MASS SPECTRA OF IMIDAZOLE DERIVATIVES.

3.* PENTASUBSTITUTED 1-HYDROXY-3-IMIDAZOLINE-3-OXIDES AND 3-IMIDAZOLINE-3-OXIDE-1-OXYLS

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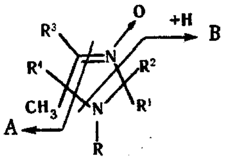
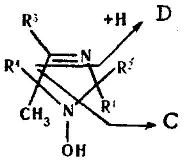
Stable nitroxyl radicals have recently found much wider application in various fields of science and technology. They have been used, for example, as spin markers, antioxidants, the working substances of lasers, stabilizers, etc., [3], which explains the increased interest of investigators in studying various aspects of the behavior of these compounds. In the literature information is available concerning the fragmentation under electron impact of nitroxyl radicals and their precursors in the pyrrolidine [4], piperidine and derivatives [5-7], isoindoline [8], and benzopyrroloindole [9] series, and certain other compounds [10, 11].

In our previous studies the mass spectra of pentasubstituted 3-imidazoline-3-oxides [1], 3-imidazoline-1-oxyls and their precursors — the 1-hydroxy-3-imidazolines [2] — have been examined. On the basis of an analysis also of the high resolution spectra of the labeled compounds it was shown that the molecular ions (M^+) of the sterically hindered 3-imidazoline-3-oxides and 1-hydroxy-3-imidazolines were degraded mainly along two routes, with the formation of type A ions and B ions (Scheme 1) and C and D ions (Scheme 2) respectively. A somewhat more complicated fragmentation picture was observed in the spectra of the pentasubstituted 3-imidazoline-1-oxide (Scheme 3). In the majority of the spectra of these stable radicals intense lines due to the fragment ions $[M - 30]^+$ and $[M - 45]^+$ were also present.

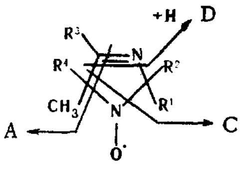
Scheme 1



Scheme 2



Scheme 3



In the present work the mass spectra of the following pentasubstituted 1-hydroxy-3-imidazoline-3-oxides (I) and 3-imidazoline-3-oxide-1-oxyls (II) have been studied.

It seemed pertinent to compare the spectra of these compounds with the previously studied representatives of the 3-imidazoline series and to attempt to widen the possibility of using mass spectrometry for establishing the structure of stable nitroxyl radicals. The application of other spectroscopic methods for studying the structure of these molecules, for example, nuclear magnetic resonance, because of the short relaxation times, resulting from the unpaired electron, does not enable reliable structural characteristics of the molecules to be obtained.

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*For communications 1 and 2, see [1, 2] respectively.

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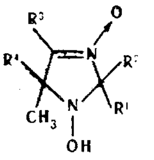
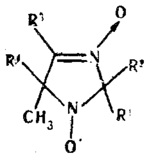


I



II

I **a** $R^1=R^2=R^3=R^4=CH_3$; **b** $R^1=R^2=CD_3$, $R^3=R^4=CH_3$; **c** $R^1=R^2=R^3=R^4=CH_3$, 3-^{15}N; **d** $R^1=R^2=R^3=R^4=CH_3$, $R^3=C_2H_5$; **e** $R^1=R^2=R^4=CH_3$, $R^3=i\text{-}C_3H_7$; **f** $R^1=R^2=CH_3$, $R^3+R^4=(CH_2)_4$; **g** $R^1=R^2=R^4=CH_3$, $R^3=C_6H_5$; **h** $R^1=R^2=R^4=CH_3$, $R^3=C_6H_4F\text{-}p$; II **a** $R^1=R^2=R^3=R^4=CH_3$; **b** $R^1=R^4=CH_3$, $R^1=R^2=CD_3$; **c** $R^1=R^2=R^3=R^4=CH_3$, 3-^{15}N; **d** $R^1=R^2=R^4=CH_3$, $R^3=C_2H_5$; **e** $R^1=R^2=R^4=CH_3$, $R^3=i\text{-}C_3H_7$; **f** $R^1=R^2=CH_3$, $R^3+R^4=(CH_2)_4$; **g** $R^1=R^2=R^4=CH_3$, $R^3=C_6H_5$; **h** $R^1=R^2=R^4=CH_3$, $R^3=C_6H_4F\text{-}p$; and $R^1+R^2=(CH_2)_5$, $R^4=CH_3$, $R^3=C_6H_5$

Pentasubstituted 1-Hydroxy-3-Imidazoline-3-Oxides (Ia-h).

