MASS SPECTRA OF 1-ALKOXYAZIRIDINES

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The mass spectra of 12 di-, tri-, and tetramethyl-substituted 1-alkoxyaziridines were investigated, and the principal pathways of their fragmentation under the influence of electron impact, which include cleavage of the N–O and C–O bonds of the alkoxy group or cleavage at two bonds of the aziridine ring, were ascertained. The compositions of the resulting ions were confirmed by high-resolution mass-spectrometric data. The four examined parallel fragmentation processes explain the appearance of all of the principal ions in the mass spectra of alkoxyaziridines. The established principles open up the possibility of identification of 1-alkoxy-aziridines in complex mixtures with isomeric compounds.

Data on the preparation of 1-alkoxyaziridines by oxidation of alkoxy amines with lead tetraacetate in the presence of olefins have been presented in earlier communications [1, 2]. A detailed analysis of the complex reaction mixtures, which, in addition to the stereoisomeric alkoxyaziridines, contain their structural isomers and other side products, is necessary to ascertain the role of the alkoxy centers in these reactions. The most expedient method for the investigation of these mixtures is chromatographic mass spectrometry; however, for its efficient use one must know the regularities and peculiarities of the mass spectra of alkoxyaziridines. The literature data on the mass spectra of alkyl-substituted alkoxyaziridines are extremely scanty and are limited to incomplete information regarding the mass spectra of 1-methoxytetramethylaziridine [3] and the stereoisomeric 1-n-butoxy-2,3-dimethylaziridines [4]. A great deal more study has been devoted to 1-alkoxyaziridine derivatives with functional groups attached to the ring carbon atoms [5], but rearrangement processes in the molecular ions that substantially change the form of the mass spectra and hinder elucidation of the principles of dissociative ionization (fragmentation) of the simplest alkoxyaziridines are possible when complex substituents are present.

We have made a detailed study of the mass spectra of 12 di-, tri-, and tetramethyl-substituted 1-alkoxyaziridines, including four pairs of syn and anti invertomers that differ with respect to the configuration of the nitrogen atom.* Analysis of the mass spectra presented in Table 1 and a comparison of them with the literature data for aziridines containing different substituents make it possible to uncover a number of interesting peculiarities and regularities that are extremely valuable not only for an understanding of the behavior of the aziridine molecules during electron impact but also for the determination of the structures of compounds of this class.

The conclusions set forth below were used for the chromatographic mass-spectrometric analysis and mass-fragmentation analysis of the complex reaction mixtures containing aziridines. The mass spectra of more than 30 aziridines detected in these mixtures are in complete agreement with the established principles.

Molecular Ions

The molecular ions of all of the investigated aziridines are of low intensity [no more than 10–11% of the intensity of the maximum peak (W_M less than 2.3%)]; this constitutes evidence for the low stabilities of these compounds with respect to electron impact. Trimethylaziridines II–IV are more stable than the other aziridines (Table 2). A decrease in the

*The assignment of the configurations of the invertomers was made from RMP data on the basis of the considerations set forth in [1].

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TABLE 1. Mass Spectra of 1-Alkoxyaziridines at Ionizing-Electron Energies of 70 and 12 eV (m/e values in relative percent)*

Ia. 1-Methyl-2,3-cis-dimethylaziridine (syn form)

70 eV: 101 (2) $[M]^{+\cdot}$, 86 (3), 72 (2), 71 (4), 70 (100), 69 (2), 68 (7), 58 (2), 56 (20), 55 (10), 54 (7), 53 (2), 45 (2), 44 (4), 43 (9), 42 (80), 41 (36), 40 (2), 39 (5), 31 (3), 30 (6), 29 (18); m* 66,0 (70→68) 39,1 (43→41), 37,1 (41→39)
12 eV: 101 (4), 86 (2), 71 (4), 70 (100), 42 (3)

Ib. 1-Methoxy-2,3-cis-dimethylaziridine (anti form)

70 eV: 101 (4) $[M]^{+\cdot}$, 86 (5), 85 (4), 84 (2), 75 (10), 72 (6), 71 (7), 70 (100), 69 (3), 68 (9), 60 (2), 59 (33), 58 (6), 57 (2), 56 (28), 55 (22), 54 (14), 53 (3), 45 (6), 44 (5), 43 (30), 42 (90), 41 (43), 40 (3), 39 (11), 31 (9), 30 (9), 29 (33); m* 39,1 (43→41), 37,1 (41→39)
12 eV: 101 (4), 86 (2), 75 (2), 72 (2), 71 (5), 70 (100), 59 (6), 56 (2), 42 (5)

