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Dedicated to Full Member of the Russian Academy of Sciences M.G. Voronkov on his 90th anniversary

Fragmentation of Pyrazolecarbaldehyde Thio- and Dithioacetals under Electron Impact and Chemical Ionization

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Abstract—The mass spectra of 1-substituted 3,5-dimethyl-1*H*-pyrazole-4-carbaldehyde bis(2-hydroxyethyl) dithioacetals and thioacetals were studied for the first time. The main fragmentation pathways of their molecular ions generated under electron impact and chemical ionization were similar. Primary decomposition of the molecular ions of bis(2-hydroxyethyl) dithioacetals involves elimination of 2-sulfanylethanol molecule with formation of the corresponding 1,3-oxathiolane radical cation. Fragmentation of the molecular ions $[M]^{+\cdot}$ and $[M + H]^+$ derived from 2-(3,5-dimethyl-1*H*-pyrazol-4-yl)-1,4,6-oxadithiocanes includes cleavage of the eight-membered heteroring and elimination of $C_4H_9OS^{\cdot}$. Substituents in the heteroring of pyrazolecarbaldehydes inhibit decomposition processes related to the aldehyde group.

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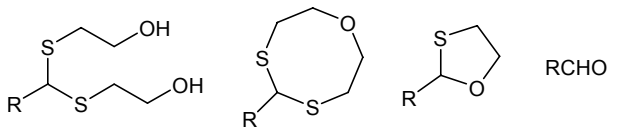
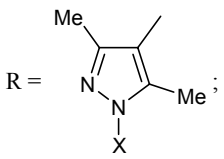
Compounds containing a pyrazole fragment are used as components of many medicines possessing anti-inflammatory, antidiabetic, analgesic, and other kinds of pharmacological activity [1, 2]. In addition, they are highly effective pesticides, in particular insectoacaricides [3], and are successfully used in the synthesis of coordination compounds as efficient catalysts [4]. Therefore, pyrazole derivatives attract strong interest. Pyrazolecarbaldehydes open wide prospects in further modification and synthesis of pyrazole derivatives which could exhibit biological activity and be useful as dyes, fluorophores, etc. From the viewpoint of practical application of pyrazole derivatives in human activity, of particular importance is their identification by instrumental methods which could ensure reliable determination of their concentration in various media.

In continuation of our studies in the field of synthesis and properties of functionalized pyrazoles, in the present work we examined the behavior of previously unknown pyrazolylcarbaldehyde bis(2-hydroxyethyl) dithioacetals **Ia**–**Ie**, pyrazolyl-substituted 1,4,6-oxadithiocanes **IIa**–**IIe** and 1,3-oxathiolanes **IIIa**–**IIIe**, and pyrazolecarbaldehydes **IVa**–**IVe** under electron impact (EI) and chemical ionization with a view to reveal analytical ions ensuring their reliable mass spectrometric identification. The complete mass spectra (EI) of all compounds **I**–**IV** are given in Table 1.

The presence in molecules **I** and **II** of a labile dithioacetal functionality in addition to a pyrazole ring makes them interesting models for both chemical and mass spectrometric studies. Moreover, these compounds may equally be regarded as functionally substituted pyrazoles and dithioacetals derived from 2-sulfanylethanol and the corresponding pyrazolecarbaldehyde. Therefore, their fragmentation under electron



Ia–Ie **IIa–IIe** **IIIa–IIIe** **IVa–IVe**



;

X = Me (**a**), Pr (**b**), *i*-Pr (**c**), CH_2=$CHCH_2$ (**d**), $PhCH_2$ (**e**).

Table 1. Complete electron impact mass spectra of pyrazolecarbaldehyde bis(2-hydroxyethyl) dithioacetals **Ia**–**Ie**, pyrazolyl-substituted 1,4,6-oxadithiocanes **IIa**–**IIe** and 1,3-oxathiolanes **IIIa**–**IIIe**, and pyrazolecarbaldehydes **IVa**–**IVe**

