In the ^{13}C NMR spectra of adducts I-VIII (Table 4), in addition to the downfield signals characteristic of the carbon atoms of the thietane dioxide ring [3], in the regions of 54-59 and 58-60 ppm there are signals for the carbon atoms of the oxirane ring. The chemical shifts of the $C_{(1)}$, $C_{(4)}$-$C_{(7)}$ atoms are shifted appreciably downfield with increase in the number of methyl groups at position 5.

EXPERIMENTAL

The mass spectra were obtained on a Varian MAT-311 instrument with direct injection of the sample into the ion source at 70 eV and an ionization chamber temperature of 200°C. The ^{13}C NMR spectra were recorded on a Jeol PS-100 spectrometer in deuterochloroform with HMDS as internal standard under the conditions of full proton decoupling and single resonance.

LITERATURE CITED

1. I. G. Tishchenko, G. I. Polozov, and A. F. Abramov, Vestn. Belorus. Un-Ta, No. 2, 12 (1980).
2. B. Lamm, Acta Chem. Scand, Ser. B, 29, 332 (1975).
3. L. N. Koikov, P. B. Terent'ev and N. S. Kulikov, Zh. Org. Khim., 17, No. 5, 1087 (1981).
4. L. N. Koikov, P. B. Terent'ev, I. P. Gloriozov, V. N. Torocheshnikov, V. N. Baidin, and Yu. G. Bundel', Khim. Geterotsikl. Soedin., No. 5, 643 (1983).
5. G. I. Polozov, I. G. Tishchenko, and A. F. Abramov, Zh. Org. Khim., 16, 765 (1980).
6. G. Stork and I. J. Borowitz, J. Am. Chem. Soc., 84, 313 (1962).
7. H. J. Jacobsen, S. O. Lawesson, J. T. B. Marshall, G. Schroll, and D. H. Williams, J. Chem. Soc., No. 3, 940 (1966).
8. R. J. Radel, B. T. Keen, and W. W. Paudler, J. Heterocycl. Chem., 14, 1389 (1977).
9. A. I. Ermakov and Yu. N. Sheinker, Khim. Geterotsikl. Soedin., No. 1, 65 (1981).
10. D. S. Yufin, Yu. T. Struchkov, L. N. Koikov, P. B. Terentev', and Yu. G. Bundel', Khim. Geterotsikl. Soedin., No. 5, 651 (1983).

FRAGMENTATION OF SUBSTITUTED 2-SILA-1,3-DIOXACYCLOALKANES UNDER ELECTRON IMPACT

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The mass spectrometric dissociation of 2-sila-1,3-dioxacycloalkanes takes place mainly with loss of the substituent from position 2 of the heterocycle. The fragment formed here eliminates the molecular of carbonyl compounds or alkenes.

The organosilicon analogs of cyclic acetals find use as water-repellant liquids [1]. The methyl- and phenyl-substituted 1,3-dioxa-2-silacycloalkanes are used as components of lubricants [2] and copolymers for most of the organosilicon polymers produced by modern industry [3]. The aim of the present work was to study the mass spectra of substituted 2-sila-1,3-dioxacyclohexanes I-IX and substituted 2-sila-1,3-dioxacyclopentanes X-XII:

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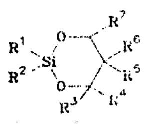
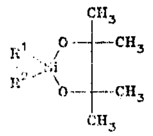


