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FRAGMENTATION PATHWAYS OF SINGLY- AND DOUBLY-CHARGED IONS IN THE MASS SPECTRA OF Si-, N- AND C-SUBSTITUTED 1,3-DIOXA-6-AZA-2-SILACYCLOOCTANES

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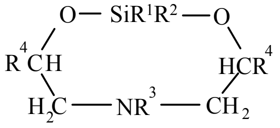
The fragmentation pathways of singly- and doubly-charged ions in the mass spectra of Si-, N-, and C-substituted 1,3-dioxa-6-aza-2-silacyclooctanes upon electron impact have been studied. The directions for the fragmentation of the singly- and doubly-charged molecular ions differ markedly. All the doubly-charged fragmentation ions are formed by the loss of neutral molecules from M^{++} *and contain nitrogen and silicon atoms.*

Keywords: 1,3-dioxa-6-aza-2-silacyclooctanes, singly- and doubly-charged ions, mass spectra.

The fragmentation pathways of singly-charged molecular ions of Si-, N-, and C-substituted 1,3-dioxa-6-aza-2-silacyclooctanes have been studied in rather considerable detail [1]. The mass spectra of these compounds were found to have numerous peaks for doubly-charged ions but no attempts have yet been undertaken to interpret these peaks. We studied the mass spectra of 11 1,3-dioxa-6-aza-2-silacyclooctanes (**1a-k**) in order to reveal common pathways for the decomposition of the doubly-charged molecular ions and compare them with the reported directions for the fragmentation of singly-charged molecular ions.



1a $R^1 = R^2 = R^3 = Me$, $R^4 = H$; **b** $R^1 = Ph$, $R^2 = R^3 = Me$, $R^4 = H$; **c** $R^1 = Ph$, $R^2 = OMe$; $R^3 = Me$, $R^4 = H$; **d** $R^1 = R^2 = Ph$, $R^3 = Me$, $R^4 = H$; **e** $R^1 = R^2 = Ph$, $R^3 = R^4 = H$; **f** $R^1 = R^2 = Me$, $R^3 = Ph$, $R^4 = H$; **g** $R^1 = R^2 = R^3 = R^4 = Me$; **h** $R^1R^2 = CH_2CH{=}CHCH_2$, $R^3 = R^4 = Me$; **i** $R^1R^2 = CH_2CH{=}CHCH_2$, $R^3 = Et$, $R^4 = H$; **j** $R^1R^2 = CH_2CH{=}CHCH_2$, $R^3 = Pr$, $R^4 = H$; **k** $R^1 = R^2 = R^3 = Me$, $R^4 = CF_3$

While the peaks of the singly-charged molecular ions are present in the spectra of all the compounds studied **1a-k**, the peak of the doubly-charged molecular ion with *m/z* 149.5 (299^{++}) is observed only in the mass spectrum of **1d**. The decomposition pathways of the singly-charged molecular ions of heterocycles **1a-g**, in which the silicon atom is not spirocyclic, have been described in detail [1, 2]. Thus, here we only examine the