Compound no.	m/z (I_{rel}, %)[a]
Ia	276 (<1) $[M]^{+\cdot}$, 277 (<1) $[M + 1]^+$, 199 (9), 198 (32), 197 (4), 156 (7), 153 (7), 147 (6), 144 (4), 143 (4), 141 (7), 139 (22), 138 (51), 137 (100),123 (5), 111 (3), 110 (3), 109 (5), 82 (4), 81 (3), 79 (4), 78 (12), 69 (3), 68 (3), 67 (5), 66 (14), 65 (7), 63 (3), 62 (3), 61 (8), 60 (32), 59 (18), 58 (7), 57 (4), 56 (33), 55 (4), 54 (4), 53 (6), 52 (4), 50 (3), 49 (3), 48 (15), 47 (24), 46 (12), 45 (34), 44 (10)
Ib	304 (<1) $[M]^{+\cdot}$, 305 (6) $[M + 1]^+$, 229 (6), 228 (15), 227 (100), 226 (38), 225 (9), 183 (5), 181 (6), 167 (19), 166 (19), 165 (14), 151 (22), 139 (8), 138 (17), 137 (37), 125 (8), 124 (52), 123 (38), 110 (3), 109 (7), 97 (7), 89 (6), 82 (8), 80 (5), 78 (7), 68 (3), 67 (4), 66 (3), 65 (4), 61 (13), 60 (21), 59 (12), 58 (3), 54 (3), 53 (3), 52 (3), 48 (10), 47 (16), 46 (5), 45 (19), 44 (5)
Ic	304 (<1) $[M]^{+\cdot}$, 305 (9) $[M + 1]^+$, 228 (14), 227 (100), 226 (18), 225 (6), 185 (10), 181 (4), 167 (8), 166 (11), 165 (7), 151 (18), 141 (4), 139 (7), 138 (3), 137 (3), 125 (5), 124 (21), 123 (28), 109 (9), 97 (7), 89 (6), 82 (3), 78 (7), 68 (3), 67 (3), 66 (3), 65 (3), 61 (10), 60 (8), 59 (9), 52 (3), 48 (4), 47 (9), 46 (4), 45 (22)
Id	302 (<1) $[M]^{+\cdot}$, 303 (1) $[M + 1]^+$, 227 (4), 226 (12), 225 (72), 224 (63), 223 (11), 181 (5), 180 (2), 179 (9), 166 (3), 165 (32), 164 (71), 163 (100), 150 (3), 149 (27), 147 (5), 139 (3)138 (3), 137 (15), 136 (6), 135 (16), 124 (3), 123 (18), 122 (9), 121 (10), 120 (3), 119 (3), 118 (3), 109 (8), 108 (6), 107 (3), 106 (3), 97 (4), 95 (8), 94 (11), 93 (3), 92 (3), 89 (5), 82 (7), 81 (7), 80 (7), 79 (4), 78 (12), 77 (4), 69 (3), 68 (5), 67 (8), 66 (7), 65 (8), 63 (3), 62 (3), 61 (16), 60 (37), 59 (22), 58 (5), 57 (3), 56 (7), 55 (9), 54 (6), 53 (6), 52 (5), 51 (4), 49 (3), 48 (16), 47 (26), 46 (9), 46 (34), 44 (8)
Ie	352 (<1) $[M]^{+\cdot}$, 276 (4), 275 (84), 274 (100), 273 (7), 230 (6), 229 (6), 215 (11), 214 (56), 213 (75), 200 (4), 199 (29), 197 (3), 186 (4), 185 (29), 171 (3), 137 (5), 123 (5), 122 (5), 92 (9), 91 (100), 89 (10), 82 (3), 78 (13), 77 (3), 66 (4), 65 (28), 63 (5), 61 (14), 60 (8), 59 (11), 58 (3), 55 (3), 52 (3), 51 (6), 48 (4), 47 (8), 46 (3), 45 (18), 43 (3)
IIa	260 (2) $[M + 2]^{+\cdot}$, 259 (9) $[M + 1]^+$, 258 (10) $[M]^{+\cdot}$, 156 (5), 155 (7), 154 (100), 153 (45), 139 (4), 138 (3), 137 (5), 123 (5), 111 (2), 109 (3), 91 (4), 80 (2), 66 (4), 56 (6)
IIb	289 (3), 288 (5) $[M + 2]^{+\cdot}$, 287 (21) $[M + 1]^+$, 286 (9) $[M]^{+\cdot}$, 184 (5), 183 (9), 182 (100), 181 (11), 167 (15), 154 (5), 153 (4), 152 (4), 151 (3), 149 (10), 141 (4), 140 (9), 139 (17), 124 (4), 123 (4), 109 (4), 97 (4), 89 (3)
IIc	288 (5) $[M + 2]^{+\cdot}$, 287 (21) $[M + 1]^+$, 286 (8) $[M]^{+\cdot}$, 184 (4), 183 (8), 182 (100), 181 (9), 167 (13), 149 (10), 140 (9), 139 (16), 123 (5), 109 (3)
IId	286 (3) $[M + 2]^{+\cdot}$, 285 (16) $[M + 1]^+$, 284 (10) $[M]^{+\cdot}$, 182 (5), 181 (15), 180 (100), 179 (23), 165 (7), 153 (7), 152 (4), 147 (30), 139 (5), 138 (6), 106 (3), 89 (3), 80 (2), 59 (3)
IIe	335 (7) $[M + 1]^+$, 334 (3) $[M]^{+\cdot}$, 232 (5), 231 (17), 230 (100), 229 (23), 215 (7), 214 (3), 199 (5), 197 (8), 185 (3), 1677 (3), 156 (4), 139 (3), 92 (4), 91 (42), 65 (3)
IIIa	199 (11) $[M + 1]^+$, 198 (18) $[M]^{+\cdot}$, 163 (11), 153 (2), 139 (5), 138 (92), 137 (100), 110 (5), 99 (3), 85 (12), 83 (11), 82 (10), 80 (3), 79 (3), 69 (4), 66 (21), 65 (6), 60 (10), 59 (10), 53 (4), 49 (3), 48 (5), 47 (28), 46 (7), 45 (5)
IIIb	227 (8) $[M + 1]^+$, 226 (60) $[M]^{+\cdot}$, 181 (12), 167 (16), 166 (43), 165 (14), 152 (5), 151 (57), 140 (3), 139 (10), 138 (8), 137 (7), 125 (11), 124 (51), 123 (100), 114 (3), 96 (6), 95 (7), 83 (4), 82 (13), 81 (6), 80 (13), 69 (4), 68 (7), 59 (10), 57 (3), 56 (3), 55 (3), 54 (3, 53 (3), 52 (3), 51 (4)
IIIc	227 (6) $[M + 1]^+$, 226 (36) $[M]^{+\cdot}$, 225 (7), 211 (3), 181 (5), 167 (19), 166 (61), 165 (14), 152 (7), 151 (53), 138 (8), 137 (11), 125 (11), 124 (58), 123 (100), 109 (3), 108 (3), 94 (4), 82 (8), 65 (6), 61 (5), 60 (6), 59 (7), 58 (5), 45 (8)
IIId	225 (9) $[M + 1]^+$, 224 (28) $[M]^{+\cdot}$, 223 (5), 179 (11), 165 (29), 164 (49), 163 (91), 149 (20), 137 (14), 136 (4), 135 (12), 123 (20), 122 (9), 121 (8), 120 (7), 108 (6), 94 (11), 82 (11), 80 (12), 79 (6), 78 (4), 68 (4), 67 (6), 66 (12), 65 (10), 60 (10), 59 (9), 58 (8), 57 (3), 56 (5), 55 (4), 54 (5)
IIIe	275 (6) $[M + 1]^+$, 274 (17) $[M]^{+\cdot}$, 273 (3), 215 (15), 214 (21), 213 (38), 200 (3), 199 (32), 186 (4), 185 (15), 171 (6), 151 (3), 144 (3), 137 (3), 123 (3), 122 (4), 92 (8), 91 (100), 65 (27), 63 (5), 60 (12)