Ic. 1-Methoxy-2,3-trans-dimethylaziridine

70 eV: 101 (2) $[M]^{+\cdot}$, 86 (3), 72 (2), 71 (3), 70 (100), 69 (2), 68 (7), 58 (2), 56 (21), 55 (11), 54 (8), 53 (2), 45 (2), 44 (4), 43 (9), 42 (86), 41 (38), 40 (3), 39 (6), 33 (2), 31 (3), 30 (6), 29 (20); m* 66,0 (70→68), 39,1 (43→41), 37,1 (41→39)
12 eV 101 (3), 86 (2), 71 (4), 70 (100), 42 (4)

IIa. 1-Methoxy-2,2,3-trimethylaziridine (syn form)

70 eV: 115 (9) $[M]^{+\cdot}$, 101 (2), 100 (27), 88 (3), 87 (62), 85 (11), 84 (92), 83 (3), 82 (4), 75 (2), 74 (3), 73 (4), 72 (10), 70 (15), 69 (29), 68 (22), 67 (4), 59 (19), 58 (5), 57 (9), 56 (12), 55 (32), 54 (4), 53 (4), 45 (8), 44 (28), 43 (48), 42 (100), 41 (69), 40 (7), 39 (27), 33 (4), 31 (8), 30 (8), 29 (20); m* 66,0 (115→87), 37,1 (41→39), 24,2, 23,2, 21,2 (84→42), 7,3

12 eV 115 (14), 101 (2), 100 (28), 88 (3), 87 (97), 85 (8), 84 (100), 83 (2), 73 (2), 72 (2), 70 (2), 69 (2), 68 (3), 59 (3), 57 (4), 43 (3), 42 (11)

IIb. 1-Methoxy-2,2,3-trimethylaziridine (anti form)

70 eV: 115 (9) $[M]^{+\cdot}$, 101 (2), 100 (20), 88 (2), 87 (45), 85 (7), 84 (98), 83 (3), 82 (4), 74 (2), 72 (9), 70 (15), 69 (25), 68 (19), 67 (3), 59 (2), 58 (3), 57 (7), 56 (11), 55 (28), 54 (4), 53 (3), 45 (2), 44 (25), 43 (26), 42 (100), 41 (24), 40 (6), 39 (24), 38 (2), 33 (3), 31 (3), 30 (7), 29 (14): m* 66,0 (115→87), 37,1 (41→39), 24,1, 23,1, 21,2 (84→42)
12 eV: 115 (14), 100 (16), 88 (3), 87 (71), 85 (7), 84 (100), 83 (2), 70 (2), 68 (2), 57 (3), 42 (7)

IIIa. 1-Ethoxy-2,2,3-trimethylaziridine (syn form)

70 eV: 129 (10) $[M]^{+\cdot}$, 114 (16), 102 (2), 101 (41), 100 (2), 86 (15), 85 (7), 84 (100), 83 (3), 82 (3), 73 (8), 71 (6), 70 (39), 69 (19), 68 (14), 67 (2), 60 (5), 59 (4), 58 (15), 57 (11), 56 (6), 55 (22), 45 (6), 44 (14), 43 (32), 42 (73), 41 (47), 40 (4), 39 (13), 31 (3), 30 (4), 29 (29); m* 79,2 (129→101), 37,1 (41→39)
12 eV. 130 (2), 129 (18), 114 (14), 102 (5), 101 (93), 85 (6), 84 (100), 73 (5), 70 (5), 55 (11), 41 (9)

IIIb. 1-Ethoxy-2,2,3-trimethylaziridine (anti form)

70 eV: 129 (10) $[M]^{+\cdot}$, 114 (13), 102 (2), 101 (39), 100 (2), 86 (13), 85 (7), 84 (100), 83 (2), 82 (3), 73 (8), 71 (4), 70 (42), 69 (19), 68 (13), 67 (2), 60 (5), 59 (3), 58 (14), 57 (10), 56 (6), 55 (23), 45 (10), 44 (14), 43 (34), 42 (71), 41 (49), 40 (4), 39 (15), 31 (3), 30 (4), 29 (29); m* 79,2 (129→101), 37,1 (41→39)
12 eV: 129 (15), 114 (9), 102 (4), 101 (70), 85 (6), 84 (100), 73 (3), 70 (5), 55 (9), 41 (8)

