Fragmentation of Silaspiroalkanes in EI Mass Spectrometry

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The fragmentations of six silaspiroalkanes combined with four-, five-, and six-membered rings in EI mass spectrometry have been studied by a B/E linked scanning technique and an *ab initio* MO method. The main fragmentation process from the molecular ion is the consecutive losses of two ethylene molecules which occur *via* the cleavage of an Si-C bond in each ring of silaspiroalkanes. From the *ab initio* MO calculation, we found that the initial bond fission occurred in an Si-C bond of the molecular ion. At that time, the cleavage of an Si-C bond occurs in the smaller ring more easily than in the larger one, since the strain on the smaller ring is larger. We found the metastable decomposition due to a CH₃ loss from the molecular ions of 4-silaspiro[3.5]nonane, 5-silaspiro[4.4]nonane, and 4-silaspiro[3.4]octane.

1. Introduction

The chemistry of organosilicon compounds is one of the growing areas in organic chemistry, including the mass spectrometry of organic compounds.^{1), 2)} However, the systematical investigation on fragmentation mechanisms of alkylsilanes in EI mass spectrometry has not been extensive.

We have systematically studied the fragmentation mechanisms of alkylsilanes in EI mass spectrometry during the last five years.³⁾ The EI mass spectra of linear alkylmonosilanes were characterized by (i) the formation of the silyl cation due to the cleavage of an Si-C bond; (ii) the formation of (CH₃)₃Si⁺; (iii) and the formation of the [R₁R₂R₃SiCH₂=CH₂]⁺ ion (R₁, R₂, R₃=CH₃ or H) with σ-π conjugation, which were elucidated with the *ab initio* MO calculation.⁴⁾ Our next goal was to elucidate the fragmentation mechanism of silacycloalkane ions, which is expected to be the effect of ring structures. Recently, we have studied the fragmentation of silacycloalkanes, that is, silacyclobutane, silacyclopentane, silacyclohexane and their 1-methyl and 1,1-dimethyl derivatives in EI mass spectrometry.⁹⁾ The fragmentation process of silacyclohexane is shown in Scheme 1.

Scheme 1.

The investigation in the fragmentation mechanism of silaspiroalkane ions has not been reported so far except for 4-silaspiro[3.3]heptane.⁸⁾ In addition, no investigation has been reported the *ab initio* MO calculation of silaspiroalkane ions. In the present

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Fig. 1. Molecular structures of silaspiroalkanes: (1) 6-silaspiro[5.5]undecane; (2) 5-silaspiro[4.5]decane; (3) 4-silaspiro[3.5]nonane; (4) 5-silaspiro[4.4]nonane; (5) 4-silaspiro[3.4]octane; (6) 4-silaspiro[3.3]heptane.

Scheme 2.

study, we have investigated the fragmentation processes of the six silaspiroalkane ions combined with four-, five-, and six-membered rings shown in Fig. 1.

2. Experimental

Each of compounds (1)–(5) was prepared according to the procedure of Dubac *et al.*,⁵⁾ using THF in place of ether. We transformed 1,1-dichloro-1-silacycloalkanes (a)–(c) into the silaspiroalkanes (1)–(5) with the diGrignard reagents $\text{BrMg}(\text{CH}_2)_m\text{MgBr}$, $m=4,5$ from the corresponding dibromoalkanes, $(\text{Br}(\text{CH}_2)_m\text{Br})$, $m=4,5$, in THF at 0°C according to the routes shown in Scheme 2. All compounds (1)–(5) were purified by gas chromatography.

The EI mass spectra of compounds (1)–(5) were measured using a Hitachi RMU-6M mass spectrometer operating at a pressure of ca. 10^{-7} Torr. The electron energies to ionize the above samples (1)–(5) were changed in the range of 10–70 eV in order to confirm the energy dependence of the fragmentation. Some metastable peaks (m^*) were observed in the EI mass spectra of compounds (1)–(5), which were produced due to the metastable decompositions in the first-field-free region (1st FFR). In addition, the

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Fig. 2. EI mass spectra of 6-silaspiro[5.5]undecane (1) at 70 eV and 12.5 eV.

