MASS SPECTRA OF BENZOXAZOLONE DERIVATIVES

P. B. Terent'ev, D. A. Simov,
V. B. Kalcheva, and Kh. S. Boicheva

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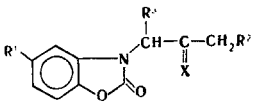
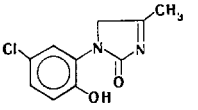
N-Acetonylbenzoxazolones containing a substituent in the acetonyl residue, as well as their hydrazones and oximes, decompose under the influence of electron impact to give primarily fragments of N-methylene- or N-methylbenzoxazolones. For the oximes and hydrazones the characteristic ions are $(M - OH)$ and $(M - NH_2)$, which evidently have cyclic structures. The isomeric aryl triazinones undergo fragmentation via the scheme of the retrodiene synthesis. The characteristic ions that make it possible to distinguish the isomeric benzoxazolones, arylimidazolones, and aryltriazinones were found.

One of us has previously described the synthesis of N-acetonyl-2-benzoxazolone and its reaction with a number of nucleophilic agents [1-3]. According to the IR and NMR spectroscopic data, its reaction with, for example, hydroxylamine [1] proceeded at the ketone carbonyl group without involvement of the benzoxazolone ring. However, in the reaction with such nucleophilic agents as primary amines, the reaction proceeds through the formation of a number of intermediates, the alkylamine group of which attacks the carbonyl carbon atom of the benzoxazolone ring, as a result of which N-(2-hydroxyphenyl)imidazolone derivatives are formed. Finally, hydrazine hydrate was found to be capable of reacting in both directions to give both benzoxazolone derivatives and substituted 4-(2-hydroxyphenyl)-2,3,4,5-tetrahydro-1,2,4-triazin-3-ones [3].

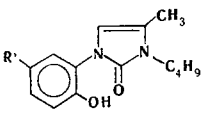
In order to find differences in the mass-spectral behavior of the indicated three groups of compounds we studied the fragmentation, under the influence of electron impact, of Ia-*l*, IIIa, b, and IVa, b (Table 1).



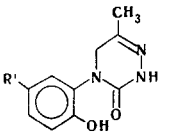
Ia-*l*



II



IIIa, b



IVa, b

I a R^1=Cl, R^2=R^3=H, X=O; b R^1=Cl, R^2=Br, R^3=H, X=O; c R^1=Cl, R^2=$N(CH_2CH_2)_2O$, R^3=H, X=O; d R^1=R^3=H, R^2=$N(CH_2CH_2)_2O$, X=O; e R^1=R^2=R^3=H, X=NOH; f R^1=Cl, R^2=R^3=H, X=NOH; g R^1=Cl, R^2=R^3=H, X=$NOCOCH_3$; h R^1=R^2=R^3=H, X=NNH_2; i R^1=Cl, R^2=R^3=H, X=NNH_2; j R^1=Cl, R^2=H, R^3=CH_3, X=O; k R^1=Cl, R^2=H, R^3=CH_3, X=NOH; *l* R^1=Cl, R^2= 3-benzoxazolonyl, R^3=H, X=O; III, IV a R^1=H; b R^1=Cl

The principal processes of dissociative ionization of Ia-*l* consist (Scheme 1) in primary detachment of a $COCH_2R^2$ radical [2] to give fragment F_1 with subsequent fragmentation, which is characteristic for benzoxazolone itself, i.e., ejection of CO or CO_2 [4] with the formation of ions F_5 and F'_5.

It is interesting to note that in the spectrum of *l* there are F_1 ions that contain chlorine and F_1 ions that do not contain halogen, and the latter have higher intensities; this indicates higher probability of charge localization in the molecular ion on the non-chlorine-containing residue of the benzoxazolone ring. The F_5 ion

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TABLE 1. Mass Spectra of Ia-*l*, II, IIIa, b, and IVa, b [m/e (Relative Intensity, %)]*

Ia (*M*) 227 (36,1), 226 (11,5), 225 (100), 185 (21,4), 184 (34,2), 183 (100), 182 (100), 154 (6,1), 140 (9,8), 138 (29,7), 113 (18,2), 111 (56,5), 102 (12,7), 97 (6,1), 83 (6,6), 81 (6,2), 75 (22,3), 69 (21,6), 63 (17,5)