IVa. 1-Isopropoxy-2,2,3-trimethylaziridine (syn form)

70 eV: 143 (4) $[M]^{+\cdot}$, 126 (2), 115 (12), 102 (2), 101 (3), 86 (23), 85 (5), 84 (66), 73 (24), 71 (6), 70 (6), 69 (13), 68 (8), 67 (4), 60 (4), 58 (4), 57 (7), 56 (2), 55 (5), 53 (2), 45 (8), 44 (8), 43 (100), 42 (28), 41 (38), 40 (3), 39 (10), 29 (5); m* 91,6 (143→115), 52,9 (101→73), 37,1 (41→39)
12 eV: 143 (15), 126 (9), 115 (46), 101 (30), 86 (15), 85 (6), 84 (100), 73 (22), 72 (15), 57 (13), 43 (15)

IVb. 1-Isopropoxy-2,2,3-trimethylaziridine (anti form)

70 eV: 143 (4), $[M]^{+\cdot}$, 126 (2), 115 (10), 102 (2), 101 (7), 87 (4), 86 (17), 85 (4), 84 (69), 73 (19), 71 (4), 70 (5), 69 (12), 68 (5), 60 (2), 58 (2), 57 (3), 56 (6), 55 (2), 53 (5), 45 (7), 44 (8), 43 (100), 42 (27), 41 (36), 40 (2), 39 (8), 29 (36); m* 91,6 (143→115), 52,9 (101→73), 37,1 (41→39)
12 eV. 143 (12), 126 (6), 115 (35), 101 (20), 86 (9), 85 (6), 84 (100), 73 (29), 57 (12), 43 (15)

*The peaks with intensities less than 2% of the intensity of the maximum peak (except for the molecular ions) and with m/e values less than 29 are not presented.

TABLE 1. (Continued).

V. 1-Methoxy-2,2,3,3-tetramethylaziridine

70 eV: 130 (0,8), 129 (0,5) $[M]^{+\cdot}$, 114 (4), 99 (8), 98 (100), 87 (7), 84 (5), 83 (20), 82 (4), 72 (4), 70 (2), 69 (13), 68 (3), 67 (2), 58 (2), 57 (10), 56 (10), 55 (9), 54 (2), 53 (2), 43 (7), 42 (92), 41 (50), 40 (5), 39 (23), 30 (4), 29 (12); m* 70,2 (98→83), 37,1 (41→39), 35,0 (39→37), 34,4, 33,1, 29,6 (57→41), 24,2 (69→41), 21,2 (83→42), 18,0 (98→42), 17,2 (98→41)
12 eV: 129 (0,6), 114 (3), 99 (8), 98 (100), 87 (10), 57 (2), 42 (3).

VI. 1-Ethoxy-2,2,3,3-tetramethylaziridine

70 eV: 144 (0,1), 143 (0,2) $[M]^{+\cdot}$, 128 (3), 101 (4), 100 (2), 99 (6), 98 (100), 85 (2), 84 (16), 83 (9), 82 (3), 73 (2), 70 (2), 69 (19), 59 (14), 58 (9), 57 (8), 56 (6), 55 (5), 43 (6), 42 (52), 41 (30), 40 (2), 39 (10), 31 (2), 29 (8).
12 eV: 143 (0,4), 128 (2), 101 (7), 99 (5), 98 (100), 84 (2), 42 (2)

VII. 1-n-Butoxy-2,2,3,3-tetramethylaziridine

70 eV: 172 (0,2), 171 (0,1) $[M]^{+\cdot}$, 100 (4), 99 (7), 98 (100), 84 (11), 83 (8), 82 (2), 73 (4), 69 (8), 58 (5), 57 (11), 56 (4), 55 (4), 43 (5), 42 (32), 41 (23), 40 (2), 39 (4), 29 (12); m* 70,3 (98→83), 56,9 (84→69), 37,1 (41→39), 36,5 (83→55), 29,6 (57→41), 21,3 (83→42), 18,0 (98→42).
12 eV: 171 (0,4), 99 (8), 98 (100), 84 (3), 42 (2).

ionizing-electron energy to 12 eV only slightly increases the relative intensities of the molecular ions.

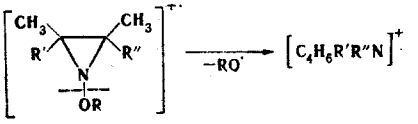
The intensities of the $[M + 1]^+$ ion peaks are anomalously higher than the intensity of the low-intensity molecular ions and are poorly reproduced; this is probably associated with the ease of protonation of these systems in the admission system of the mass spectrometer.