The main fragmentation path of the molecular ions (M^+) of compound Ia (Fig. 1,a) gives rise to the formation of the hydrocarbon ion $[C_5H_9]^+$.* Loss of a fragment of 73 amu (C_3H_7NO) with formation of ions of composition C_5H_9NO, m/e 99,† and with approximately an equal probability of formation of ions at 74$[C_3H_8NO]^+$, which requires the migration of a hydrogen atom to the charged fragment, represents two other important disintegration pathways of this compound. These fragmentation paths can also be traced in the spectra of the other 4-alkyl-substituted 1-hydroxy-3-imidazoline-3-oxides (Id, Ie, Fig. 1d,e) Thus in the spectra of compounds Id and Ie ion peaks are observed at 113, 83 and 127, 97 respectively, the characteristic shifts of which on the mass scale give confirmation that the ions are of a similar nature to those at 99 and 69 in the spectrum of compound Ia. We also note that the ion peak at 74 $[C_3H_8NO]^+$ has the same m/e value in the spectra of compounds Id and Ie.

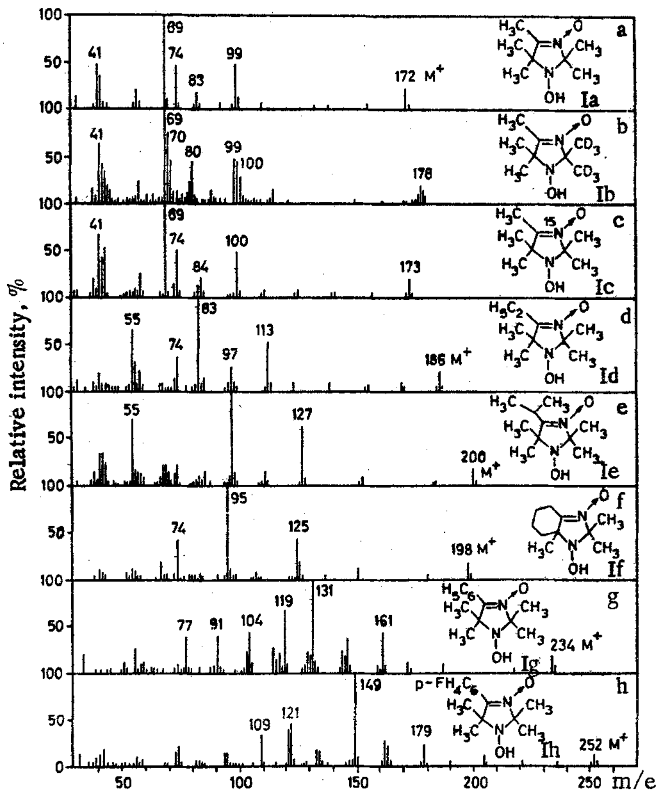


Fig. 1. Mass spectra of 1-hydroxy-3-imidazoline-3-oxides Ia-h.

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*Here and in the sequel the elemental compositions given are calculated from the accurate values of the mass numbers.

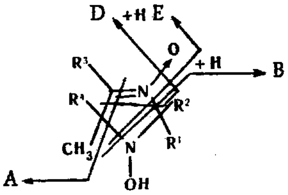
†Here and in the sequel the number characterizing the ion is the mass to charge ratio.

Previously it has been found that for the 3-imidazoline-3-oxides [1] there is a characteristic formation of hydrocarbon ions containing the substituents at positions 4 and 5 of the imidazoline ring (type A ions, Scheme 1). This fragmentation path apparently also occurs for compounds Ia-f since when both the substituents R^3 and R^4 are changed, the peaks due to the hydrocarbon ions shift by the corresponding number of mass units, and in the spectrum of the oxide Ib (2,2-ditrideuteromethyl derivative) the position of the peak is essentially maintained.

