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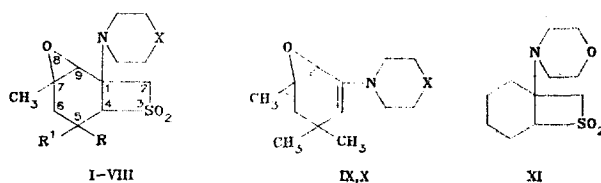
MASS SPECTRA AND ^{13}C NMR SPECTRA OF THE ADDUCTS OF EPOXYENAMINES WITH SULFENE

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The behavior of the adducts of alicyclic epoxyenamines with sulfene under electron impact and also their ^{13}C NMR spectra were studied. The initial fragmentation of these compounds, which takes place with the ejection of sulfene, is accompanied by a specific hydrogen rearrangement of the molecular ion. The degree of substitution of the cyclohexane ring has a significant effect on the nature of the subsequent dissociation, which leads to extensive degradation of the oxirane ring.

The readily occurring reaction of sulfene with alicyclic epoxyenamines leads to the formation of aminoepoxythietane dioxides [1], which represent a new type of previously uninvestigated heterocyclic system including three and four-membered heterocycles annellated with the cyclohexane ring. It seemed of interest to determine which of the heterocycles would be decomposed first by the action of electron impact and to trace the main directions in the mass-spectrometric fragmentation of the compounds. In this connection in the present work we investigated the mass-spectrometric behavior of 1-amino-8-oxa-3-thiatricyclo[5.2.0.0^{7,9}]nonane 3,3-dioxides (I-VIII) by means of the DADI technique and the high-resolution mass spectra and studied their ^{13}C NMR spectra.



I R=H, II-X R=CH₃; I-IV R¹=H, V-X R¹=CH₃; I, II, V, IX X=O, III, VII, X
X=CH₂, IV, VIII X=(CH₂)₂ (VI X=-)

The molecular ion peaks (M^+) in the mass spectra of adducts I-VIII (Table 1) have low intensity, which demonstrates the low stability of the molecules to electron impact. In the general case the stability of M^+ depends little on the nature of the amine substituent and decreases with increase in the number of methyl groups at position 5 (Table 2) on account of the appearance of new energetically favorable dissociation paths for M^+ on account of possible rearrangement.

The initial dissociation of M^+ is extremely similar to the previously investigated fragmentation of the cyclic adducts of sulfene and enamines [2-4], involving retro[2+2]-cleavage

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TABLE 1. Mass Spectra of Compounds I-XI*