I-IX



X-XII

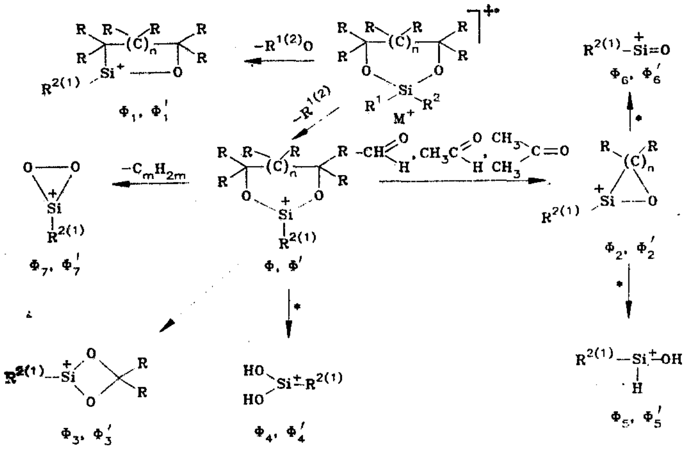
I, II, V-X, XII $R^1 = CH_3$, III, IV, XI $R^1 = C_2H_5$; I, II, X $R^2 = CH_3$, III, IV, XI $R^2 = C_2H_5$, V-IX, XII $R^2 = C_6H_5$; II, IV, VI, VII, IX $R^3 = CH_3$; VII, IX $R^4 = CH_3$; VIII $R^5 = R^6 = CH_3$; IX $R^7 = CH_3$; where not indicated, R = H

Earlier [4] we studied the main dissociation paths of 2,2-dimethyl-2-sila-1,3-dioxacyclohexanes. In the present work we established the effect of substituents at the silicon atom and also the size of the heterocycle on the stability of the molecular ions (M^+) and analyzed the general fragmentation pattern of these compounds under electron impact.

Analysis of the mass-spectrometric data (Tables 1 and 2) shows that the stability of M^+ in the investigated 2-sila-1,3-dioxacycloalkanes I-XII corresponds to 0.8-8.8% of the total ion current. An aromatic substituent at position 2 somewhat increases the stability of M^+ in the 2-phenyl-substituted compounds V-IX, XII. A similar relationship was observed earlier [5, 6] during the discussion of the mass spectra of cyclic organosilicon compounds, and also in 2-aryl-1,3-dioxacyclanes [7].

At the first stage in the dissociation of M^+ (Scheme) the $R^{1(2)}$ and $R^{1(2)}O$ particles are eliminated with the formation of ions of the Φ and Φ_1 types, respectively (Table 2). Simple cleavage of the $Si-R^{1(2)}$ bond leads to the formation of ions which give a signal with maximum intensity for all the compounds except VIII, IX, and XI. The preferential elimination of the alkyl group from position 2 of the heterocycle has been mentioned for 1,3-dioxolanes and 1,3-oxathiolanes [7] and also for silicon-containing heterocycles having two geminal substituents at the silicon atom [8, 9]. The second process takes place with migration of the alkyl (or aryl) group from position 2 of the heterocycle to the oxygen atom, and its probability is significantly lower. The presence of two different substituents at the silicon atom in compounds V-IX, XII gives rise to the simultaneous appearance of two ions of the Φ_1 type. In the Scheme and in Table 2 these alternative ions are marked by a subscript and a prime.

Analysis of the mass-spectral data makes it possible to isolate four main dissociation paths for the Φ ion, leading to the formation of the Φ_2, Φ_3, Φ_4, and Φ_7 ions.



R = H, CH_3; n = 0, 1

A characteristic feature of the investigated compounds is the elimination, by the fragment ion $\Phi(\Phi')$, of a molecule of formaldehyde (the 4,6-unsubstituted compounds) or of molecules of acetaldehyde (the 5,5-disubstituted compounds) and acetone (the 4,4-disubstituted compounds) with the formation of a whole "family" of ions of the Φ_2 type. Dissociation with the elimination of the formaldehyde molecule predominates in these competing parallel processes, and the ketone molecule is eliminated least readily. A feature of the dissociation of M^+ in compounds X-XII is the preferred elimination of the acetone molecule from the ion $\Phi(\Phi')$. It should be noted that in the majority of the spectra the $\Phi \rightarrow \Phi_2$ transition is supported by

