2-Amino-1-benzyl-3-heteroarylpyrrolo[2,3-b]quinoxalines. Anhydrous finely powdered potassium carbonate (0.55 g, 4 mmole) was added to a solution of 2-benzylamino-3-chloroquinoxaline (0.54 g, 2 mmole) and the corresponding heteroarylacetonitrile (2 mmole) in DMF (15 ml). The reaction mixture was cooled, diluted with water (50 ml), acidified with acetic acid and the precipitate was filtered, washed with water, and dried in air.

2-Amino-1-benzyl-3-(benzimidazol-2-yl)pyrrolo[2,3-b]quinoxaline (V), yield 0.71 g (93%); 2-amino-1-benzyl-3-(1-methylbenzimidazol-2-yl)pyrrolo[2,3-b]quinoxaline (VI), yield 0.75 g (94%); 2-amino-1-benzyl-3-(benzothiazol-2-yl)pyrrolo[2,3-b]quinoxaline (VII), yield 0.75 g (94%); 2-amino-1-benzyl-3-(4-methylthiazol-2-yl)pyrrolo[2,3-b]quinoxaline (VIII), yield 0.70 g (95%).

2-Amino-1-benzyl-3-(pyridin-2-yl)pyrrolo[2,3-b]quinoxaline (IX, $C_{22}H_{18}N_5$). Yield 0.62 g (89%) as a yellow microcrystalline powder with mp 212-213°C (from aqueous DMF), IR spectrum 1595 (C=N), 3290 cm^{-1} (N-H). PMR spectrum (DMSO-D_6): 9.1 (2H, br.s, NH_2); 8.94 (1H, d, $^3J_{34}$ = 8 Hz, 3-H pyridine); 8.1-7.2 (9H, m), including 7.28 (5H, s, arom. benzyl protons); 7.08 (1H, dd, $^3J_{H_5,H_6}$ = 4.5, $^3J_{54}$ = 7 Hz, 5-H pyridine); 5.58 ppm (2H, s, CH_2); 2-amino-1-benzyl-3-(quinolin-2-yl)pyrrolo[2,3-b]quinoxaline (X, $C_{26}H_{19}N_5$). Yield 0.79 g (95%) as a yellow microcrystalline powder with mp 246-247°C (aqueous DMF). IR spectrum: 1600 (C=N), 3195 cm^{-1} (N-H). PMR spectrum: (DMSO-D_6): 9.5 (2H, br.s, NH^2); 9.20 (1H, d, $^3J_{34}$ = 9 Hz, 3-H quinoline); 8.36 (1H, d, $^3J_{43}$ = 9 Hz, 4-H quinoline); 8.2-7.2 (13H, m), including 7.31 (5H, s, arom. benzyl protons); 5. 63 ppm (2H, s, CH_2).

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SYNTHESIS AND PROPERTIES OF AZOLES AND THEIR DERIVATIVES.

23.* ELECTRON IMPACT MASS SPECTROMETRY OF REGIO- AND STEREOISOMERIC DIARYLNITRO-Δ²-ISOXAZOLINES

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UDC 543.51:547.786

It was shown that the general paths of dissociation of molecular ions of 3-phenyl-4(5)-aryl-5(4) nitro-Δ^2-isoxazolines involve the primary elimination of the $NO_2^{\cdot}$, HNO_2, and $OCHNO_2$ particles, and also the formation of the $C_6H_5CN^{+\cdot}$, $C_6H_5^{+}$, ions and substituted tropylium cations. The 3,5- and 3,4-diaryl isomers differ most sharply in the probability of formation of $[RC_6H_4C\overset{+}{\equiv}O]$ ions, the peaks of which are maximal in the first case. The mass spectra of cis- and trans-isomers in the 3,5-diarylisoxazoline series differ little quantitatively.

Derivatives of nitro-Δ^2-isoxazolines have lately attracted increased interest in connection with their structural features [2], the possibility of using them as intermediates in the synthesis of other heterocyclic compounds [2-8], and also in relation to examination

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*For Communication 22, see [1].