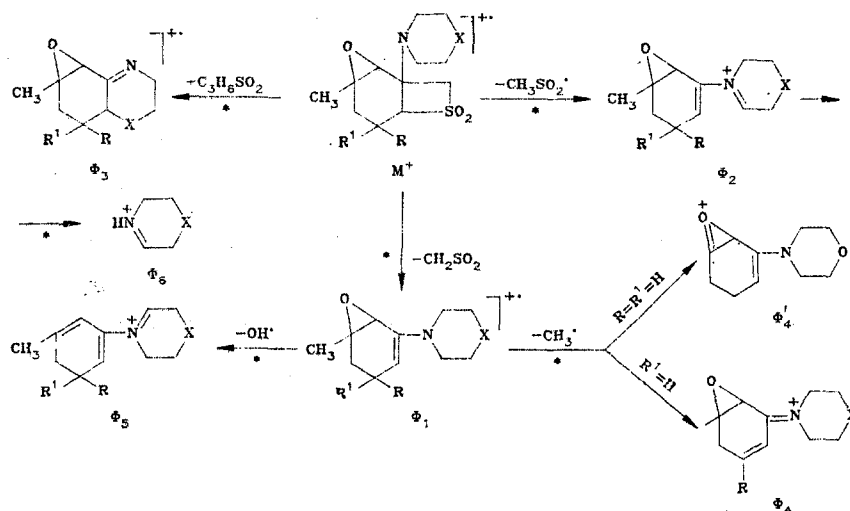
Compound	m/z values (relative intensity, %)
I	273 (11), 195 (100), 194 (95), 180 (45), 178 (34), 152 (11), 67 (11), 56 (12), 55 (20), 43 (37), 42 (11), 41 (31)
II	287 (23), 210 (11), 209 (81), 208 (100), 195 (18), 194 (98), 193 (11), 182 (11), 181 (38), 180 (14), 166 (14), 152 (11), 112 (13), 108 (16), 86 (21), 81 (14), 79 (16), 77 (14), 69 (14), 67 (29), 55 (32), 54 (15), 53 (16), 43 (63), 42 (23), 41 (57)
III	285 (7), 207 (45), 206 (90), 193 (13), 192 (100), 190 (55), 188 (11), 179 (15), 164 (23), 150 (11), 136 (12), 84 (33), 67 (12), 55 (21), 43 (29), 42 (13), 41 (41)
IV	299 (11), 221 (50), 220 (100), 206 (64), 204 (32), 193 (12), 178 (12), 98 (11), 55 (17), 43 (20), 41 (23)
V	301 (6), 223 (43), 222 (79), 209 (25), 208 (100), 206 (16), 195 (36), 180 (11), 112 (13), 93 (11), 91 (11), 86 (13), 81 (13), 79 (13), 77 (12), 67 (17), 56 (20), 55 (23), 53 (14), 43 (55), 42 (18), 41 (47)
VI	285 (4), 207 (30), 206 (54), 193 (19), 192 (100), 190 (16), 179 (20), 96 (11), 70 (22), 55 (17), 43 (22), 41 (24)
VII	299 (5), 221 (35), 220 (67), 207 (17), 206 (100), 193 (25), 84 (15), 55 (16), 43 (20), 42 (11), 41 (24)
VIII	313 (5), 235 (29), 234 (69), 221 (17), 220 (100), 207 (20), 98 (13), 55 (21), 43 (17), 41 (22)
IX	223 (33), 209 (30), 208 (100), 166 (11), 165 (22), 114 (18), 112 (22), 93 (18), 79 (14), 77 (14), 70 (14), 56 (15), 55 (20), 43 (37), 41 (55)
X	221 (16), 207 (13), 206 (100), 163 (11), 112 (11), 110 (15), 84 (33), 83 (30), 69 (28), 57 (11), 56 (11), 55 (17), 44 (12), 43 (16), 41 (55)
XI	245 (30), 167 (37), 166 (100), 165 (43), 152 (13), 138 (14), 136 (12), 122 (13), 109 (12), 108 (24), 95 (13), 94 (13), 86 (13), 81 (22), 79 (23), 77 (14), 67 (20), 56 (15), 55 (24), 54 (14), 53 (15), 42 (15), 41 (38)

*The peaks of M^+ and of the ions with an intensity of more than 10% of the maximum are given.

of the thietane ring and elimination of a molecule of sulfene or alkylsulfene. One of the characteristic dissociation paths in compounds I-VIII is also realized with loss of sulfene and the formation of the ϕ_1 ion (see the scheme), the fraction of which in the total ion current is highest for compound (I) and decreases appreciably for the substituted derivatives II-VIII (Table 2).

The main dissociation path for M^+ involves the formation of the stable fragment $[M - CH_3SO_2]^+$ (the ϕ_2 ion); the probability of this process for compounds II-VIII is 1.2-2.4 times larger than the probability of the elimination of sulfene. We note that the formation of the ϕ_1 and ϕ_2 ions is the result of independently occurring single-stage processes of the dissociation of M^+ , since the metastable transition $\phi_1 - H \cdot \rightarrow \phi_2$ is not observed.

Scheme

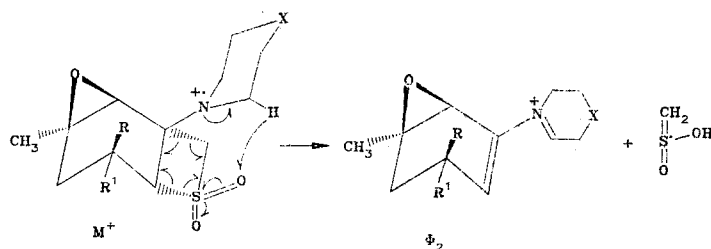


A characteristic feature in the mass spectra of the precursors of the adducts, i.e., the epoxyenamines IX, X [5], is the absence of peaks for the $[M - H]^+$ ions, and at the same time the W_M values of the latter are significantly higher (4.7 and 3.2%, respectively, Table 1).

