Mass Spectrometry of Allyloxy Di- and Trimethylsilanes

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The mass spectra of allyloxydimethylsilanes and allyloxytrimethylsilanes were examined. Isotopic labelling and metastable peaks support the proposed fragmentation patterns. Siliconium ions dominate the spectra. Loss of neutral fragments from $[M-15]^+$ and $[M-1]^+$ ions is important. These fragmentation patterns are discussed in terms of interaction of siliconium ions with the carbon-carbon double bond of the allyloxy ligand. Increased substitution on the allyloxy ligand apparently decreases the interaction of siliconium ions with the carbon-carbon double bond.

Unlike reactions of silicon compounds in solution,¹ the reactions of silicon compounds in a mass spectrometer are often dominated by siliconium ions. The interaction of siliconium ions with remote functional groups is well-documented in the high vacuum conditions of a mass spectrometer.² These interactions often lead to predictable fragmentation patterns.

The volatility and ease of preparation of silyl ethers make them the derivatives of choice for gas chromatographic mass spectrometric analysis of mixtures of alcohols. Knowledge of the fragmentation patterns of trimethylsilyl ethers of alcohols is essential information for the determination of structure.³⁻⁸ The use of dimethylsilyl ethers for this purpose has been less widespread despite their higher volatility. Similarities and differences in the fragmentation of these two types of ethers have been noted.⁹

One such difference is the relatively high abundance (5-20%) of the $[M-17]^+$ ions in the mass spectra of dimethylsilyl ethers.⁹ The $[M-17]^+$ ions are normally less than 1% relative abundance for trimethylsilyl ethers of alcohols. The $[M-17]^+$ peak is unusually large in the mass spectrum of allyloxydimethylsilane (1). We were interested in the possibility that this $[M-17]^+$ ion might arise from the interaction of a siliconium ion with the carbon-carbon double bond of the allyloxy ligand. In this paper, we report and analyze the mass spectra of several allyloxydimethyl-

silyl and -trimethylsilyl ethers (Tables 1-3). We find that interaction of the siliconium ions with the carbon-carbon double bond is important.

The mass spectrum of **1** is dominated by four siliconium ions. The peak at m/z 75,¹⁰ ion *a*, is the base peak. The other dominant ions include the $[M-15]^+$ ion (*b*), the $[M-17]^+$ ion (*c*) and the dimethyl-siliconium ion (*d*) at m/z 59. In addition to these ions, there are six peaks of intermediate (approx. 20-40%) relative abundance. These peaks occur at m/z 115 $[M-1]^+$ (*e*), m/z 85, m/z 73, m/z 71, m/z 61 (*f*) and m/z 45 (g). The complete mass spectrum of **1** is listed in Table 1.

The assignment of most of the major peaks is straightforward. Scheme 1 outlines the probable mode of formation of most of the major ions. Ion *a* is often present in the mass spectra of alkoxysilanes.^{10,11} Alkenes are known to be eliminated from alkoxy-substituted siliconium ion.¹¹ This process, ion *e* to an ion *a*, may occur by the loss of allene, and it is supported by observation of an appropriate metastable peak (see Table 1). Exact mass measurement of ion *a* as determined by peak matching (calc. for SiC₂H₇O 75.0266; found 75.0259) is consistent with the proposed structure. Calculated and observed exact masses for all ions *b* and *e* are also expected in the mass



Scheme 1

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Table 1. Mass spectra of dimethylsilyl ethers