The intensities of the $[M - 1]^+$ ions for the investigated alkoxyaziridines do not exceed tenths of a percent and are much lower than the intensities of the molecular ions, whereas the peaks of the $M^{+\cdot}$ and $[M - 1]^+$ ions have close intensities in the mass spectra of any of the alkyl- and aryl-substituted aziridines (except for the 1-alkoxy derivatives).

Principal Fragmentation Pathways

The principal fragmentation pathways of the molecular ions of 1-alkoxyaziridines are four parallel processes, which are indicated in the case of IIIa in Figure 1. Two of them include cleavage of the C–O and N–O bonds in the alkoxy group, and the other two include cleavage of the aziridine ring.

1. The most typical fragmentation process for I-VIII upon electron impact is splitting out of the alkoxy group:



This fragmentation pathway has been previously noted for 1-methoxytetramethylaziridine [3] and derivatives of 1-alkoxyaziridinecarboxylic acids [5]. The empirical formula of the resulting ion in the case of aziridine II was confirmed by measurement of the precise mass with a high-resolution spectrometer (m/e 84.0816, $M_{C_5H_{10}N}$ = 84.0813). In accordance with [5, 6], the ions formed by splitting out of a radical from the nitrogen atom of the aziridines have the $\rangle C{=}\overset{+}{N}{=}C\langle$ acyclic structure.

The $[M - RO\cdot]^+$ ions in the spectra of the investigated 1-alkoxyaziridines have the maximum intensity (except for IIa,b and IVa,b). The contribution of these fragments to the total ion current (Table 2) ranges from 13–17% (trimethylaziridines) to 20–41% (di- and tetramethyl derivatives).

When the ionizing-electron energy is reduced to 12 eV, the fraction $[M - RO\cdot]^+$ ions in

TABLE 2. Fractions of the Molecular and Principal Fragment Ions in the Mass Spectra of 1-Alkoxyaziridines at 70 and 12 eV (in parentheses) (percent of the total ion current Σ_{29})

Fragmentation pathway and ions*	Ia	Ib	Ic	IIa	IIb	IIIa	IIIb	IVa	IVb	V	VI	VII
$M^{+\cdot}$	0,7 (3,4)	0,7 (3,4)	0,6 (2,3)	2,3 (5,4)	1,6 (6,1)	1,8 (8,4)	1,7 (7,2)	0,9 (5,3)	0,9 (4,8)	0,14 (0,4)	0,04 (0,3)	0,06 (0,3)
1. $[M-RO]^+$	31 (90)	20 (80)	30 (90)	13 (37)	17 (46)	17 (39)	17 (46)	15 (37)	17 (43)	27 (85)	32 (86)	41 (89)
$[C_2H_4N]^+$	24 (3)	17 (4)	25 (3)	13 (4)	16 (3)	12 (0)	11 (0)	6 (0)	6 (0)	22 (2)	16 (2)	12 (2)
2. $[R]^+$	†	†	†	†	†	5 (0)	5 (0)	23 (5)	25 (6)	†	0	4 (0)
3. $[M-C_nH_{2n}]^{+\cdot}$	0,3 (0)	0	0	8 (35)	8 (32)	7 (36)	7 (32)	2,6 (14)	1,7 (8)	1,2 (5)	1,2 (5)	0
4. ‡	22 (1)	19 (1)	21 (1)	22 (2)	19 (2)	22 (6)	23 (6)	15 (0)	15 (0)	29 (2)	27 (2)	12 (3)

*The letter R refers to the alkyl group of the OR alkoxy group.

†The $[CH_3]^+$ ions (m/e 15) were not recorded.

‡The sum of the intensities of the $[M - RON]^{+\cdot}$ ion peaks and the secondary hydrocarbon ions is presented for the fourth pathway.