In the case of pentamethyl-3-imidazoline-3-oxide [1] formation of the ion of composition $N^1HRC^2R^1R^2$ ($[M - 98]^+$, see Scheme 1, path B) is brought about by cleavage of the N^1—C^5 and C^2—N^3 bonds. This fact suggests that the ion $[C_3H_8NO]^+$ in the spectrum of compound Ia could arise as a result of an analogous process. Loss of a fragment of 73 amu, on the other hand, is a distinctive feature of the spectra of pentasubstituted 1-hydroxy-3-imidazolines [2] and for this scission of at least two bonds N^1—C^2 and C^4—C^5 is necessary (path B, Scheme 2). It can be accepted that the fragmentation pattern of the oxide If (in the spectra ion peaks are present at 74 and $[M - 73]^+$, Fig. 1f) provides proof of the scission of the N^1—C^5 and C^2—N^3 bonds during formation of both types of ion, however it is possible that the occurrence of these processes is due to an effect of the ring substituent on the degradation of M^+.

Indisputable proof of the participation (retention or elimination) of groups of atoms of the original molecule in the disintegration process is provided by analysis of the mass spectra of the D_6- and 3-^{15}N-analogs of compound Ia (see Fig. 1b,* c). The ion peak at 99 $[C_5H_9NO]^+$ essentially maintains its position in the spectrum of the deuteroanalog Ib and is shifted by a unit in the spectrum of compound Ic. This unambiguously points to the inclusion in the composition of the ions under discussion of the substituents at positions 4 and 5 and the atom N-3, and consequently, the loss of fragment $N^1C^2R^1R^2$ when the ions $[M - 73]^+$ are formed. This fragmentation path is formally represented in Scheme 4 by type E ions.

Scheme 4



From Table 1 and Fig. 1a,c it is seen that the ion $[C_3H_8NO]^+$ essentially retains 6 atoms of deuterium and does not contain the ^{15}N marker, which indicates the inclusion of the substituents at atoms $C_{(2)}$ and $N_{(1)}$ of the imidazoline ring in their composition (by Scheme 4, path B). (Evidence of the existence of a fragmentation path leading to formation of type A ions has been given above.)

Attention should be drawn firstly to the content of seven deuterium atoms in ion B, secondly to the differing content of one and two atoms of deuterium in the type A and E ions, In the first case the percentage content of seven deuterium atoms, taking account of a possible exchange of the hydrogen of the hydroxyl group with deuterium during synthesis [12], suggests that migration of the hydrogen atoms which accompanies the formation of ion B occurs mainly from the methyl group in position 5. The differing contents of deuterium in the ions A and E apparently indicate the existence of several, possibly independent of one another, formation paths of these ions. From analysis of the spectra of compounds Ia-c it is also seen that at least a large proportion of the ions at 42 ($[C_2H_4N]^+$, type D ions, Scheme 4) contain the $N_{(3)}$ atom and do not contain the methyl group at atom $C_{(2)}$ of the imidazoline ring.

Introduction of aryl substituents (Fig. 1g, h) considerably reduces the stability of the molecular ions to electron impact [1] (the values of W_M for compounds Ia and Id are 3.7 and 2.34 against 1.64 and 1.2 for compounds Ig and Ih respectively) and complicate the degradation processes of M^+. Nevertheless in the spectra of these compounds peaks are present of

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*The intensities of the ion peaks at 179 and 180 indicate an excessive content of deuterium contrary to expectation. Apparently a significant exchange of the protons of the hydroxyl and allyl methyl groups occurs with deuterium during synthesis of the compound (see, e.g., [12]).

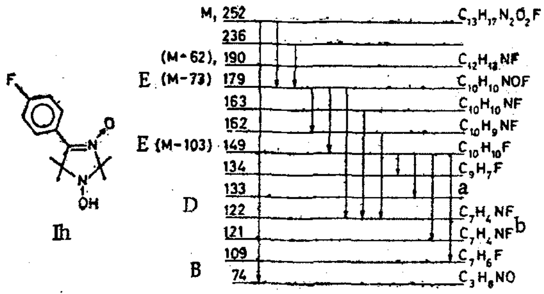
TABLE 1. Deuterium Content in the Molecular Ions and Ions $[C_5H_9NO]^+$, $[C_3H_8NO]^+$ and $[C_5H_9]^+$