TABLE 1. Mass Spectra of Compounds I-XII*

Compound	m/z value (peak intensity, % of maximum)
I	132 (5), 117 (100), 101 (4), 87 (17), 75 (11), 61 (7), 59 (9), 43 (8), 31 (18), 45 (18)
II	146 (5), 131 (100), 103 (38), 101 (29), 87 (17), 77 (22), 75 (29), 45 (25), 43 (13), 28 (13)
III	160 (10), 131 (100), 129 (2), 103 (11), 101 (2), 91 (9), 89 (1), 75 (2), 73 (5), 45 (4)
IV	174 (7), 145 (100), 117 (14), 115 (12), 101 (5), 91 (7), 84 (8), 45 (8), 32 (18), 28 (16)
V	194 (33), 179 (100), 146 (26), 133 (21), 131 (14), 117 (93), 87 (31), 77 (7), 75 (21), 28 (21)
VI	208 (24), 193 (100), 163 (24), 139 (16), 137 (24), 130 (22), 121 (24), 116 (17), 105 (17), 77 (25)
VII	222 (27), 207 (100), 177 (25), 165 (17), 139 (12), 137 (32), 129 (12), 105 (13), 77 (8), 45 (13)
VIII	222 (5), 207 (16), 137 (31), 105 (18), 77 (26), 51 (18), 45 (100), 43 (47), 41 (65), 39 (41)
IX	236 (6), 137 (23), 78 (31), 77 (53), 59(24), 46 (54), 44 (100), 43 (62), 42 (92), 40 (46)
X	174 (52), 159 (100), 143 (10), 133 (18), 117 (24), 116 (65), 101 (24), 77 (24), 75 (43), 43 (29)
XI	202 (23), 173 (50), 91 (51), 85 (98), 59 (97), 57 (100), 45 (60), 43 (96), 41 (97), 31 (92)
XII	236 (45), 171 (75), 150 (100), 121 (88), 59 (96),58 (75), 44 (50), 43 (50), 51 (88), 30 (75)

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*The ten strongest peaks are given.

TABLE 2. Peak Intensities of the Characteristic Ions for Compounds I-XII (% of total ion current)

Compound	M^+	Φ	Φ'	Φ_1	Φ'_1	Φ_2	Φ'_2	Φ_3	Φ'_3	Φ_4	Φ'_4	Φ_5	Φ'_5	Φ_6	Φ'_6	Φ_7	Φ'_7
I	2,0	40,0	—	1,6	—	6,8	—	—	—	1,6	—	2,8	—	3,6	—	4,4	—
II	1,2	24,0	—	1,7	—	6,9* 4,1	—	9,1	—	5,3	—	2,2	—	2,4	—	7,0	—
III	4,8	48,0	—	—	—	5,8	—	5,3	—	4,3	—	1,0	—	2,4	—	0,5	—
IV	2,7	38,0	—	0,8	—	4,6 (1,9)	—	5,3	—	2,7	—	—	—	1,1	—	3,0	—
V	4,6	14,0	13,0	0,8	2,1	3,6	4,3	0,4	0,7	0,3	2,4 †	0,6	1,7	1,1	1,7	1,1	2,9
VI	4,3	18,0	1,4	1,8	3,1	4,3 (2,0)	0,7 (5,6)	2,5	0,4	2,9	4,5	1,4	1,4	4,3	0,9	4,3	0,2
VII	6,5	24,0	0,2	0,5	2,9	6,0 (1,9)	1,9 (0,2)	3,4	0,2	2,9	1,9	1,0	2,6	1,4	—	7,7	0,2
VIII	0,9	2,7	0,7	—	0,7	0,5 (0,3)	0,5 —	1,0	0,2	0,7	4,4	0,5	1,9	2,4	2,2	5,3	0,2
IX	0,8	1,2	0,1	0,9	0,3	1,4 (0,4)	0,5 (0,5)	0,4	0,4	0,8	6,9	0,3	2,1	0,9	3,1	3,0	0,9
X	8,8	17,0	—	1,7	—	3,9	—	4,1	—	—	—	—	—	—	—	7,3	—
XI	1,6	3,5	—	0,4	—	0,8	—	0,8	—	—	—	—	—	—	—	0,4	—
XII	3,6	2,7	8,0	1,8	1,4	0,9	0,5	0,6	0,6	—	—	—	—	—	—	1,7	1,5

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*The component ions in relation to the substituents R^3 to R^7; the ions with the smallest m/z values are given in parentheses.
†The $[R^2]^+$ ions make a contribution to the intensity of the peaks for these ions.

the presence of peaks for metastable ions. The formation of cyclic ions like ions of the Φ_2 type (Scheme) was observed in [7] during examination of the dissociative ionization of substituted 1,3-dioxanes. Ring contraction as a result of fragmentation has been observed in the mass spectra of silicon-containing heterocycles [5, 8, 9].