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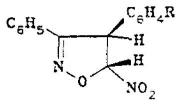
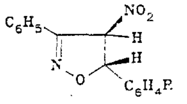
of their biological activity [9, 10]. The latter prompted the investigation of compounds of this class by various chemical methods. However, these compounds have not yet been sufficiently investigated mass spectrometrically.

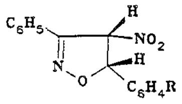
In the present work, we have studied the influence of structural factors on the character of dissociation of the molecular ion (M^+) of 3-phenyl-4(5)-aryl-5(4)nitro-Δ^2-isoxazolines I-XV, which were selected as model compounds. Thus, we set out to study both the general and specific paths of dissociation, and to reveal diagnostically important paths of fragmentation among them, suitable for differentiation of regio- and stereoisomers. The high-voltage (70V) mass spectra of these compounds are shown in the experimental part.



I-VII



VIII-XII



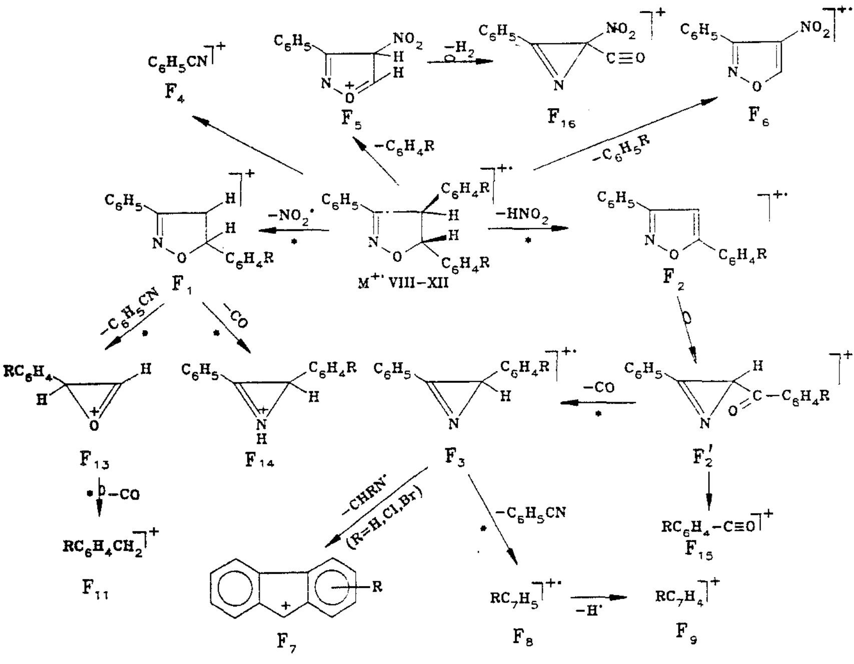
XIII-XV

I, VIII R=H, II R=*m*-CH_3, III R=*p*-CH_3, IV, IX, XIII R=*p*-CH_3O, V, X R=*m*-Cl;
VI, XI, XIV R=*p*-Cl, VII, XII, XV R=*p*-Br

It should be noted that in the series of Δ^2-isoxazoline derivatives, similar investigations have been carried out only for the regioisomeric derivatives of trans-3-aryl-4(5)-phenyl-5(4)-acyl-Δ^2-isoxazolines [11]. The fragmentation paths of these compounds found by these authors differ from those observed by us for nitroisoxazolines I-XV.

Examination of the mass spectra shows that the dissociation of M^+ of the compounds studied proceeds by several paths and includes the most important features of dissociative ionization of acyclic nitro compounds [12] of diarylisoxazoles [13, 14] and diaryl-Δ^2-isoxazlines [11, 13] (schemes 1 and 2).

