

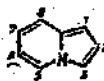
FEATURES OF MASS-SPECTRAL FRAGMENTATION OF METHYLNITROINDOLIZINES

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The mass spectrometric method is very informative for the study of the structure of nitroheteroarenes [1]. Results of the study of primary processes of mass spectral fragmentation of a series of isomeric methylnitroindolizines, containing ortho-situated CH_3 and NO_2 groups in various positions of the indolizine ring, are presented in this communication. The main directions of fragmentation are the following processes with participation of the NO_2 group (characteristic of nitroarenes and nitroheteroarenes on the whole): 1) elimination of the NO_2 group; 2) cleavage of NO_2 as a result of the nitro-nitrite rearrangement; 3) elimination of the HO radical as a result of the "ortho-effect" [2]. The obtained experimental data are presented in the table, together with earlier obtained mass spectrometric results of 2-methyl-6-nitro- and 2-methyl-8-nitroindolizines. It is seen from data of the table that in the case of 6- and 8-nitroindolizines elimination of the nitro group plays an important role, while for indolizines with an NO_2 group in the pyrrole ring the nitro-nitrite rearrangement is more characteristic. An analogous dependence was observed earlier for isomeric nitroindoles [3].




Substituent	M	$[\text{M}-\text{NO}]^+$	$[\text{M}-\text{NO}_2]^+$	$[\text{M}-\text{OH}]^+$
		M^+	M^+	M^+
2-Me-6- NO_2 [3]	176	—	0.75	—
2-Me-8- NO_2 [4]	176	0.01	0.88	—
2,7-Me ₂ -6- NO_2	190	0.06	1.12	0.60
2,7-Me ₂ -8- NO_2	190	0.12	1.35	0.16
2-Me-1- NO_2	176	0.29	0.04	0.69
2-Me-3- NO_2	176	0.40	0.20	0.17
2-Me-1,6-(NO_2) ₂	221	0.11	0.08	0.31
2-Me-3,6-(NO_2) ₂	221	0.23	0.12	0.17

The most important result is the observed dependence of the intensity of the $[\text{M}-\text{OH}]^+$ peak on the arrangement of CH_3 and NO_2 groups in relation to the tetraene skeleton of indolizine, characterized by a significant degree of localization of double and single bonds [5]. It was found that the $[\text{M}-\text{OH}]^+/M^+$ ratio is several times greater for isomers, containing the



fragment than for

isomers, containing the  fragment when the substituents are present both in the pyrrole and in the pyridine portion of the indozine molecule (table). The found dependence can be helpful during the structural determination of isomeric methylnitroindolizines.

The synthesis of introindolizines and a detailed analysis of mass spectra will be published later. The authors are grateful to Doctor of Chemical Sciences P. B. Terent'ev for helpful discussion.

Experimental part. Mass spectra were obtained on an MKh-1303 instrument at an ionization energy of 70 eV with direct sample introduction into the ion source.

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