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Mass Spectra of New Heterocycles: X.* Fragmentation of the Molecular Ions of 1-Alkyl(cycloalkyl, aryl)-3-alkoxy(aryl)-2-methylsulfanyl-1*H*-pyrroles

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Abstract—The mass spectra of previously unknown 1-alkyl(cycloalkyl, aryl)-3-alkoxy(aryl)-2-methylsulfanyl-1*H*-pyrroles were studied. Fragmentation of all 3-alkoxy-substituted pyrroles under electron impact (70 eV) follow both ether and sulfide decomposition paths; In particular, 1-R-substituted 3-methoxy-2-methylsulfanyl-1*H*-pyrroles (R = Me, Et, *i*-Pr, *s*-Bu, *cyclo*-C_5H_9, *cyclo*-C_6H_{11}, Ph) lose methyl radical group from both methoxy and methylsulfanyl groups. The mass spectra of 1-*sec*-butyl- and 1-cycloalkylpyrroles also contained a strong peak (10–49%) from odd-electron $[M - C_nH_{2n}]^{+\cdot}$ ion formed via cleavage of the N–R bond with synchronous hydrogen transfer. Cleavage of the O–Alk bond in the fragmentation of 3-alkoxy-1-isopropyl-2-methylsulfanyl-1*H*-pyrroles (Alk = Et, *i*-Pr, *t*-Bu) was accompanied by rearrangement process leading to the corresponding alkene and odd-electron 1-isopropyl-2-methylsulfanyl-1*H*-pyrrol-3-ol ion. The main fragmentation path of 1-alkyl-2-methylsulfanyl-3-phenyl-1*H*-pyrroles (Alk = Me, *i*-Pr) under electron impact involves dissociation of the S–Me bond with formation of rearrangement 1*H*-[1]benzothieno[2,3-*b*]pyrrol-8-ium ion.

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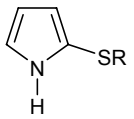
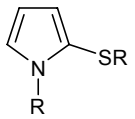
The importance of pyrroles and pyrrole-containing structures in biology and various practical applications is difficult to overestimate. Pyrrole ring constitutes a structural unit of such vitally important natural compounds as chlorophyll, hemoglobin, vitamin B_{12}, prodigiosins, bile pigments, etc., pharmaceutical substances, and useful intermediate products in synthetic organic chemistry, materials science, nonlinear optics, and supramolecular chemistry [2]. It was proved that introduction of heteroatoms and heteroatom-containing substituents into pyrrole ring could radically change physical, chemical, and biological properties of pyrrole compounds and materials based thereon [3]. Alkylsulfanyl-substituted pyrroles are especially promising for the design of biologically active compounds and optoelectronic materials [3, 4]. Therefore, synthesis of alkylsulfanyl-substituted pyrrole structures and detailed study on their properties, including their behavior under electron impact, seem to be important.

Mass spectrometric fragmentation of pyrroles was the subject of a few publications [5, 6]; decomposition pathways of only pyrrole itself and its alkyl and carbonyl derivatives were studied in sufficient detail [6]. Mass spectra of pyrroles with heteroatom-containing substituents, e.g., alkoxy and alkylsulfanyl groups, were not reported prior to our studies [1, 7–9]. We were the first to record the mass spectra of two series of alkylsulfanyl-substituted pyrroles, 2-[alkyl(alkenyl, alkynyl)sulfanyl]-1*H*-pyrroles **I** [7] and 1-alkyl-2-alkylsulfanyl-1*H*-pyrroles **II** [8] and reveal general relations holding in their decomposition under electron impact.