Scheme 1



Thus, for example, under electron impact (EI) conditions, trans-3-phenyl-4-aryl-5-nitro-Δ^2-isoxazolines I-VII form unstable $M^{+\cdot}$, and their peaks are virtually absent in the mass spectra. The fairly intense peaks with the maximal mass number correspond to the $[M-NO_2]^+$ (F_1) and $[M - HNO_2]^+$ (F_2) ions. Formation of the F_2 ions takes place with the participation of the hydrogen atom at the 4-position of the azoline ring and leads to pseudomolecular ions of the corresponding diarylisoxazoles. This is confirmed, in particular, by comparison of the mass spectra of 3,4-diphenyl-5-nitro-Δ^2-isoxazoline (I) and 3,4-diphenylisoxazole (XVI). It should be noted that the process of thermal (120-150°C) dehydronitration of these compounds proceeds in a similar manner [15].

Another path of dissociation of M^+ of compounds I-VII involves a parallel cleavage of the N—O and $C_{(4)}$-$C_{(5)}$ bond and the elimination of the $OCHNO_2$ molecule. Thus azirine ions

F_3 are formed, the peak intensity of which in the case of isoquinoline I reaches 79% of the maximal value. A similar process was previously observed [16] in the dissociation of 3-aryl-Δ^2-isoxazolines, which led to the $[M - CH_2O]^+$ ions. The F_3 ions can also be formed by the "isoxazole mechanism" [13, 17], i.e., as a result of a skeletal rearrangement of the F_2 ion into diarylazirine F_2', followed by the elimination of a carbon monoxide molecule. This path is indicated by the presence of corresponding metastable transitions in the spectra.

Further fragmentation of the F_3 ion proceeds by a scheme characteristic for diaryl derivatives of azirine [17, 18] and leads to the appearance of three characteristic ions: $[F_3 - CHRN]^+$ (F_7, R = H, 165),* $[F_3 - C_6H_5CN]^+$ (F_8) and $[F_3 - C_6H_5CN - H]^+$ (F_9). It should be noted that while the aryl residue at the $C_{(4)}$ atom in the azoline ring contains a unique marker in the form of chlorine (compounds V, VI) or bromine atoms (VII), the peaks of the halogen-substituted fluorenyl ions F_7 199/201 (R = Cl) and 243/245 (R = Br) have low intensity. This fact is probably due to the more facile cleavage of the C_{aryl}-Hal bond, in comparison with the cleavage of the C_{aryl}-H bond.

Intense peaks of the $[C_6H_5CN]^+$ ions (F_4, 103) are observed in the spectra of all the compounds of this series, which arise both from the M^+, as a result of a synchronous cleavage of the N-O and $C_{(3)}$-$C_{(4)}$ bonds [11, 16], as well as from fragmentary ions. Their intensity depends on the nature of substituents on the phenyl ring, which are present at the 4-position of the azoline ring, and is probably due to the degree localization of the charge on this or another part of the molecule. The simultaneous elimination of the C_6H_4R radical and the molecule of C_6H_5R, leading to the formation of 191 (F_5) and 190 (F_6) ions, respectively, is manifested to a lesser extent.