Ib (*M*) 307 (5,8), 305 (38,2), 303 (31,4), 185 (8,1), 184 (50,2), 183 (31,2), 182 (100). 171 (5,1), 169 (15,2), 140 (12,7), 138 (41,6), 113 (18,8), 111 (58,7), 102 (26,1) 99 (6,7) 76 (16,3), 75 (28,4), 63 (16,1)

Ic (*M*) 310 (0,9), 282 (1,0), 182 (0,8), 169 (0,7), 138 (0,7), 113 (0,8), 111 (2,5), 100 (100), 76 (8,5), 63 (12,5)

Id (*M*) 276 (12,7), 248 (8,9), 148 (12,1), 135 (22,3), 100 (100), 77 (5,1), 70 (14,2)

Ie (*M*) 206 (58,1), 189 (62,7), 161 (8,2), 148 (14,3), 147 (10,0), 146 (18,4), 135 (42,1), 120 (21,8), 106 (12,3), 104 (8,2), 91 (11.8), 85 (12,3), 81 (12,8), 79 (16,7), 78 (21,4), 77 (100), 74 (9,8), 65 (27,5)

If (*M*) 242 (26,1), 241 (8,3), 240 (81,2), 225 (32,3), 224 (11,8), 223 (100), 195 (8,2), 188 (6,7), 187 (8,2), 183 (8,1), 182 (21,8), 181 (12,7), 180 (32,1), 171 (11,7), 170 (12,9), 169 (42,4), 168 (14,5), 156 (9,7), 154 (28,3), 140 (14,6), 138 (6,7), 126 (8,1), 113 (14,7), 111 (44,8), 102 (12,1), 99 (6,8), 78 (6,6), 77 (11,2), 76 (40,0), 75 (30,1), 63 (18,5)

Ig (*M*) 284 (21,1), 283 (6,8), 282 (64,2), 242 (34,0), 241 (10,8), 240 (100), 225 (30,0), 224 (9,0), 223 (91,8), 199 (8,4), 195 (12,0), 188 (9,2), 184 (28,3), 183 (16,5), 182 (68,8), 181 (10,0), 180 (28,3), 171 (30,0), 170 (11,0), 169 (95,6), 157 (20,0), 156 (24,2), 155 (66,2), 154 (81,3), 140 (11,0), 183 (31,8). 127 (5,0), 125 (15,2), 113 (25,8), 111 (78,2), 102 (10,1), 101 (9,2), 99 (27,3), 75 (70,0), 65 (20,8)

Ih (*M*) 205 (100), 161 (15,2), 149 (16,8), 148 (26,2), 146 (12,0), 136 (36,8), 135 (31,3), 120 (34,3), 112 (6,1), 93 (8,2), 91 (6,4)

Ii (*M*) 241 (34,1), 240 (11,2), 239 (100), 255 (5,1), 223 (14,8), 183 (5,3), 182 (12,0), 181 (16,5), 180 (20,7), 172 (5,8), 171 (14,6), 170 (24,6), 169 (41,3), 156 (22,3), 154 (68,8), 127 (10,0), 113 (12,0), 112 (10.8), 99 (14,7), 78 (24,0), 73 (6,4), 71 (22,7)

Ij (*M*) 241 (5,1), 239 (14,9), 198 (33.8), 197 (12.0), 196 (100), 160 (5,2), 153 (7,4), 117 (71,2), 113 (6,4), 111 (19,2)

Ik (*M*) 256 (6,7), 254 (19,8), 239 (14.7), 237 (46,8), 197 (8,0), 196 (9,2), 195 (14,6), 171 (15,3), 170 (20,0), 169 (58,7), 168 (40.1), 154 (6,2), 127 (6,1), 117 (10,8), 113 (14,2), 111 (42,8), 86 (100,0), 85 (42.3), 76 (12,4), 75 (10,3), 63 (16,7)

Il (*M*) 360 (10,5). 358 (32,3), 224 (10,1), 195 (12,1), 190 (22,7), 184 (5,7), 182 (17,7), 161 (25,2), 148 (100), 111 (12,1), 104 (11,6), 77 (72.7), 51 (7,5), 43 (8,6)

II (*M*) 226 (31,3), 225 (12,7), 224 (100), 185 (6,1), 183 (19.0), 156 (22,0), 154 (61,7), 127 (8,4), 101 (6,1), 99 (18,3), 73 (14,4), 63 (16,7)