Table 1. (Contd.)

Compound no.	m/z (I_{rel}, %)[a]
IVa	138 (55) $[M]^{+\cdot}$, 137 (100) $[M-1]^+$, 85 (9), 84 (4), 83 (33), 82 (7), 81 (5), 79 (5), 68 (3), 67 (3), 66 (4), 65 (3), 59 (4), 56 (12), 49 (4), 48 (5), 47 (6), 47 (7)
IVb	167 (7) $[M+1]^+$, 166 (66) $[M]^{+\cdot}$, 165 (4), 164 (7), 152 (5), 151 (34), 138 (4), 137 (5), 125 (12), 124 (27), 123 (100), 96 (4), 95 (7), 85 (10), 83 (27), 82 (4), 81 (3), 67 (7), 65 (5), 54 (5), 48 (7), 47 (8)
IVc	167 (7) $[M+1]^+$, 166 (93) $[M]^{+\cdot}$, 165 (5), 152 (3), 151 (58), 138 (5), 136 (3), 126 (3), 125 (5), 124 (38), 123 (100), 110 (3), 97 (3), 96 (4), 85 (20), 83 (32), 82 (4), 76 (3), 68 (10), 67 (9), 66 (8), 65 (6), 54 (8), 49 (10), 48 (9)
IVd	165 (22) $[M+1]^+$, 164 (100) $[M]^{+\cdot}$, 163 (89), 149 (11), 137 (17), 136 (4), 135 (13), 124 (4), 123 (26), 122 (7), 121 (8), 109 (5), 108 (8), 106 (3), 95 (8), 94 (13), 93 (3), 82 (14), 81 (7), 80 (8), 69 (9), 68 (8), 67 (10), 65 (13), 56 (5), 55 (4), 54 (5), 53 (3)
IVe	216 (5) $[M+2]^+$, 215 (29) $[M+1]^+$, 214 (84) $[M]^{+\cdot}$, 213 (37) $[M-1]^+$, 200 (5), 199 (39), 186 (5), 185 (16), 172 (2), 171 (8), 158 (5), 145 (5), 137 (5), 124 (6), 123 (5), 107 (3), 92 (8), 91 (100), 89 (4), 65 (26)

[a] Ion peaks with a relative intensity of less than 3% were omitted.

impact can follow pathways typical of both classes of compounds or take a quite different pathway.

The total ion chromatograms of dithioacetals **Ia**–**Ie** (injector, interface, and ion source temperatures were equal to 200°C) contained four peaks. The mass spectrum of the first peak (*m*/*z* 78) matched the reference spectrum of 2-sulfanylethanol (**V**) [5]. The mass spectrum of the second peak was typical of the corresponding pyrazolecarbaldehyde **IV**. The other two peaks with different retention times but the same molecular weight were assigned to 1,3-oxathiolanes **III**. Presumably, bis(2-hydroxyethyl) dithioacetals **Ia**–**Ie** underwent partial thermal decomposition upon chromatography (Scheme 1). It should be noted that thermolysis of bis(2-hydroxyethyl) dithioacetal **Ia**–**Ie** with formation of pyrazolecarbaldehyde and 2-sulfanylethanol is a reverse process to their formation in solution [6].