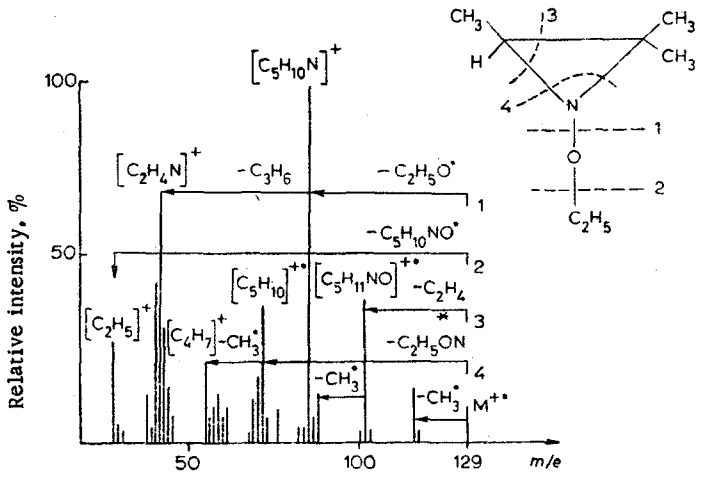
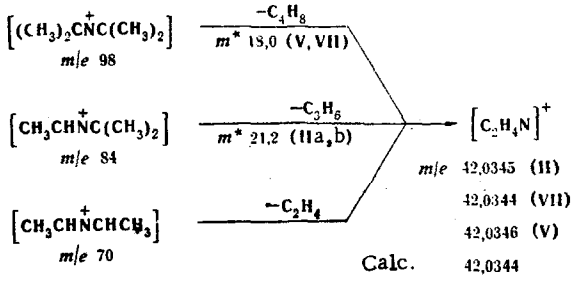


Fig. 1. Principal fragmentation pathways of 1-alkoxyaziridines upon electron impact [in the case of 1-ethoxy-2,2,3-trimethylaziridine (IIIa)].

the ion current increases sharply (up to 80-90% in the mass spectra of di- and tetramethylaziridines), but remains lower as before in the case of trimethylaziridines (37-46%); this is associated with the presence in the latter of a competitive process involving fragmentation of the molecular ions (see below).

Splitting out of an OR group in compounds of different classes containing an N–O bond (for example, some of the simplest O-alkyl ethers of oximes) also takes place, although to a considerably lesser degree [7]. However, if one examines aziridines with different substituents attached to the nitrogen atom, cleavage of the N–X bond is sufficiently characteristic and was almost always observed for (in addition to 1-alkoxyaziridines) N-acyl- [8-10], N-phthalimido- [11], N-alkyl- [6], N-aryl- [6, 12], and N-haloaziridines [5, 13]. This sort of cleavage of the N–X bond during electron impact substantially distinguishes aziridines from other nitrogen heterocycles and amines.

The next step in the fragmentation of $[M - RO^\cdot]^+$ ions can be considered to be splitting out of neutral particles corresponding in composition to the olefin molecule (C_2H_4 for dimethylaziridines, C_3H_6 for trimethylaziridines, and C_4H_8 for tetramethylaziridines), which leads in all cases to the same ion with m/e 42:

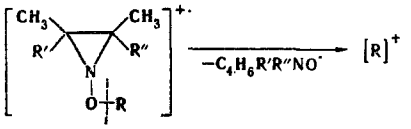


The proposed scheme is confirmed by the presence of the corresponding metastable peaks and determination of the composition of the ions with m/e 42 by means of high-resolution mass spectrometry. These ions basically have the composition $[C_2H_4N]^+$ and only a very small number of them form $[C_3H_6]^{+\cdot}$ particles. At an ionization energy of 12 eV the intensity of the ion peaks with m/e 42 decreases sharply (for example, from 25 to 3% Σ_{29} for Ic); this constitutes evidence for a two-step mechanism for its formation.

When tetramethylaziridines V-VII, which have different alkoxy groups, are compared, it may be noted that as the mass of the OR groups increases, the fraction of the $[C_6H_{12}N]^+$ ion (m/e 98) in the ion current increases (from 27 to 41%), and the fraction of the $[C_2H_4N]^+$ ion decreases (from 22 to 12%). It seems most rational to us to explain this tendency by a decrease in the energy of excitation of the $[C_6H_{12}N]^+$ fragment ion in the case of a heavier

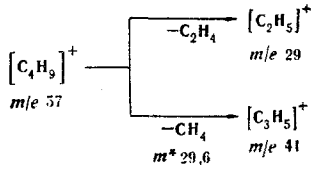
alkoxy group and, consequently, a decrease in the degree of its subsequent fragmentation. The $[C_2H_4N]^+$ ion is one of the major ions in the spectra of not only alkoxyaziridines but of all the known alkylaziridines [6].