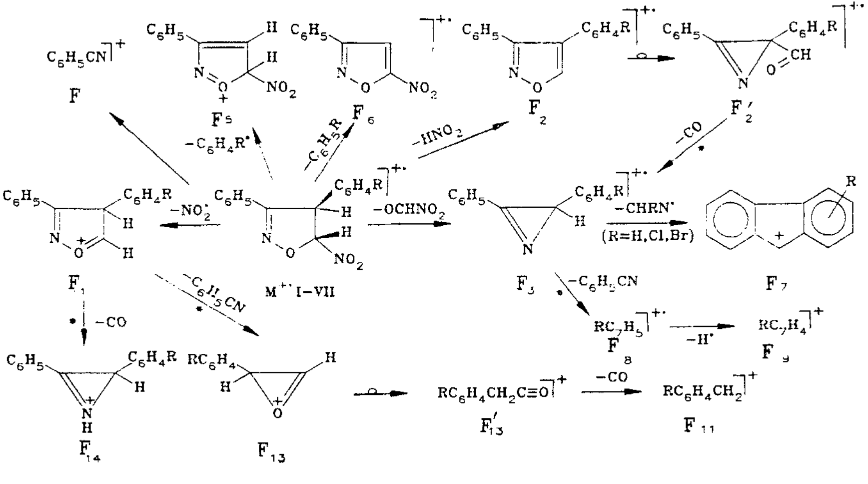
The peaks of the phenyl (F_{10}, 77) and tropylium cations (F_{11}, 91), and also the peaks of the F_{12} (89) ions have a high intensity in the mass spectra of isoxazolines I-VII. The latter probably have the structure of dehydrotropylium ions, formed at the expense of the phenyl substituent at the 3-position of the azoline ring. The occurrence of F_{11} ions can be related to the elimination of carbon monoxide from the small ring of the F_{13} ion , which in turn forms from F_1 ions as a result of splitting of a benzonitrile molecule. It is pospossible that the splitting off of carbon monoxide is the result of a preliminary rearrangement of the F_3 ion into a carbonyl derivative F'_{13} [19].

A competing path of fragmentation of the F_1 ion is the parallel formation of the $[F_1 - CO]^+$ ions (F_{14}), whose peaks are intense in the spectra of adducts I, II, and V.

The fragmentation paths of the F_1 ion are confirmed by the appearance of the corresponding metastable transitions in the spectra.

The mass spectra of trans-3-phenyl-4-nitro-5-aryl-Δ^2-isoxazolines VIII-XII in general coincide with the spectra of the above discussed regioisomers. The difference that appears in the relative intensities of M^+ and the fragmentary ions in the spectra of the isomeric pairs is apparently due to the structure of these ions (Scheme 2). In particular, the presence of the nitro group at the $C_{(4)}$ atom and the aryl residue at the $C_{(5)}$ atom increases the stability of the M^+ under EI conditions, and their low-intensity peaks are observed in the spectra of compounds VIII-XII.

Scheme 2



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*The numbers characterizing the ion define the m/z value.