Table 1. Metastable Decompositions of Silaspiroalkanes

Compound	Parent ion, m/z	Daughter ion, m/z	
		Measurement of $m^{*a)}$	B/E Linked scanning method
 (1)	168 $M^{+•}$	140 (116.7)	140, 126
	140	112 (89.6)	125, 112, 98
	112		97, 84
 (2)	154 $M^{+•}$	126 (103.1)	126, 98
	126	98 (76.2)	98
	98		83, 70, 55, 43
 (3)	140 $M^{+•}$	112 (89.6)	125, 112, 98
	112	84 (63.0)	97, 84
	84		69, 56, 43
 (4)	140 $M^{+•}$	112 (89.6)	125, 112, 98
	112	84 (63.0)	97, 84, 56
	84		69, 56, 43
 (5)	126 $M^{+•}$	98 (76.2)	111, 98, 84
	98	83 (70.3), 70 (50.0)	83, 70, 55, 43
	70		55, 43

^{a)} The value in parentheses is the apparent mass-to-charge ratio $m^*=m_2^2/m_1$ observed for the metastable decomposition: $m_1^+ \rightarrow m_2^+ + n$.

metastable decompositions in the 1st FFR were monitored by a constant B/E linked scanning technique using a Hitachi M-2000 mass spectrometer.

3. *Ab initio* MO Calculation

The equilibrium geometries of neutral molecules and their molecular cations for 4-

Fig. 3. EI mass spectra of 5-silaspiro[4.5]decane (2) at 70 eV and 12.5 eV.

silaspiro[3.5]nonane (3), 5-silaspiro[4.4]nonane (4), 4-silaspiro[3.4]octane (5), and 4-silaspiro[3.3]heptane (6) were calculated using the GAUSSIAN 88 and 92 programs.^{6), 7)} The 3-21G* and 3-21G basis sets have been used for the geometry optimization without applying any symmetry constraints because an appropriate basis set would be 3-21G for relatively large molecules, and a polarized 3-21G* basis set for small molecules in organosilicon compounds.^{1b)}

4. Results and Discussion

4.1 Mass spectra

6-Silaspiro[5.5]undecane. Figure 2 shows the EI mass spectra of 6-silaspiro[5.5]undecane at 70 eV and 12.5 eV. In this figure, the most abundant ion is the molecular ion at m/z 168. The m/z 140 ion was the second most abundant ion in the range of 10–70 eV. This means that a C_2H_4 loss from the molecular ion (M^{++}) is dominant in the range of 10–70 eV. In the 70 eV-EI mass spectrum of 6-silaspiro[5.5]undecane, the m/z 112 ion is also abundant, which is due to a C_2H_4 loss from $[M-C_2H_4]^{++}$. We confirmed the metastable decompositions for these processes from the detections of m^* and the detections of product ions by a constant B/E linked scanning technique. Table 1 shows the parent ions and product ions obtained from the observations of metastable decompositions. A metastable peak ($m^* 168 \rightarrow 140$; calcd. 116.7, obsd. 116.7) for a C_2H_4 loss from M^{++} , and a metastable peak ($m^* 140 \rightarrow 112$; calcd. 89.6, obsd. 89.6) for a C_2H_4 loss from $[M-C_2H_4]^{++}$ were observed in 6-silaspiro[5.5]undecane (1) (see Table 1).

The m/z 126 ion is produced due to a C_3H_6 loss from M^{++} ; the m/z 98 ion is due to a C_3H_6 loss from $[M-C_2H_4]^{++}$; the m/z 125 ion is due to a CH_3 loss from $[M-C_2H_4]^{++}$; and the m/z 97 ion is due to a CH_3 loss from $[M-2C_2H_4]^{++}$. All of these metastable decompositions were detected clearly by a B/E linked scan (see Table 1).

5-Silaspiro[4.5]decane. The observed EI mass spectra of 5-silaspiro[4.5]decane at 70 eV and 12.5 eV are given in Fig. 3. The most abundant ion is $[M-C_2H_4]^{++}$ at m/z 126. The m/z 98 ion is produced due to a C_2H_4 loss from $[M-C_2H_4]^{++}$. Figure 3 shows that the consecutive losses of two ethylene molecules from the molecular ion are dominant in the

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Fig. 4. EI mass spectra of 4-silaspiro[3.5]nonane (3) at 70 eV and 12.5 eV.