TABLE 2. Intensities of the Peaks for the Characteristic Ions in the Mass Spectra of Compounds I-VIII as Percentages to the Total Ion Current (Σ_{40} , %)

Compound	W_M	Φ_1	Φ_2	Φ_3	Φ_4	Φ_5	Φ_6
I	1,6	11,6	11,1	0,7	5,2 (Φ'_4)	4,0	1,0
II	2,1	5,9	7,3	2,8	7,2	5,2	1,5
III	0,9	4,7	8,8	1,5	9,8	5,5	3,2
IV	2,1	7,7	15,5	1,9	9,9	4,9	1,7
V	0,8	4,7	7,8	3,6	9,9	1,6	1,3
VI	0,9	4,4	7,9	2,9	14,6	2,3	3,2
VII	1,1	5,4	10,3	3,9	15,4	1,2	2,3
VIII	0,8	4,7	11,2	3,2	16,2	1,1	2,1

The main peak in the mass spectra of these compounds is the peak for the $[M - CH_3]^+$ ion. On the other hand, in the spectrum of the amino sulfone XI [6] the peak for the $[M - CH_3SO_2]^+$ ion is the maximum in intensity. These data indicate direct participation of the four-member heterocycle in the formation of the ions with structure Φ_2 . The most likely process is dissociation of M^+ by a mechanism of the McLafferty rearrangement type involving the mobile hydrogen atoms of the α -methyl group in the nitrogen-containing heterocycle. This is typical of enamino ketones [7], 3-amino-1,2,4-triazine 1-oxides [8], and functionally substituted piperidines [9]. According to the data from x-ray crystallographic analysis of the adduct of sulfene with E-1-dimethylamino-1-phenyl-1-propene [10], the carbon atom of the N-methyl group lies in the plane of the sulfonyl group and the nitrogen atom. Examination of molecular models of adducts I-VIII demonstrates the steric proximity of the oxygen atom of the sulfonyl group and the hydrogen atoms of the above-mentioned α -methylene group. Such molecular geometry undoubtedly promotes the migration of one of the hydrogen atoms to the sulfonyl group and subsequent elimination of the CH_2SO_2H radical, which is realized through a cyclic transition state as a result of a concerted process:



One of the characteristic fragmentation paths in the investigated compounds is the direct formation of the $[M - C_3H_6SO_2]^+$ ion (Φ_3) from M^+ . Its peak is particularly strong in the spectra of adducts V-VIII. This ion is evidently formed through the simultaneous occurrence of two processes, i.e., cleavage of the four-membered and nitrogen-containing rings with the ejection of sulfene and ethylene molecules, respectively. This suggesting is consistent with the data on the fragmentation of the enamines of cyclanones and cycloamines [7], the mass spectra of which contain a strong peak for the $[M - C_2H_4]^+$ ion, formed as a result of the dissociation of the nitrogen-containing ring. However, the peaks of the $[M - C_2H_4]^+$ ions, which would have the structure of the Φ_3 ion, are absent in the spectra of epoxyamines IX, X.

A characteristic dissociation path of M^+ is also the elimination of a molecule of SO_2 with the subsequent ejection of a hydrogen atom. The spectra of all the compounds contain a peak for the $[M - CH_2SOH]^+$ ion, and in the spectrum of compound I there is in addition a peak for the $[M - OH]^+$ ion; this is probably due to rearrangement processes in M^+ . The spectra of adducts II-VIII always contain a peak for the $[M - CH_3]^+$ ion. The intensities of all the above-mentioned peaks are low (less than 1% of the total ion current), and these paths are consequently insignificant in the overall dissociation of M^+ .

The subsequent dissociation of the Φ_1 ion involves primarily the loss of the methyl group and the formation of the $[\Phi_1 - CH_3]^+$ ions, which give a signal of high intensity (maximum for compounds V-VIII). In the case of adduct I this process is evidently realized with the removal of the methyl group from the oxirane ring and localization of the charge at the oxygen atom (the Φ'_4 ion); for compounds II-VIII the removal of the methyl radical from position 5 is

TABLE 3. Elemental Composition of the Ions in the Mass Spectra of Compounds I and VII