Table 2. Mass spectra of deuterated allyloxydimethylsilanes

m/z 145 144 143 131	dimethyi silane 1 [*]	enyloxy)dimethyl- silane 5 ⁵	But-2-enyloxy- dimethylsilane 6 ^c	enyl-2-oxy) dimethylsilane 9 ^d	m/z	Allyloxy- dimethylsilane	Allyloxydimethyl- silane-Si-d ₁	(2,3,3-d ₃ -Allyloxy) dimethylsilane
145 144 143 131						1	2	3
145 144 143 131				0.3	100	•	-	, ,
144 143 131 130				0.3	120			2.2
143 131 120				24	119			4.1
131				2.4	118		1.4	11.4
120		1.5	1.7	4.1	11/	1.0	1.4	
100		9.9	13.4	11.8	116	2.1		
129		8.7	7.1	97.9	115	18.5	10.0	
127				2.8	106			8.1
119			5.7		105			22.5
118			•	1.6	104			100.0
117	10	37	43	12.3	103	2.8		43.4
116	2 1	10.5	10.8	85	102	7.2	100.0	91.3
115	19.5	10.0	100.0	14	101	73.4		93.4
112	10.5	22.2	11 5	33	100	8.5	27.8	45.2
113		16	1.5	5.5	99	86.0	10.9	
		1.0	1.0	5.0	97	2.0		
103	2.8		1.4		01	2.0		
102	7.2	1.4	1.9	1.3	91			1.8
101	73.4	9.0	11.7	8.2	90		5.5	7.6
100	8.5	1.0	1.3		89	4.9	10.3	26.4
99	86.0	9.2	10.6°	2.9	88	2.6	4.0	34.4
97	2.0	5.6	3.7		87	3.7	5.8	37.8
80	49	64	58		86	2.8	3.5	22.3
99	2.6	50	75		85	18.3	5.7	4.6
00 97	2.0	147	15.1	52	84			1.4
87	2.7	2.2	24	5.2	78			13.5
00	10 of	10 0	2.7	2.4	77	3.8		36.0
00	10.5	10.0	20.5	5.4	76	7.7	12.7	88.3
77	3.8	3.6	3.9	4.0	75	100.0	98.1	92.2
76	7.7	6.4	6.6	7.6	74	32	9.0	48.4
75	100.0	84.1	86.4	100.0	73	16.0	48.4	50.5
74	3.2	2.0	2.1		70	10.0	93	33.0
73	16.0 ⁹	1.3	3.2	1.4	71	22.2	15.2	00.0
71	22.3	2.0	2.1	1.0	71	22.0	10.2	
69	1.0	1.5	1.4	2.4	63	1.2		14.6
63	12	1.0	2.3		62	2.0	4.9	59.7
62	20	1.5	35	1.0	61	33.5	23.9	59.3
61	33.5	20.8	52.0	12.7	60	7.4	23.0	64.3
60	7 4	20.0	5.8	2.0	59	74.0	20.5	89.7
50	74.0	2.4	44.8	13.5	58	9.0	19.3	45.0
59	0.0	20.7	4.8	1 1	57	6.3	16.4	16.8
56	5.0	2.5	4.0	1.1	56		5.0	6.4
57	0.3	1.4	4.4 9 E	21	55	6.9	5.5	5.7
55	0.9	3.0	0.0	2.1	53	3.4	3.3	4.7
53	3.4	1.0	4.3	£.£	48			14.3
47	8.1	1.7	5.5	1.8	47	81	4.8	22.1
45	41.7	4.9	16.6	5.2	46	0.1	8.2	54.8
^a Metastal	ble ions:	19.8-20.3 45 ² /1	101 = 20.0; 30	-30.5 59 ² /115 =	45	41 7	25.8	61.9

* Metastable ions: $19.8-20.3 \ 45^2/101 = 20.0; \ 30-30.5 \ 59^2/115 = 30.3; \ 36.5-37.2 \ 61^2/101 = 36.8; \ 48.5-49 \ 75^2/115 = 48.9; \ 49.5-50.3 \ 71^2/101 = 49.9; \ 62.5-63 \ 85^2/115 = 62.8; \ 65.5-66 \ 87^2/115 = 65.8; \ 96.8-97.3 \ 99^2/101 = 97.0.$

b.c Metastable ions: 17.2-17.8 $45^2/115 = 17.6$; 26.5-27.5 $59^2/129 = 27.0$; 32-32.8 $61^2/115 = 32.4$; 43-44 $75^2/129 = 43.6$; 62.5-63 $85^2/115 = 62.8$; 65.5-66.5 $87^2/115 = 65.8$; 78.8-79.3 $101^2/129 = 79.1$; 85-85.5 $99^2/115 = 85.2$; 98.5-99 $113^2/129 = 98.8$; 101.3-102.3 $115^2/130-101.73$; 110.8-111.5 $113^2/115 = 111.03$.

