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Mass spectra of 3,6-dihalo-4,4-dimethyl-1,4-selenasilafulvenes and 2,4-dihalo-2-dihalomethyl-3,3-dimethyl-1-selena-3-silacyclopent-4-enes

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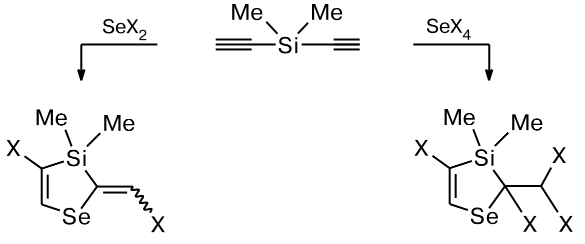
The behavior of new heterocyclic systems, *viz.*, 3,6-dihalo-4,4-dimethyl-1,4-selenasilafulvenes **1a,b** and 2,4-dihalo-2-dihalomethyl-3,3-dimethyl-1-selena-3-silacyclopent-4-enes **2a,b** (Hal = Cl, Br), was studied under conditions of electron ionization and thermal decomposition. Their fragmentation is accompanied by skeletal rearrangements, and the positive charge is localized mainly on ions containing silicon. Selenasilafulvenes **1a,b** form stable molecular ions. Selenasilacyclopent-4-ene **2a** decomposes partially and compound **2b** decomposes completely in the gas phase with the elimination of a hydrogen halide and a halogen molecules.

Key words: 3,6-dihalo-4,4-dimethyl-1,4-selenasilafulvene, 2,4-dihalo-2-dihalomethyl-3,3-dimethyl-1-selena-3-silacyclopent-4-ene, mass spectra, molecular ion, electron impact, fragmentation, rearrangement, elimination.

Electrophilic addition of organylselenyl halides to acetylenes is the main method for the synthesis of 2-halovinyl selenides.[1—3] The reaction of selenium tetrahalides with acetylene affords bis(2-halovinyl)selenium dihalides.[4] We have previously[5,6] studied the addition of the selenium tetra- and dihalides to diethynyldimethylsilane. These reactions unexpectedly gave earlier unknown heterocyclic systems: 3,6-dihalo-4,4-dimethyl-1,4-selenasilafulvenes **1a,b** and 2,4-dihalo-2-dihalomethyl-3,3-dimethyl-1-selena-3-silacyclopent-4-enes (**2a,b**).



1 **2**

X = Cl (**a**), Br (**b**)

In continuation of these studies,[7] we studied the fragmentation of these compounds under electron ionization and showed that the character of their decomposition is determined by the size and saturation extent of the heterocycle and the nature of halogen and its position in the ring.[8] The compounds under study contain exocyclic halogen atoms in both the heterocycle and side chain. In addition, the five-membered unsaturated heterocycle contains two endocyclic heteroatoms. Therefore, it seemed of interest to study specific features of the behavior of these compounds under electron ionization conditions.

Upon electron ionization, halogen-containing selenasilafulvenes **1a,b** form stable molecular ions, whose peaks are maximum. Their contributions* to the total ion current are 23.2 and 32.2%, respectively. In both cases, an intense peak of the $[M - Me]^+$ ion (10.4 and 7.4%) is observed, which is characteristic of compounds containing the dimethylsilyl group.[9—14] Other fragmentation ions can be divided into two groups.

The first group includes ions containing simultaneously halogen and silicon atoms: $[MeSiX_2]^+$, $[Me_2SiX]^+$, $[MeSi{=}C{=}CHX]^+$, and $[SiX]^+$ (X = Cl, Br). In the mass spectra of compounds **1a,b**, the peaks of these rearrangement ions are highly intense: their overall contribution to the total ion current is 27.4 and 31.5%, respectively (Table 1).

Trimethylsilyl esters of haloalcohols and halogen-substituted carboxylic acids[15] and halogen-containing 2-silanocaranes[16] are characterized by skeleton rearrangements caused by halogen atom migration to the silylic center. In this case, the bromodimethylsilycenium cation

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* The term "contribution" implies the ratio of the sum of peak intensities of all isotope varieties of the ion under consideration to the total ion current.