Fig. 5. EI mass spectra of 5-silaspiro[4.4]nonane (4) at 70 eV and 12.5 eV.

fragmentation process of 5-silaspiro[4.5]decane at the low energy electron bombardment (12.5 eV). In Table 1, a metastable peak ($m^* 154 \rightarrow 126$; calcd. 103.1, obsd. 103.1) for a C_2H_4 loss from $M^{+•}$, and a metastable peak ($m^* 126 \rightarrow 98$; calcd. 76.2, obsd. 76.2) for a C_2H_4 loss from $[M - C_2H_4]^{+•}$ were observed in compound (2). Table 1 shows that the m/z 70 ion is produced due to a C_2H_4 loss from $[M - 2C_2H_4]^{+•}$. From these results, we found that the consecutive losses of three ethylene molecules from the molecular ion occurred in metastable decompositions of a 5-silaspiro[4.5]decane ion.

From the result of a B/E linked scan, we find that the m/z 98 ion is produced due to a C_4H_8 loss from $M^{+•}$; the m/z 83 ion is due to a CH_3 loss from $[M - 2C_2H_4]^{+•}$; the m/z 55 ion is due to a C_3H_7 loss from $[M - 2C_2H_4]^{+•}$; and the m/z 43 ion is directly produced from $[M - 2C_2H_4]^{+•}$ (see Table 1). The peak intensities of these fragment ions become larger in the high energy bombardment. (See 70 eV-EI mass spectrum in Fig. 3.)

4-Silaspiro[3.5]nonane and 5-silaspiro[4.4]nonane. Figures 4 and 5 show the 70 eV- and 12.5 eV-EI mass spectra of 4-silaspiro[3.5]nonane (3) and 5-silaspiro[4.4]nonane

Fig. 6. EI mass spectra of 4-silaspiro[3.4]octane (5) at 70 eV and 12.5 eV.

(4), respectively. In the EI mass spectra of two silaspirononanes (3) and (4), there are large peaks at m/z 112 and 84. In Table 1, a metastable peak ($m^* 140 \rightarrow 112$; calcd. 89.6, obsd. 89.6) for a C_2H_4 loss from M^{+} , and a metastable peak ($m^* 112 \rightarrow 84$; calcd. 63.0, obsd. 63.0) for a C_2H_4 loss from $[M - C_2H_4]^{+}$ were observed in compounds (3) and (4). The metastable decomposition for another C_2H_4 loss from $[M - 2C_2H_4]^{+}$ was detected by a B/E linked scan (see Table 1).

In both of silaspirononanes (3) and (4), Table 1 shows that the m/z 125 ion is produced due to a CH_3 loss from M^{+} ; the m/z 98 ion is due to a C_3H_6 loss from M^{+} ; the m/z 97 ion is due to a CH_3 loss from $[M - C_2H_4]^{+}$; the m/z 69 ion is due to a CH_3 loss from $[M - 2C_2H_4]^{+}$; the m/z 43 ion is due to either or both of $SiCH$ and C_3H_5 losses from $[M - 2C_2H_4]^{+}$. In compound (4), the metastable decomposition for a C_4H_8 loss from $[M - C_2H_4]^{+}$ to produce the m/z 56 ion was detected clearly by a B/E linked scan (see Table 1).

4-Silaspiro[3.4]octane. Figure 6 shows the EI mass spectra of 4-silaspiro[3.4]octane (5) at 70 eV and 12.5 eV. There is only a large peak at m/z 98 except for the molecular ion peak (m/z 126) in the 12.5 eV-EI mass spectrum. In the 70 eV-EI mass spectrum of silaspirooctane, a large peak at m/z 70 appears. In Table 1, a metastable peak ($m^* 126 \rightarrow 98$; calcd. 76.2, obsd. 76.2) for a C_2H_4 loss from M^{+} , and a metastable peak ($m^* 98 \rightarrow 70$; calcd. 50.0, obsd. 50.0) for a C_2H_4 loss from $[M - C_2H_4]^{+}$ were observed in compound (5).