^d Metastable ions: 26.5-27.2 $59^2/129 = 27.0$; 36.8-37.5 $73^2/143 = 37.3$; 95-96 $117^2/144 = 95.1$; 124.8-125.3 $127^2/129 = 125$.

*9.3% ion t, 1.3% ion p.

f 4.4% ion I, 13.9% ion k.

⁹ 2.1% ion *i*, 13.9% trimethylsiliconium ion.

spectrum of **1**. The fragmentation of a methyl radical or hydrogen atom from a quaternary silyl center to form siliconium ions $[M-15]^+$ (b) and $[M-1]^+$ (e) is a

favorable process.¹²⁻¹⁴ The exact mass measurement of these ions (Table 4) supports these assignments.

Ion d may be formed either by loss of an alkoxy radical from the molecular ion of **1** or by elimination of acrolein from ion e. This second process is supported by an appropriate metastable peak. The geneses of ions f, the hydroxymethylsiliconium ion, and g, the methylsiliconium ion from ion b are related to the formation of ions a and d from ion e. Thus, elimination of allene from ion b yields ion f, and elimination of acrolein from ion b yields ion g. Appropriate metastable peaks are observed for these processes.

The assignment of structure to ion c is not as straightforward. The loss of 17u can be accounted for in several ways. Richter and Hunnemann⁹ have reported that metastable peaks support sequential loss

Lable 3. Mass spectra of trimethylslivi ethe	Table	3.	Mass	spectra	of	trimethy	vlsilvl	ether
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m/z	Allyloxy- trimethyl silane 4 ^a	(2-Methylprop-2- enyloxy)trimethyl- silane 7 ⁵	But-2-enyloxy- trimethylsilane 8°	(2-Methylbut-3- enyl-2-oxy) trimethylsilane 10 ^d
159				0.3
158				2.3
1 477				
14/		1.4	1 5	4.1
140		1.4	1.5	A 1
140		31.6	4.4 317	12.8
143		51.0	15	100.0
100	0.7		1.0	1.0
132	0.7		4 1	1.3
131	1.4	4.4	4.1	10.5
130	17.0	100.0	100.0	2.0
127		100.0	100.0	14
447	4 5			1.4
11/	4.5			
110	10.9			2.0
112	100.0	21	3.0	2.0
111	1.5	5.1	12	
400			1.2	
103	1.2	1.1	1.2	2.6
00	1.9	3.5	0.0	3.0
33 97	15.0	2.0	4.3	1.9
37	1.5			
89	1.1			
88	3.0	1.1	1.8	
07 96	10.4 E 1			
85	49.6	2.1	2.3	1.4
77	14	1 0	41	10
76	22	37	75	39
75	26.1	47.3	97.9	50.0
74	5.9	2.3	4.7	4.6
73	50.9	19.7	39.4	42.5
71	3.5			
61	14.0	17	45	32
60	7.4		1.7	0.2
59	66.5	3.6	7.7	4.7
58	14.4	2.2	3.6	1.1
47	9.5		1.4	
55	9.9	1.2	4.1	1.2
53	4.1		2.0	1.4
47	11.3	1.0	4.4	1.9
46	3.7			
45	49.1	2.6	10.7	5.0

^a Metastable ions: 29.8–30.5 $59^2/115 = 30.3$; 62.5–63 $85^2/115 = 62.8$; 65.5–66.3 $87^2/115-65.8$; 84.5–85.5 $99^2/115 = 85.23$. ^{b.c} Metastable ions: 43.3–43.8 $75^2/129 = 43.6$; 78.5–79.5 $101^2/129 = 79.1$; 98.5–99.3 $113^2/129 = 98.9$; 115–116 $129^2/144 = 115.6$.