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Table 1. Main characteristic peaks in the mass spectra (70 eV) of 3,6-dihalo-4,4-dimethyl-1,4-selenasilafulvenes (**1a,b**) and 2,4-dihalo-2-dihalomethyl-3,3-dimethyl-1-selena-3-silacyclopent-4-enes (**2a,b**) and thermolysis products **3a,b** and **4a,b**

Ion, fragment	*m/z*[a] (*I* (%))						
	1a[b]	**1b**	**2a**	**3a**	**3b**[c]	**4a**[d]	**4b**[e]
$M^{+\cdot}$	258 (23.2)	346 (32.2)	328 (2.82)	258 (13.2)	346 (5.7)	293 (9.0)	424 (4.0)
$[M - Me]^+$	243 (10.4)	331 (7.4)	—	—	331 (0.8)	—	—
$[C_2HHalSe]^{+\cdot}$	140 (5.2)	184 (2.2)	140 (10.1)	140 (11.8)	184 (13.6)	140 (24.5)	184 (25.9)
$[MeSiHal_2]^+$	113 (6.2)	201 (5.7)	113 (6.1)	113 (9.2)	201 (12.0)	113 (14.4)	201 (14.2)
$[MeSiC_2HHal]^+$	103 (4.5)	147 (6.6)	103 (2.8)	103 (20.8)	147 (14.1)	103 (7.0)	147 (4.2)
$[Me_2SiHal]^+$	93 (10.3)	137 (11.6)	93 (23.6)	93 (10.8)	137 (14.1)	93 (10.3)	137 (15.1)
$[HalSi]^+$	63 (6.4)	107 (7.6)	63 (5.5)	63 (6.6)	107 (21.7)	63 (4.9)	107 (20.4)
C_4H_7Si	83 (2.0)	83 (5.8)	83 (1.0)	83 (2.6)	83 (2.8)	83 (1.0)	83 (1.3)
C_3H_3Si	67 (2.0)	67 (2.0)	67 (1.0)	67 (1.8)	67 (0.4)	—	67 (0.2)
C_3H_2Si	66 (1.3)	66 (1.4)	66 (3.3)	66 (1.3)	66 (0.3)	—	—
C_3HSi	65 (4.3)	65 (1.2)	65 (5.5)	65 (3.7)	65 (0.2)	65 (3.0)	65 (0.3)
C_2H_3Si	55 (1.7)	55 (2.8)	—	55 (1.2)	—	—	—
C_2HSi	53 (5.9)	53 (7.6)	53 (1.9)	53 (5.7)	53 (2.4)	53 (1.0)	53 (0.84)
CH_3Si	43 (3.4)	43 (4.5)	43 (0.7)	43 (2.2)	43 (0.3)	43 (0.6)	43 (0.2)
C_3H_3	39 (1.6)	39 (1.4)	39 (0.6)	39 (0.8)	39 (0.3)	39 (0.4)	39 (0.3)

[a] Calculated to the isotopes ^{35}Cl, ^{80}Se, and ^{79}Br.

[b] *m/z* (*I* (%)): 145 $[M - MeSiCl_2]^+$ (2.8), 105 $[Me_2SiCCl]^+$ (12.0), and 63 $[SiCl]^+$ (6.6).

[c] *m/z* (*I* (%)): 108—107 $[C_2H_4Se]^{+\cdot}$ + $[BrSi]^+$ (20.5), and 159 $[BrSe]^+$ (3.0).

[d] *m/z* (*I* (%)): 128 $[CHClSe]^+$ (13).

[e] *m/z* (*I* (%)): 159 $[BrSe]^+$ (5.7).