Ia–If



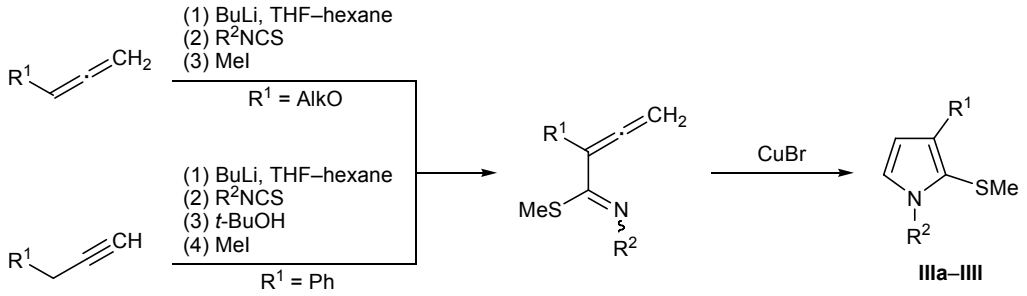
IIa–IId

R = Me (**a**), Et (**b**), Pr (**c**), Bu (**d**), $H_2C{=}CHCH_2$ (**e**), $HC{\equiv}CCH_2$ (**f**).

The nature of substituent R in 1,2-disubstituted pyrroles **II** affects the fragmentation pattern of their molecular ions to a much stronger extent than does the

* For communication IX, see [1].

Scheme 1.



R^1 = OMe, R^2 = Me (**a**), Et (**b**), *i*-Pr (**c**), *s*-Bu (**d**), *cyclo*-C_5H_9 (**e**), *cyclo*-C_6H_{11} (**f**), Ph (**g**); R^2 = *i*-Pr, R^1 = OEt (**h**), OPr-*i* (**i**), OBu-*t* (**j**); R^1 = Ph, R^2 = Me (**k**), *i*-Pr (**l**).

substituent in 2-alkylsulfanyl-1*H*-pyrroles **Ia**–**Id**. The reason is that the first step in the decomposition of the latter is elimination of the alkyl substituent, which gives rise to common 1,3-thiazin-1-ium ion with *m*/*z* 98. Further decomposition of that ion follows the same scheme for all compounds. Analogous process with compounds **II** leads to ions having different substituents on the nitrogen atom, so that their further decomposition paths are also different. Fragmentation patterns of the molecular ions of 2-allylsulfanyl- and 2-(prop-2-yn-1-ylsulfanyl)-1*H*-pyrroles **Ie** and **If** involve mainly isomeric bicyclic structures [7], whereas common decomposition pathways of pyrroles **IIb**–**IId** are elimination of the R radical from the alkylsulfanyl group and elimination of alkene molecule [8].

The present work continues our systematic studies on the mass spectra of new heterocyclic compounds [1, 7–10] obtained from isothiocyanates and allene- and acetylene-based carbanions [11]. We were the first to study the behavior of previously unknown 1-substituted 3-alkoxy- and 3-phenyl-2-methylsulfanyl-1*H*-pyrroles **IIIa**–**IIIl** under electron impact (70 eV). Compounds **IIIa**–**IIIl** were synthesized according to Scheme 1 [12]. Very recently we reported [9] on the mass spectrum of only one representative of this series, 1-isopropyl-3-methoxy-2-methylsulfanyl-1*H*-pyrrole (**IIIc**), in comparison with its structural isomers, 5-methoxy-2,2-dimethyl-6-methylsulfanyl-2,3-dihydropyridine and 3-methoxy-7-methyl-2-methylsulfanyl-4,5-dihydro-3*H*-azepine. Characteristic ions ensuring reliable identification of each isomer in reactions mixture were found.

Unlike pyrrole and its alkyl derivatives that are moderately stable to ionization under electron impact [6], almost all the examined pyrroles **IIIa**–**IIIi**, **IIIk**, and **IIIl** gave rise to stable molecular ions (I_{rel} 64–100%). Only in the mass spectrum of 3-*tert*-butoxy-1-isopropyl-2-methylsulfanyl-1*H*-pyrrole (**IIIj**), the relative intensity of the molecular ion peak did not exceed 12%. The complete mass spectra of pyrroles **IIIa**–**IIIl** are given in Table 1.