D Number	$C_8H_{16}N_2O_2$, m/e	M^+, %	$[C_5H_9NO]^+$, m/e	E, %	$[C_3H_8NO]^+$, m/e	B, %	$[C_5H_9]^+$, m/e	A, %
D_0	172	14	99	100	74	20	69	100
D_1	173	12	100	89	75	5	70	81
D_2	174	13	101	51	76	9	71	40
D_3	175	19	102	6	77	15	72	8
D_4	176	25			78	23		
D_5	177	49			79	51		
D_6	178	100			80	100		
D_7	179	83			81	15		
D_8	180	39			82	6		
D_9	181	11						

type A ions (131 and 149 for compounds Ig and Ih respectively), type E ions (161 and 179) and type B ions (74). Apparently the aryl substituents impart great stability to the ions $[M - O]^+$ and $[M - (NO+OH)]^+$ compared with alkyl substituents, which is apparent in the increased number of fragment ion peaks. In the spectrum of Ig in addition metastable ion peaks are observed, for example, at 129.1, 127.1, 114.88, 63.2 corresponding to the transitions 161 → 144, 204 → 161, 146 → 129, 161 → 119, 131 → 91 (the calculated m/e values of the metastable ions are respectively 128.9, 127.2, 114.1, 88, 63.2), however the multivariability of the compositions of the majority of the ions in the spectrum of compound Ig (see Experimental section) makes determination of their genetic bonds difficult. A simpler degradation picture is observed in the case of compound Ih.

The metastable transitions (Scheme 5) found in the spectrum of this compound by the defocusing method [13] suggest that a possible source of the type A ions in the spectrum of this compound could be type E ions, which in turn are formed both directly from M^+, and from the ion $[M - 16]^+$. Ion B is formed as a result of a single-stage breakdown of the molecular ions, and the nitrogen containing ion D proves to be a daughter ion in relation to the three ion species at 170, 163 and 162.* However these details do not obscure the main fact: for compounds Ia-h, as for the 3-imidazoline-3-oxides [1], formation of type A and B ions is a characteristic. The presence of a hydroxy group at atom N-1 changes the ratio of the peak intensities of these ions and in addition, facilitates the occurrence of one other process — the formation of type E ions (Scheme 4).

Scheme 5



a) The ion composition was not determined.
b) Apparently formed from ions 149 of a different composition, which are not recorded on the normal mass spectrum.

Pentasubstituted 3-Imidazoline-3-oxide-1-oxyls (IIa-i);

Molecular ions of the nitroxyl IIa (Fig. 2a) lose a methyl radical and NO group, the intensities of the ions which are formed in this way are 10 and 13% respectively. In the

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*It should, however, be kept in mind that the defocusing method [13] which we used for constructing Scheme 5 does not enable all possible ion relations to be recorded in the spectrum. Nevertheless from the data obtained it follows that the overall fragmentation picture is rather complex.

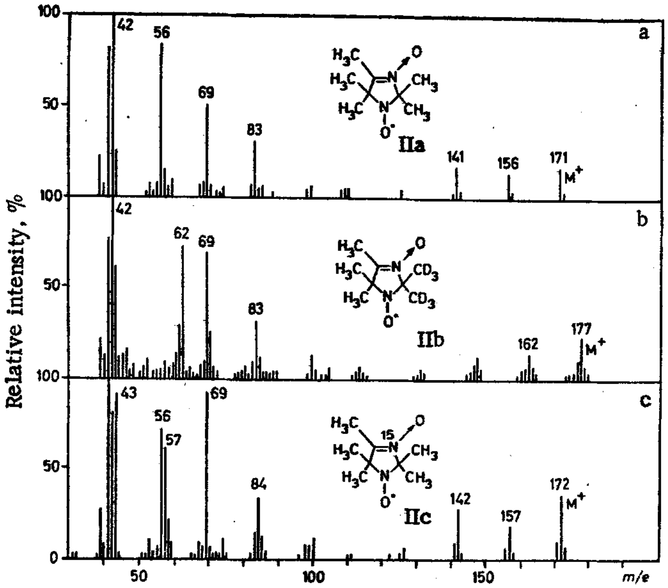

Fig. 2. Mass spectra of the 3-imidazoline-3-oxide-1-oxyls IIa-c.

spectrum of compound IIa strong peaks are observed both for hydrocarbon ions — 69 $[C_5H_9]^+$, 41 $[C_3H_5]^+$ and for nitrogen-containing ions — 83 $[C_5H_9N]^+$, 56 $[C_3H_6N]^+$, 42 $[C_2H_4N]^+$.* A quite definite conclusion concerning the degree of participation — loss or retention — of atoms and groups of atoms of the original molecule in the M^+ fragmentation process follows from analysis of the spectra of the 2,2-ditrideuteromethyl- and 3-^{15}N-analogs of compound IIa (Fig. 2b,c).