From the result of a B/E linked scan in Table 1, the m/z 111 ion is produced due to a CH_3 loss from M^{+} ; the m/z 84 ion is produced due to a C_3H_6 loss from M^{+} ; the m/z 83 ion is due to a CH_3 loss from $[M - C_2H_4]^{+}$. The m/z 55 ions are produced due to a C_3H_7 loss from $[M - C_2H_4]^{+}$ and due to a CH_3 loss from $[M - 2C_2H_4]^{+}$, that is, by two different processes. We detected two different processes to produce the m/z 43 ions: one is produced from $[M - C_2H_4]^{+}$, and the other is due to a C_2H_3 loss from $[M - 2C_2H_4]^{+}$ (see Table 1). In the former process, there are two possibilities, one or both of which could occur: one is a C_4H_7 loss from $[M - C_2H_4]^{+}$, and the other possibility is an SiC_2H_3 loss. These fragment ions appeared in the 70 eV-EI mass spectrum (see Fig. 6).

Table 2. Calculated UHF total energies for the neutral molecules (M) and molecular ions (M⁺⁺) of silaspiroalkanes (3)–(6)^{a)}

Compounds	3-21G*//3-21G*	3-21G*//3-21G	3-21G//3-21G
3	–598.049729	–598.048047	–597.958422
3 ⁺⁺		–597.775812	–597.691602
4	–598.073627	–598.072342	–597.985695
4 ⁺⁺		–597.784514	–597.701173
5	–559.225328		
5 ⁺⁺	–558.950955		
6	–520.376436		
6 ⁺⁺	–520.097394		

^{a)} Total energies are given in hartrees.

4.2 *Ab initio* MO calculation

Since the fragmentation in mass spectrometry starts from the molecular cation radical, we calculated the molecular cation radical by the *ab initio* MO method. The calculated total energies of the neutral molecules 3–6 and the molecular cations 3⁺⁺–6⁺⁺ are summarized in Table 2. The standard polarized split valence 3-21G* basis set was used for the geometry optimization of 3, 4, 5, 5⁺⁺, 6, and 6⁺⁺, and the 3-21G basis set was used for that of 3, 3⁺⁺, 4, and 4⁺⁺. The optimized energies of molecular ions were calculated using the 3-21G*//3-21G*, 3-21G*//3-21G, and 3-21G//3-21G basis sets. Table 2 shows that 5-silaspiro[4.4]nonane ion 4⁺⁺ is by 0.24 eV more stable than 4-silaspiro[3.5]nonane ion 3⁺⁺ at the 3-21G*//3-21G level of theory.

The optimized geometries of the neutral molecules 3–6 and the molecular cations 3⁺⁺–6⁺⁺ are shown in Fig. 7. Comparing the molecular cation with the neutral molecule, one of four Si–C bond distances is lengthened in compound (3)–(6). In 4-silaspiro[3.5]nonane (3), one of four Si–C bonds is lengthened from 1.89 Å in the neutral molecule (3a) to 2.63 Å in the molecular cation (3b). In 5-silaspiro[4.4]nonane (4), one of four Si–C bonds is lengthened from 1.90 Å in the neutral molecule (4a) to 2.46 Å in the molecular cation (4b). In 4-silaspiro[3.4]octane (5), one of four Si–C bonds is lengthened by 0.61 Å from 1.89 Å in the neutral molecule (5a) to 2.50 Å in the molecular cation (5b). In 4-silaspiro[3.3]heptane (6), one of four Si–C bonds is lengthened by 0.56 Å from 1.89 Å in the neutral molecule (6a) to 2.45 Å in the molecular cation (6b). From this result, we find that the initial bond fission occurs in an Si–C bond of the molecular ion. The cleavage of an Si–C bond in the smaller ring occurs more easily than that in the larger one since the strain energy on the smaller ring is larger.

4.3 The structures of molecular ions and the fragmentations of silaspiroalkane ions

In the EI mass spectra of the five silaspiroalkanes (1)–(5), it is common that the molecular ion peaks are higher than those of the corresponding alkylsilanes. As seen from Figs. 2–6, the relative intensity of the molecular ion decreases with the reduction of ring size in the silaspiroalkane. This means that the stability of the molecular ion depends on the ring size. The *ab initio* MO calculation showed that one of four Si–C bond distances is lengthened in compounds (3)–(6), comparing the molecular cation with