2. Another general pathway of fragmentation of the molecular ions of 1-alkoxyaziridines is cleavage of the C–O bond in the alkoxy group, which takes place simultaneously with splitting out of the entire alkoxy group:

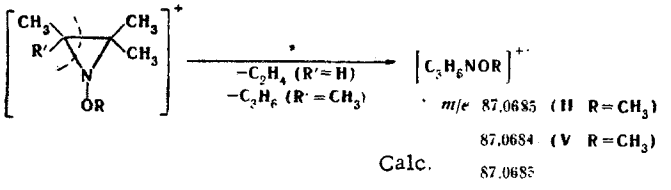


This sort of process has also been observed for derivatives of 1-alkoxyaziridine-2-carboxylic acids [5].

The intensity of the $[R]^+$ ions is usually low, except for 1-isopropoxy-2,2,3-trimethylaziridines IVa,b, in which the peaks with m/e 43 ($[C_3H_7]^+$) become the maximum peaks. It may be assumed that in this case, in which the R radicals are secondary or tertiary, the corresponding ions in the mass spectra will be among the most intense. The subsequent fragmentation of the $[R]^+$ ions via the schemes that are usual for carbonium ions is confirmed in the case of 1-n-butoxyaziridine VII:



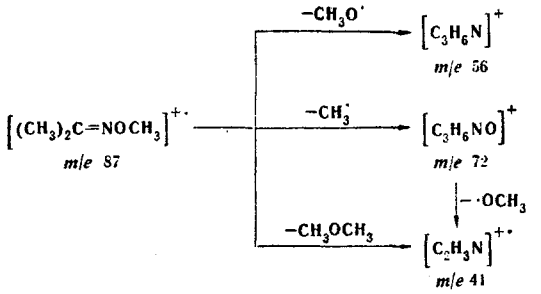
3. In addition to the two processes examined, cleavage of the aziridine ring itself with the loss of a neutral olefin molecule (C_2H_4 or C_3H_6) is characteristic for the molecular ions of 1-alkoxyaziridines:



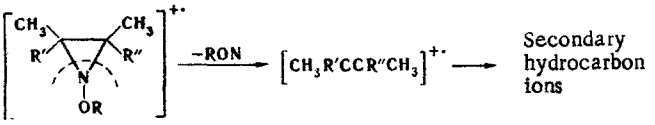
In the case of trimethylaziridines the $[M - C_2H_4]^+$ ions are among the most intense in the mass spectra (fragmentation of this type is observed to a slight extent in the spectra of di- and tetramethylaziridines).

The compositions of the $[C_3H_6NOR]^+$ ions were established for II and V by means of high-resolution mass spectrometry. The one-step character of the formation of these fragments is confirmed by the presence of the corresponding metastable peaks: IIa,b m* 66.0 (115→87), IIIa, b m* 79.2 (129→101), and IVa,b m* 91.6 (143→115).

The acetoneimine structure $[(CH_3)_2C{=}NH]^{+\cdot}$ was assigned to the analogous $[M - C_3H_6]^{+\cdot}$ ions in the spectrum of 2,2,3,3-tetramethylaziridine [6]. If this assumption is adopted, the $[C_3H_6NOR]^{+\cdot}$ ions in our case can be regarded as molecular ions of acetoxime ethers $[(CH_3)_2C{=}NOR]^{+\cdot}$, and their subsequent fragmentation may thus be similar to the fragmentation of oxime ethers under electron impact. In fact, secondary $[C_3H_6N]^+$ (calculated m/e 56.0500; found for II and V, respectively, 56.0504 and 56.0503) and $[C_2H_3N]^{+\cdot}$ ions (calculated m/e 41.0265; found for II and V, respectively, 41.0268 and 41.0269), which are characteristic for the methyl ether of acetone oxime [7], are observed in the spectra of aziridines II and V:



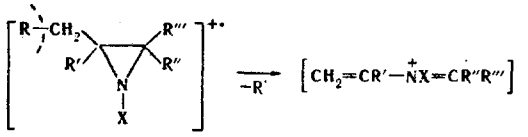
4. Cleavage of the aziridine ring at both C–N bonds is to a certain extent in our case a reversible reaction for the preparation of 1-alkoxyaziridines:



The subsequent fragmentation of the resulting $[C_nH_{2n}]^{+\cdot}$ hydrocarbon ions is similar to the fragmentation under electron impact of olefins, as a result of which a number of secondary fragment ions with m/e 41, 42, 55, 56, 69, 83, etc. are obtained. The hydrocarbon nature of the ions with these masses is confirmed by the results of measurements of the m/e values of some of the indicated fragments in the spectra of aziridines II, V, and VII.