From comparison of the spectra of Fig. 2a-c, it is seen that during formation of the ion $[M - 15]^+$ the CH_3 group is lost but not CD_3. This suggests that in the case of compound IIa in a way analogous to the decomposition of the 3-imidazoline-1-oxides [2], a methyl group is lost from the atom $C_{(5)}$ of the imidazoline ring. Loss of the NO group from the molecular ion also involves atom $N_{(1)}$ of the ring, since the ^{15}N marker is completely retained by the ions $[C_8H_{15}NO]^+$ in the spectrum of compound IIc.

Peaks due to hydrocarbon ions of the type $[C_5H_9]^+$ (69) and $[M - 102]^+$ are also present in the spectrum of compound Ia. The compositions of these, as shown earlier, result from the substituents at atoms $C_{(4)}$ and $C_{(5)}$ of the imidazoline ring (Schemes 1,3,4, path A). Judging by the retention of the value of m/e for the peaks due to the ion $[C_5H_9]^+$ in the spectrum of the deuteroanalog IIb and in the case of pentamethyl-3-imidazoline-3-oxide-1-oxyl IIa, these ions include the same part of the molecule and characterize the substituents R^3, R^4 and R^5.

The ion $[C_3H_5]^+$, 41, apparently, basically contains the part of the molecule with the atoms $C_{(4)}$ and $C_{(5)}$ which is indicated by the ratio of the peak intensities of the ions $[C_3H_5]^+$ and $[C_3D_5]^+$ in the spectrum of compound IIb.

Nitrogen-containing Ions. Peaks due to ions of composition C_5H_9N, 83, and $[M - 88]^+$ are observed in the spectrum of pentamethyl-3-imidazoline-1-oxyl and, as was shown [2], for their formation the scission of at least the two bonds $C_{(4)}$—$C_{(5)}$ and $N_{(1)}$—$C_{(2)}$ is necessary and elimination of the fragment $C^5R^4R^5NO$ (Scheme 3, path C). Retention of the m/e value of the peak due to the ion $[C_5H_9N]^+$ in the spectrum of the deuteroanalog of IIb and its shift by one unit in the spectrum of compound IIc indicates the loss of the $N^1C^2R_2$ part of the molecule during formation of these ions. Thus the ion $[M - 88]^+$ is determined by the substituents at atoms $C_{(4)}$, $C_{(5)}$, and $N_{(3)}$ of pentamethyl-3-imidazoline-3-oxide-1-oxyl, and the eliminated group is the substituent at atom $C_{(2)}$.

In the spectrum of the deuteroanalog IIb the line due to the ion at 56, $[C_3H_6N]^+$, is shifted by 6 units towards higher m/e values, which indicates the retention of atom $C_{(2)}$ with its substituents in the ion composition. Also from the spectrum of compound IIc it is seen that the ion $[C_3H_6N]^+$ includes both the atoms $N_{(1)}$ and $N_{(3)}$ since the content of the ^{15}N

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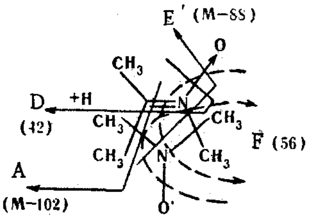
*For accurate m/e values and elemental compositions see experimental section.

isotope in this ion is 45%.

The ion 42, $[C_2H_4N]^+$, almost completely retains the ^{15}N marker and does not contain deuterium. This indicates the inclusion of the atoms $C_{(4)}$ and $N_{(3)}$ of the ring and the methyl group in its composition. Also it should be noted that formation of the ion $[C_2H_4N]^+$ is accompanied by migration of a hydrogen atom mainly from the methyl group of position 5 (compare with [2]).