Analysis of the mass spectra showed that the molecular ions of 3-alkoxy-substituted 2-methylsulfanyl-1*H*-pyrroles **IIIa**–**IIIj** decompose along two concurrent paths, ether and sulfide (channels *1* and *2*, respectively; Schemes 2–7). The main fragmentation path of the molecular ion of 3-methoxy derivatives **IIIa**–**IIIf** involves elimination of methyl radical from either methoxy (ion **A**) or methylsulfanyl group (ion **A′**). Further decomposition of $[M - Me]^+$ can also take two pathways due to different fragmentation patterns of ions **A** and **A′** (Table 2; Schemes 2, 3). In particular, the fragmentation of **IIIa** involves successive elimination of neutral CO species and SH radical from ion **A** with formation of odd-electron ion with *m*/*z* 81 (**D**) which may be assigned 1-methylpyrrole structure (Scheme 2, channel *1*). The same ion is formed in the decomposition of ion **A′** as a result of successive elimination of CS molecule (ion **C**) and OH radical (Scheme 2, channel *2*). The assumed structure of ion **D** is confirmed by the presence in the mass spectrum of a series of ions typical of decomposition of 1-methylpyrrole [13], *m*/*z* (I_{rel}, %): 80 (9) $[M - H]^+$, 57 (15) $[M - C_2H_2]^{+\cdot}$, 54 (9) $[M - HCN]^{+\cdot}$, 53 (14) $[M - H - HCN]^+$, 42 (72) $[C_2H_4N]^+$.

Scheme 3 shows the main fragmentation pathways of 3-methoxypyrroles **IIIb**–**IIIf** in which the aliphatic substituent on the nitrogen atom is different than methyl group ($R^2 \neq Me$). Unlike pyrrole **IIIa**, fragmentation of ions **A** and **A′** derived from compounds **IIIb**–**IIIf** begins with expulsion of alkene molecule from the R^2 substituent, leading to $[\mathbf{A}\ (\mathbf{A'}) - C_nH_{2n}]^+$ ion with *m*/*z* 128 (**E** or/and **E′**). The abundance of the latter sharply increases in going from pyrrole **IIIb** (R^2 = Et;

Table 1. Complete mass spectra[a] of 1-alkyl(cycloalkyl, aryl)-3-alkoxy(aryl)-2-methylsulfanyl)pyrroles **IIIa**–**IIIl** (electron impact, 70 eV)