^d Metastable ions: 37–37.8 $73^2/143 = 37.3$; 39–39.8 $75^2/143 = 39.3$; 129–130 $143^2/158 = 129.4$.

of H_2 and methyl radical from the molecular ions of dimethylsilyl ethers of aliphatic alcohols to give the $[M-17]^+$ ions. In contrast, metastable peaks in the mass spectrum of **1** support sequential loss of methyl radical and H_2 from the molecular ion of **1** as the origin of the $[M-17]^+$ ion. Thus, ion b loses H_2 to form ion c. This process is supported by an appropriate metastable peak. Alternatively, loss of a hydrogen atom followed by loss of methane could also account for the formation of ion c although this process is not supported by observation of metastable peaks.

Table	4.	Observed	and	calculated	masses	for
		ions				

lons (Scheme)	Observed mass	Empirical formula	Calculated mass
a (1)	75.0259	SiC ₂ H ₇ O	75.0266
Ь (1, 2)	101.0425	SiC₄H ₉ O	101.0425
c (1, 2)	99.0267	SiC ₄ H ₇ O	99.0266
d (1,7)	a	SiC ₂ H ₇	-
e (1, 2)	115.0583	SiC ₅ H ₁₁ O	115.0579
f (1,7)	⁸	SICH ₅ O	
g (1)	⁸	SiCH₅	
h (2)	71.0312	SiC ₃ H ₇	71.0317
i (2)	73.0101	SiC ₂ H ₅ O	73.0110
j (2, 6)	87.0272	SiC ₃ H ₇ O	87.0266
k (2)	85.0475	SiC₄H₅	85.0474
1 (2)	85.0115	SiC₃H₅O	85.0110
m (6)	129.0743	SiC ₆ H ₁₃ O	129.0736
n (6)	115.0586	SiC₅H₁₁O	115.0579
o (6)	113.0428	SiC ₅ H ₉ O	113.0423
p (6)	99.0625	SiC ₅ H ₁₁	99.0630
q (6)	101.0422	SiC₄H₀O	101.0423
r (6)	85.0474	SiC₄H ₉	85.0474
s (6)	99.0273	SiC₄H ₇ O	99.0266
t (7)	117.0740	SiC ₅ H ₁₃ O	117.0736
u (7)	143.0879	SiC ₇ H ₁₅ O	143.0892
v (7)	129.0741	SiC ₆ H ₁₃ O	129.0736

* Exact mass was not measured.

We propose a cyclic structure for ion c as shown in Scheme 2. This process would involve an intramolecular electrophilic attack by siliconium ion b on the remote carbon-carbon bond to form ion b'. Ion b'then loses hydrogen to form ion c. In a similar manner, ion e could cyclize to form e' which could eliminate methane to form ion c. Previous studies^{2,15-17} have shown that siliconium ions undergo intramolecular electrophilic aromatic attack to form cyclic carbocations which then eliminate a neutral species to form other siliconium ions (Scheme 3). The reaction of siliconium ions with ethene may be similar. This reaction is proposed to proceed through a collision complex which then decomposes by elimination of hydrogen or methane.¹⁸

$${}^{+}SiH_{3}+C_{2}H_{4} \rightarrow [SiC_{2}H_{7}]^{+*}$$

$$[SiC_{2}H_{7}]^{+*} \rightarrow [SiC_{2}H_{5}]^{+}+H_{2}$$

$$[SiC_{2}H_{7}]^{+*} \rightarrow [SiCH_{3}]^{+}+CH_{4}$$

The cyclization of ions b and e followed by elimination of neutral species other than H_2 or methane provides pathways by which the other principal ions observed in the mass spectrum of 1 are formed. For example, elimination of formaldehyde from ion b'yields the methylvinylsiliconium ion h at m/z 71. This assignment is supported by the exact mass of ion h, and the process by the observation of an appropriate metastable peak. Elimination of methane from ion b'may yield ion l. Although no metastable peak is observed from this process, the detection of a peak at m/z 85 with the exact mass required for this ion (calc. for SiC₃H₅O 85.0110; found 85.0115) may support this assignment. Finally, ethene may be eliminated from ion b' to form ion *i*. Again no metastable is observed for this process, but the high resolution mass spectrum of 1 has a peak at m/z 73 distinct from the trimethylsiliconium ion which is also present. The