On the basis of the data which have been presented and retaining the symbols of the previously discussed Schemes 1-4, the most important fragmentation paths of compound IIa can be represented by the following scheme:

Scheme 6



The regularities which have been found are also retained in the mass spectrometric disintegration of other nitroxyl radicals IId-i (Fig. 3a-f). The elemental composition of the hydrocarbon ions, corresponding to the loss of 102 amu in the case of the nitroxyls IId-f, h,i, and 142 amu in the case of the nitroxyl IIg, and the characteristic shifts of the peaks of these ions makes it possible to state that their composition, as for compound IIa, is determined by the substituents on the fourth and fifth atoms of the ring (ion A in Scheme 6). Ion peaks at 41-43 are observed in the spectra of all the compounds, however, they apparently do not provide much structural information and indicate only a deep-seated breakdown of the molecule with formation of fragments, which includes atoms $C_{(4)}$ and $C_{(5)}$ as well as fragments of their substituents (cf. 70, 69, 55, 58 in the spectrum of compound IIe and 55, 56 in the spectra of compounds IId and IIi). From analysis of the spectra of the nitroxyls IId-i three types of nitrogen-containing ions E, D, and F are readily identified. In fact as a result of the loss from the molecular ions of the compounds IId-f, h, i of a fragment of 88, and in the case of the compound IIg of 128 amu, strong peaks due to quite stable ions appear at 97, 111, 145, 163 and 109 respectively. At the same time comparison with the spectra of compound IIa-c leads to the conclusion that during their formation the atoms $N_{(1)}$ and $C_{(2)}$ with their substituents are lost. Type F ions (56, $[C_3H_6N]^+$) are present in the spectra of compounds IId-f, and in the spectrum of compound IIg possibly the ion peak at 96 corresponds. Finally in the spectra of compounds IId-i lines due to type D ions are readily detected with the general formula R^3CNH, for example, 104 (IIf,g) and 122 (IIh).

The data presented indicate the correctness of Scheme 6 for all the pentasubstituted 3-imidazoline-3-oxide-1-oxyls which we examined, and this in turn permits the structural elements of these molecules to be determined using the compositions of the ions and of the eliminated fragments.

We have noted some special features in the behavior of compounds IIa-i under electron impact. An increase in the number of carbon atoms of the alkyl group at the $C_{(4)}$ atom increases the stability of the molecular ions, the values of W_M change in the following order: 2.84 (IIa, $R^3 = CH_3$), 4.74 (IId, $R^3 = C_2H_5$) and 6.20 (IIe, $R^3 = i\text{-}C_3H_7$), and the stability of M^+ for the 4-arylsubstituted 3-imidazoline-3-oxide-1-oxyls is somewhat greater than for the 4-methyl derivatives (e.g., W_M for compound IIf ($R^3 = C_6H_5$) is 5.58). By comparing the mass spectra of the nitroxyls IIa-i with the spectra of other stable radicals of the imidazoline series – the pentasubstituted 3-imidazoline-1-oxyls [2] – it may be noted that the intense ion peak $[M - 45]^+$ characteristic for the previously studied radicals is absent in the spectra of compounds IIa-e (in the spectra of compounds IIg-i the intensity of this peak is ∿ 10%). It is doubtful whether the ion peak $[M - 30]^+$ can be included among the characteristic peaks since its intensity changes within wide limits: from 40% in the case of compound IIe to complete absence in the spectra of compounds IIh, i (other differences and similarities in the five fragments are noted above). A characteristic of compounds IIa-e, g, h is that their reduction in the ion source, in comparison with radicals, which do not contain an

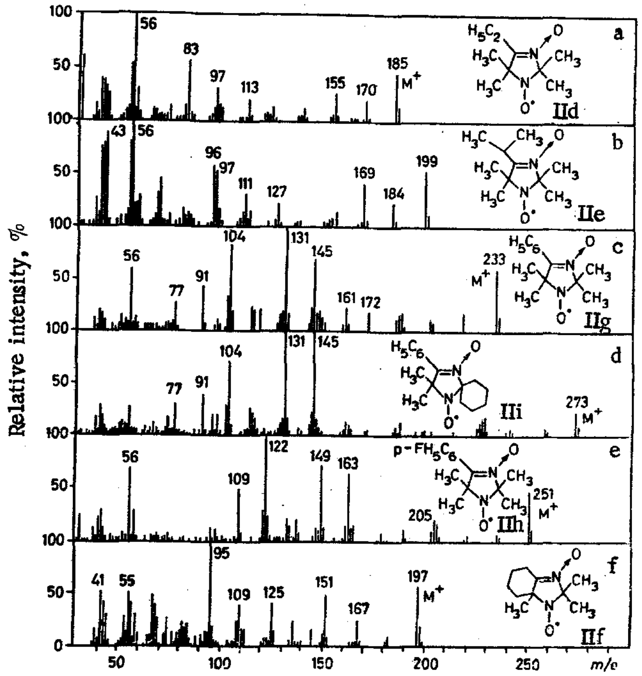


Fig. 3. Mass spectra of the 3-imidazoline-3-oxide-1-oxyls IId-i.