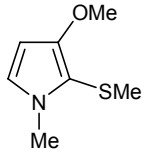
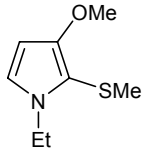
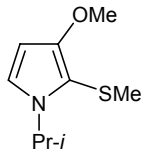
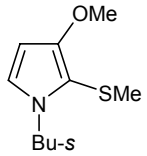
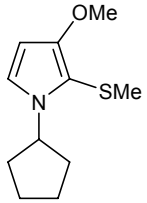
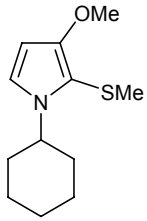
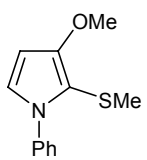
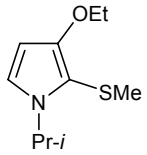
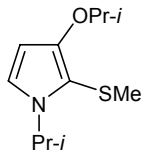
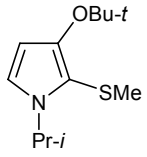
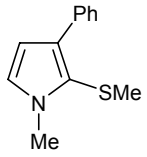
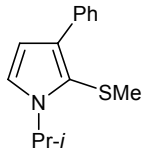
Compound no.	Formula	*m*/*z* (I_{rel}, %)
IIIa		157 (100) $[M]^{+\cdot}$, 158 (13) $[M + 1]^{+\cdot}$, 159 (5) $[M + 2]^{+\cdot}$, 144 (5), 143 (10), 142 (62) $[M - Me]^+$, 127 (4), 126 (3), 124 (3), 115 (3), 114 (13), 113 (3), 112 (6), 110 (12), 109 (12), 101 (3), 100 (3), 98 (20), 97 (3), 96 (5), 94 (3), 88 (5), 86 (4), 85 (4), 84 (7), 83 (4), 82 (14), 81 (52), 80 (9), 75 (3), 73 (15), 72 (8), 71 (5), 70 (10), 69 (9), 68 (7), 67 (7), 66 (6), 59 (6), 58 (14), 57 (15), 56 (7), 55 (16), 54 (9), 53 (14), 52 (7), 51 (3), 49 (8), 48 (10), 47 (17), 46 (6), 45 (27), 44 (8), 43 (7), 42 (72), 41 (26) $[C_2H_3N]^{+\cdot}$, 40 (8), 39 (18) $[C_3H_3]^+$, 38 (4), 37 (3)
IIIb		171 (77) $[M]^{+\cdot}$, 172 (13) $[M + 1]^{+\cdot}$, 173 (8) $[M + 2]^{+\cdot}$, 158 (5), 157 (9), 156 (100) $[M - Me]^+$, 143 (<1) $[M - C_2H_4]^+$, 141 (11), 140 (4), 128 (32) $[M - Me - C_2H_4]^+$, 127 (4), 124 (9), 123 (9), 112 (21), 110 (4), 108 (8), 101 (4), 100 (9), 99 (3), 98 (3), 97 (3), 96 (15), 95 (35), 94 (5), 86 (4), 85 (6), 84 (16), 83 (4), 82 (7), 81 (3), 80 (20), 74 (5), 73 (8), 72 (4), 71 (4), 70 (7), 69 (10), 68 (8), 67 (16) $[C_4H_4N]^{+\cdot}$, 66 (3), 59 (6), 56 (11), 55 (6), 54 (11), 53 (14), 52 (11), 47 (4), 46 (3), 45 (14), 44 (4), 43 (4), 42 (8), 41 (15) $[C_2H_3N]^{+\cdot}$, 40 (4), 39 (11) $[C_3H_3]^+$, 38 (3)
IIIc		185 (100) $[M]^{+\cdot}$, 186 (11) $[M + 1]^{+\cdot}$, 187 (6) $[M + 2]^{+\cdot}$, 172 (3), 171 (4), 170 (68) $[M - Me]^+$, 155 (4), 143 (3) $[M - C_2H_4]^+$, 142 (5), 138 (3), 130 (4), 129 (5), 128 (80) $[M - Me - C_3H_6]^+$, 126 (3), 112 (10), 110 (3), 101 (3), 100 (27), 99 (3), 98 (4), 97 (4), 96 (14), 95 (3), 94 (4), 86 (4), 85 (5), 84 (26), 83 (3), 82 (4), 80 (6), 77 (3), 74 (3), 73 (5), 71 (3), 70 (5), 69 (7), 68 (6), 67(27) $[C_4H_4N]^{+\cdot}$, 66 (3), 59 (4), 58 (4), 57 (4), 56 (4), 55 (5), 54 (8), 53 (11), 52 (8), 47 (3), 45 (9), 43 (21), 42 (8), 41 (32) $[C_2H_3N]^{+\cdot}$, 40 (4), 39 (15) $[C_3H_3]^+$