The Φ_2 ions can then eliminate a molecule of the alkene and a molecule of the cycloalkene (or alkyne) with the formation of the Φ_6 and Φ_5 ions, respectively. Both these transitions are confirmed by the presence of metastable ions in the spectra of the compounds.

There are at least three other paths for the dissociation of the Φ ion: 1) An ion of the Φ_7 type is formed after the elimination of the alkene molecule. The appearance of such ions has been observed before [10] during the analysis of the mass spectra of diphenyldialkoxysilanes.

In the spectra of our investigated compounds these ions have appreciable intensity, and in the 2-phenyl-substituted compounds V-IX, XII their intensity amounts to 32% on account of the stabilizing effect of the phenyl substituent. 2) An ion of the Φ_3 type, containing a four-membered ring (three-membered in the case of 2-sila-1,3-dioxacyclopentanes) with three heteroatoms, is formed after the elimination of the molecule of the respective alkene from the Φ ion. The Φ_3 ion can then, evidently, eliminate a molecule of the aldehyde or ketone, being converted into the Φ_6 ion (Scheme). 3) The elimination of the cycloalkene from the Φ ion is confirmed by the presence of metastable peaks in the spectra. This process leads to the formation of Φ_4 ions.

Thus, considerable similarity is found in the fragmentation paths of 2-sila-1,3-dioxacyclohexanes I-IX and their five-membered analogs X-XII. In both cases the direction of dissociation is determined by the nature of the substituent at the endocyclic silicon atom.

EXPERIMENTAL

Compounds I, III were synthesized by the method in [11], and compounds II, IV-XII by the method in [12]. The purity of the compounds (not lower than 98%) was monitored by GLC (3 m × 3 mm column, SE-30 on Chromaton N-AB, column temperature 50-250°C, programmed heating at 6 deg/min, helium, 2 liters/h). The mass spectra of compounds (I-XII) were recorded on an MI-1201 instrument at 70 eV with an ionization chamber temperature of 70°C. The samples were delivered to the source at room temperature through a probe connected to the tube by a fine control valve.

LITERATURE CITED

1. J. Jack, British Patent No. 857153; Chem. Abst., 55, 18648 (1961).
2. S. D. I. Brown, US Patent No. 3505378; Chem. Abst., 73, 5760 (1970).
3. M. G. Voronkov, V. G. Mileshkevich, and Yu. A. Yuzhelevskii, The Siloxane Bond [in Russian], Nauka, Moscow (1976), p. 7.
4. R. S. Musavirov, I. A. Borisova, L. B. Gazizova, E. P. Nedogrei, S. S. Zlot-skii, and D. L. Rakhmankulov, Zh. Obshch. Khim., 53, 1583 (1983).
5. V. Yu. Orlov, Usp. Khim., 42, 1184 (1973).
6. V. N. Bochkarev, T. L. Krasnova, and E. A. Chernyshev, Zh. Obshch. Khim., 42, 1339 (1972).
7. A. A. Polyakova and R. A. Khmel'nitskii, Mass Spectrometry in Organic Chemistry [in Russian], Khimiya, Leningrad (1972), p. 139.
8. V. N. Bochkarev, A. N. Polivanov, N. G. Komalenkova, S. A. Bashkirova, and E. A. Chernyshev, Zh. Obshch. Khim., 43, 2703 (1973).
9. V. N. Bochkarev, A. N. Polivanov, N. G. Komalenkova, S. A. Bashkirova, and E. A. Chernyshev, Zh. Obshch. Khim., 43, 785 (1973).
10. B. Y. K. Ho, L. Spialter, and L. D. Smithson, Org. Mass Spectrom., 10, 361 (1975).
11. R. S. Musavirov, L. F. Lapuka, E. P. Nedogrei, V. I. Larionov, I. A. Kudashova, E. A. Kantor, S. S. Zlot-skii, and D. L. Rakmankulov, Dokl. Akad. Nauk SSSR, 270, 616 (1983).
12. R. Calas and P. Nicov, Comp. Rend. Chemic Organosilicique, 249, 1011 (1959).