N-oxide group, occurs only to a negligible extent.*

In evaluating the possibilities of mass spectrometry for the analysis of stable nitroxyl radicals and their precursors in the pentasubstituted 3-imidazoline series it is possible to identify two main factors. Firstly the compositions of the molecular ions, characteristic fragment ions and eliminated fragments enables the compositions of all the substituents on the cyclic carbon atoms to be determined (only in the case of the N^3-oxides did we obtain incomplete information — only the sum of the amu of the substituents R^3, R^4, and R^5). Secondly the method allows an assessment to be made at a qualitative level of the ratio of the diamagnetic and paramagnetic forms in a mixture of compounds. This follows from a simple comparison of the spectra of the radicals and their precursors. It should be particularly noted that for such an interpretation of the spectra the choice of system for introducing the sample into the ionizing chamber and the conditions for recording the spectrum are of considerable importance.

EXPERIMENTAL

For the synthesis of compounds I and II see [14].

The mass spectra of all the samples were measured on an AEI MS902 instrument using a direct insertion system (temperature was varied from —30°C to +100° depending on volatility of the sample). Accelerating voltage 6 kV, ionizing voltage 70 eV, cathode emission current 100 μA. Accurate values of the mass numbers were determined at a resolution of ∿10,000, elemental compositions were calculated on a "Nairi" computer according to the program described in [16].

Below are given the identification codes of the compounds, the found and calculated values of the mass number, and the elemental composition of the fragment ions M^+:

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*An exception is compound IIf (Fig. 3f)— the ratio of the intensities of the ion peaks for $[M + H]^+$ and M^+ is 0.37. The spectrum contains a large number of peaks, a proportion of which are due to breakdown of $[M + H]^+$ ions (cf. with the spectrum of If, Fig. 1f).

Ia, $C_8H_{16}N_2O_2$

99,0685	99,0684	C_5H_9NO
74,0606	74,0606	C_3H_8NO
69,0704	69,0704	C_5H_9
42,0471	42,0469	C_3H_6, 13%
42,0344	42,0344	C_2H_4N, 86%
41,0393	41,0391	C_3H_5

Ie, $C_{10}H_{20}N_2O_2$

127,1002	127,0997	$C_7H_{13}NO$
97,1019	97,1017	C_7H_{13}
131,0732	131,0734	C_9H_9N, 45%
130,0679	130,0656	C_9H_8N
129,0714	129,0704	$C_{10}H_9$
119,0858	119,0860	C_9H_{11}, 17%
119,0608	119,0609	$C_7H_7N_2$, 60%
119,0372	119,0371	C_7H_5NO, 17%
117,0702	117,0704	C_9H_9
115,0563	115,0547	C_9H_7
104,0632	104,0626	C_8H_8, 5%
104,0503	104,0500	C_7H_6N, 95%
103,0534	103,0547	C_8H_7, 3%
103,0426	103,0421	C_7H_5N, 97%
91,0556	91,0548	C_7H_7
56,0509	56,0500	C_3H_6N

Ih, $C_{13}H_{17}FN_2O_2$

179,0745	179,0746	$C_{10}H_{10}FNO$
149,0767	149,0766	$C_{10}H_{10}F$
134,0533	134,0531	C_9H_7F
122,0406	122,0405	C_7H_5FN
121,0327	121,0327	C_7H_4FN
109,0457	109,0453	C_7H_6F
74,0604	74,0606	C_3H_8NO
73,0521	73,0527	C_3H_7NO

IIa, $C_8H_{15}N_2O_2$

141,1149	141,1153	$C_8H_{15}NO$
83,0733	83,0738	C_5H_9N
69,0704	69,0704	C_5H_9
56,0509	56,0500	C_3H_6N
42,0469	42,0469	C_3H_6, 25%
42,0339	42,0344	C_2H_4N, 75%
41,0395	41,0391	C_3H_5, 90%

Ig, $C_{13}H_{18}N_2O_2$

218,1414	218,1419	$C_{13}H_{18}N_2O$
187,1354	187,1360	$C_{13}H_{17}N$
172,1117	172,1126	$C_{12}H_{14}N$
161,0843	161,0840	$C_{10}H_{11}NO$, 22%
161,0729	161,0714	$C_9H_9N_2O$, 78%
146,0964	146,0969	$C_{10}H_{12}N$
145,0883	145,0891	$C_{10}H_{11}N$
144,0808	144,0813	$C_{10}H_{11}N$
131,0863	131,0860	$C_{10}H_{11}$, 55%