IIId		199 (84) $[M]^{+\cdot}$, 200 (10) $[M + 1]^{+\cdot}$, 201 (5) $[M + 2]^{+\cdot}$, 185 (5), 184 (50) $[M - Me]^+$, 170 (4), 156 (3), 155 (3), 152 (4), 143 (10) $[M - C_2H_4]^+$, 142 (3), 130 (5), 129 (6), 128 (100) $[M - Me - C_4H_8]^+$, 124 (4), 112 (5), 110 (3), 100 (18), 98 (4), 97 (3), 96 (10), 86 (3), 85 (4), 84 (19), 83 (3), 82 (4), 80 (5), 78 (3), 73 (4), 70 (4), 69 (4), 68 (5), 67 (25) $[C_4H_4N]^{+\cdot}$, 59 (3), 58 (3), 57 (11), 56 (3), 55 (8), 54 (6), 53 (8), 52 (5), 45 (7), 43 (3), 42 (6), 41 (30) $[C_2H_3N]^{+\cdot}$, 40 (2), 39 (13) $[C_3H_3]^+$
IIIe		211 (86) $[M]^{+\cdot}$, 212 (13) $[M + 1]^{+\cdot}$, 213 (5) $[M + 2]^{+\cdot}$, 198 (4), 197 (8), 196 (69) $[M - Me]^+$, 181 (4), 179 (4), 178 (3), 164 (5), 163 (3), 146 (4), 144 (4), 143 (15), 142 (3), 138 (4), 136 (3), 132 (5), 130 (10), 129 (8), 128 (100) $[M - Me - C_5H_8]^+$, 127 (3), 120 (3), 112 (6), 110 (3), 101 (3), 100 (21), 99 (4), 98 (7), 97 (7), 96 (8), 95 (4), 94 (3), 91 (3), 86 (3), 85 (6), 84 (19), 83 (4), 82 (6), 81 (3), 80 (6), 79 (5), 74 (4), 73 (5), 71 (8), 70 (6), 69 (15), 68 (9), 67 (36) $[C_4H_4N]^{+\cdot}$, 66 (4), 65 (7), 59 (4), 58 (4), 57 (10), 56 (6), 55 (10), 54 (8), 53 (10), 52 (7), 51 (4), 47 (4), 45 (10), 44 (3), 43 (10), 42 (7), 41 (62) $[C_2H_3N]^{+\cdot}$, 40 (6), 39 (24) $[C_3H_3]^+$
IIIf		225 (81) $[M]^{+\cdot}$, 226 (15) $[M + 1]^{+\cdot}$, 227 (5) $[M + 2]^{+\cdot}$, 212 (4), 211 (9), 210 (67) $[M - Me]^+$, 179 (3), 178 (11), 145 (3), 144 (5), 143 (49), 142 (6), 130 (9), 129 (13), 128 (100) $[M - Me - C_6H_{10}]^+$, 126 (3), 112 (8), 110 (4), 100 (20), 99 (3), 98 (10), 97 (7), 96 (9), 94 (3), 86 (3), 85 (4), 84 (19), 83 (13), 82 (8), 81(11), 80 (7), 79 (7), 78 (3), 77 (4), 74 (3), 73 (5), 71 (3), 70 (6), 69 (6), 68 (7), 67 (28) $[C_4H_4N]^{+\cdot}$, 66 (3), 65 (4), 59 (4), 58 (3), 57 (3), 56 (7), 55 (65), 54 (13), 53 (20), 52 (8), 51 (4), 47 (4), 45 (10), 44 (4), 43 (7), 42 (7), 41 (77) $[C_2H_3N]^{+\cdot}$, 40 (4), 39 (32)
IIIg		219 (100) $[M]^{+\cdot}$, 220 (3) $[M + 1]^{+\cdot}$, 221 (6) $[M + 2]^{+\cdot}$, 206 (6), 205 (10), 204 (72) $[M - Me]^+$, 190 (4), 189 (7), 188 (9), 186 (10), 176 (12), 173 (7), 172 (7), 171 (10), 170 (22), 162 (4), 161 (5), 160 (8), 151 (6), 143 (21), 135 (9), 129 (4), 117 (8), 111 (4), 104 (14), 91 (8), 77 (38) $[Ph]^+$, 69 (5), 58 (3), 51 (14), 44 (4), 39 (4) $[C_3H_3]^+$