IIIa 246 (100), 229 (6,8), 203 (19,3), 202 (8,9), 190 (37,0), 149 (6,8), 147 (35.9), 127 (5,7), 120 (68,8), 111 (15,6), 94 (5,2), 93 (7.3), 10 (9.4), 69 (17.2), 65 (18,8), 57 (26,6), 56 (32,8), 43 (12,5), 42 (49,0)

IIIb 282 (34,7), 281 (10,6), 280 (100), 240 (6,1), 239 (5,2), 238 (18,8). 237 (12,7), 226 (21,4), 225 (6,3), 224 (63,6), 183 (10,6), 181 (14,8). 156 (21,1), 154 (63,6), 129 (5,0), 127 (16,8), 112 (6,3), 111 (14.1), 99 (10,8), 23 (26,3)

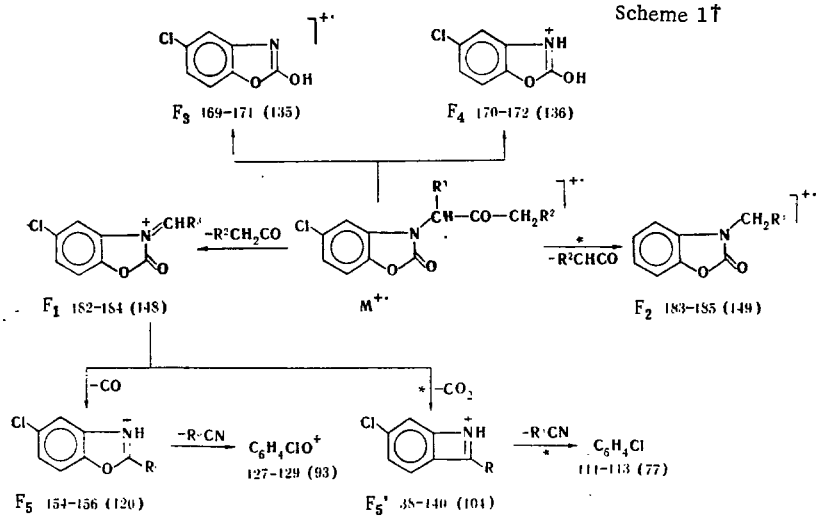
IVa 205 (100), 136 (59,5), 135 (48,0), 120 (40,3), 95 (7,7), 93 (12,0), 83 (15,2), 81 (23.2)

IVb 241 (31,6), 240 (10,9), 239 (100,0), 172 (5,4), 171 (8,6), 170 (20,6), 169 (25,7), 156 (13,4), 154 (36,1), 153 (9,1), 137 (9.4), 136 (7,9), 136 (6,3), 127 (6,2), 101 (5,1), 99 (15,8), 76 (5,3), 75 (5,8), 63 (10,8)

*Ions having intensities > 5% are presented; ions having intensities > 0.5% are presented for Ic.

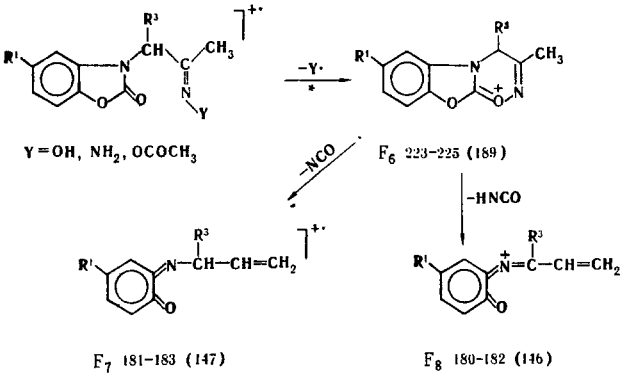
subsequently does not eliminate CO but, like benzoxazoles, eliminates HCN and only then CO.* This indicates that the F_5 ion probably has the cyclic benzoxazole structure rather than an open structure. The composition of ions F_1-F_4 in the mass spectra of Ie, i were determined by means of the high-resolution mass spectra.

Scheme 1†



In addition to the F_1 fragment ion, the mass spectra of Ia-*l* are characterized by a series of rearranged ions F_2-F_4, and their formation, as well as the formation of the F_1 ion, is confirmed, as a rule, by the corresponding metastable ions.