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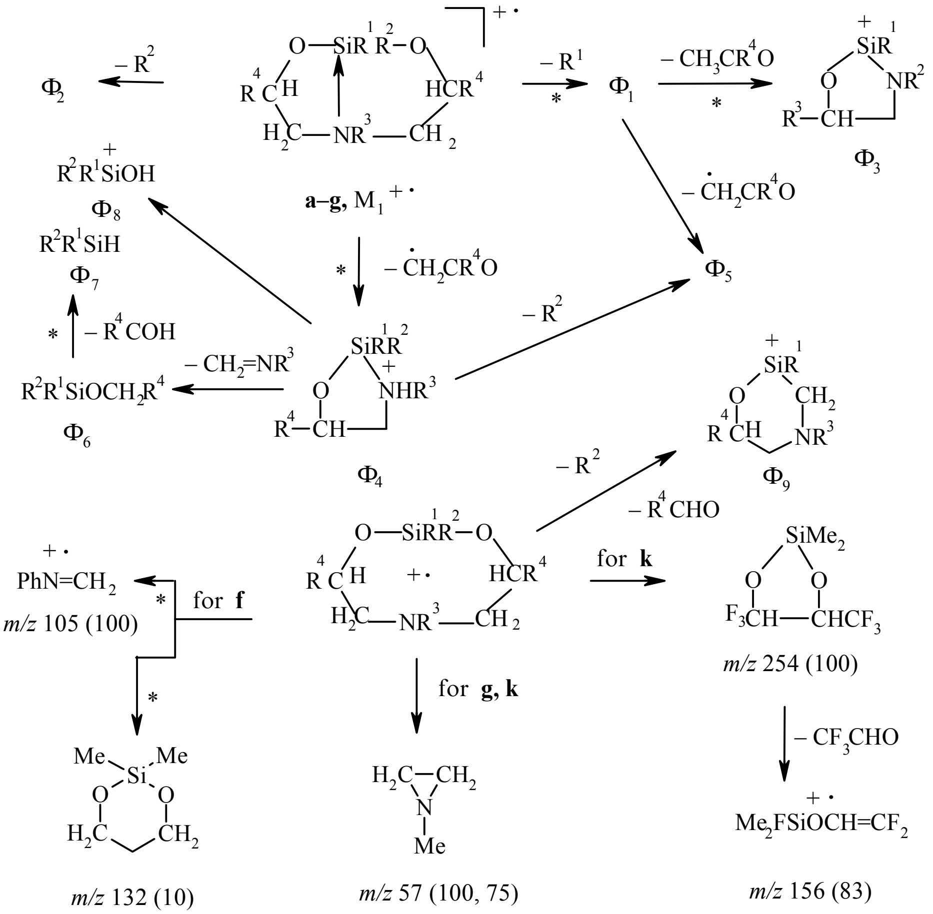
major fragmentation pathways relative to the criteria for analyzing transannular interaction in the gas phase developed in our previous work [3, 4].

A common decomposition pathway for the singly-charged molecular ions of heterocycles **1a-g** is consecutive loss of one of the substituents at the silicon atom as a free radical and neutral CH_3CR^4O molecule to form ions $Φ_1$ and $Φ_3$, respectively (Scheme 1). The probability of loss of a phenyl radical is much higher than for the methyl radical, which is characteristic for pentacoordinated silicon derivatives [3].

Scheme 1



If there is at least one methyl group at the silicon atom in **1a-g**, as in the case of methylsilatrane [3], radical $CHCR^4O$ is lost from the singly-charged molecular ion, leading to ion $Φ_4$, which then consecutively loses neutral molecules of methylenimine and aldehyde, converting to ions $Φ_6$ and $Φ_7$ (scheme 1). The fragmentation of ion $Φ_4$ leads to hydroxysilicenium cation $Φ_8$. In accord with [3], the formation of all these ions indicates that the bicyclic form $[M_1]^{+\cdot}$ of molecular ions of **1a-g** exists in the gas phase. This form features an Ni→Si dative bond. Additional evidence for this conclusion lies in the finding that, of fragments $[M - R^4CHO]^{+\cdot}$, $[M - R^1 - R^4CHO]^{+\cdot}$, and $[M - R^2 - R^4CHO]^{+\cdot}$ typical for the decomposition of the monocyclic form of $[M]^{+\cdot}$ of the molecular ions [4], the first two fragments are lacking in the spectra of **1a-g**, while the latter is observed only for R^2 = Me (ion $Φ_9$ in Scheme 1 and Table 1).

The resonance interaction of the phenyl group with the nitrogen atom in **1f** stabilizes the monocyclic form $[M]^{+\cdot}$. Thus, the largest peak in the spectrum for this compound is found for the pseudomolecular ion of N-phenylmethylenimine with *m/z* 105. The peak for $[M - PhN{=}CH_2]^{+\cdot}$ with *m/z* 132 is also found in the spectrum

TABLE 1. Values of Relative Intensity, *m/z* (%) for Singly-charged Ions in the Mass Spectra of **1a-g**

Ion	**a**	**b**	**c**	**d**	**e**	**f**	**g**
M^+	175 (48)	237 (10)	253 (15)	299 (1)	285 (0.2)	237 (83)	203 (26)
Φ_1		160 (100)	176 (100)				
Φ_2		222 (25)	222 (9)				
Φ_3	116 (16)	116 (10)	132 (8)	178 (7)	164 (7)	178 (10)	130 (9)
Φ_4	132 (12)	194 (3)	210 (5)	—	—	194 (2)	146 (3)
Φ_5	117 (100)	179 (15)	—	—	—	179 (2)	131 (2)
Φ_6	89 (44)	151 (21)	167 (39)	213 (5)	213 (3)	89 (18)	103 (2)
Φ_7	59 (12)	121 (11)	137 (20)	183 (15)	183 (4)	59 (7)	59 (9)
Φ_8	75 (15)	137 (8)	153 (4)	199 (2)	199 (3)	75 (10)	75 (19)
Φ_9	130 (11)	192 (4)	192 (1)	—	—	192 (8)	144 (8)

