DISINTEGRATION OF 1-SILALACTONES UNDER THE INFLUENCE OF ELECTRON IMPACT

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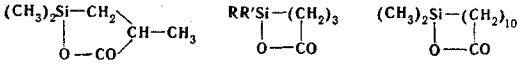
It is shown that the paths of fragmentation of 1-silalactones under the influence of electron impact are determined by the ring size and remain virtually unchanged when the methyl groups attached to the silicon atom are replaced by a chlorine atom or an ethyl group. The possibility of the identification of isomeric silalactones on the basis of their mass spectra was established.

The present communication is devoted to a study of the paths of disintegration of previously synthesized [1, 2] silalactones (I-III) under the influence of electron impact and to the exposure of the possibility of the identification of compounds of this class on the basis of their mass spectra.



I

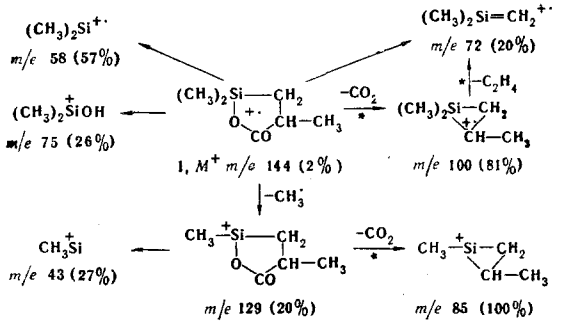
II a–c

III

II a $R = R' = CH_3$; b $R = CH_3$, $R' = Cl$; c $R = C_2H_5$, $R' = Cl$

The mass spectra of all of the investigated compounds contain molecular ion peaks of low intensity (~1%). The peaks of the $(M-1)^+$ ions have intensities of the same order. The fragmentation of five-membered lactone I is very simple. Two of the most intense peaks in the spectrum correspond to ions formed during ejection of a CO_2 molecule from the molecular ion and from the $(M-Me)^+$ ion with m/e 129 (the loss of a methyl group from the silicon atom is characteristic for the methyl derivatives of silicon-containing heterocycles [3, 4]). The formation of the remaining ions in the spectrum of I (the structures, m/e values, and relatiive intensities of these ions are presented in Scheme 1) requires no commentary. The elimination of CO_2 from the silalactones is similar to the ejection of SO_2 from silasultines during electron impact [5].

Scheme 1†



† The transitions denoted with an asterisk are confirmed by the presence of the corresponding metastable peaks. Ions of low mass numbers may arise not only directly from the molecular ion but also in several steps.

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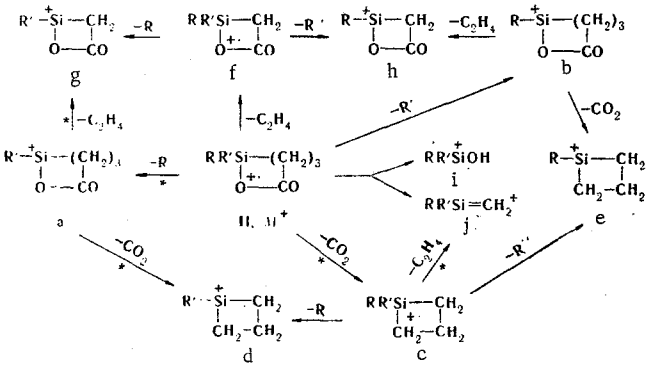
TABLE 1. m/e Values (relative intensities, %) of the Characteristic Ions in the Mass Spectra of Six-Membered Silalactones IIa-c

Ion	IIa	IIb*	IIc
M^+	144 (1)	164 (2)	178 (1)
$(M-1)^+$	143 (1)	163 (1)	177 (1)
a	129 (12)	149 (1)	149 (4)
b		129 (1)	143 (3)
c	100 (35)	120 (60)	134 (64)
d		105 (9)	105 (13)
	85 (8)		
e		85 (2)	99 (1)
f	116 (98)	136 (25)	150 (42)
g		121 (15)	121 (52)
	101 (65)		
h		101 (5)	115 (5)
i	75 (16)	95 (25)	109 (22)
j	72 (100)	92 (100)	106 (100)

*The m/e values for Cl^{35} are given for the chlorine-containing ions. The ratios of the intensities of the isotopic peaks are in agreement with the calculated values in all cases.