Table 1. (Contd.)

Compound no.	Formula	*m*/*z* (I_{rel}, %)
IIIh		199 (100) $[M]^{+\cdot}$, 200 (15) $[M + 1]^{+\cdot}$, 201 (7) $[M + 2]^{+\cdot}$, 184 (11) $[M - Me]^+$, 182 (3), 172 (5), 171 (7) $[M - C_2H_4]^{+\cdot}$, 170 (85) $[M - Et]^+$, 167 (5), 156 (24) $[M - C_2H_4 - Me]^+$, 155 (4), 154 (3), 153 (4), 142 (11), 140 (4), 138 (4), 130 (5), 129 (8), 128 (88) $[M - Et - C_3H_6]^+$, 127 (3), 126 (3), 124 (6), 122 (4), 115 (4), 114 (43) $[M - C_2H_4 - Me - C_3H_6]^+$, 113 (4), 112 (28), 111 (4), 110 (6), 108 (3), 101 (5), 100 (18), 99 (3), 97 (7), 96 (13), 95 (4), 94 (9), 87 (3), 86 (13), 85 (7), 84 (29), 83 (6), 82 (11), 81 (7), 80 (13), 79 (4), 77 (3), 74 (6), 73 (7), 72 (5), 71 (6), 70 (8), 69 (17), 68 (8), 67 (14), 66 (3), 65 (4), 61 (3), 59 (11), 58 (7), 57 (12), 56 (7), 55 (20), 54 (11), 53 (20), 52 (12), 51 (5), 49 (9), 48 (3), 47 (6), 46 (3), 45 (15), 44 (22), 43 (56) [*i*-Pr]$^+$, 42 (20), 41 (64) $[C_2H_3N]^{+\cdot}$, 40 (11), 39 (26) $[C_3H_3]^+$
IIIi		213 (64) $[M]^{+\cdot}$, 214 (8) $[M + 1]^{+\cdot}$, 215 (3) $[M + 2]^{+\cdot}$, 198 (1) [*M* – Me]+, 172 (5), 171 (25) $[M - C_3H_6]^{+\cdot}$, 170 (51) [*M* – *i*-Pr]$^+$, 158 (5), 157 (9), 156 (100) $[M - C_3H_6 - Me]^+$, 130 (3), 129 (12), 128 (58) $[M - i\text{-Pr} - C_3H_6]^+$, 122 (3), 116 (3), 115 (5), 114 (76) $[M - C_3H_6 - Me - C_3H_6]^+$, 112 (20), 110 (4), 101 (3), 100 (17), 96 (12), 95 (3), 94 (5), 87 (3), 86 (13), 85 (5), 84 (22), 83 (5), 82 (10), 81 (3), 80 (14), 74 (5), 73 (8), 71 (3), 70 (6), 69 (6), 68 (8), 67 (13), 60 (3), 59 (8), 58 (5), 57 (5), 56 (4), 55 (9), 54 (13), 53 (15), 52 (14), 47 (5), 46 (3), 45 (15), 44 (7), 43 (92) [*i*-Pr]$^+$, 42 (25), 41 (96) $[C_2H_3N]^{+\cdot}$, 40 (9), 39 (39) $[C_3H_3]^+$