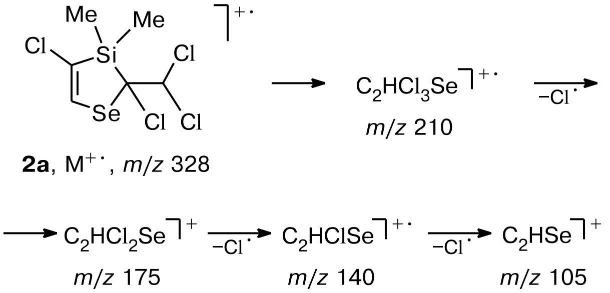
is formed *via* the β-elimination mechanism, which agrees with the known behavior of silyl-substituted *gem*-dihalocyclopropanes in solution.[17]

The second group contains silicon-containing ions without a halogen atom. Their overall contribution in the mass spectra of compounds **1a** and **1b** is 20.6 and 25.3%, respectively.

Thus, almost all fragmentation ions contain the silicon atom. Selenium-containing ions are mainly the molecular and $[M - Me]^+$ ions. Halogen-containing ions take more than 65% of the total ion current. The presence of heteroatoms in the fragment is confirmed by the ratio of intensities of isotope peaks of the considered ion. The routes of decomposition of compounds **1a,b** indicate that the halogen nature exerts no effect on the fragmentation character.

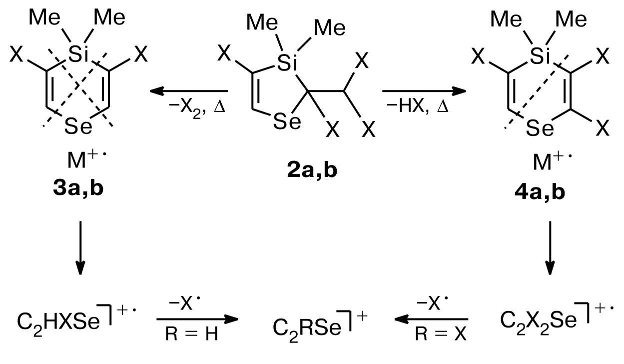
The additional introduction of two halogen atoms into a selenasilafulvene molecule affects substantially their reactivity in the gas phase. Four chlorine atoms possess strong electron-withdrawing properties and thus decrease the stability of the molecules to electron ionization. As a result, 2,4-dichloro-2-dichloromethyl-3,3-dimethyl-1-selena-3-silacyclopent-4-ene (**2a**) forms a low-intensity molecular ion, whose fragmentation direction is mainly related to the formation of silicon-containing rearrangement ions characteristic of the decomposition of selenasilafulvenes **1a,b** (see Table 1). The second direction of decomposition is caused by the C(2)—Si and C(5)—Se bond cleavage, resulting in the formation of the 2,2,3-trichloroselenirane radical cation with *m/z* 210. The further decomposition of this ion proceeds through the successive elimination of the chlorine atoms (Scheme 1).

Scheme 1



We failed to obtain the mass spectrum of bromine-containing analog **2b** by the direct injection of the sample into the ion source. The compound decomposed on transition to the gas phase at 170 °C. When $CHCl_3$ solutions of the studied compounds were chromatographically injected, 2,4-dihalo-2-dihalomethyl-3,3-dimethyl-1-selena-3-silacyclopent-4-enes **2a,b** decomposed in the injector of the chromatograph (250 °C) to eliminate molecules of halogen (intermediates **3a,b**) or hydrogen halide (intermediates **4a,b**, Scheme 2). Chlorine-containing selenasilacyclopentene **2a** decomposes only partially. Its chromatogram consists of three peaks corresponding to compound **2a** with $M^{+\bullet}$ = 328 (^{35}Cl, ^{80}Se) and intermediates **3a** with $M^{+\bullet}$ = 258 and **4a** with $M^{+\bullet}$ = 293. Bromine-containing analog **2b** decomposes completely and, therefore, its chromatogram contains only two peaks corresponding to intermediates **3b** with $M^{+\bullet}$ = 346 (^{79}Br^{80}Se) and **4b** with $M^{+\bullet}$ = 424.

