MASS SPECTROMETRIC STUDY OF 8-NITROISOXAZOLIZIDINES

II. Disubstituted 8-Nitroisoxazolizidines*

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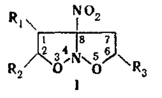
The mass spectra of dimethyl- and methylphenyl-8-nitroisoxazolizidines have been studied, and the possibility of establishing the position of the substituents on the basis of an analysis of these spectra has been shown. The main routes of the fragmentation of compounds of this class under the influence of electron impact are discussed.

We have previously shown [1] that the structure of the monosubstituted 8-nitroisoxazolizidines can be successfully established on the basis of analysis of their mass spectra. The present paper is devoted to a study of the mass spectrometric behavior of the disubstituted 8-nitroisoxazolizidines Ia–e:



I

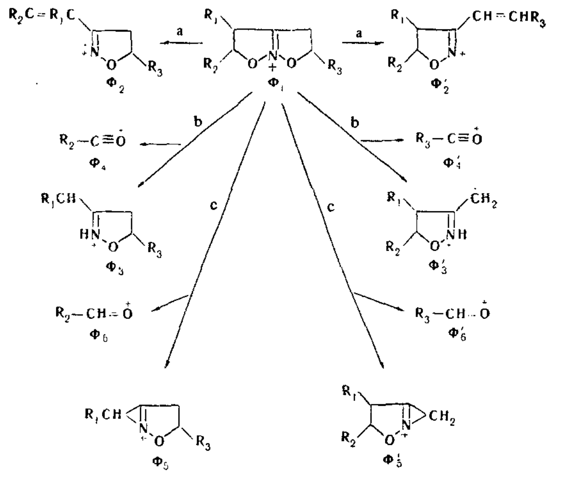
I a $R_1=H$, $R_2=R_3=CH_3$;
b $R_1=R_3=CH_3$, $R_2=H$;
c $R_1=H$, $R_2=CH_3$, $R_3=C_6H_5$;
d $R_1=CH_3$, $R_2=H$, $R_3=C_6H_5$;
e $R_1=C_6H_5$, $R_2=H$, $R_3=CH_3$.

As in the mass spectra of the monosubstituted compounds of this class, the peak of the molecular ion is absent from the mass spectra of the disubstituted 8-nitroisoxazolizidines Ia–e taken on a MKh-1303 instrument at a temperature of 140–150° C with an electron energy of 25–40 eV. The "heaviest" ion in the mass spectra is the $[M-46]^+$ ion Φ_1, corresponding to the elimination of the NO_2 group from the molecular ion. From the m/e value of the Φ_1 ion, it is easily possible to determine the molecular weight of the compound under investigation.

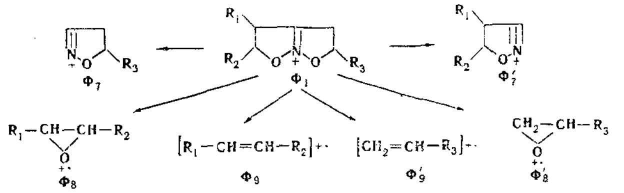
The most probable position of the localization of the positive charge in the ion Φ_1 is the nitrogen atom, and the main routes of fragmentation of the ion are connected with the rupture of a N—O bond with the simultaneous or successive rupture of a C—O or C—C bond, which is frequently accompanied by the migration of a hydrogen atom from the residual charged fragment to the eliminated residue, or conversely.

The following routes of degradation are the most characteristic for the Φ_1 ions: a) elimination of a ·OH radical as a result of the rupture of N—O and $C_2(C_6)$—O bonds, accompanied by the migration of the hydrogen atom from the remaining charged fragment (Φ_2 or Φ_2', see Scheme 1) to the oxygen; b) rupture of N—O and C_1—C_2 (C_7—C_6) bonds with the migration of a hydrogen atom from the acyl fragment eliminated with the formation of the ion radical Φ_3 or Φ_3' (it must be mentioned that as a result of this type of degradation the charge may also be localized on the acyl fragment—the ions Φ_4 or Φ_4', see Scheme 1); c) rupture of the bonds described above but without migration of a hydrogen atom, leading to the formation of the ions Φ_5 and Φ_5' or aldehydic ion-radicals (Φ_6 or Φ_6' see Scheme 1); d) rupture of N—O and C_1—C_8 (C_7—C_8) bonds with the elimination of an olefin oxide and the formation of the ions Φ_7 or Φ_7'—the peaks of the ions due to the localization of the charge on the olefin oxide fragment Φ_8 and Φ_8' are of low intensity (see Scheme 2); c) rupture of the $C_2(C_6)$—O and $C_1(C_7)$—C_8 bonds with the formation of an olefin ion-radical (Φ_9 or Φ_9')—the localization of the charge on the second fragment is less probable.

