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MASS SPECTRA OF DERIVATIVES OF BENZALDEHYDE SELENAZOLYLHYDRAZONES

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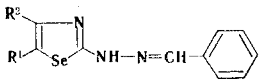
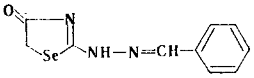
UDC 547.789.9'571'574.3:543.51

The mass spectra of benzaldehyde selenazolylhydrazones Ia-d and benzaldehyde selenazolidenehydrazones II and III were studied. Splitting out of benzonitrile as a result of a rearrangement of the McLafferty type is characteristic for the fragmentation of the M^+ ions of Ia-d. The subsequent fragmentation of the $M - C_6H_5CN$ ion occurs due to ejection of the SeH group or a molecule of carbodiimide from the selenazole ring or due to cleavage of ring side substituents. The principal fragments in the mass spectra of II and III are formed as a result of the ejection of groups of SeH and SeCHCO atoms.

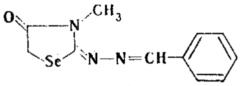
In a continuation of our research [1, 2] on the synthesis and analysis of derivatives of benzaldehyde heterylhydrazones that have high biological activity, in the present research we studied the principal pathways in the fragmentation of benzaldehyde selenazolylhydrazones Ia-d and benzaldehyde selenazolidenehydrazones II and III under the influence of electron impact.



Ia-d



II



III

I a $R^1 = H$, $R^2 = C_6H_5$; b $R^1 + R^2 = (CH_2)_4$; c $R^1 + R^2 = (CH_2)_3$; d $R^1 = H$, $R^2 = CH_2Cl$

The mass spectra of analytically valuable derivatives of carbonyl compounds, viz. nitro- and, particularly, dinitrophenylhydrazones, have been investigated in greatest detail [3]. Their spectra are characteristic and make it possible in a number of cases to determine the position and character of the substituents in the residue of the carbonyl compound from the mass numbers of the fragment ions [4]. The processes of dissociative ionization of arylhydrazones of aromatic aldehydes and ketones that are accompanied by skeletal rearrangements have been examined in quite some detail [5, 6]. It has been established that for all of the compounds mentioned above one of the chief processes in the fragmentation of their molecular ions (M^+) is cleavage of the nitrogen–nitrogen bond.

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0009-3122/82/1806-0575$07.50

TABLE 1. Mass Spectra of Benzaldehyde Selenazolylhydrazones Ia-d and Benzaldehyde Selenazolidenehydrazones II and III*

Compound	m/z values (relative intensities, %)
Ia	51 (13), 76 (7), 77 (46), 78 (8), 89 (17), 90 (14), 91 (7), 102 (42), 103 (20), 104 (33), 105 (17), 116 (10), 129 (7), 131 (6), 142 (6), 144 (6), 169 (11), 182 (100), 196 (12), 224 (54), 246 (6), 250 (5), 327 (33, M+).
Ib	51 (34), 67 (50), 77 (100), 78 (49), 79 (61), 89 (15), 90 (21), 92 (25), 94 (24), 103 (11), 104 (35), 105 (25), 106 (37), 107 (9), 118 (13), 119 (60), 120 (18), 121 (74), 122 (11), 133 (10), 145 (8), 147 (8), 159 (8), 160 (8), 174 (45), 202 (67), 224 (10), 228 (22), 305 (55, M+).
Ic	51 (4), 77 (12), 78 (6), 79 (8), 80 (17), 81 (26), 90 (6), 104 (18), 105 (43), 106 (62), 107 (72), 108 (9), 119 (6), 131 (5), 133 (5), 145 (25), 160 (27), 170 (7), 185 (33), 186 (44), 187 (66), 188 (64), 210 (8), 214 (12), 291 (100, M+).
Id	51 (57), 77 (100), 78 (19), 89 (18), 90 (31), 91 (17), 103 (25), 104 (68), 105 (20), 106 (10), 115 (11), 117 (16), 119 (18), 153 (22), 161 (70), 196 (92), 218 (4), 222 (11), 264 (6), 299 (57, M+).
II	51 (13), 77 (61), 89 (36), 90 (67), 91 (11), 92 (6), 94 (15), 103 (11), 104 (100), 105 (22), 106 (5), 117 (7), 118 (9), 119 (8), 146 (63), 147 (7), 172 (11), 186 (5), 190 (17), 267 (61, M+).
III	51 (10), 57 (49), 77 (32), 89 (13), 90 (84), 91 (13), 94 (4), 103 (3), 104 (100), 105 (15), 106 (9), 116 (8), 117 (13), 118 (25), 119 (5), 131 (13), 132 (15), 133 (10), 136 (9), 149 (8), 160 (29), 165 (8), 178 (4), 184 (4), 200 (5), 204 (9), 239 (3), 253 (3), 281 (93, M+).