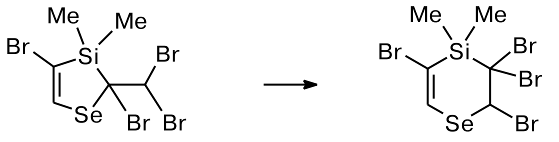
Scheme 2



X = Cl (**a**), Br (**b**)

Thermal reactions of ring expansion due to the exocyclic methylene group have been known long ago.[18—20] The molecular ions of selenasilafulvenes **1a,b** and intermediates **3a,b** are of the same values; however, their mass spectra differ, *i.e.*, these compounds are structural isomers. Probably, thermal decomposition produces stable unsaturated six-membered heterocycles (see Scheme 2).

The quantum-chemical calculations were carried out by the DFT(B3LYP)/LANL2DZ method and showed an insignificant difference between the total energies of molecules of the five-membered (**2b**) and six-membered (**2b′**) heterocycles (0.84 kcal mol^{-1}), which can indicate the easy transformation of the five-membered heterocycle into the six-membered one.



The proposed structures of thermolysis products **3a,b** and **4a,b** correspond to the data of their mass spectra. The stability of molecular ions of the formed intermediates is much lower than that of five-membered cycles **1a,b** (see Table 1). They decompose *via* two competitive routes. The main of them involves the formation of the indicated silicon-containing rearrangement ions, which are common for all intermediates and for studied molecules **1a,b**. The contribution of the ions formed upon the decomposition of compounds **3a,b** is higher than that in the case of **4a,b** (47.4, 61.9 and 36.6, 53.9, respectively, see Table 1).

The second direction is ring splitting into two parts with the C(3)—Si and C(6)—Se bond cleavage, and the charge is localized on the selenium-containing fragment. As a result, odd-electron ions $[C_2X_2Se]^{+\bullet}$ and $[C_2HXSe]^{+\bullet}$, respectively, are formed (see Scheme 2). This decomposition is characteristic of derivatives of cyclobutanes and saturated four-membered heterocycles in which the charge is localized on a part of the molecule with a lower ionization energy, which agrees with the Stevenson—Audier rule.[21—23] The mass spectra of intermediates **4a,b** show no peaks of ions formed by the C(2)—Se and C(5)—Si bond cleavage. However, this direction of decomposition cannot be excluded for analogs **3a,b**, because it also produces the radical cation $[C_2HXSe]^{+\bullet}$. Probably, this explains the high intensity of the ion, whose contribution is more than twofold higher than the contribution of a similar ion formed from intermediate **3b**. The $[C_2X_2Se]^{+\bullet}$ radical cation easily eliminates the halogen atom to form the stable ion $[C_2XSe]^+$ with the maximum intensity in the spectrum.

Thus, the decomposition of halogen-containing selenasilafulvenes **1a,b** and selenasilacyclopent-4-enes **2a,b** is associated with skeleton rearrangements, and the positive charge is localized mainly on the silicon atom. Selenasilacyclopent-4-ene **2a** decomposes partially and **2b** decomposes completely at 250 °C with the elimination of HX and X_2 molecules.

Experimental

Mass spectra were obtained on LKB-2091 and HP5971A GC-MS spectrometers (quadrupole analyzer). The energy of ionizing electrons was 70 eV. The direct and chromatographic injections of samples were used. For the direct injection, the temperature was selected in such a way to obtain a qualitative mass spectrum without the thermal destruction of the sample. The temperature of the ion source was 170 and 250 °C. Capillary columns of 25 m×0.5 mm with the OV-70 and SE-54 stationary liquid phases were used for the chromatographic injection. Helium served as the carrier gas, and the temperature-programmed regime from 50 to 240 °C with a rate of 8 deg min^{-1} was used. The injector temperature was 250 °C. Chromatograms were measured by the total ion current.

Quantum-chemical calculations were carried out by the DFT(B3LYP)/LANL2DZ density functional method with the complete optimization of the geometry using the GAUSSIAN-98 standard program package.[24]

The substances for the study (*Z*/*E*: **1a** 5 : 1; **1b** 6 : 1) were synthesized by known procedures.[5,6]

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