In the electron impact mass spectra of compounds **Ia**–**Ie** introduced directly into the ion source, the intensity of the molecular ion peaks was less than 1%. An exception was compound **Ib** which displayed in the mass spectrum a weak $[M+H]^+$ peak with *m*/*z* 305 (6%). The primary fragmentation of bis(2-hydroxyethyl) dithioacetals **Ia**–**Ie** follows a path typical of acetals [7]. The molecular ion decomposes *in statu nascendi* via cleavage of the acetal C–S bond with elimination of $C_2H_5S^{\cdot}$ radical or C_2H_6OS molecule (Scheme 2). The $[M-C_2H_5OS]^+$ ion can have structure **A** or **A′**, and the $[M-C_2H_6OS]^{+\cdot}$ radical cation, structure **B** or **B′**. Further decomposition of these ions involves expulsion of sulfur-containing radical $C_2H_5S^{\cdot}$ with formation of ions **C** and **D** (Table 2). This fragmentation path is energetically favorable if the $[M-C_2H_6OS]^{+\cdot}$ ion has the structure of 1,3-oxathiolane radical cation **B** and $[M-C_2H_5OS]^+$ is protonated 1,3-oxathiolane **A**.

The above assumption was confirmed by studying the mass spectra of 1,3-oxathiolanes **IIIa**–**IIIe**. These compounds under electron impact displayed strong molecular ion peaks (Table 1, Scheme 3), which is typical of 2-aryl-1,3-oxathiolanes and oxathianes [8, 9]. In the fragmentation of unsubstituted 1,3-oxathiolane, its 2-alkyl derivatives, and 1,3-oxathiane, the charge resides mainly on sulfur-containing fragments. Therefore, $[M-CHO]^+$, $[M-CH_2O]^{+\cdot}$, and $[HCS]^+$ ions are the most abundant. By contrast, the main fragmentation pathway of pyrazolyl-substituted 1,3-oxathiolanes **IIIa**–**IIIe** is elimination of sulfur-containing fragment

Scheme 1.

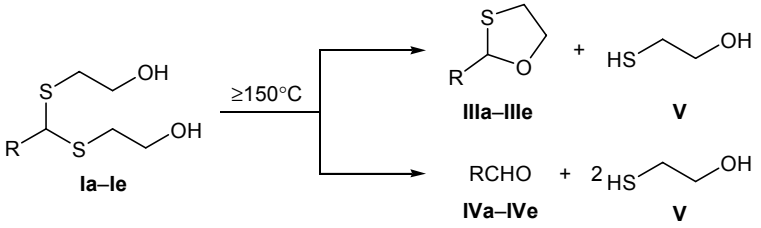


Table 2. Principal ions in the electron impact mass spectra of pyrazolecarbaldehyde bis(2-hydroxyethyl) dithioacetals **Ia**–**Ie**

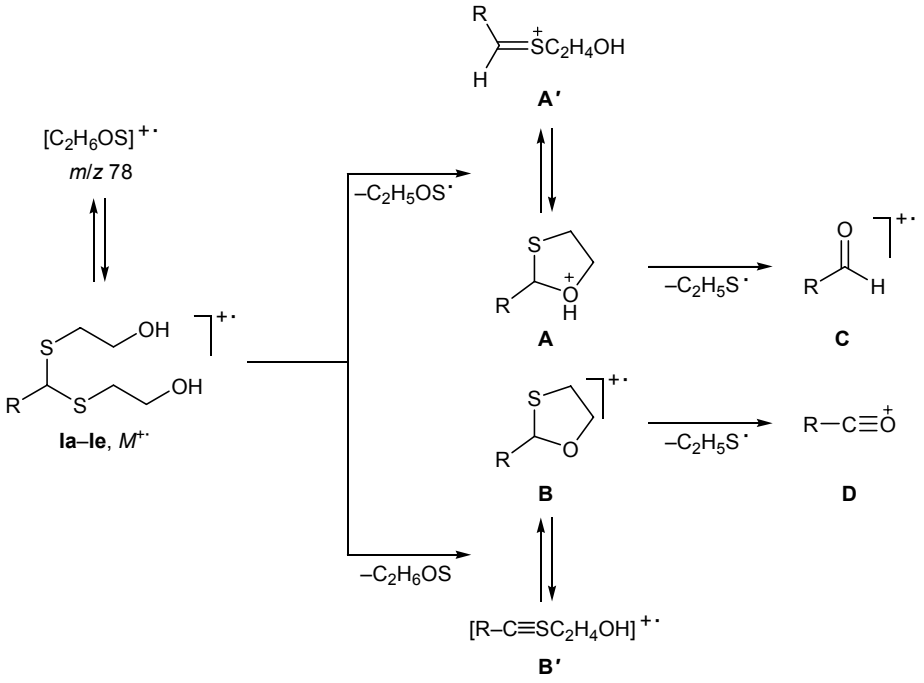
Ion	*m*/*z* (I_{rel}, %)				
	Ia	**Ib**	**Ic**	**Id**	**Ie**
M^+	276 (<1)	304 (<1)	304 (<1)	302 (<1)	352 (<1)
$[M + H]^+$	277 (<1)	305 (6)	305 (9)	303 (1)	353 (–)
$[M - C_2H_5OS]^+$, **A**, **A′**	199 (9)	227 (100)	227 (100)	225 (72)	275 (84)
$[M - C_2H_6OS]^+$, **B**, **B′**	198 (33)	226 (38)	226 (18)	224 (63)	274 (100)
$[\mathbf{A} - C_2H_5S]^{+\cdot}$, **C**	138 (51)	166 (19)	166 (11)	164 (71)	214 (56)
$[\mathbf{B} - C_2H_5S]^+$, **D**	137 (100)	165 (14)	165 (7)	163 (100)	213 (75)
$[R]^+$	109 (5)	137 (37)	137 (3)	135 (16)	185 (29)
$[C_3H_5OS]^+$, *m*/*z* 89	(1)	(6)	(6)	(5)	(10)
$[C_2H_6OS]^{+\cdot}$, *m*/*z* 78	(12)	(7)	(7)	(12)	(13)
$[C_3H_4S]^{+\cdot}$, *m*/*z* 60	(32)	(21)	(8)	(37)	(8)
$[C_2H_5S]^+$, *m*/*z* 61	(8)	(13)	(10)	(16)	(14)