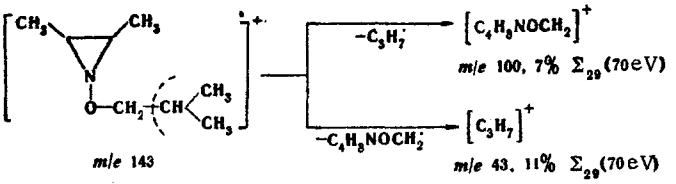
The only example of this type of fragmentation is observed for nitrogen-unsubstituted 2,2,3,3-tetramethylaziridine [6], the mass spectrum of which contains $[M - NH]^{+\cdot}$ fragment ions.

The examined four principal schemes for the fragmentation of methyl-substituted 1-alkoxyaziridines sufficiently fully describe the behavior of compounds of this type under electron impact. However, when the methyl groups are replaced by more complex groups, the possibility of cleavage of the carbon–carbon bonds in the alkyl groups, which is particularly likely in the β position relative to the aziridine ring [6], appears:



This process may become one of the major fragmentation pathways for alkyl-substituted 1-alkoxyaziridines, in addition to the pathways examined above.

Cleavage of the C–C bonds of the alkoxy group itself in some cases also leads to rather intense peaks. It follows from our data that this sort of fragmentation is most characteristic for 1-isobutoxyaziridines (for example, for 1-isobutoxy-2,3-cis-dimethylaziridine):



Analytical Application

The analytical application of the examined principles of the behavior of 1-alkoxyaziridines during electron impact primarily entails the detection and identification of these compounds in the reaction mixtures. The $[M - RO\cdot]^+$ peaks are the principal feature for the identification of 1-alkoxyaziridines. We have shown that the intensities of the analogous peaks in the spectra of the oxime ethers are several times lower than in the spectra of the isomeric aziridines. Recording of the mass fragmentation spectra with respect to the mass of the $[M - RO\cdot]^+$ ions makes it possible to immediately isolate the components of the reaction mixture for which the contribution of these fragments to the ion current is quite large.

The set of fragment ions formed as a result of the four major fragmentation processes makes it possible to subsequently determine the structures of the 1-alkoxyaziridines, despite the considerable (in some cases) variations in the ratios of the intensities of the individual lines.

Insofar as the possibility of the identification of the syn- and anti-invertomers from the mass spectra is concerned, the observed differences in the intensities of the peaks of the four investigated pairs of invertomers do not make it possible to formulate any principles common to all of the alkoxyaziridines.

EXPERIMENTAL

The mass spectra were obtained with an LKB-2091 chromatographic mass spectrometer at ionization energies of 70 and 12 eV, an ionization current of 25 μA, an accelerating voltage of 3.5 kV, a separator temperature of 140-150°C, and an ion-source temperature of 180°C.

In addition to LKB columns [1.8 m by 2 mm with 2% SE-30 on Chromosorb W (80-100 mesh) and a 17 m by 0.25 mm capillary column with SE 30], a Hewlett–Packard 2 m by 2 mm steel column with 10% Carbowax 20 M on Chromosorb W (60-80 mesh) was used for chromatographic separation of the reaction mixtures. The compounds were introduced in the form of 5-10% solutions in methylene chloride (in 0.2-0.4 μl doses).

No special search was made for the metastable ions. The precise masses of the individual ions in the spectra of II, V, and VII were determined with an A.E.I.Ms-50 high-resolution mass spectrometer in the Institute of Organic Synthesis of the Academy of Sciences of the Latvian SSR by A. P. Gaukhman, to whom the authors express their sincere gratitude.

Alkoxyaziridines. The alkoxyaziridines were obtained by oxidation of the corresponding alkoxy amines with lead tetraacetate in excess olefin [1]. A 0.01-mole sample of lead tetraacetate and 10 ml of methylene chloride were added in small portions with vigorous stirring in the course of 15 min to a cooled (to −45°C) mixture of 0.01 mole of alkoxy amine,* 0.05 mole of olefin, and 15 ml of dry methylene chloride, and the mixture was stirred at −45°C for 30 min, after which the cooling bath was gradually removed, and the mixture was stirred at room temperature for 30 min. The resulting solution was washed with water (three 30-ml portions) to remove the acetic acid and dried with magnesium sulfate for 24 h. The solution was concentrated *in vacuo* (with a water aspirator) at room temperature.

