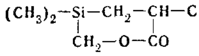
MASS SPECTROMETRIC STUDY OF 2- AND 4-SILALACTONES

V. N. Bochkarev, N. S. Fedotov,
I. G. Rybalka, and Z. F. Mironov

UDC 543.51:547.245'8'892'896

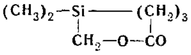
In contrast to the previously investigated 1-silalactones, ejection of a CO_2 molecule from the molecular ion is not characteristic in the disintegration of 2- and 4-silalactones under electron impact. Migration of the silicon atom to the oxygen atom during fragmentation of the 2- and 4-silalactones was observed. The dependence of the paths of disintegration of the silalactones on the ring size and the number of methylene links was established. The possibility of the identification of isomeric 2-silalactones on the basis of their mass spectra was observed.

We have previously investigated [1] the paths of fragmentation of 1-silalactones under electron impact. It seemed of interest to ascertain the effect of the introduction of one or several links between the silicon atom and the ester oxygen atom on the direction of the mass-spectral disintegration of silalactones In order to achieve this, we investigated the mass spectra of isomeric 2-silalactones I and II, which differ with respect to ring size, and silalactone III.



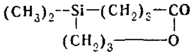
$$\begin{array}{l}(CH_3)_2-Si-CH_2-CH-CH_3\\ \qquad\quad\;\, | \qquad\quad\;\; |\\ \qquad\;\;\; CH_2-O-CO\end{array}$$

I



$$\begin{array}{l}(CH_3)_2-Si——(CH_2)_3\\ \qquad\quad\;\, | \qquad\quad\;\; |\\ \qquad\;\;\; CH_2-O-CO\end{array}$$

II



$$\begin{array}{l}(CH_3)_2-Si-(CH_2)_3-CO\\ \qquad\quad\;\, | \qquad\qquad\quad\;\; |\\ \qquad\;\; (CH_2)_3——O\end{array}$$

III

The molecular ion peaks are practically absent in the mass spectra of I-III, but peaks of $(M-1)^+$ions, the formation of which is associated with α cleavage with respect to the ester oxygen atom, and peaks of $(M-CH_3)^+$ ions, which arise as a result of elimination of a methyl radical from the silicon atom, are observed in all cases. The mass spectrum of six-membered 2-silalactone I differs sharply from the previously investigated spectra of 1-silalactones [1] with respect to the absence of an $(M-CO_2)$ peak and the presence of a maximally intense peak of an ion with m/e 88 (see scheme 1). The ejection of a formaldehyde molecule from this ion leads to an ion with a dimethylsilene structure with m/e 58. The $88^+ \to 58^+$ transition is confirmed by the presence of a metastable peak with m* 38.8 (calculated value 38.2). An ion with m/e 115, $(M-CH_3-28)^+$, is observed in the spectrum of I. Inasmuch as it has been shown [1] that the ejection of an ethylene molecule is not characteristic for silalactones in which the silicon atom and the carbonyl group are separated by two carbon atoms, it can be assumed that this ion is formed as a result of

TABLE 1. Relative Intensities (%) of the Characteristic Ions in the Mass Spectra of Isomeric 2-Silalactones I and II

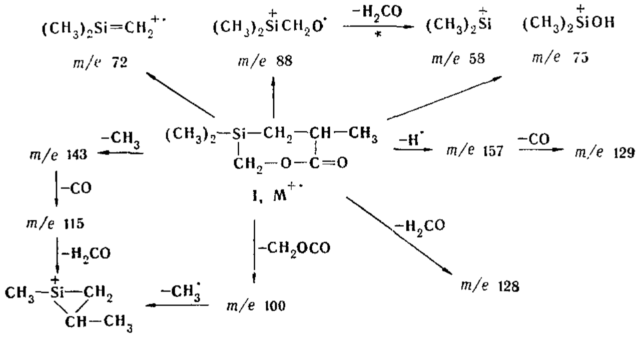
m/e	157	143	130	129	128	115	113	100	88	85	75	72	58
I	1	7	—	3	3	37	15	7	100	22	7	11	61
II	4	15	24	31	9	74	—	56	36	32	25	100	54

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 910-912, July, 1974. Original article submitted June 14, 1973.

©1976 Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for $15.00.

elimination of a CO molecule from the $(M-CH_3)^+$ ion (a process analogous to the ejection of SO during the fragmentation of silasultines [2]).