TABLE 1. Mass Spectra of Compounds I-XVI

Compound	m/z (intensity in % of maximal peak*)
1	2
I	50 (31), 51 (68), 52 (11), 61 (5), 62 (17), 63 (49), 64 (18), 65 (18), 74 (8), 75 (12), 76 (28), 77 (55), 78 (5), 87 (5), 88 (8), 89 (100), 90 (99), 91 (98), 92 (9), 102 (4), 103 (48), 104 (12), 105 (5), 115 (5), 116 (23), 117 (5), 118 (25), 119 (10), 164 (4), 165 (38), 166 (9), 167 (6), 178 (9), 179 (6), 190 (5), 191 (6), 192 (19), 193 (79), 194 (38), 195 (6), 220 (7), 221 (84), 222 (53), 223 (8)
II	50 (17), 51 (54), 52 (12), 53 (7), 62 (6), 63 (20), 64 (6), 65 (12), 74 (5), 75 (9), 76 (16), 77 (83), 78 (38), 79 (19), 89 (14), 90 (8), 91 (11), 102 (12), 103 (70), 104 (50), 105 (100), 106 (13), 115 (6), 116 (5), 130 (15), 131 (5), 132 (8), 133 (24), 165 (17), 166 (4), 178 (6), 179 (6), 190 (3), 191 (4), 192 (6), 193 (10), 205 (3), 206 (15), 207 (44), 208 (39), 209 (6), 235 (37), 236 (61), 237 (11)
III	50 (16), 51 (45), 52 (11), 53 (6), 62 (5), 63 (16), 64 (5), 65 (10), 74 (4), 75 (7), 76 (14), 77 (65), 78 (29), 79 (13), 89 (10), 90 (5), 91 (7), 102 (9), 103 (48), 104 (30), 105 (100), 106 (10), 115 (4), 116 (4), 130 (12), 131 (4), 132 (5), 133 (43), 134 (5), 165 (7), 193 (4), 206 (7), 207 (23), 208 (11), 235 (20), 236 (33), 237 (6)
IV	50 (24), 51 (66), 52 (10), 53 (4), 62 (8), 63 (19), 64 (7), 65 (11), 74 (6.0), 75 (11), 76 (29.4), 77 (100), 78 (23), 79 (7), 87 (4), 88 (5), 89 (21), 90 (18), 91 (46), 92 (10), 102 (6), 103 (17), 104 (8), 105 (13), 106 (3), 115 (4), 116 (4), 119 (10), 120 (16), 121 (69), 122 (7), 133 (5), 135 (3), 146 (13), 147 (3), 148 (4), 149 (47), 150 (8), 151 (4), 152 (7), 153 (5), 165 (6), 174 (5), 178 (6), 180 (12), 181 (3), 208 (38), 209 (7), 223 (14), 224 (4), 236 (7), 251 (24), 252 (12)
V	50 (28), 51 (65), 52 (9), 61 (6), 62 (19), 63 (44), 64 (8), 65 (4), 73 (11), 74 (9), 75 (17), 76 (19), 77 (61), 78 (5), 85 (3), 86 (6), 87 (10), 88 (11), 89 (100), 90 (21), 91 (4), 97 (4), 99 (10), 101 (4), 102 (4), 103 (18), 104 (8), 114 (8), 115 (5), 116 (8), 123 (20), 124 (17), 125 (79), 126 (12), 127 (24), 150 (10), 151 (3), 152 (13), 153 (4), 154 (4), 163 (6), 164 (5), 165 (29), 166 (6), 190 (9), 191 (8), 192 (24), 193 (34), 194 (5), 226 (4), 227 (37), 228 (37), 229 (18), 230 (13), 255 (30), 256 (47), 257 (16), 258 (16), 259 (3)
VI	50 (27), 51 (69), 52 (9), 61 (4), 62 (17), 63 (40), 64 (7), 65 (4), 73 (10), 74 (8), 75 (15), 76 (19), 77 (62), 78 (5), 86 (5), 87 (8), 88 (8), 89 (86), 90, (19), 99 (8), 101 (4), 102 (3), 103 (13), 104 (81), 114 (7), 115 (4), 116 (6), 123 (15), 124 (16), 125 (100), 126 (12), 127 (29), 150 (13), 151 (3), 152 (11), 153 (25), 154 (5), 155 (9), 165 (17), 166 (4), 190 (5), 191 (5), 192 (11), 193 (21), 194 (3), 227 (22), 228 (13), 229 (9), 230 (4), 255 (24), 256 (38), 257 (14), 258 (14)