from $[M]^{+\cdot}$ with formation of $[M - C_2H_4S]^{+\cdot}$ radical cation (**C**, Scheme 3). Analogous pattern was observed for fragmentation of nitrobenzaldehyde thioacetals [6]. It should be noted that introduction of a strong electron-withdrawing substituent dramatically reduced the stability of the molecular ion, and the corresponding peak was almost not observed in the mass spectra.

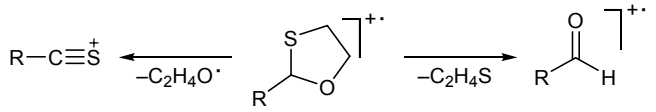
Further decomposition pattern of ion **C** completely coincides with that typical of the molecular ions of pyrazolecarbaldehydes **IVa**–**IVe** (see below). Elimination of oxygen-containing fragment $C_2H_5O^{\cdot}$ from the molecular ion $[M]^{+\cdot}$ of 1,3-oxathiolanes **IIIa**–**IIIe** with formation of $[M - C_2H_5O]^+$ ion (**E**) is a minor pathway. Presumably, the reason is higher electronegativity of the oxygen atom.

Thus the electron impact mass spectra of bis(2-hydroxyethyl) ditihoacetals **Ia**–**Ie** (upon direct sample admission into the ion source) completely coincide with the spectra of the corresponding 1,3-oxathiolanes **IIIa**–**IIIe**. This indicates that primary fragmentation of the molecular ion of **Ia**–**Ie** gives rise to 1,3-oxathiolane radical cation via elimination of C_2H_6OS molecule.

Scheme 2.



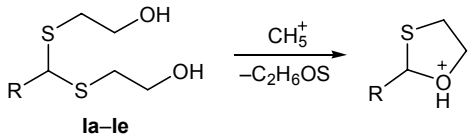
Scheme 3.



m/*z*	153 (2)	198 (18)	138 (92) (**a**)
	181 (12)	226 (60)	166 (43) (**b**)
	181 (5)	226 (36)	166 (61) (**c**)
	179 (11)	224 (28)	164 (49) (**d**)
	229 (–)	274 (17)	214 (21) (**e**)

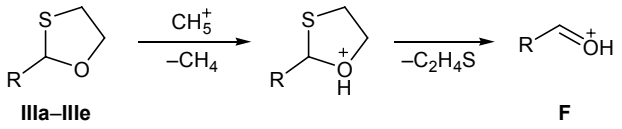
The chemical ionization mass spectra of bis(2-hydroxyethyl) dithioacetals **Ia**–**Ie** were also very similar to the positive ion chemical ionization (PICI) spectra of 1,3-oxathiolanes **IIIa**–**IIIe**. As under electron impact, expulsion of 2-sulfanylethanol molecule (**V**) from the molecular ion of bis(2-hydroxyethyl) dithioacetal **Ia**–**Ie** gives the corresponding protonated 1,3-oxathiolane **IIIa**–**IIIe** (Scheme 4, Table 3).

Scheme 4.



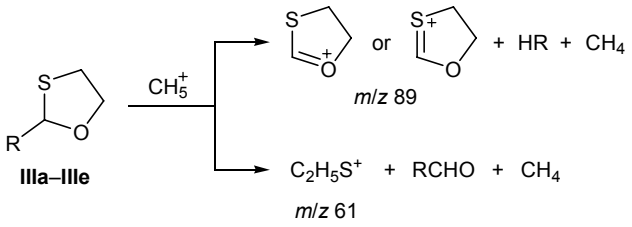
In the PICI spectra of 1,3-oxathiolanes **IIIa**–**IIIe** the molecular ions $[M + H]^+$ are fairly abundant (Table 4). The most typical fragmentation pathway (as under electron impact) involves elimination of C_2H_4S molecule with formation of ion **F**. Most probably, the latter has the structure of protonated pyrazolecarbaldehyde **IVa**–**IVe** (Scheme 5).