Scheme 2



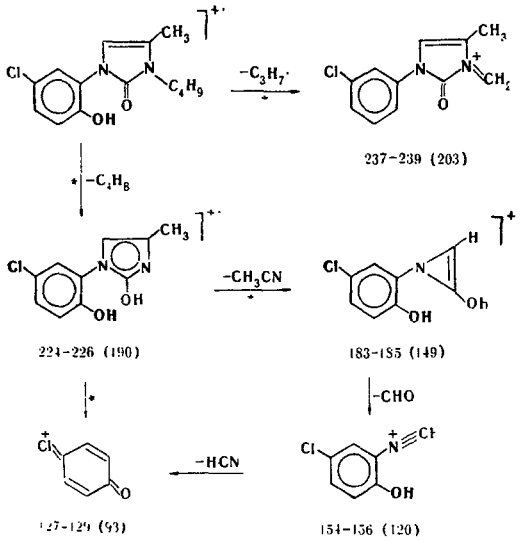
The structures of Ie-i as benzoxazolone derivatives are confirmed by the presence of F_1 ions in the mass spectra. In addition to them, the F_6 ion (Scheme 2), which is formed by loss of 17 amu (OH) by the molecular ions of Ie, f, 59 amu (C_2H_2O+OH) by the Ig molecular ion, and 16 amu (NH_2) by the Ic, i molecular ions, is characteristic for them. As one should have expected, in the mass spectrum of Ik the mass number of the F_6 ion undergoes a 14 amu shift. Measurement of the precise composition of the F_6 ion and the fragment formed from it in the mass spectra of Ie, i by means of the high-resolution mass spectra made it possible to establish that it subsequently eliminates primarily NCO and HNCO to give, respectively, F_6 and F_8 ions. This proves that the F_6 ion in all likelihood has a cyclic rather than a linear structure.

The mass spectra of II and IIIb are characterized by the presence of fragments (see Scheme 3) with m/e 183-185, 154-156, and 127-129, which are also present in the mass spectra of Ia-c, g, i, *l*. However, the groups of ions with m/e 169-171 and 170-172 (i.e., respectively, the F_3 and F_4 ions) are absent in their mass spectra, and this makes it possible to distinguish them confidently from the isomeric benzoxazolone

*The loss of Cl or HCl proceeds only in the subsequent stages of the fragmentation of the F_5 and F'_5 ions.

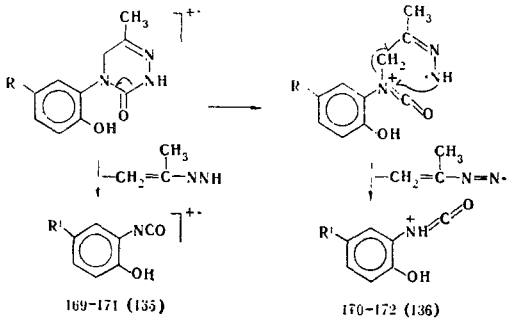
†Here and subsequently, the m/e values when R^3 = H are presented under the formulas; the m/e values of the same ions that do not contain chlorine are presented in parentheses. The fragmentation pathways confirmed by metastable ions are indicated by asterisks.

Scheme 3



derivatives. Finally, ions with m/e 169-171 and 170-172 are observed in the mass spectra of triazinone IVb and the isomeric hydrazone Ii (for IVa, respectively, ions with m/e 135 and 136), but ions with m/e 182-184 and 183-185 (for IVa, m/e 148, 149) are completely absent.

Scheme 4



The formation of the first group of ions in the mass spectra of IVa, b is explained by retrodiene fragmentation of their molecular ions, which proceeds both without transfer and with transfer of a hydrogen atom to the charge-bearing fragment.

Thus the affiliation of a compound with the benzoxazolone, arylimidazolone, or triazinone series can be established by means of the mass-spectrometric method.

EXPERIMENTAL

The mass spectra were recorded with an MKh-1303 spectrometer with introduction of the substances into the ion source at an ionizing-electron energy of 50 eV, an accelerating voltage of 2 kV, and an emission current of 150 μA. The high-resolution mass spectra were recorded with a JMS-01 SG-2 spectrometer (JEOL) with double focusing at an ionization energy of 75 eV. The purity of all of the substances was monitored by thin-layer chromatography in no less than three systems.

LITERATURE CITED

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