IIe, $C_{10}H_{19}N_2O_2$

184,1218	184,1212	$C_9H_{16}N_2O_2$*
169,1474	169,1467	$C_{10}H_{19}NO$*
127,1004	127,0997	$C_7H_{13}NO$*
11,1007	111,1048	$C_7H_{13}N$*
97,1029	97,1017	C_7H_{13}*, 93%
97,0868	97,0891	$C_6H_{11}N$, 7%
96,0822	96,0813	$C_6H_{10}N$*
70,0654	70,0657	C_4H_8N
69,0704	69,0704	C_5H_9, 23%
69,0584	69,0578	C_4H_7N, 64%
69,0342	69,0340	C_4H_9O, 13%
56,0509	56,0500	C_3H_6N
55,0560	55,0548	C_4H_7

IIg, $C_{13}H_{17}N_2O_2$

218,1056	218,1055	$C_{12}H_{14}N_2O_2$
202,1116	202,1106	$C_{12}H_{14}N_2O$
188,1078	188,1075	$C_{12}H_{14}NO$
187,1348	187,1360	$C_{13}H_{17}N$
186,1274	186,1282	$C_{13}H_{16}N$
161,0833	161,0840	$C_{10}H_{11}NO$
145,0893	145,0891	$C_{10}H_{11}N$
131,0858	131,0860	$C_{10}H_{11}$
129,0780	129,0789	$C_6H_{11}NO_2$
104,0495	105,0500	C_7H_6N
91,0548	91,0547	C_7H_7

IIh, $C_{13}H_{16}FN_2O_2$

122,0405	122,0405	C_7H_5FN

LITERATURE CITED

1. L. Yu. Ivanovskaya, B. G. Derendyaev, V. V. Martin, and V. S. Kobrin, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim., 5, No. 12, 136 (1977).
2. L. Yu. Ivanovskaya, B. G. Derendyaev, V. S. Kobrin, and L. B. Volodarskii, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim., 5, No. 12, 141 (1977).
3. É. G. Rozantsev, Free Iminoxyl Radicals [in Russian], Khimiya, Moscow (1970).
4. B. A. Andersson and G. Tölsch, Chem. Scr., 2, 21 (1972).
5. A. Morrison and A. P. Devies, Org. Mass Spectrom., 3, 353 (1970).
6. R. G. Kostyanovskii and Kh. Khafizov, Dokl. Akad. Nauk SSSR, 198, No. 2, 363 (1971).
7. A. B. Shapiro, V. M. Suskina, B. V. Rozynov, and É. G. Rozantsev, Izv. Akad. Nauk SSSR, Ser. Khim., No. 12, 2828 (1969).
8. B. V. Rozynov, V. D. Sholle, V. N. Golubev, and É. G. Rozantsev, Izv. Akad. Nauk SSSR, Ser. Khim., No. 9, 1989 (1973).
9. A. B. Shapiro, B. V. Rozynov, É. G. Rozantsev, N. F. Kucherova, L. A. Aksanova, and N. N. Novikova, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 867 (1971).
10. V. G. Zaikin, Z. S. Ziyavidinova, and N. S. Vul'fson, Izv. Akad. Nauk SSSR, Ser. Khim., No. 8, 1734 (1974).
11. B. V. Rozynov, M. V. Sudnik, A. B. Shapiro, V. L. Sodovskaya, I. A. Bogdanova, O. S. Reshetova, L. G. Nekhamkina, E. S. Brodskii, M. F. Romantsev, and É. G. Rozantsev, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 816 (1975).
12. L. B. Volodarskii and G. A. Kutikova, Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 937 (1971).
13. R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, Metastable Ions, Elsevier, Amsterdam–London–New York (1973).
14. L. B. Volodarskii, Khim. Geterotsikl. Soedin., No. 10 1299 (1973).
15. M. I. Gorfinkel' and S. A. Nekhoroshev, Avtometriya, No. 3, 126 (1972).
16. B. G. Derendyaev, S. A. Nekhoroshev, and L. M. Pokrovskii, Avtometriya (1978, in press).

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*Was determined by means of a computer treatment of the high-resolution spectra.