VII	50 (40), 51 (96), 52 (11), 61 (6), 62 (28), 63 (58), 64 (12), 65 (4), 74 (11), 75 (16), 76 (25), 77 (79), 78 (8), 86 (8), 87 (13), 88 (25), 89 (100), 90 (43), 91 (5), 102 (5), 103 (15), 104 (11), 114 (12), 115 (14), 116 (7), 118 (64), 119 (7), 143 (12), 163 (4), 164 (5), 165 (27), 166 (6), 167 (9), 168 (3), 169 (24), 170 (5), 171 (16), 190 (7), 191 (9), 192 (20), 193 (28), 194 (10), 196 (10), 197 (7), 198 (5), 199 (6), 271 (14), 272 (7), 273 (14), 274 (5), 299 (29), 300 (22), 301 (31), 302 (20), 303 (3)
VIII	50 (22), 51 (56), 52 (8), 62 (6), 63 (20), 64 (5), 65 (10), 74 (6), 75 (7), 76 (13), 77 (98), 78 (8), 88 (3), 89 (18), 90 (6), 91 (46), 92 (4), 102 (3), 103 (9), 105 (100), 106 (9), 116 (6), 119 (4), 144 (4), 165 (16), 189 (12), 190 (4), 191 (13), 192 (4), 193 (7), 194 (11), 221 (7), 222 (10), 268 (M^{+}; 1)
IX	50 (13), 51 (25), 52 (6), 62 (5), 63 (17), 64 (12), 65 (7), 74 (4), 75 (6), 76 (13), 77 (50), 78 (9), 79 (4), 89 (11), 90 (4), 91 (7), 92 (18), 102 (6), 103 (6), 107 (10), 115 (4), 121 (60), 122 (6), 132 (3), 135 (100), 136 (10), 146 (4), 149 (49), 150 (8), 151 (6), 152 (10), 153 (3), 165 (4), 176 (7), 177 (8), 178 (38), 179 (17), 180 (4), 189 (4), 207 (11), 208 (5), 251 (14), 252 (4), 298 (M^{+}; 4)
X	50 (26), 51 (43), 52 (6), 62 (8), 63 (25), 64 (6), 73 (4), 74 (10), 75 (35), 76 (20), 77 (37), 78 (3), 85 (3), 87 (6), 88 (4), 89 (22), 90 (6), 91 (3), 94 (6), 95 (4), 99 (4), 101 (4), 102 (4), 103 (7), 104 (4), 111 (49), 112 (5), 113 (18), 114 (5), 115 (5), 116 (6), 125 (28), 126 (4), 127 (20), 139 (100), 140 (9), 141 (33), 144 (6), 149 (3), 150 (4), 163 (5), 164 (4), 165 (14), 187 (3), 188 (4), 189 (23), 190 (7), 191 (14), 192 (4), 193 (12), 227 (7), 228 (11), 229 (4), 230 (4), 255 (4), 256 (12), 258 (4), 302/304 (M^{+}: 2/0,6)
XI	50 (22), 51 (40), 52 (6), 62 (7), 63 (23), 64 (5), 65 (5), 73 (5), 74 (8), 75 (29), 76 (17), 77 (34), 78 (3), 85 (4), 88 (4), 89 (25), 90 (6), 91 (3), 94 (8), 95 (4), 99 (4), 101 (5), 102 (5), 103 (6), 104 (6), 111 (43), 112 (5), 113 (17), 114 (5), 115 (6), 116 (5), 125 (46), 126 (6), 127 (16), 139 (100), 140 (10), 141 (40), 142 (4), 144 (3), 149 (3), 150 (6), 151 (3), 152 (4), 153 (12), 155 (4), 163 (6), 164 (3), 165 (16), 166 (3), 187 (4), 188 (4), 189 (28), 190 (9), 191 (20), 192 (5), 193 (14), 199 (3), 227 (8), 228 (8), 229 (3), 255 (4), 256 (20), 257 (5), 258 (7), 302/304 ($M^{+\cdot}$, 2/0,6)
XII	50 (34), 51 (42), 52 (6), 55 (4), 56 (8), 62 (8), 63 (24), 64 (6), 65 (6), 74 (12), 75 (26), 76 (35), 77 (41), 78 (5), 83 (8), 84 (6), 87 (4), 88 (6), 89 (25), 90 (13), 91 (8), 94 (10), 95 (9), 102 (6), 103 (13), 104 (17), 105 (4), 113 (4), 114 (6), 115 (7), 116 (6), 118 (37), 119 (7), 133 (6), 139 (4), 152 (4), 155 (29), 157 (28), 163 (6), 164 (4), 165 (19), 166 (4), 169 (13), 171 (13), 183 (100), 184 (9), 184 (9), 185 (99), 186 (9), 187 (5), 188 (5), 189 (37), 190 (11), 191 (20), 192 (6), 193 (25), 194 (5), 197 (6), 198 (3), 199 (5), 200 (5), 271 (7), 272 (5), 273 (6), 274 (5), 299 (8), 300 (22), 301 (10), 302 (21), 303 (4), 346/348 (M^{+}, 1/1)