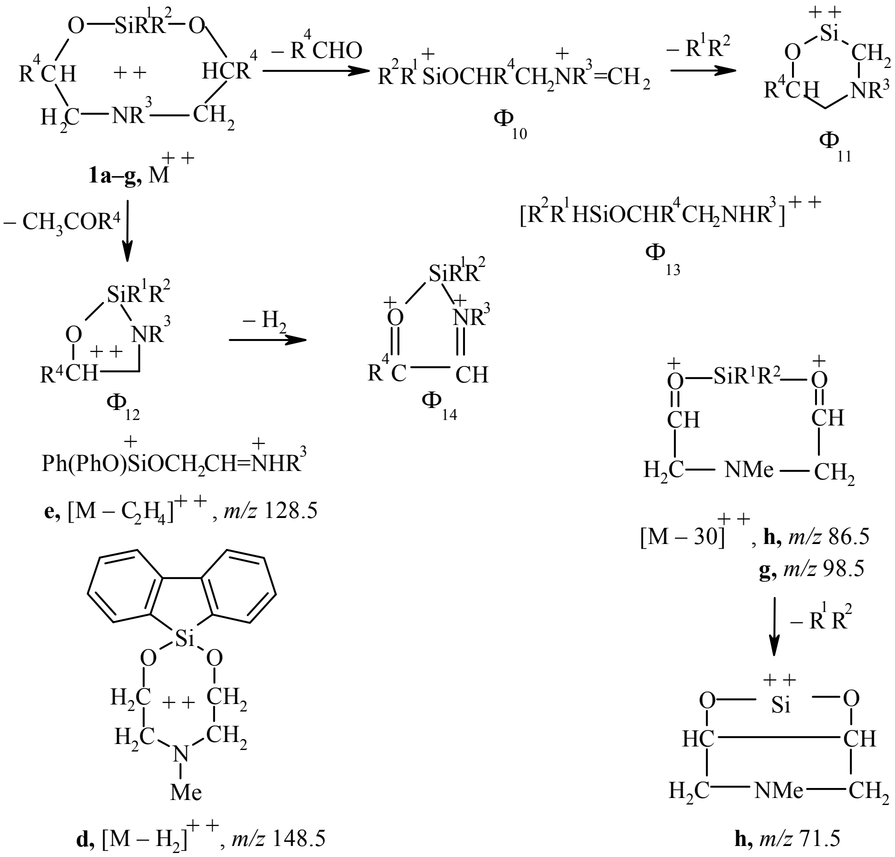
of **1f**. The bulky substituents at $C_{(4)}$ and $C_{(8)}$ in molecule **1g** hinder transannular interaction. Thus, the major peak in the spectrum of this compound is the pseudomolecular ion of N-methylaziridine with *m/z* 57 (the peak for ion $[M - 57]^{+\cdot}$ with *m/z* 146 overlaps the peak for ion Φ_4). The correctness of the assumption that the bulk of the substituents at $C_{(4)}$ and $C_{(8)}$ affects the ratio of the monocyclic $[M]^{+\cdot}$ and bicyclic $[M_1]^{+\cdot}$ forms of the molecular ion was indicated by the mass spectrum of **1k**, where $R^1 = R^2 = R^3$ = Me and $R^4 = CF_3$. The three major peaks in the spectrum of this compound correspond to ions $[M - C_2H_4NMe]^+$ with *m/z* 254 (100%), $[C_2H_4NMe]^{+\cdot}$ with *m/z* 57 (75%), and $[M - C_2H_4NMe - CF_3CHO]^+$ with *m/z* 156 (83%). All these ions are formed from the monocyclic form of the molecular ion $[M]^{+\cdot}$ with *m/z* 311 (42%). This also accounts for the high intensity of the peak for $[M - H]^+$ with *m/z* 310 (22%) characteristic for methylamine derivatives. The peaks for ions Φ_3–Φ_6 formed from the bicyclic form of the molecular ion $[M1]^{+\cdot}$ are virtually lacking in the spectrum of **1e**. Of the other fragmentation ions, we should note $[M - Me]^+$ with *m/z* 296 (46%) and $[M - CF_3]^+$ with *m/z* 242 (14%). Derivative **1k** is the only example among the heterocycles studied to give a spectrum lacking peaks for doubly-charged ions. This failure may be related to diminished electron density on the ring atoms due to the strong inductive effect of the trifluoromethyl substituents. The mass spectra of **1a-k** are represented in Table 1 and Scheme 1.