Scheme 3

exact mass measurement supports this assignment (calc. for SiC₂H₅O 73.0110; found 73.0101). The detection of a peak at m/z 73 other than the trimethylsiliconium ion should serve as a caution to chemists who automatically assign peaks at m/z 73 to the trimethylsiliconium ion.

Analogously, elimination of formaldehyde and ethene from ion e' yields ions k and j respectively. Both of these processes are supported by metastable peaks. Exact mass measurements are consistent with the structures assigned. It should be noted that ion k



nominally has the same mass as ion l. However, the high resolution mass spectrum of 1 shows two peaks at m/z 85.

The mass spectra of deuterium-labelled allyloxydimethylsilanes reveal that the deuterium atoms are scrambled throughout the cyclic ions b' and e' before elimination of neutral species. Thus, in the mass spectrum of allyloxydimethylsilane-Si- d_1 (2), H₂ as well as HD is lost from ion b' (Scheme 4). In the mass spectrum of $(2,3,3-d_3-\text{allyloxy})$ dimethylsilane (3), formaldehyde- d_2 , formaldehyde- d_1 and formaldehyde are all lost from ions b' and e' (Scheme 5). The mass spectra of the deuterated allyloxydimethylsilanes are compiled in Table 2.



Scheme 5

Given this data, it was of interest to determine whether similar processes were significant in the mass spectra of other allyloxysilanes. If these interactions were general, the mass spectrum of allyloxytrimethylsilane (4) should be similar, but less complicated than the mass spectrum of 1.

As expected, the mass spectrum of 4 (See Table 3) shows similar fragmentation patterns to that of 1. The base peak is ion e. All of the processes discussed previously from ion e occur in the mass spectrum of 4. These processes, outlined in Schemes 1 and 2, are supported by appropriate metastable peaks. A metastable peak supports the loss of methane from ion e'. No metastable peak for this process was found in the mass spectrum of 1; however, the observation of this metastable in the mass spectrum of 2 supports the same process from ion e' in the mass spectrum of 1.

Substitution of methyl groups for hydrogen atoms on the allyloxy ligand in both the 2 and 3 positions generally decreases the relative abundance of ions that result from the interaction of the initially formed siliconium ion with the carbon-carbon double bond of the allyloxy ligand. This result is surprising because methyl-substituted ethenes are known to react more readily than ethene with most electrophiles.¹⁹ Scheme 6 outlines the fragmentations of 2-methylprop-2enyloxydimethylsilane (2-methallyloxydimethylsilane, 5) and but-2-enyloxydimethylsilane (crotyloxydimethylsilane, 6).

The same basic fragmentation patterns are observed from ions m and n as are observed from ions b and e. An important difference is observed, however, in the loss of the olefin from ions m and n. These ions would be expected to lose both propene and ethene. There is no evidence for the loss of propene from either ion mor ion n. Instead, ethene is eliminated to form ions qand r. The process, ion n' to ion j is supported by the observation of an appropriate metastable peak; the process, ion m' to ion q, is also supported by an appropriate metastable peak. The losses of formaldehyde and methane also are exclusive. Acetaldehyde and ethane could be eliminated, but there is no evidence for these processes. Complete mass spectra of 5 and 6 are listed in Table 1.

The trimethylsilyl ethers of 2-methylprop-2-en-1-ol (7) and but-en-1-ol (8) fragment and rearrange in a similar manner to their dimethylsilyl counterparts. Their mass spectra are listed in Table 3. The proposed processes from ion m (Scheme 6) are supported by metastable peaks. The exact mass measurements are consistent with the proposed structures of ions.