IIIj		227 (12) $[M]^{+\cdot}$, 228 (2) $[M + 1]^{+\cdot}$, 229 (1) $[M + 2]^{+\cdot}$, 212 (2) [*M* – Me]+, 173 (4), 172 (7), 171 (49) $[M - C_4H_8]^{+\cdot}$, 170 (8) [*M* – *t*-Bu]+, 158 (5), 157 (9), 156 (100) $[M - C_4H_8 - Me]^+$, 129 (9), 128 (11) $[M - t\text{-Bu} - C_3H_6]^+$, 116 (3), 115 (5), 114 (54) $[M - C_4H_8 - Me - C_3H_6]^+$, 112 (11), 100 (5), 96 (6), 94 (3), 86 (8), 85 (3), 84 (9), 83 (3), 82 (7), 80 (8), 74 (3), 73 (4), 70 (3), 69 (3), 68 (4), 67 (7), 59 (5), 58 (4), 57 (30), 56 (6), 55 (8), 54 (7), 53 (9), 52 (8), 47 (3), 45 (9), 44 (4), 43 (38) [i-Pr]+, 42 (15), 41 (83) $[C_2H_3N]^{+\cdot}$, 40 (8), 39 (30) $[C_3H_3]^+$
IIIk		203 (100) $[M]^{+\cdot}$, 204 (19) $[M + 1]^{+\cdot}$, 205 (7) $[M + 2]^{+\cdot}$, 190 (7), 189 (17), 188 (85) $[M - Me]^+$, 187 (13), 186 (7), 175 (3), 174 (7), 173 (47) $[M - Me - Me]^+$, 172 (15), 171 (6), 161 (10), 155 (7), 154 (4), 149 (3), 148 (6), 147 (52) $[M - Me - MeCN]^+$, 146 (7), 145 (6), 144 (3), 140 (4), 129 (4), 128 (14), 127 (5), 121 (3), 116 (3), 115 (20), 114 (4), 113 (4), 103 (8), 101 (37), 94 (41), 89 (11), 88 (5), 87 (4), 86 (12), 84 (12), 80 (4), 79 (5), 78 (4), 77 (17) [Ph]+, 76 (4), 75 (6), 74 (9), 71 (8), 69 (10), 65 (5), 64 (4), 63 (15), 62 (6), 54 (3), 52 (3), 51 (14), 50 (7), 45 (21), 42 (23), 41 (5) $[C_2H_3N]^{+\cdot}$, 40 (2), 39 (16) $[C_3H_3]^+$, 38 (3)
IIIl		231 (77) $[M]^{+\cdot}$, 232 (12) $[M + 1]^{+\cdot}$, 233 (5) $[M + 2]^{+\cdot}$, 218 (3), 217 (8), 216 (50) $[M - Me]^+$, 189 (5), 176 (5), 175 (13), 174 (100) $[M - Me - C_3H_6]^+$, 173 (14), 172 (4), 155 (5), 154 (5), 147 (22) $[M - Me - C_3H_6 - HCN]^+$, 146 (3), 128 (3), 116 (3), 115 (15), 103 (3), 102 (4), 89 (5), 86 (3), 77 (5) [Ph]+, 69 (3), 65 (3), 63 (5), 51 (4), 45 (5), 43 (10), 41 (14) $[C_2H_3N]^{+\cdot}$, 39 (8) $[C_3H_3]$+