The decomposition of the doubly-charged molecular ions of **1a-g** proceeds differently. This occurs because the probability of forming the bicyclic forms in these electron-deficient ions is diminished due to the N→Si dative bond. A common direction for the decomposition of ions $[M]^{++}$ of heterocycles **1a-g** is the consecutive loss of neutral molecules R^4CHO and R^1,R^2, leading to ions Φ_{10} and Φ_{11}, respectively (Scheme 2). Ion Φ_{10} loses not a diphenyl molecule but rather a benzene molecule, leading to $[M - H_2CO - C_6H_6]^{++}$ with *m/z* 88.5, only in the case of compound **1e** containing an endocyclic NH group. Both processes are observed in the spectrum of **1d**· Ion Φ_{10} $[M - H_2CO]^{++}$ eliminates both a diphenyl molecule to give ion Φ_{11} and a benzene molecule, converting to an ion with *m/z* 95.5. The loss of benzene also proceeds directly from $[M]^{++}$ to give an ion with *m/z* 110.5. The peaks of these ions have high intensity for doubly-charged ions (2-7%), while the intensity of ion Φ_{11} with *m/z* 57.5 in the spectrum of **1a** reaches even 15%. The peaks of ions Φ_{12} $[M - CH_3CH]^{++}$ have intensity of about 0.5%. The scission of the same bonds accompanied by the migration of two hydrogen atoms to the charged fragment leads to ion Φ_{13} $[M - CHCO]^{++}$. Ion Φ_{14} is the product of the dehydrogenation of ion Φ_{12} (Scheme 2). The *m/z* values and relative intensities of these ions are given in Table 2.

TABLE 2. *m/z* Values of Doubly-charged Ions in the Mass Spectra of **1a-g**

Ion	**a**	**b**	**c**	**d**	**e**	**f**	**g**
M^{++}	—	—	—	149.5	—	—	—
Φ_{10}	72.5	103.5	111.5	134.5	127.5	103.5	79.5
Φ_{11}	57.5	57.5	57.5	57.5	—	88.5	64.5
Φ_{12}	65.5	96.5	—	127.5	—	96.5	72.5
Φ_{13}	66.5	97.5	—	—	—	97.5	—
Φ_{14}	64.5	—	—	—	—	95.5	—

Scheme 2



Peaks for doubly-charged ions are found in the spectra of some compounds, which are lacking in the spectra of others. Thus, the spectrum of **1c** features a peak for ion $[M - 2H_2CO]^{++}$ with *m/z* 96.5 formed as the result of loss of a formaldehyde molecule from ion Φ_{10} due to the OCH_2 group attached to the silicon atom.

The spectrum of **1d** has a peak for ion $[M - H_2]^{++}$ with *m/z* 148.5 arising from the dehydrocondensation of the two phenyl substituents leading to a silafluorene species. A peak for ion $[M - C_2H_4]^{++}$ with *m/z* 128.5 is found for **1e** with high intensity (4%).

The formation of this ion is likely accompanied by migration of a phenyl substituent from the silicon atom to an oxygen atom (Scheme 2). There are no peaks for ions $[M - C_2H_4]^{++}$ in the spectra of compounds **1a** and **1f** but peaks are found for ions $[M - C_2H_4 - H_2CO]^{++}$ with *m/z* 58.5 and 89.5, respectively. Finally, the spectrum of **1g** features a strong peak for ion $[M - 2CH_3]^{++}$ with *m/z* 86.5. We might have assumed that this ion arises due to loss of the two substituents at the silicon atom, R^1 and R^2, although the presence of ion

$[M - 2CH_3]^{++}$ with *m/z* 98.5 in the spectrum of **1h**, in which there are no methyl groups at the silicon atom, indicates that the formation of both these ions is related to loss of two C-methyl substituents.