Scheme 5.



The two other fragment ions with *m*/*z* 89 and 61 (Table 4) can be formed as a result of decomposition of $[M + H]^+$ or ionization via anion abstraction (Scheme 6).

Scheme 6.



Apart from the above ions, the PICI mass spectra contained fairly intense peaks of cluster ions $[M + C_2H_5]^+$ and $[M + C_3H_5]^+$ formed by electrophilic addition. These ions, as well as $[M + H]^+$, readily lose C_2H_4S molecule, yielding two important characteristic ions $[(M + C_2H_5) - C_2H_4S]^+$ and $[(M + C_3H_5) - C_2H_4S]^+$ (Tables 3, 4).

We can conclude that the main fragmentation pathways of the molecular ions of pyrazolecarbaldehyde dithioacetals **I** and pyrazolyl-substituted 1,3-oxathiolanes **III** under electron impact and chemical ioniza-

Table 3. Positive ion chemical ionization mass spectra of pyrazolecarbaldehyde bis(2-hydroxyethyl) dithioacetals **Ia**–**Ie** (reactant gas methane)

Ion	*m*/*z* (I_{rel}, %)				
	Ia	**Ib**	**Ic**[a]	**Id**	**Ie**[b]
$[M - C_2H_5OS]^+$, **A**	199 (73)	227 (100)	227 (85)	225 (100)	275 (20)
$[\mathbf{A} + C_2H_5]^+$	227 (12)	255 (15)	255 (10)	253 (12)	303 (2)
$[\mathbf{A} + C_3H_5]^+$	239 (5)	267 (5)	267 (2)	265 (4)	315 (–)
$[(\mathbf{A} + C_2H_5) - C_2H_4S]^+$	167 (25)	195 (15)	195 (20)	193 (12)	243 (20)
$[(\mathbf{A} + C_3H_5) - C_2H_4S]^+$	179 (5)	207 (3)	207 (5)	205 (4)	255 (2)
$[\mathbf{A} - C_2H_4S]^+$	139 (100)	167 (55)	167 (100)	165 (80)	215 (100)
$[C_3H_5OS]$, *m*/*z* 89	(13)	(10)	(15)	(15)	–
$[C_2H_5OS]$, *m*/*z* 61	(20)	(8)	(18)	(12)	(25)

[a] *m*/*z* 125 (3) $[(\mathbf{A} - C_2H_4S) - C_3H_6]^+$ (**Ic**).
[b] *m*/*z* 91 (17) $[C_7H_7]^+$, 119 (5) $[C_7H_7N_2]^+$ (**Ie**).

Table 4. Positive ion chemical ionization mass spectra of 2-pyrazolyl-1,3-oxathiolanes **IIIa**–**IIIe** (reactant gas methane)

Ion	*m*/*z* (I_{rel}, %)				
	IIIa	**IIIb**	**IIIc**	**IIId**	**IIIe**
$M^{+\cdot}$	198 (6)	226 (2)	226 (8)	224 (5)	274 (3)
$[M + H]^+$	199 (77)	227 (12)	227 (65)	225 (61)	275 (21)
$[M + C_2H_5]^+$	227 (7)	255 (3)	255 (9)	253 (10)	303 (3)
$[M + C_3H_5]^+$	239 (4)	267 (1)	267 (3)	265 (3)	315 (1)
$[(M + C_2H_5) - C_2H_4S]^+$	167 (11)	195 (11)	195 (12)	193 (12)	243 (15)
$[(M + C_3H_5) - C_2H_4S]^+$	179 (3)	207 (4)	207 (4)	205 (4)	255 (4)
$[(M + H) - C_2H_4S]^+$	139 (100)	167 (100)	167 (100)	165 (100)	215 (100)
$[C_3H_5OS]^+$, *m*/*z* 89	(12)	(3)	(13)	(13)	(4)
$[C_2H_5S]^+$, *m*/*z* 61	(15)	(18)	(17)	(19)	(17)

Table 5. Positive ion chemical ionization mass spectra of pyrazolecarbaldehydes **IVa**–**IVe** (reactant gas methane)

Ion	*m*/*z* (I_{rel}, %)				
	IVa	**IVb**	**IVc**	**IVd**	**IVe**
$M^{+\cdot}$	138 (6)	166 (5)	166 (6)	164 (10)	214 (15)
$[M + H]^+$	139 (100)	167 (100)	167 (100)	165 (100)	215 (100)
$[M + C_2H_5]^+$	167 (15)	195 (13)	195 (17)	193 (16)	243 (12)
$[M + C_3H_5]^+$	179 (4)	207 (4)	207 (6)	205 (5)	255 (4)
$[M - CHO]^+$	111 (3)	125 (3)	125 (5)	137 (4)	–