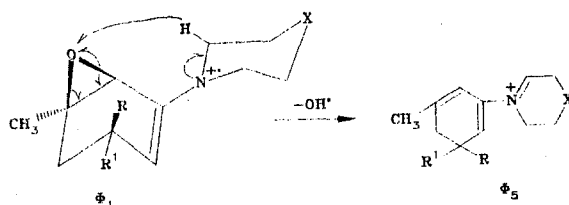
Com- pound	Ion	Elemental composition	Accurate mass		Com- pound	Ion	Elemental composition	Accurate mass	
			found	calcu- lated				found	calculated
I	M ⁺	C ₁₂ H ₁₉ NO ₄ S	273,1025	273,1016	VII	M ⁺	C ₁₅ H ₂₅ NO ₃ S	299,1547	299,1538
	Φ ₁	C ₁₁ H ₁₇ NO ₂	195,1277	195,1258		Φ ₁	C ₁₄ H ₂₃ NO	221,1803	221,1779
	Φ ₂	C ₁₁ H ₁₆ NO ₂	194,1205	194,1180		Φ ₂	C ₁₄ H ₂₂ NO	220,1724	220,1700
	Φ ₃	C ₉ H ₁₃ NO ₂	167,0955	167,0946		Φ ₃	C ₁₂ H ₁₆ NO	193,1471	193,1466
	Φ ₄	C ₁₀ H ₁₄ NO ₂	180,1049	180,1024		Φ ₄	C ₁₃ H ₂₀ NO	206,1552	206,1544
	Φ ₅	C ₁₁ H ₁₆ NO	178,1244	178,1232					

TABLE 4. ¹³C NMR Spectra of Compounds I-VIII, ppm

Compound	C ₍₁₎	C ₍₂₎	C ₍₄₎	C ₍₅₎	C ₍₆₎	C ₍₇₎	C ₍₉₎
I	48,38	68,72	73,07	21,97	16,61	54,36	58,24
II	48,92	68,88	79,75	30,05	20,50	55,37	58,16
III	49,23	69,66	80,22	30,13	22,36	55,13	58,39
IV	49,39	63,89	80,66	28,19	24,22	55,75	58,71
V	51,71	66,47	82,16	34,71	23,12	57,23	58,01
VI	49,46	63,36	82,62	30,36	27,10	58,39	59,48
VII	51,56	64,62	83,07	32,74	28,56	58,11	58,32
VIII	51,79	66,24	83,71	34,71	23,04	58,47	59,17

most likely (the Φ₄ ion). The maximum intensity of the peak for this ion is probably explained by the ease of the elimination of the methyl group on account of its steric interaction with the oxygen atom of the oxirane ring and the subsequent formation of a cyclic structure with conjugated bonds and with stabilization of the charge at the nitrogen atom.

The subsequent dissociation paths of the main fragment ions Φ₁-Φ₄ largely characterize the processes involved in the dissociation of the oxirane ring, which are accompanied by the elimination of OH, CH₃CO, and CHO radicals. The corresponding fragment ions and also the Φ₃ and Φ₄ ions are capable of undergoing dehydrogenation processes. The elimination of the OH radical from the Φ₁ ion, which leads in the case of compounds I-IV to high-intensity peaks for the Φ₅ ion (up to 5.5% of the total ion current) can also be explained by a characteristic rearrangement with the participation of the oxirane oxygen atom and the α-hydrogen atom of the nitrogen-containing ring:



For compounds V-VIII, which have two methyl substituents at the C₍₅₎ atom, the elimination of the methyl group, which competes with the rearrangement, becomes the predominant process. The peaks of all the remaining ions in the mass spectra have low intensity, and their fraction in the total ion current is not greater than 1-2%. Apart from the above-mentioned peaks, common peaks for the whole series of compounds are the strong peaks for ions with m/z 41, 43, 55, 67, 69, 77, 79, and 91 and also the Φ₆ ion, which corresponds to the residue of the cyclic amine.

The total fraction of M⁺ and all the ions discussed above is greater than 40%, which indicates a fairly high degree of selectivity in the dissociation of the compounds.

The high-resolution mass spectra of adducts I, VII (Table 3) confirm the elemental compositions of M⁺ and the main fragment ions. The paths presented in the Scheme and the order of their formation follow from analysis of the DADI spectra of compounds I, III, VII.

Thus, the thietane dioxide and nitrogen containing rings in the investigated compounds are cleaved with much greater probability than the oxirane ring, the dissociation of which is due primarily to the possibility of a specific hydrogen rearrangement.

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 $\text{C}(1)$, $\text{C}(4)$ - $\text{C}(7)$ 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 deuteriochloroform with HMDS as internal standard under the conditions of full proton decoupling and single resonance.

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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-diox-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: