MASS-SPECTROMETRIC BEHAVIOR OF CONDENSED 1,3-AZINES WITH OXO, THIOXO, OR IMINO FUNCTIONS IN THE 4 POSITION

1. 2,3-DIHYDRO-4H-1,3-BENZOTHIAZINE-2,4-DITHIONE AND ITS MONO- OR DIOXO ISOLOGS

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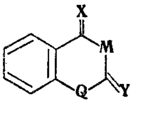
The principle pathway of fragmentation under electron impact of the molecular ions (M^+) of 2,3-dihydro-4H-1,3-benzothiazine-2,4-dithione and its mono- and dioxo isologs is cleavage of the retrodiene fragmentation type with the formation of monotypic A ions. In some cases successive two-step elimination of neutral fragments leads to the A ion. The large values (4.0-12.5) of the ratios of the intensities of the peaks of the A and M^+ ions is a characteristic feature for 4-oxo derivatives. This value ranges from 0.6 to 1.5 for the 2-oxo derivatives.

Under electron impact 2-imino-2,3-dihydro-4H-1,3-benzo-4-thiazinones [1, 2], 4-imino-2,3-dihydro-4H-1,3-benzo-2-thiazinones [2], and 1,3-benzoxazin-4-ones with the general formula Z (M and Q are heteroatoms, X and Y = O, S, and NR) undergo primary cleavage of the retro-Diels—Alder (RDA) type (RDA cleavage) with the formation of a "diene" ion radical and a neutral "phylodiene" fragment. Depending on the ionization potentials of these fragments [3], the positive charge is localized primarily either on the diene or phylodiene fragments. In particular, in the case of the imino-1,3-benzothiazinones mentioned above



Z

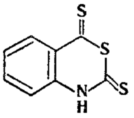


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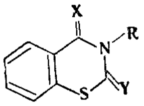
TABLE 1. Intensities of the Peaks of the Molecular and Principal Fragment Ions in the Mass Spectra of II-XIII (%Σ_{39})



Compound	Structural type	X	Y	R	M	W_M	M-H	M-R	M-SH	M-CS	M-CHS	M-RCN	M-RNCY	$\frac{M-RNCY}{M}$
II	A	S	S	H	211	16,2	3,20	3,20	0,49	1,80	—	1,14	14,5	0,89
III	A	S	S	CH_3	225	14,3	2,29	0,43	2,15	0,29	1,0	0,86	9,85	0,69
IV	A	S	S	C_6H_5	287	3,5	0,10	5,00	0,30	0,45	1,25	0,35	3,70	1,06
V	B	S	O	H	195	15,9	0,64	—	—	0,79	—	—	13,3	0,84
VI	B	S	O	CH_3	209	8,3	0,72	12,0	0,24	—	—	—	12,0	1,45
VII	B	S	O	C_6H_5	271	7,1	—	—	—	—	—	—	3,9	0,55
VIII	C	O	S	H	195	2,7	—	—	0,25	—	—	—	24,6	9,1
IX	C	O	S	CH_3	209	6,5	1,04	—	—	—	—	1,82	26,0	4,0
X	C	O	S	C_6H_5	271	6,4	—	—	—	—	—	1,89	37,8	5,9
XI	D	O	O	H	179	7,8	—	—	—	—	—	—	31,3	4,0
XII	D	O	O	CH_3	193	4,6	—	—	—	—	—	—	32,8	7,1
XIII	D	O	O	C_6H_5	255	3,6	—	—	—	—	—	—	45,0	12,5

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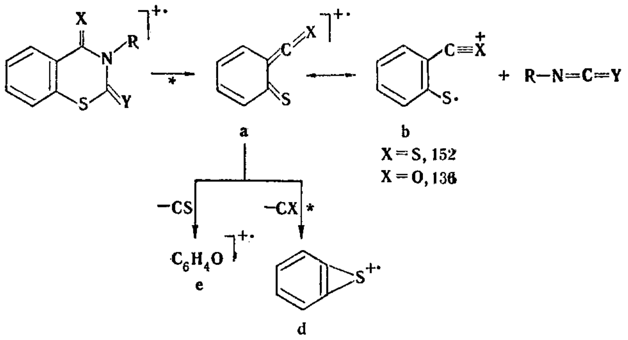
the ion peaks that correspond to the phylodiene are characterized by appreciable intensity [2]. At the same time, in our next publication we will show that processes involving the fragmentation of the molecular ions of the RDA type virtually do not occur in the dissociative ionization of 3,1-benzothiazin-4-thiones that have the same structure of the Z type, as well as in the case of 1,2-dihydro-4H-3,1-benzothiazin-2,4-dithione [1]. In this connection, we became interested in the character of the mass-spectral fragmentation of the isomeric (with respect to I) 1,3-benzothiazine-2,4-dithione (II), as well as its N-methyl- and N-phenyl derivatives (III and IV, structures of the A type, see Table 1). Since the literature thus far has not contained any information regarding the mass-spectral behavior of 1,3-benzothiazine-4-thiones, and only spotty information regarding 3,1-benzothiazine-4-ones has been available [1, 2, 4], we investigated the corresponding 4-thioxo-2-oxo derivatives (V-VII with a structure of the B type), 2-thioxo-4-oxo derivatives (VIII-X with a structure of the C type), and 2,4-dioxo derivatives (XI-XIII with a structure of the D type) of these compounds.

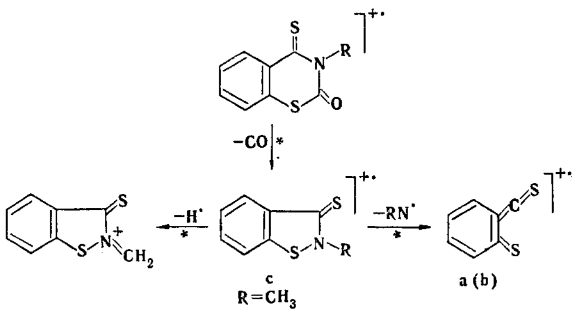
Of the six investigated 1,3-benzothiazine-4-thione derivatives, molecular-ion peak is the maximum peak only in the case of II, III, and V. In the case of the N-phenyl derivatives the intensity of the peak of this ion does not exceed 38-70% (see Table 2). The molecular ions of all of the compounds of this group undergo fragmentation with the formation of ion radical a, mesomeric b (152*), and a neutral isocyanate or isothiocyanate (R—N=C=Y) fragment (Scheme 1).

Scheme 1



The peak of the a (b) ion is the maximum peak in the mass spectrum of VI (see Table 2). The one-step character of its formation from the molecular ion via a pathway of the RDA fragmentation type is confirmed in a number of cases by the corresponding peaks of the metastable ions. In addition to this, a second two-step pathway for the formation of the a ion due to the successive elimination of a CO (ion c) of the imine RN residue (ion a, Scheme 2) is observed in the case of VI.

Scheme 2



The formation of the a (b) ion from fragment c is probably energically favorable. The intensities of the peaks of the a (b) ions (II-VII) relative to the molecular peak range from 60 to 140%. This fragment subsequently eliminates a CS molecule to give ion d (108).

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*Here and subsequently, the numbers that characterize the ions are the mass-to-charge ratios (m/e).

TABLE 2. Mass Spectra of II-XIII*

Compound	m/e values (relative intensities, %)
II	211 (100), 210 (20), 177 (11), 153 (22), 152 (89), 108 (66), 77 (8), 76 (14), 69 (30), 50 (13), 45 (13)
III	225 (100), 224 (16), 192 (15), 153 (16), 152 (69), 108 (59), 77 (12), 76 (13), 69 (27), 50 (11), 45 (16)
IV	287 (70), 242 (25), 210 (100), 152 (74), 109 (14), 108 (70), 82 (18), 77 (30), 69 (89), 51 (27), 45 (21)
V	195 (100), 167 (16), 153 (10), 152 (84), 108 (60), 76 (23), 69 (33), 63 (14), 50 (14), 45 (14), 39 (12)
VI	209 (69), 181 (16), 153 (27), 152 (100), 108 (65), 77 (26), 76 (16), 69 (50), 63 (20), 50 (20), 45 (44)
VII	271 (38), 243 (9), 194 (100), 152 (21), 109 (11), 108 (33), 77 (24), 69 (19), 51 (34), 50 (11), 39 (13)
VIII	195 (11), 137 (10), 136 (100), 109 (10), 108 (49), 82 (8), 69 (15), 63 (9), 50 (9), 45 (10), 39 (14)
IX	209 (25), 168 (17), 137 (13), 136 (100), 108 (39), 69 (30), 63 (11), 58 (9), 50 (11), 45 (13), 39 (9)
X	271 (17), 270 (4), 168 (5), 137 (10), 136 (100), 108 (22), 105 (8), 77 (8), 69 (11), 51 (8), 50 (5)
XI	179 (25), 137 (9), 136 (100), 108 (44), 82 (9), 69 (27), 63 (10), 58 (6), 50 (8), 45 (7), 39 (7)
XII	193 (14), 137 (10), 136 (100), 108 (39), 82 (9), 69 (25), 63 (9), 58 (7), 50 (7), 45 (7), 39 (7)
XIII	255 (8), 137 (10), 136 (100), 108 (19), 82 (4), 77 (2), 69 (10), 63 (4), 58 (3), 51 (4), 39 (4)

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*The molecular ion peak and the 10 most intense peaks are presented.