Scheme 1



Scheme 2



In determining the positions of the substitutents in the 8-nitroisoxazolizidines studied, the fullest information is given by a consideration of the route for the degradation of the ion Φ_1 connected with the elimination of an acyl radical (b). In actual fact, in the case of the symmetrically disubstituted 8-nitroisoxazolizidine Ia only the elimination of an acetyl radical is possible with the formation of a single ion-radical $\Phi_3=\Phi_3'$ with m/e 99 (figure, 1), while the mass spectrum of the unsymmetrical isomer Ib (figure, 2) has the peaks of the two possible ion-radical (Φ_3' with m/e 99, corresponding to the elimination of an acetyl group, and Φ_3, corresponding to the elimination of a formyl group).

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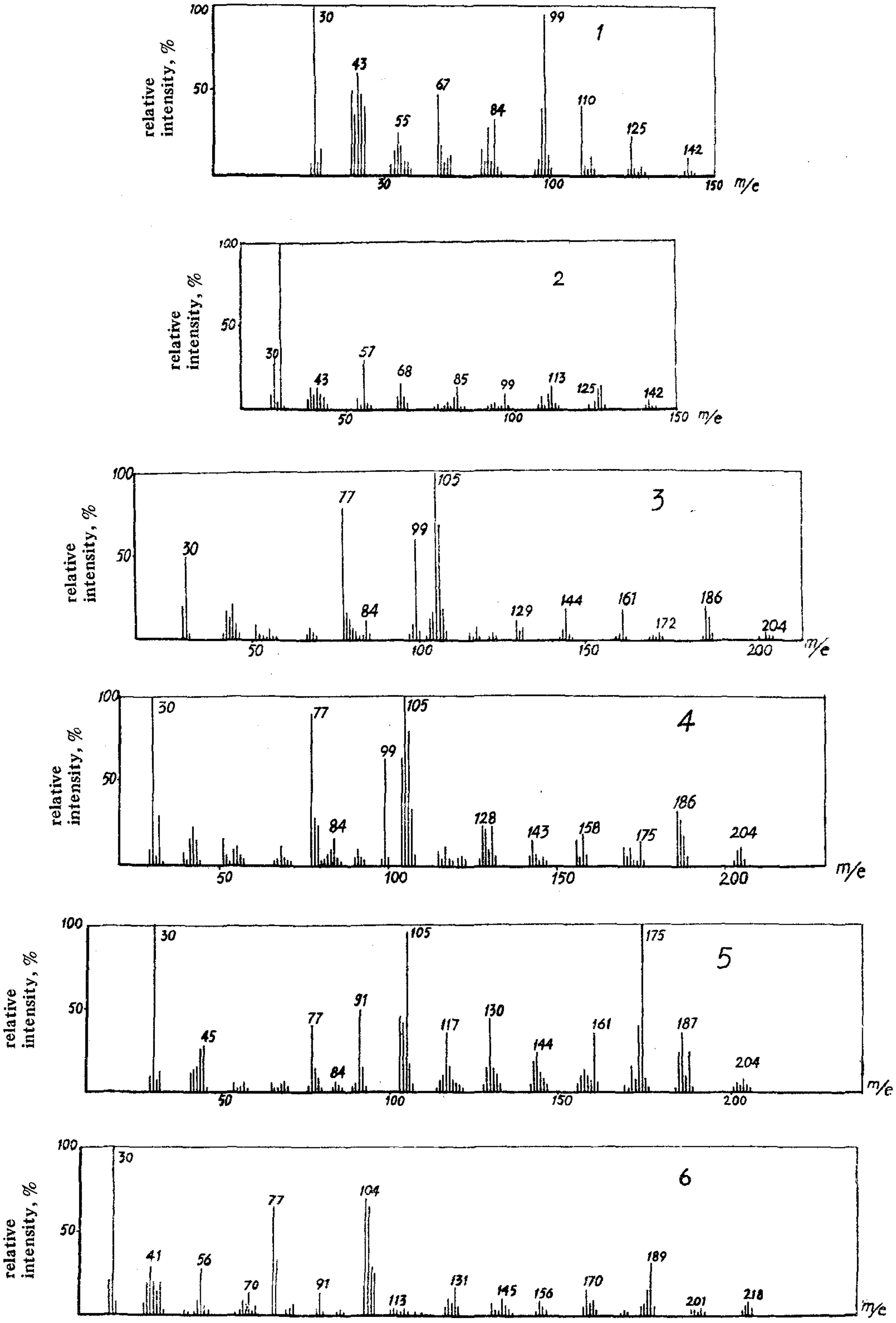
*For part I, see [1].