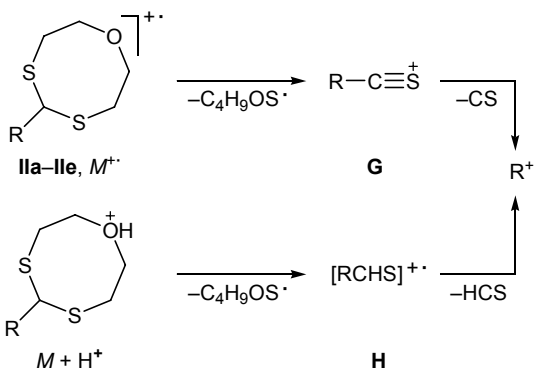
tion are similar. In both cases, the molecular ions of bis(2-hydroxyethyl) dithioacetals **I** are unstable, and they rapidly decompose to give the corresponding 1,3-oxathiolane **III** radical cation. There exists strong analogy between thermal decomposition of compounds **Ia**–**Ie** and **IIIa**–**IIIe** and fragmentation of their molecular ions under mass spectrometric analysis.

Pyrazolecarbaldehydes **IVa**–**IVe** displayed in the electron impact mass spectra a strong peak from the molecular ion (Table 1), which is typical of compounds containing an aromatic ring [9]. The main fragmentation pathway is determined by the presence of a heteroaromatic ring and is related to cleavage of C–C and C–N bonds with formation of $[M - Me]^+$ and $[M - X]^+$ ions. As might be expected, compound **IVd** decomposes mainly following a path typical of alkylbenzenes [9], and the base peak in the spectrum is that corresponding to $[C_7H_7]^+$ (*m*/*z* 91).

Pyrazolecarbaldehydes **IVa**–**IVe** readily undergo protonation in the gas phase. In their chemical ionization mass spectra (reactant gas methane) peaks of protonated molecular ions have the maximal intensity (Table 5). The PICI mass spectra of **IVa**–**IVd** contained the only fragment ion peak $[M - CHO]^+$; no such peak was observed in the spectrum of **IVe**. The mass spectra (EI) of **IVa**–**IVe** lacked $[M - CHO]^+$ ion peak. In addition, aldehydes **IVa**–**IVe** displayed in the PICI spectra peaks from $[M + H]^+$ ions (100%) and fairly intense peaks from cluster ions $[M + Alk]^+$. Thus substituents in the heteroring of aldehydes **IVa**–**IVe** inhibit fragmentation processes typical of alicyclic aldehydes.

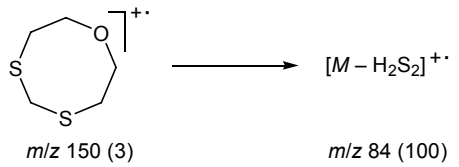
Unlike bis(2-hydroxyethyl) dithioacetals **Ia**–**Ie**, the electron impact mass spectra of pyrazolyl-substituted oxadithiocanes **IIa**–**IIe** contained weak molecular ion peaks (I_{rel} 3–10%, Table 1) and $[M + H]^+$ peaks (I_{rel} 7–

Scheme 7.



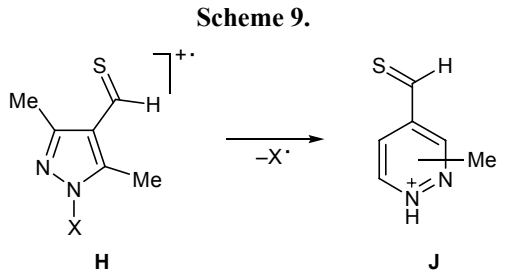
21%, Table 1). The latter are likely to appear due to the presence of traces of water in the ion source. The main fragmentation pathway of $[M]^{+\cdot}$ and $[M + H]^+$ is cleavage of the eight-membered heteroring with elimination of $C_4H_9OS^{\cdot}$ and formation of ions **G** and **H** (Scheme 7). This pattern is typical of 1,3-diselenanes of the thiophene series [10] but is different from the decomposition of 1,4,6-oxadithiocane which mainly loses H_2S_2 species (Scheme 8) [11].

Scheme 8.



It is known that elimination of $HS^{\cdot}$ and $HS_2^{\cdot}$ radicals is characteristic of fragmentation of all 2-aryl-1,3-dithianes [8]. The presence of a heteroaromatic ring in molecules **IIa**–**IIe** completely suppresses these processes, as well as elimination of H_2S_2; however, characteristic is the second series of ions arising from expulsion of the X substituent from the pyrazole ring in ion **H** (Scheme 9, Table 1)

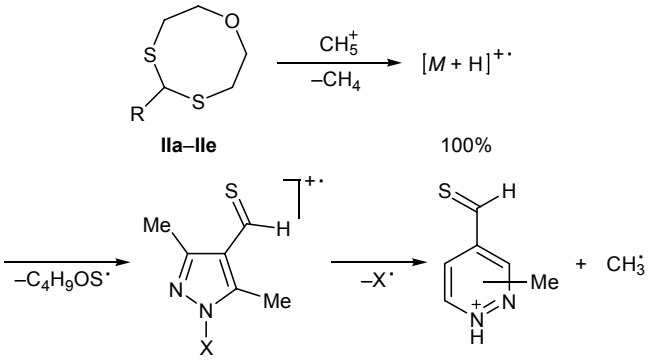
Scheme 9.