C ₁ -Si ₄ -C ₉ 119.4	Si ₄ -C ₁ -H ₁₀ 113.3	C ₇ -C ₆ -H ₁₈ 109.0
C ₃ -Si ₄ -C ₉ 121.9	Si ₄ -C ₁ -H ₁₁ 121.0	C ₇ -C ₆ -H ₁₉ 108.9
C ₅ -Si ₄ -C ₉ 104.2	Si ₄ -C ₂ -H ₁₂ 108.6	C ₈ -C ₇ -H ₂₀ 109.2
C ₁ -C ₅ -C ₆ 110.3	Si ₄ -C ₂ -H ₁₃ 143.0	C ₈ -C ₇ -H ₂₁ 108.7
Si ₄ -C ₉ -C ₈ 110.2	Si ₄ -C ₃ -H ₁₄ 121.0	C ₇ -C ₈ -H ₂₂ 108.9
C ₅ -C ₆ -C ₇ 112.7	Si ₄ -C ₃ -H ₁₅ 113.2	C ₇ -C ₈ -H ₂₃ 109.0
C ₆ -C ₇ -C ₈ 113.6	C ₆ -C ₅ -H ₁₈ 108.6	C ₈ -C ₉ -H ₂₄ 109.8
C ₇ -C ₈ -C ₉ 112.8	C ₆ -C ₅ -H ₁₇ 109.9	C ₈ -C ₉ -H ₂₅ 108.6

C₃-Si₄ 2.629

C ₁ -Si ₄ -C ₉ 126.4	Si ₄ -C ₁ -H ₁₀ 110.6	C ₇ -C ₆ -H ₁₈ 109.6
C ₃ -Si ₄ -C ₉ 109.7	Si ₄ -C ₁ -H ₁₁ 114.1	C ₇ -C ₆ -H ₁₉ 109.5
C ₃ -Si ₄ -C ₅ 105.1	C ₁ -C ₂ -H ₁₂ 110.0	C ₆ -C ₇ -H ₂₀ 109.8
C ₄ -C ₅ -C ₆ 109.1	C ₁ -C ₂ -H ₁₃ 109.7	C ₈ -C ₇ -H ₂₁ 108.1
Si ₄ -C ₉ -C ₈ 109.1	C ₂ -C ₃ -H ₁₄ 120.8	C ₇ -C ₈ -H ₂₂ 109.5
C ₆ -C ₇ -C ₇ 113.2	C ₂ -C ₃ -H ₁₅ 118.4	C ₇ -C ₈ -H ₂₃ 109.6
C ₅ -C ₇ -C ₈ 113.8	C ₆ -C ₅ -H ₁₆ 108.3	C ₈ -C ₉ -H ₂₄ 111.1
C ₇ -C ₈ -C ₉ 113.3	C ₆ -C ₅ -H ₁₇ 111.1	C ₈ -C ₉ -H ₂₅ 108.4

Si ₅ -C ₄ -H ₁₆ 110.2	C ₈ -C ₅ -H ₁₈ 110.2
Si ₅ -C ₄ -H ₁₇ 114.8	C ₇ -C ₈ -H ₂₃ 109.0

C ₂ -C ₃ 1.545	Si ₅ -C ₉ -C ₈ 102.3
Si ₅ -C ₄ 2.462	C ₂ -C ₃ -H ₁₅ 110.2
	C ₁ -C ₂ -C ₃ 109.5

C ₁ -C ₂ -C ₃ 100.1	C ₂ -C ₃ -Si ₄ 87.7
C ₁ -Si ₄ -C ₃ 79.7	C ₃ -Si ₄ -C ₈ 119.0
C ₁ -Si ₄ -C ₅ 123.8	Si ₄ -C ₁ -H ₉ 113.1
C ₂ -C ₁ -Si ₄ 87.7	C ₆ -C ₇ -C ₈ 107.8

C ₃ -Si ₄ 2.507	C ₁ -C ₂ -C ₃ 107.1
	C ₆ -C ₇ -C ₈ 108.5

Fig. 7. Optimized geometries of silaspiroalkanes: (3a) 4-silaspiro[3.5]nonane; (3b) 4-silaspiro[3.5]nonane cation; (4a) 5-silaspiro[4.4]nonane; (4b) 5-silaspiro[4.4]nonane cation; (5a) 4-silaspiro[3.4]octane; (5b) 4-silaspiro[3.4]octane cation; (6a) 4-silaspiro[3.3]heptane; (6b) 4-silaspiro[3.3]heptane ion. The 3-21G* basis set was used for (3a), (4a), (5a), (5b), (6a), and (6b). The 3-21G basis set was used for (3b) and (4b). Bond lengths in Å; bond angles in degrees.

the neutral molecule (see Fig. 7). From this result, we found that the initial bond fission occurred in an Si-C bond of the molecular ion. The cleavage of an Si-C bond in the smaller ring occurs more easily than that in the larger one. Since the strain on the smaller ring is larger, it can be predicted that the cleavage of an Si-C bond in the smaller ring occurs more easily than that in the larger one.