TABLE 1 (Continued.)

1	2
XIII	50 (15), 51 (36), 52 (6), 62 (6), 63 (6), 64 (16), 65 (10), 74 (4), 75 (8), 76 (15), 77 (72), 78 (15), 79 (5), 88 (3), 89 (15), 90 (6), 91 (10), 92 (24), 102 (7), 103 (7), 104 (3), 107 (15), 115 (5), 116 (4), 117 (3), 119 (3), 121 (100), 122 (9), 126 (3), 132 (4), 135 (100), 136 (16), 139 (4), 149 (80), 150 (12), 151 (13), 153 (4), 165 (5), 176 (7), 177 (10), 178 (43), 179 (23), 180 (5), 189 (6), 191 (4), 207 (16), 208 (7), 251 (16), 252 (6), 298 ($M^{+\cdot}$, 6)
XIV	50 (22), 51 (44), 52 (6), 62 (7), 63 (24), 64 (6), 65 (6), 73 (4), 74 (8), 75 (30), 76 (17), 77 (38), 78 (4), 82 (5), 87 (5), 88 (4), 89 (27), 90 (7), 91 (3), 94 (18), 95 (11), 99 (6), 101 (5), 102 (4), 103 (6), 104 (7), 111 (53), 112 (6), 113 (24), 114 (7), 115 (6), 116 (5), 125 (68), 126 (7), 127 (22), 139 (100), 140 (17), 141 (65), 142 (5), 144 (3), 149 (4), 150 (6), 151 (3), 152 (4), 153 (21), 155 (7), 163 (7), 164 (4), 165 (18), 166 (3), 187 (4), 188 (5), 189 (36), 190 (12), 191 (27), 192 (7), 193 (22), 194 (4), 199 (4), 225 (4), 227 (11), 228 (12), 229 (5), 230 (4), 256 (40), 257 (8), 258 (13), 302/304 ($M^{+\cdot}$, 3/1)
XV	50 (33), 51 (46), 52 (7), 62 (9), 63 (26), 64 (7), 65 (7), 74 (11), 75 (27), 76 (37), 77 (43), 78 (4), 83 (10), 87 (5), 88 (6), 89 (28), 90 (17), 91 (6), 94 (4), 95 (12), 96 (11), 102 (6), 103 (10), 104 (13), 105 (4), 113 (5), 114 (6), 115 (8), 116 (7), 118 (48), 119 (9), 139 (8), 144 (4), 152 (4), 155 (28), 157 (27), 163 (7), 164 (4), 165 (20), 166 (5), 169 (15), 171 (14), 183 (100), 184 (9), 185 (100), 186 (9), 187 (5), 188 (5), 189 (39), 190 (14), 191 (21), 192 (7), 183 (28), 194 (7), 197 (6), 199 (5), 271 (6), 272 (6), 273 (6), 274 (5), 299 (4), 300 (21), 301 (9), 302 (19), 303 (5), 346/348 ($M^{+\cdot}$, 1/1)
XVI	50 (26), 51 (85), 52 (10), 61 (4), 62 (20), 63 (61), 64 (19), 65 (7), 74 (7), 75 (9), 76 (13), 77 (58) 78 (5), 86 (4), 87 (7), 88 (11), 89 (100), 90 (81), 91 (8), 103(4), 104 (7), 116 (28), 118 (5), 139 (4), 144 (3), 163 (5), 164 (6), 165 (47), 166 (11), 190 (6), 191 (7), 192 (21), 193 (56), 194 (9), 221 ($M^{+\cdot}$, 74), 222 (23)

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*Peaks with intensity of <3% are not listed.

Elimination of the NO_2 radical (F_1) and the HNO_2 molecule (F_2) from M^+ is also typical for this series of compounds. However, the peak intensity of these ions is lower than that of similar ions in the preceding series of compounds. At the same time, a splitting of the C_6H_5R molecule and C_6H_4R radical is observed leading to the F_6 and F_5 ions. The F_6 ion can lose a further molecule of hydrogen to form the F_{16} (189) ions. Peaks of the F_{16} ions are absent in the spectra of regioisomeric isoxazolines I-VII, and therefore they are of interest analytically.