* The peaks of ions with intensities $\geq 3\%$ are presented; the isotopic peaks of the selenium-containing fragments are omitted, and the peaks of ions that contain the most abundant ^{80}Se isotope are indicated.

TABLE 2. Stabilities (W_M) of the Molecular Ions and Relative Intensities of the Peaks of the Characteristic Fragments (in percent of the total ion current) in the Mass Spectra of Ia-d, II, and III

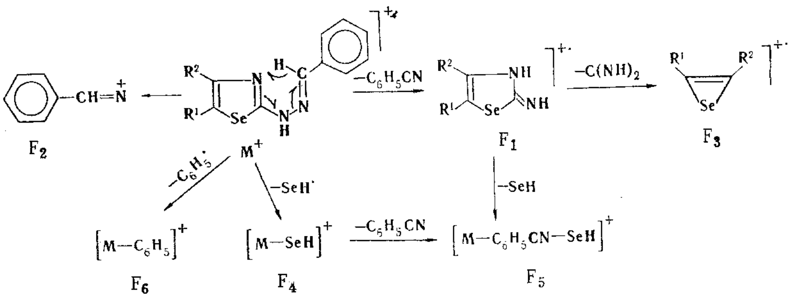
Compound	W_M	F_1	F_2	F_3	F_4	F_5	F_6
Ia	8,1	13,7	3,2	21,5	0,6	—	1,2
Ib	7,1	10,6	1,7	1,4	0,5	3,6	2,2
Ic	23,5	18,3	1,6	5,5	0,7	6,5	2,7
Id	12,3	19,1	5,3	—	0,3	1,1	2,1
II	21,6	—	12,7	—	0,6	—	4,2
III	28,2	2,0	12,1	—	0,5	—	2,8

The mass spectra of Ia-d, II, and III (Table 1) are characterized by intense peaks of M^+ ions, which, judging from the W_M values (Table 2), have high stabilities. The peaks of doubly charged molecular ions of hydrazones recorded in the spectra of the investigated compounds also constitute evidence for this.

A characteristic feature of the fragmentation of the M^+ ions of Ia-d is splitting out of a neutral molecule of benzonitrile as a result of a rearrangement of the McLafferty type and the formation of an $[M - C_6H_5CN]^+$ fragment ion (F_1, scheme and Table 2), the peak of which has considerable intensity in the spectra of these compounds. Simple cleavage of the N–N bond leads preferably to the formation of $Ph-CH=\overset{+}{N}$ ions (F_2). The subsequent fragmentation of the F_1 ion occurs due to cleavage of the selenazole ring with splitting out of a molecule of carbodiimide with the formation of F_3 ions. A peculiarity of the fragmentation of the benzaldehyde selenazolylhydrazones is ejection of an SeH$^{\cdot}$ radical from both M^+ with the formation of an $[M - SeH]^+$ ion (F_4), which gives a low-intensity signal in the spectra, and from the F_1 fragment with the formation of F_5 ions, the peaks of which are the second most intense peaks in the mass spectra of Ib, c. The ease of splitting out of a selenium atom or an SeH$^{\cdot}$ radical was noted in the spectra of derivatives of selenodiazole [7] and benzoselenophene [8], whereas ejection of a sulfur atom was not observed in the case of the thio analogs. The ejection of a phenyl group from the M^+ ions of Ia-d leads to the formation of low-intensity F_6 fragments.

Splitting out of a chlorine atom from the chloromethyl group of Id and a molecule of benzonitrile in different sequences leads to the appearance of a low-intensity $[M - Cl]^+$ ion with m/z 264 and an $[M - C_6H_5CN, - Cl]^+$ ion of significant intensity with m/z 161.

Disruption of the aromatic character of the heteroring (II and III) makes rearrangement with splitting out of benzonitrile from M^+ less likely. The principal fragments in the mass spectra of II and III are formed as a result of ejection of groups of SeH and SeCHCO atoms, while the F_2 ion peak has the maximum intensity



in the spectrum (Table 2). A peculiarity of the mass spectrum of III is an intense peak of an ion with m/z 57, which probably has the $[CH_3NCO]^+$ structure.

EXPERIMENTAL

Compounds I-III were obtained by the methods described in [1, 2, 9, 10]. The mass spectra were recorded with an MS-1302 mass spectrometer by direct introduction of the samples into the ion source at an ionizing voltage of 60 eV at 30-120°C.

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