The EI mass spectra of silaspiroalkanes (1)–(5) have large peaks at m/z ($M-28$) and ($M-28 \times 2$). From this result, we conclude that the main decomposition process is the consecutive losses of two ethylene molecules. In relation to this result, it was reported that $\text{CH}_2=\text{Si}=\text{CH}_2^+$ is produced by the consecutive losses of two ethylene molecules from each ring in 4-silaspiro[3.3]heptane, which has two four-membered rings.⁸⁾ Moreover, we have already confirmed that a similar decomposition occurs in silacyclohexane⁹⁾; that is, the consecutive losses of two ethylene molecules were observed after the cleavage of an Si-C bond. On the other hand, only one C_2H_4 loss from the molecular ion occurs in silacyclopentane.⁹⁾ From these results, we expect that the consecutive losses of two ethylene molecules occur *via* the cleavage of an Si-C bond in each ring of silaspiroalkanes. In the case of 6-silaspiro[5.5]undecane (1), 5-silaspiro[4.5]decane (2), and 4-silaspiro[3.5]nonane (3) with a six-membered ring, the consecutive losses of two ethylene molecules may also occur in the same ring.

In compounds (1)–(4), the metastable decomposition for another C_2H_4 loss from $[\text{M}-2\text{C}_2\text{H}_4]^+$ was detected by a B/E linked scan (see Table 1). From this result, we found that the consecutive losses of three ethylene molecules from the molecular ion also occurred in metastable decompositions of these four silaspiroalkane ions.

As shown in Table 1, the methyl losses from the molecular ions of (3), (4), and (5) were found by a B/E linked scan, although each intensity was very weak. However, the corresponding metastable decompositions could not be observed. In addition, $[\text{M}-\text{CH}_3]^+$ did not also appear in the conventional EI mass spectra at 70 eV. This is expected to be a slow decomposition because a CH_3 loss from the molecular ion occurs *via* a hydrogen transfer.

In compounds (1)–(5), we observed a CH_3 loss from $[\text{M}-2\text{C}_2\text{H}_4]^{++}$ by a B/E linked scan. In compounds (1), (3), (4), and (5), we also found the metastable decompositions due to a C_3H_6 loss from M^{++} and due to a CH_3 loss from $[\text{M}-\text{C}_2\text{H}_4]^{++}$. The above mentioned CH_3 loss from $[\text{M}-\text{C}_2\text{H}_4]^{++}$ is expected to occur in the same ring as did the C_2H_4 loss.

5. Conclusion

The fragmentations of six silaspiroalkanes combined with four-, five-, and six-membered rings in EI mass spectrometry have been studied by a B/E linked scanning technique and an *ab initio* MO method. In the fragmentation of the five silaspiroalkane ions (1)–(5), the main decomposition process is the consecutive losses of two ethylene molecules which occur *via* the cleavage of an Si–C bond in each ring of silaspiroalkanes. Especially in the low energy region, this consecutive losses of two ethylene molecules occur preferentially. In compounds (1)–(4), we found the metastable decomposition for another C_2H_4 loss from $[\text{M}-2\text{C}_2\text{H}_4]^{++}$ by a B/E linked scan. From the *ab initio* MO calculation, we found that the initial bond fission occurred in an Si–C bond of the molecular ion. The cleavage of an Si–C bond in the smaller ring occurs more easily than that in the larger one, since the strain on the smaller ring is larger. We found the metastable decomposition due to a CH_3 loss from the molecular ions of silaspiro[3.5]nonane, silaspiro[4.4]nonane, and silaspiro[3.4]octane. This fragmentation occurs *via* a hydrogen transfer.

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Keywords

Silaspioundecane

Silaspirodecane

Silaspirononane

Silaspirooctane

Fragmentation mechanism

Ab initio MO calculation