Peaks of $[M - HNO_2, -CO]^{+\cdot}$ (F_3), $[M - NO_2, -CO]^+$ (F_{14}) and $[M - NO_2, -C_6H_5CN]^+$ (F_{13}) ions are also observed in this series. The presence of the F_3 and F_{14} ions indicates a skeletal rearrangement of the F_2 and F_1 ions, as a result of which the elimination of a carbon monoxide molecule becomes possible. The occurrence of these processes is confirmed by the corresponding metastable transitions in the spectra.

To differentiate between the trans-nitro-substituted 3,5-(compounds (VIII-XII) and 3,4-diaryl-Δ^2-isooxazolines (I-VII), the diagnostically most important ions are $[RC_6H_4C{\equiv}O]^+$ (F_{15}), whose peaks have maximal intensity in the spectra of trans-3,5-diaryl derivatives VII-XII. Their formation may be due to the isomerization of the F_2 ions into the azirine structure $F_2^{\prime}$, followed by a cleavage of the exocyclic C-C bond [13, 14, 17]. The $RC_6H_4C{\equiv}O^+$ ions are not characteristic for trans-3,4-diaryl-Δ^2-isoxazolines I-VII. The preferred formation of the F_{16} ions is possibly the reason for the lower intensity of peaks of the ions: $RC_6H_4\overset{+}{C}H_2$ (F_{11}), $[RC_7H_3]^+$ (F_9), and also of the fluorenyl cation F_7 (R = H), formed analogously with the preceding series of compounds from the oxirane cations F_{13} and azirine ions F_3. The peaks of benzonitrile cations (F_4) also have a low intensity. At the same time, the peaks of phenyl cations (F_{10}) and tropylium ions (F_{13}), as previously, remain fairly intense.

Thus, comparison of peak intensities of the fragmentary F_1-F_{15} ions of the isomer pair apparently can also enable the differentiation between the regioisomeric diarylnitro-Δ^2-isoxazoline.

Examination of the EI mass spectra of cis-(compounds XIII-XV) and trans-(IX, XI, XII)-3-phenyl-4-nitro-5-aryl-Δ^2-isoxazolines XIII-XV showed that the fragmentation paths of the isomers practically do not differ. Therefore, the mass spectrometric method is not suitable for the differentiation of the stereoisomeric 3-phenyl-4-nitro-5-aryl-Δ^2-isoxazolines.

The elemental composition of the fragmentary F_1-F_{14} ions of the regioisomeric diphenylnitro-Δ^2-isoxazolines (I, VIII) was verified by high-resolution mass spectra. Moreover, the formation of the F_1-F_3, F_7-F_9, F_{11}, F_{13}, F_{14}, F_{16} ions is confirmed by the corresponding change in the mass number of these ions in dependence on substituent R.

It should be noted that a large number of peaks of doubly-charged ions is observed, which characterize the aromatic fragments in the spectra of all the compounds studied in the present work.

EXPERIMENTAL

The mass spectra of compounds I-XVI were obtained on a LKB-9000 spectrometer at an energy of ionizing electrons of 70 eV, emission current of 50 µA, temperature of the ionic source of 250°C, and using a system of direct introduction of the samples to the ionic source at 30-70°C. It should be noted that when the samples are heated above 120°C, a thermal splitting of HNO_2 is observed, and the mass spectra of these compounds become identical with the spectra of the corresponding diarylisoxazoles. In order to avoid thermal dissociation, the spectra of all the compounds studied were obtained at sample introduction temperatures not exceeding 70°C. The high resolution spectra were run on a MAT-311A spectrometer under similar conditions. The synthesis and physicochemical properties of the compounds are described in [2, 5].

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