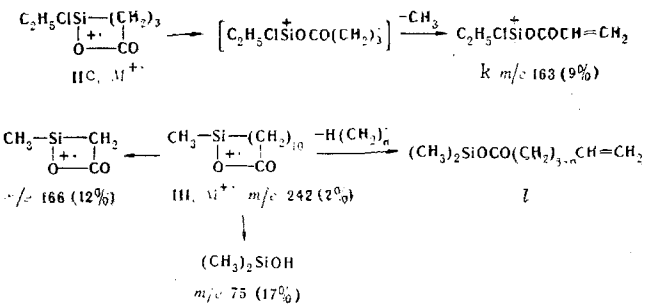
All of the ions characteristic for I are present in the mass spectrum of six-membered lactone IIa, which is the isomer of five-membered lactone I. Despite this, isomeric lactones I and IIa can be reliably distinguished on the basis of the mass spectra, inasmuch as a new type of fragmentation associated with ejection of a neutral particle with mass 28 amu from the molecular ion and the $(M-Me)^+$ ion with m/e 129 appears in the case of IIa. This particle may be ethylene or CO. A similar process was also observed in the mass spectra of silacycloketones with no less than six links in the ring, and it was shown [6] by means of

Scheme 2



the high-resolution mass spectra that this fragmentation path is due practically completely to the elimination of ethylene. Inasmuch as lactone IIa is structurally similar to the silacycloketones studied in [6], we assume that loss of an ethylene molecule is also observed in the mass spectra of lactones of the II type. A comparison of the mass spectra of IIa-c shows that a change in the nature of the substituents attached to the silicon atom does not have a substantial effect on the fragmentation paths. The structures of the characteristic ions in the mass spectra of six-membered lactones IIa-c are presented in Scheme 2, while the m/e values and relative intensities are presented in Table 1. In addition to the ions indicated in Table 1, the spectrum of IIc contains monochloro fragments $(i-C_2H_4)$ with m/e 81 (18%) and $(j-C_2H_4)$ with m/e 78 (28%), the development of which is associated with ejection of an ethylene molecule from the ethyl substituent, i.e., with conversion of the ethyl form to the hydride form. One should also note the presence in the spectrum of IIc of the $(M-15)^+$ ion with m/e 163 (9%). Inasmuch as methyl substituents attached to the silicon atom are absent in this compound, while the loss of a methyl radical from an ethyl substituent attached to a silicon atom is usually not observed, the development of this ion should be explained by ring cleavage with conversion to structure k (see Scheme 3). Ions of this type are probably also formed in the spectra of IIa, b, but they are superimposed by ions a.

Scheme 3



$n=1$, m/e 227 (11%); $n=2$, m/e 213 (5%); $n=3$, m/e 199 (15%); $n=4$, m/e 185 (17%); $n=5$, m/e 171 (9%); $n=6$, m/e 157 (4%); $n=7$, m/e 143 (9%); $n=8$, m/e 129 (100%).

Fragmentation with ring opening prevails for macrocyclic lactone III. Most of the fragment ions in the spectrum of III have structures described by general formula *l* (see Scheme 3). The structures, m/e values, and relative intensities of the characteristic ions in the mass spectrum of III are presented in Scheme 3.

One should also note that the peak with m/e 227 is a composite: an ion of the *l* type (n = 1) and an $(M-Me)^+$ ion, formed as a result of detachment of a methyl radical from the silicon atom, are superimposed

The mass spectra were recorded with an MKh-1303 mass spectrometer at 200°C and an ionizing voltage of 30 V.

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