Scheme 1

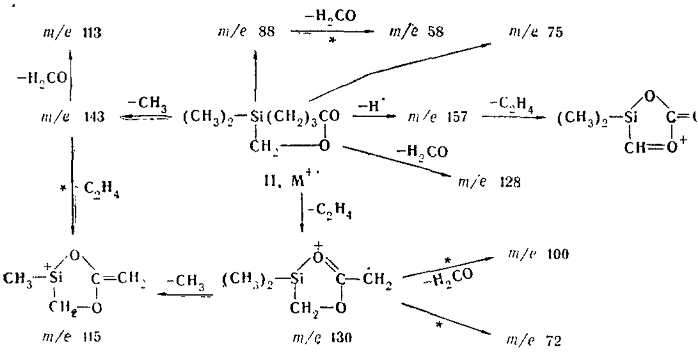


The subsequent loss of a formaldehyde molecule leads to an ion with m/e 85. An ion with m/e 72 may arise as a result of simple cleavage of two ring bonds in the molecular or fragment ions containing the $-(CH_3)_2\overset{+}{Si}CH_2-$group. The $(CH_3)_2\overset{+}{Si}OH$ ion with m/e 75 is a rearranged ion. Migration of the distant silicon atom to the oxygen atom was observed previously in the mass spectra of silacycloketones and in the mass spectrum of methyl 4-trimethylsilylbutyrate [4]. It is possible that similar migration also occurs during the formation of the ion with m/e 128, $(M-H_2CO)^+$. The paths of the formation and the m/e values of the characteristic ions in the mass spectrum of I are presented in scheme 1, while the relative intensities are presented in Table 1.

The mass spectrum of II, which is an isomer of silalactone I, contains peaks of two ions that are not observed in the spectrum of I: the $(M-CH_3-H_2CO)^+$ ion with m/e 113, and an ion with m/e 130. The development of the latter is due to the elimination of an ethylene molecule from the molecular ion, which is characteristic for compounds in which the carbonyl group and the silicon atom are separated by three methylene groups [1, 3]. It was shown that in this case the silicon atom migrates to the carbonyl oxygen atom (see scheme 2). The m/e values of the rest of the ions in the spectra of II and I are identical, but the relative intensities differ sharply (see Table 1).

The ion peak with m/e 72 in the spectrum of silalactone II is a maximum peak; this is explained by the development of this ion from the ion with m/e 130 as a result of loss of the $-CH_2CO_2-$group.

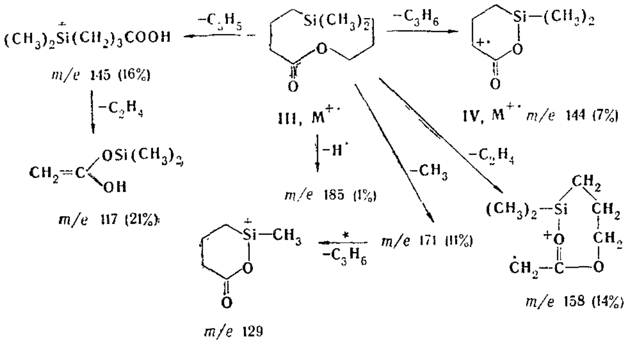
Scheme 2



The sharp increase in the intensity of the ion with m/e 115 is associated with the possibility of ejection of an ethylene molecule from the $(M-CH_3)^+$ ion with m/e 143. In this case, the silicon atom migrates to the carbonyl oxygen [3]. The $130^+ \rightarrow 72^+$ and $143^+ \rightarrow 115^+$ transitions are confirmed by the presence of the corresponding metastable peaks. The paths of formation and the m/e values of the characteristic ions in the mass spectrum of II are presented in scheme 2, while the relative intensities are presented in Table 1.

Ion peaks with m/e 185, 171, 158, 145, and 117 are observed in the mass spectrum of 4-silalactone III. The structures of these ions and their relative intensities are presented in scheme 3.

Scheme 3



In addition, the spectrum of III contains peaks of all of the ions characteristic for the spectrum of 1-silalactone IV. These are the ion peaks with m/e 144 (7%), 143 (12%), 129 (36%), 116 (22%), 101 (100%), 100 (5%), 75 (63%), 72 (19%), and 58 (3%), the structures and the paths of the formation of which were examined in [1]. We explain the similarity in the mass spectra of III and IV by the possibility of transannular interaction of the ester oxygen atom with the silicon atom in the macrocyclic system of silalactone III. Under the influence of electron impact, propylene is ejected from the molecular ion of III, and this leads to the development of the molecular ion of 1-silalactone IV, as shown in scheme 3. Similar ejection from the $(M-CH_3)^+$ ion leads to an ion with m/e 129.

The mass spectra were recorded with an MKh-1303 spectrometer at 150° and an ionizing voltage of 30 V.

LITERATURE CITED

1. V. N. Bochkarev, N. S. Fedotov, I. G. Rybalka, and V. F. Mironov, Khim. Geterotsikl. Soedin. (in press).
2. J. Dubac, P. Mazerolles, M. Joly, W. Kitching, C. W. Fong, and W. Atwele, J. Organomet. Chem., 34, 17 (1972).
3. W. P. Weber, R. A. Felix, A. K. Willard, and H. G. Boettger, J. Org. Chem., 36, 4060 (1971).
4. W. P. Weber, R. A. Felix, and A. K. Willard, J. Amer. Chem. Soc., 92, 420 (1970).