The pathways for the decomposition of the singly-charged molecular ions of spirocyclic derivatives **1h-j** has been examined in detail by Bochkarev et al. [5]. Low-intensity peaks are found for ions $[M - R_4CHO]^{++}$ as well as $[M - CH_3]^{+}$ in the spectrum of **1i** and $[M - C_2H_5]^{+}$ in the case of **1j** formed from the molecular ion form lacking an N→Si bond. This also holds for ions $[M - CH_3CR^4O]^{+\cdot}$. The major direction in the decomposition of singly-charged molecular ions of **1h-j** begins with the loss of a butadiene molecule and formation of ion Φ^{15} $[M - R^1R^2]^{+\cdot}$, where $R^1+R^2 = C_4H_6$. Analogous decomposition is found for cyclosiloxanes containing endocyclic silacyclopentane units [6]. Elimination of ethylene or propylene from the alkyl substituent at the nitrogen atom leading to ion Φ_{16} occurs in the decomposition of **1i** and **1j**. The loss of these molecules also occurs directly from the molecular ions of **1i** and **1j** to give ion Φ_{17} (Scheme 3). The *m/z* values and relative intensities of these ions are given in Table 3.

On the other hand, there is no peak for ion $[M - C_4H_6]^{++}$ in the mass spectra of the doubly-charged ions for **1h-j**. The decomposition of these heterocycles proceeds through a special scheme, which will be examined separately.

The formation of ion $[M - 2CH_3]^{++}$ with *m/z* 96.5 in the spectrum of **1h** was mentioned above. The loss of a butadiene molecule from this ion leads to a fragment with *m/z* 71.5 (scheme 2). The spectrum of **1h** also has a peak for ion Φ_{10} $[M - CH_3CHO]^{++}$ with *m/z* 91.5. The decomposition of $[M]^{++}$ for compound **1i** is reminiscent the decomposition of heterocycles **1a-g** and the corresponding spectrum has peaks for ions Φ_{10} $[M - H_2CO]^{++}$ with *m/z* 91.5 and Φ_{11} $[M - H_2CO - C_4H_6]_{++}$ with *m/z* 64.5. The spectrum of **1j** has peaks for ions Φ_{15} $[M - CH_2CO]^{++}$ with *m/z* 92.5 and Φ_{12} $[M - CH_3CHO]^{++}$ with *m/z* 64.5.

Scheme 3

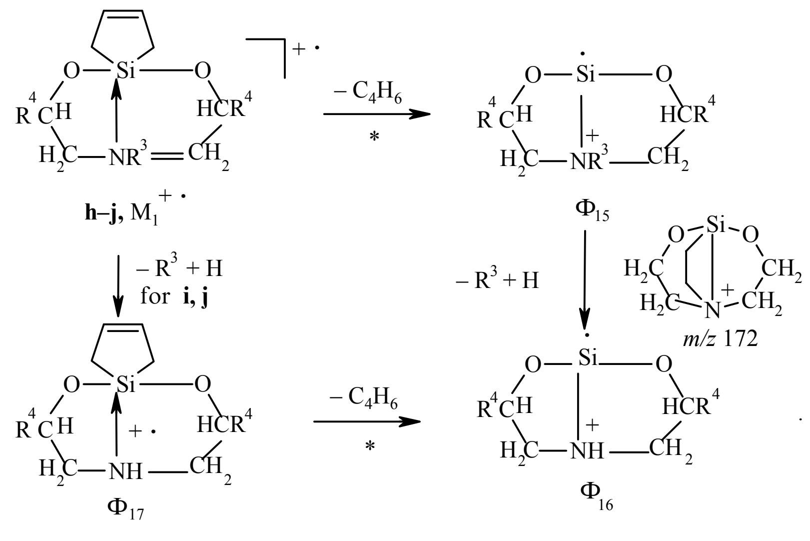


TABLE 3. *m/z* Values and Relative Intensities (%) of Singly-charged Ions in the Mass Spectra of **1h-j**

Ion	h	i	j
$M^{+\cdot}$	227 (91)	213 (40)	227 (50)
Φ_{15}	173 (100)	159 (22)	173 (23)
Φ_{16}	—	131 (100)	131 (100)
Φ_{17}	—	185 (8)	185 (28)

Thus, the directions of the electron impact fragmentation of the singly- and doubly-charged molecular ions of Si-, N-, and C-substituted 1,3-dioxa-6-aza-2-silacyclooctanes differ markedly. All the doubly-charged fragment ions are formed as the result of the loss of neutral molecules from $[M]^{++}$ and contain the nitrogen and silicon atoms.

EXPERIMENTAL

The mass spectra were taken on an MKh-1303 mass spectrometer with direct sample inlet into the ion source at 250°C. The ionizing electron energy was 70 eV. Samples of **1a-k** were prepared according to Lukevics et al. [7].

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