 and 2), the decision was made to prepare yet another one of these compounds to aid in determining the generality of this method of generation of silylenes as well as to try to obtain a 7-silanorbornadiene which is less stable toward dimethylsilylene elimination than **1** and **2**. The 7-silanorbornadienes are prepared by the Diels–Alder reaction of a silacyclopentadiene with an acetylene. For this investigation it was decided to try to prepare 7,7-dimethyl-1,2,3,4-tetraphenyl-7-silanorbornadiene (**3**) by the reaction (eq 3) of 1,1-dimethyl-2,5-diphenyl-1-



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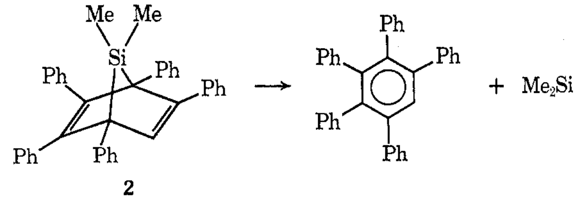

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