Further perturbation of the allyloxy ligand by placement of two methyl groups α to oxygen further decreases the relative abundance of the ions that result from interaction of the siliconium ions with the carbon-carbon double bond. The mass spectra of (2methylbut-3-enyl-2-oxy)dimethylsilane (α , α -dimethylallylloxydimethylsilane, 9) and (2-methylbut-3-enyl-2oxy)trimethylsilane $(\alpha, \alpha$ -dimethylsilylallyloxytrimethylsilane, 10) are listed in Tables 1 and 3 respectively. For these two compounds, the $[M-27]^+$ ion is much stronger than for the other dimethyl- and trimethylsilyl ethers of allylic alcohols studied. This ion undoubtedly comes from α -cleavage within the allyloxy ligand as has been observed previously as a major process for dimethylsilyl ethers of aliphatic alcohols.⁹ Determination of the exact mass of the peak at m/z 117 (ion t, Scheme 7) supports this assignment. Scheme 7 outlines the proposed processes of formation of the other major peaks in the mass spectra of 9 and 10.

In conclusion, the $[M-1]^+$ and $[M-15]^+$ ions of allyloxydimethylsilanes and the $[M-15]^+$ ions of allyloxytrimethylsilanes undergo processes by which they lose the neutral species hydrogen, methane, ethene and formaldehyde, possibly by interaction of the siliconium ions with the carbon-carbon double bond. Increased substitution on the allyloxy ligand decreases the apparent interaction of the siliconium ions with the carbon-carbon double bond.





EXPERIMENTAL

Nuclear magnetic resonance (NMR) spectra were obtained from 1% sample solutions in deuterochloroform with chloroform as an internal standard on a Varian XL-100-15 spectrometer operating in the FT mode. All samples were purified by preparative gas chromatography on a 144 in. ×0.25 in. 20% SE-30 on Chromosorb W 60/80 mesh column on a Gow-Mac 550 chromatograph. Low resolution mass spectra were determined on both a Hewlett-Packard 5985 gas chromatograph mass spectrometer and an AEI MS 9 spectrometer. A 72 in. $\times 0.25$ in. 3% OV-1 on Chromosorb W 60/80 mesh column was used in the gas chromatograph mass spectrometer. High resolution mass spectra were obtained on an AEI MS9 spectrometer. All mass spectra were run at 70 eV ionizing energy.

All silyl ethers studied are known compounds. They were identified by a combination of NMR spectroscopy, mass spectrometry, and comparison of gas chromatographic retention time with known samples. All silyl ethers studied gave satisfactory exact mass measurements by peak matching for the respective molecular ions by high resolution mass spectrometry. In those cases where NMR information has not been reported previously, we have included these data.

All silvl ethers except 2 and 3 were prepared by the condensation of commercially available alcohols with either dimethylchlorosilane or trimethylchlorosilane in the presence of tri-*n*-propylamine. The preparation of 1 is illustrative.

Allyloxydimethylsilane (1)^{20,21} was prepared by the addition of dimethylchlorosilane (20.0 g, 0.21 mol) to a vigorously stirred solution of tri-*n*-propylamine (50 cm³) and freshly distilled allyl alcohol (11 g, 0.19 mol). Stirring was continued for 3 h. Tri-*n*-propylammonium chloride was removed by filtration. The salt was washed with dichloromethane ($2 \times 10 \text{ cm}^3$). Fractional distillation of the filtrate gave 20 g (0.17 mol, 91%) crude allyloxydimethylsilane (b.p. 85 °C 755 mm⁻¹).²⁰ Allyloxydimethylsilane was further purified by preparative gas chromatography.