Mass spectra of the compounds: 1) Ia; 2) Ib; 3) Ic; 4) Id; 5) Ie; 6) II.

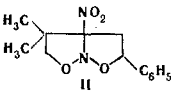
Similarly, in the mass spectrum of Ie (figure, 5) there are peaks with m/e 161 (Φ_3') and 175 (Φ_3) corresponding to the elimination of the same radicals.

In the case of Ic (figure, 3) acetyl and benzoyl radicals are eliminated from the ion Φ_1, which leads to ion radicals with m/e 161 (Φ_3) and 99 (Φ_3'), and in the case of Id (figure, 4), formyl and benzoyl radicals are eliminated, which leads to ion-radicals with m/e 175 (Φ_3) and 99 (Φ_3').

Thus, the isomeric disubstituted 8-nitroisoxazolizidines having different substituents in positions 2 and 6 are readily distinguished from one another by comparing their mass spectra.

Additional information on the nature and position of the substituents can be obtained from a consideration of the peaks of the ions Φ_4(Φ_4') and also other routes of fragmentation. For example, when a phenyl substituent is present in the molecule of the 8-nitroisoxazolizidine, very intense peaks with m/e 106 and 105, corresponding to the ion-radical of benzaldehyde (Φ_6 or Φ_6') or benzoyl (Φ_4 or Φ_4') appear, the intensities of which vary little with a change in the position of the substituent. However, information on the position of a phenyl substituent can be given by the peak of the tropylium ion with m/e 91. In the mass spectra of the 8-nitroisoxazolizidines containing a phenyl substituent in position 1, there is an intense peak of an ion with m/e 91 (Ie, figure, 5), while in the case of the isomers containing phenyl in position 2 or 6, this peak is either completely absent (Ic, figure, 3) or its intensity is very low (Id, figure, 4).

The correctness of the routes of fragmentation of disubstituted 8-nitroisoxazolizidines given above was confirmed by a study of the mass spectrum of 1,1-dimethyl-6-phenyl-8-nitroisoxazolizidine (II), in which all the peaks of the fragments containing the C_1 atom



II

are displaced by 14 mass units in comparison with the corresponding peaks in the spectrum of Id. In actual fact, as is easy to see (figure, 6), the mass spectrum of II has peaks of the following fragments (values of m/e given in brackets): Φ_1(218), Φ_2'(201), Φ_3(189), Φ_3'(113), Φ_4(29), Φ_4'(105), Φ_5(188), Φ_5'(112), Φ_6(30), Φ_6'(106), Φ_7(146), Φ_7'(98), Φ_8(72), Φ_8'(120), Φ_9(56) and Φ_9'(104).

Thus, the observed correlations between the nature of the mass spectra and the structures of the 8-nitroisoxazolizidines enable the structures of compounds of this class to be established by the mass spectrometric method.

REFERENCE

1. B. V. Rozynov, V. A. Puchkov, N. S. Vul'fson, V. A. Tartakovskii, A. A. Onishchenko, and S. S. Novikov, DAN, 169, 123, 1966.

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