Aziridines I and II were isolated from the reaction mixtures by preparative gas–liquid chromatography (GLC) with a 2 m by 18 mm steel column filled with Celite 545 with a 15% stationary phase [73% Apiezon L, 21.5% TPNA, 5% polyethylene glycol, and 0.5% (PEPA) at 50°C (for I) and 70°C (for II]; the carrier-gas (nitrogen) flow rate was 60 ml/min, the vaporizer temperature was 100-120°C, and the apparatus was a Tsvet-1 chromatograph with a flame-ionization detector. The time per cycle was 60 min, the dose was 1 ml, and the trap was cooled to −60°C.

Aziridines V and VII were isolated by distillation from a flask with a fractionating column.

1-Methoxy-2,3-cis-dimethylaziridines. These compounds were obtained from 99.6% pure cis-2-butene. Preparation Ia, which had a lower retention time, contained 90% of the pure substance according to GLC. The most intense signals in the PMR spectrum (δ) were as follows: 3.43 (s, OCH_3) and 1.04 ppm (d, J = 5 Hz, CH_3). Preparation Ib, which had a longer retention time, contained admixed Ia (16%) and other substances (∼ 30%) according to GLC. The principal signals in the PMR spectrum (δ) were as follows: 3.44 (s, OCH_3), 1.13 (d, J = 5 Hz, methyl groups of the principal component), and a weak doublet at 1.05 ppm (methyl groups of admixed Ia).

A syn configuration was assigned to Ia, the methyl groups of which are, according to the PMR spectrum, more shielded than in Ib, on the basis of the information in [1].

The mass spectra of Ia and Ib were recorded at the maxima of the chromatographic peaks of the principal components.

*The synthesis of aziridines V and VII was carried out with 0.1-0.2 mole of the alkoxy amine.

1-Methoxy-2,3-trans-dimethylaziridine (Ic). This compound was obtained from 98% pure trans-2-butene. The preparation isolated by GLC contained 96% of the pure substance. PMR spectrum, δ: two identical doublets at 1.07 and 1.27 (J = 5 Hz), multiplet of ring protons at 1.40-1.62 ppm, and singlet at 3.42 ppm (OCH_3).

1-Methoxy-2,2,3-trimethylaziridine (IIa). This compound had n_D^{20} 1.4111, n_C^{20} 1.4089, Δ_{FC} 78.0, and ω_{FCD} 18.97. The structure of the aziridine was confirmed by the IR and PMR spectra, which are completely identical to the spectra obtained in [1].

1-Methoxy-2,2,3-trimethylaziridine (IIb). This compound had n_D^{20} 1.4166, n_C^{20} 1.4143, Δ_{FC} 79.7, and ω_{FCD} 19.13. The IR and PMR spectra were in agreement with the spectra described in [1].

1-Methoxy-2,2,3,3-tetramethylaziridine (V). This compound was isolated in 27% yield and had bp 97-98°C (766 mm), d_4^{20} 0.8407, n_D^{20} 1.4194, n_C^{20} 1.4159, Δ_{FC} 87.7, and ω_{FCD} 20.81. Found, %: C 64.85; H 11.73; MR_D 38.89. $C_7H_{15}NO$. Calculated, %: C 65.07; H 11.70; MR_D 38.25.* PMR spectrum, δ: three singlets at 1.09, 1.11, and 3.40 ppm with an intensity ratio of 2:2:1. The IR spectrum is in agreement with the spectrum presented in [1, 3].

1-n-Butoxy-2,2,3,3-tetramethylaziridine (VII). This compound was isolated in 30% yield and had bp 62-64°C (32 mm), d_4^{20} 0.8499, n_D^{20} 1.4292, n_C^{20} 1.4269, Δ_{FC} 80.1, and ω_{FDC} 18.65. Found, %: C 69.79; H 12.26; MR_D 51.97. $C_{10}H_{21}NO$. Calculated, %: C 70.12; H 12.36; MR_D 52.19.* PMR spectrum, δ: 1.13 and 1.16 (s, $4CH_3$), 3.63 (t, J = 6 Hz, 2H), and 0.7-1.8 ppm (m, corresponding to 19H). The PMR and IR spectra were in complete agreement with the spectra presented in [4].

Aziridines III, IV, and VI. The compounds obtained in [1] were used.

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*The refraction of the N–O bond is 1.95 [15].