Allyloxydimethylsilane-Si- d_1 (2) was prepared by the reaction of dimethylsilylene and allyl alcohol-O- d_1 .²²

Allyl alcohol-O- d_1 was prepared by quenching lithium allyloxide, produced by reaction of *n*-butyllithium with allyl alcohol in ethyl ether at -78 °C, with deuterium oxide. Photolysis of a solution of dodecamethylcyclohexasilane^{23,24} (56 mg, 0.16 mmol), allyl alcohol-O- d_1 and hexane yielded allyloxydimethylsilane-Si- d_1 . NMR analysis of the product indicated it was at least 95% deuterated. NMR: δ 6.0 (m, 14), 5.2 (m, 1H), 5.0 (m, 1H), 4.2 (m, 2H), 0.3 (s, 6H). No Si—H absorption was detected.

(2,3,3- d_3 -Allyloxy)dimethylsilane (3) was prepared by reaction of dimethylchlorosilane and 2,2,3- d_3 -allyl alcohol in tri-*n*-propylamine.

2.3.3-d-Allyl alcohol was prepared as follows: Propargyl alcohol $(5 \text{ cm}^3, 0.09 \text{ mol})$ was treated with two equivalents of n-butyllithium in hexane/tetrahydrofuran at -78 °C with vigorous stirring. The mixture was allowed to warm to 0 °C, and it was quenched with 3.5 cm^3 (0.19 mol) D₂O. Lithium salts were removed by filtration, and propargyl alcohol- d_2 was purified by distillation through a 12 in. Vigreux column. The fraction boiling 110-111 °C was collected. Propargyl alcohol- d_2 (1.2 cm³, 0.02 mol) in 3 cm³ dry THF was added dropwise to 1.0 g lithium aluminum deuteride in 15 cm³ dry THF.²⁵ The reaction mixture was stirred and heated to 67 °C for 16 h. The mixture was then cooled to 0 °C and quenched cautiously with excess D₂O. Solids were removed by filtration, and distillation removed excess solvent. NMR analysis of the product indicated it was composed of $10\% 2,3-d_2$ allyl alcohol and 90% $2,3,3-d_3$ -allyl alcohol.

Allyloxytrimethylsilane $(4)^{26,27}$ had the following NMR spectrum: $\delta 6.1-5.7$ (m, 1H), 5.3-5.0 (m, 2H), 4.2-4.1 (m, 2H), 0.16 (s, 9H).

(2-Methylprop-2-enyloxy)dimethylsilane (5).^{28,29} Mass spectral data: see Table 1.

But-2-enyloxydimethylsilane (6).²¹ Mass spectral data: see Table 1.

(2 Methylprop-2-enyloxy)trimethylsilane(7).^{26,27} NMR: $\delta 4.85$ (br.d, 2H), 3.96 (s, 2H), 1.69 (s, 3H), 0.13 (s, 9H). Mass spectral data in Table 3.

But-2-enyloxytrimethylsilane (8).³⁰ Mass spectral data in Table 3.

(2-Methylbut-3-enyl-2-oxy)dimethylsilane (9).^{20,28} NMR: $\delta 6.09-4.91$ ABX pattern analyzed³¹ as: $\delta_{\rm X} 5.94$, $\delta_{\rm B} 5.15$, $\delta_{\rm A} 4.99$, $J({\rm AB}) = 1.5$ Hz, $J({\rm AX}) =$ 17.1 Hz, $J({\rm BX}) = 10.4$ Hz; 4.73 (sept, 1H, J = 2.8 Hz), 1.38 (s, 6H), 0.24 (d, 6H, J = 2.8 Hz). Mass spectral data in Table 1.

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(2-Methylbut-3-enyl-2-oxy)trimethylsilane (10).^{26.27} NMR: δ 6.09-4.88 ABX pattern analyzed as: $\delta_{\rm X} = 5.95$, $\delta_{\rm B} = 5.14$, $\delta_{\rm A} = 4.95$, $J({\rm AB}) = 1.5$ Hz, $J({\rm AX}) = 17.2$ Hz, $J({\rm BX}) = 10.3$ Hz; 1.36 (s, 6H), 0.17 (s, 9H). Mass spectral data in Table 3.

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