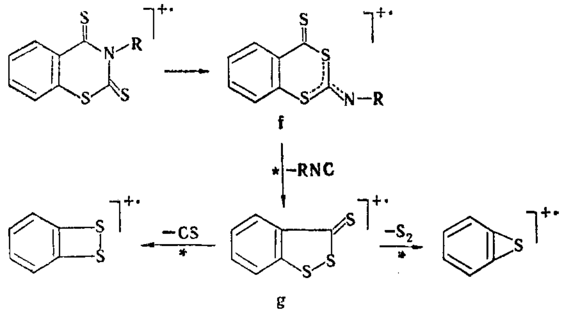
The intensities of the molecular-ion peaks in the mass spectra of the 1,3-benzothiazin-4-ones (VIII-XIII) that we investigated range from 8 to 25% (see Table 2); in all cases the peak of the a (b) ion (136) is the maximum peak. The formation of this ion directly from the molecular ion via the scheme of RDA fragmentation is confirmed by the corresponding peaks of the metastable ions. In the case of these compounds two-step processes involving the fragmentation of the molecular ion to fragment a could not be identified. The peaks of the fragment ions formed in the RDA fragmentation in the mass spectra of the isothiocyanates (VIII-X) and isocyanates (XI-XIII) are generally either of low intensity or absent. A comparison of the ratios of the intensities of the peaks of the $[M-RCNY]^+$ and M^+ ions (Table 1) shows that these values are higher by a factor of 4 to 12 in the case of VIII-XIII than in the case of II-VII; consequently, the high value of this parameter is a characteristic feature for 1,3-benzothiazine-4-thiones.

Thus the most intense peaks of ions of the a (b) type correspond to the key fragments in the mass spectra of 1,3-benzothiazine-4-thiones and 1,3-benzothiazin-4-ones, respectively, and this serves as a distinct analytical feature that makes it possible to distinguish 1,3-benzothiazine-2-thion-4-ones from the structurally isomeric 1,3-benzothiazine-4-thion-2-ones. As in the case of compounds II-VII, the a (b) fragment subsequently eliminates a CO molecule with the formation of ion radical d. The ejection of a CS molecule takes place to only a small extent (ion e, 92, see Scheme 1). The subsequent fragmentation of ion d leads to a series of fragments that are characteristic for all of the investigated 1,3-benzothiazine-4-thiones and -4-ones (see Scheme 1 and Table 2).

We did not find any other primary processes of fragmentation of the molecular ions of VIII-XIII, if one disregards the loss of a hydrogen atom in the case of N-phenyl derivative X and the elimination of an SH radical in the case of N-methyl compound IX, which takes place to a very small extent.

Just the opposite is observed in the case of 1,3-benzothiazine-4-thiones II-VII (see Table 1). Thus, for example, for II and V one of the most important processes is the splitting out of a phenyl group. In addition to this, particularly in the case of dithiones II-IV, the molecular ions readily lose SH, CS, CHS, and RCN particles. The elimination of an R—CN molecule, which also occurs in the fragmentation of IX and X, leads to a 184 ion in the case of dithiones II-IV. It may be assumed that this ion has benzotrithione structure g. The pathway of its formation from rearranged ion f is presented in Scheme 3.

Scheme 3



An examination of the fragmentation of an authentic sample with the g structure (m/e 184, 100%) shows that it undergoes fragmentation either with elimination of two sulfur atoms (ion 120, 54%) or, to a smaller extent, with ejection of a CS molecule (140, 28%). The intensities of the 120 ion peak in the mass spectra of II-IV are, respectively, 3, 6, and 4%. At the same time, the peak of this ion is completely absent in the mass spectra of the other compounds that we investigated.

Finally, it should be noted that a $C_6H_5CO^+$ ion (105), the intensities of the peak of which are 11 and 8%, respectively, is observed in the mass spectrum of X both at reduced (12 eV) and high (70 eV) ionization energies. Its formation can be explained only by migration of the phenyl group in the open form of the heterocyclic ring of the molecular ion to the carbonyl C_4 atom with subsequent fragmentation of the rearranged ion.

In conclusion, it should be emphasized that the multiline character of the mass spectra decreases in the order of the examined groups of compounds A, B, C, and D. Thus in the series of N-phenyl derivatives (IV, VII, X, and XIII) the number of ion peaks (with intensities $\geqslant 3\%$) are, respectively, 63, 27, 19, and 10.

EXPERIMENTAL

The synthesis of II-XIII was described in [5]. The electron-impact mass spectra were obtained with a Varian MAT CH-6 spectrometer at an ionization energy of 70 eV and a source temperature of 200°C with direct introduction of the samples into the ionization chamber. The elementary composition of the most important fragment ions was determined by means of the high-resolution mass spectra with an MS-902S spectrometer.

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