Analogous channels of decomposition of the molecular ions of 5-pyrazolyl-substituted 1,4,6-oxadithiocanes **IIa**–**IIe** were also observed upon chemical ionization using methane as reactant gas. Unlike chemical ionization mass spectra of bis(2-hydroxyethyl) dithioacetals **Ia**–**Ie**, the base peak in the spectra of compounds **IIa**–**IIe** was that corresponding to the protonated molecular ion. The latter then decomposes via elimination of $C_4H_9OS^{\cdot}$ radical with formation of odd-electron pyrazolecarbothialdehyde ion, which is quite untypical of chemical ionization. The subsequent fragmentation of pyrazolecarbothialdehyde ion follows general relations found for five-membered heteroaromatic structures [9] (Scheme 10).

In addition, the PICI spectra of all oxadithiocanes **IIa**–**IIe** contained $[M + C_2H_5]^+$ and $[M + C_3H_5]^+$ ion peaks formed as a result of electrophilic addition and peaks of ions arising from elimination of C_2H_4S molecule from the above ions (Table 6).

Scheme 10.



We can conclude that a combination of chemical ionization and electron impact mass spectra ensures more reliable determination of molecular weight and structure of compounds under study and increases the validity of their identification.

EXPERIMENTAL

Pyrazolecarbaldehyde bis(2-hydroxyethyl) dithioacetals **Ia**–**Ie** were obtained by dehydrochlorination with aqueous ammonia of the corresponding dithioacetal salts synthesized from pyrazolecarbaldehydes and 2-sulfanylethanol at a ratio of 1:2 [12]. Pyrazolyl-1,4,6-oxadithiocanes **IIa**–**IIe** were synthesized by reaction of aldehydes **IVa**–**IVe** with 2,2′-oxydiethanethiol at room temperature according to the procedure described in [12]. 2-Pyrazolyl-1,3-oxathiolanes **IIIa**–**IIIe** were isolated by column chromatography (silica gel, 0.060–0.2 mm; diethyl ether–methanol, 25:1) from the reaction mixtures obtained by reaction of pyrazolecarbaldehydes with an equimolar amount of 2-sulfanylethanol in the presence of Me_3SiCl. Aldehydes **IVa**–**IVe** were synthesized by Vilsmeier–Haack formylation [13] of the corresponding 1,3,5-trisubstituted pyrazoles which were prepared in turn by alkylation of 3,5-dimethyl-1*H*-pyrazole with alkyl halides, allyl bromide, and benzyl chloride under the conditions reported for alkylation of indoles [14].

The electron impact mass spectra were recorded on a Shimadzu QP-5050A mass spectrometer (quadrupole mass analyzer, a.m.u. range 34–650 D). Samples were introduced using a DI-50 direct inlet probe. The ion source and direct inlet probe temperatures were selected to ensure high-quality mass spectrum and avoid thermal decomposition of the substrate. Chromato-

Table 6. Positive ion chemical ionization mass spectra of 5-pyrazolyl-1,4,6-oxadithiocanes **IIa**–**IIe** (reactant gas methane)

Ion	*m*/*z* (I_{rel}, %)				
	IIa	**IIb**	**IIc**	**IId**	**IIe**
$[M + H]^+$	259 (100)	287 (100)	287 (100)	285 (100)	335 (100)
$[M + C_2H_5]^+$	287 (24)	315 (21)	315 (20)	313 (20)	363 (20)
$[M + C_3H_5]^+$	299 (7)	327 (6)	327 (7)	325 (8)	375 (8)
$[(M + C_2H_5) - C_2H_4S]^+$	227 (5)	255 (4)	255 (5)	253 (1)	303 (2)
$[(M + H) - C_2H_4S]^{+\cdot}$	199 (3)	227 (1)	227 (1)	225 (1)	275 (5)
$[(M + H) - C_4H_9OS]^{+\cdot}$	154 (15)	182 (22)	182 (20)	180 (15)	230 (20)
$[C_5H_9OS_2]^{+\cdot}$, *m*/*z* 149	(–)	(12)	(10)	(15)	(8)
$[(M + H) - C_4H_9OS - Me]^+$	139 (4)	167 (15)	167 (13)	165 (7)	215 (7)

graphic separation was performed using an SPB-5 capillary column (60 m × 0.25 mm × 0.25 μm), carrier gas helium, flow rate 0.7 ml/min, inlet pressure 280 kPa, split ratio 1:2; injector temperature 250°C, ion source temperature 200°C, oven temperature programming from 60 to 250°C at a rate of 10 deg/min.

The chemical ionization mass spectra (positive ion detection) were obtained on an Agilent 5975C instrument using methane as reactant gas. Samples were introduced through an Agilent 6890N chromatograph (HP-5MS capillary column, 30 m × 0.25 mm × 0.25 μm; carrier gas helium, constant flow rate).

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