[a] Ion peaks with a relative intensity lower than 3% are not given.

I_{rel} 32%) to pyrroles **IIIc**–**IIIe** having isopropyl (I_{rel} 80%), *sec*-butyl (I_{rel} 100%), cyclopentyl (I_{rel} 100%), and cyclohexyl (I_{rel} 100%) substituents on the nitrogen atom (Table 2, Scheme 3). Further decomposition of ions **E** and **E′** (*m*/*z* 128) is similar to that of ions **A** and **A′** (*m*/*z* 142) proposed for pyrrole **IIIa** (Scheme 2); it involves successive elimination of CO (**F**) and HS$^{\cdot}$ (Scheme 3, channel *1*) or CS (**G**) and HO$^{\cdot}$ (Scheme 3, channel *2*). In both cases, fairly abundant (I_{rel} 16–36%) odd-electron ion with *m*/*z* 67 (**H**) is formed, which is likely to have the structure of unsubstituted pyrrole. The mass spectra also contained ion peaks typical of fragmentation of pyrrole, *m*/*z* (I_{rel}, %): 41 (15–77) $[M - C_2H_2]^{+\cdot}$, 40 (2–6) $[M - HCN]^{+\cdot}$, 39 (11–32) $[M - CH_2N]^+$.

Apart from channels *1* and *2* corresponding to cleavage of the O–CH_3 and S–CH_3 bonds in the molecular ions (Scheme 3), 3-methoxypyrroles **IIIb**–**IIIf**

Table 2. Characteristic ions in the mass spectra of 1-alkyl(cycloalkyl)-3-methoxy-2-methylsulfanyl)-1*H*-pyrroles **IIIa**–**IIIf**

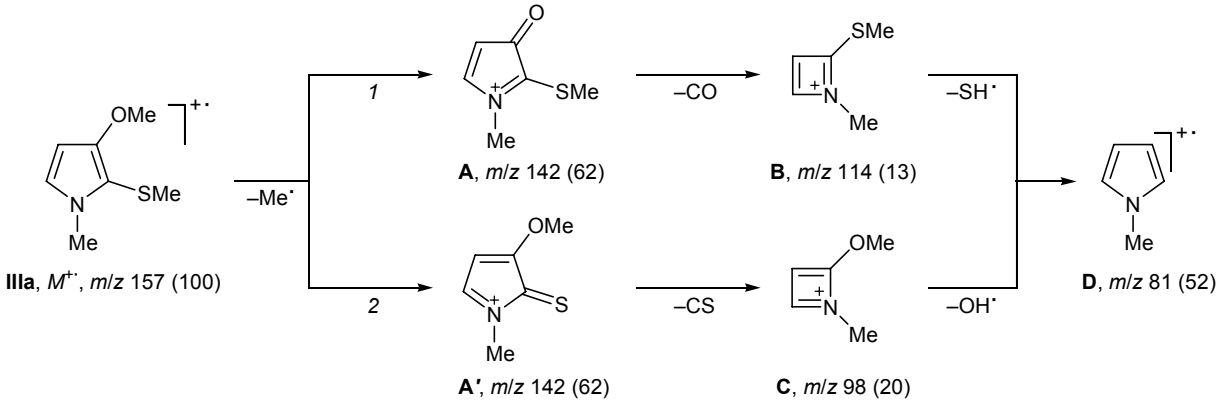
Ion		*m/z* (I_{rel}, %)					
		IIIa	**IIIb**	**IIIc**	**IIId**	**IIIe**	**IIIf**
	$[M]^{+\cdot}$	157 (100)	171 (77)	185 (100)	199 (84)	211 (86)	225 (81)
	$[M+1]^{+\cdot}$	158 (13)	172 (13)	186 (11)	200 (10)	212 (13)	226 (15)
	$[M+2]^{+\cdot}$	159 (5)	173 (8)	187 (6)	201 (5)	213 (5)	227 (5)
A, **A′**	$[M-Me]^+$	142 (62)	156 (100)	170 (68)	184 (50)	196 (69)	210 (67)
B	$[\mathbf{A}-CO]^+$	114 (13)	–	–	–	–	–
C	$[\mathbf{A}'-CS]^+$	98 (20)	–	–	–	–	–
D	$[\mathbf{B}-SH]^+$, $[\mathbf{B}-OH]^+$	81 (52)	–	–	–	–	–
E, **E′**	$[\mathbf{A}, \mathbf{A}'-C_nH_{2n}]^+$, *m/z* 128	–	(32)	(80)	(100)	(100)	(100)
F	$[\mathbf{E}-CO]^+$, *m/z* 100	–	(9)	(27)	(18)	(21)	(20)
G	$[\mathbf{E}'-CS]^+$, *m/z* 84	–	(16)	(26)	(19)	(19)	(19)
H	$[C_4H_5N]^{+\cdot}$, *m/z* 67	–	(16)	(27)	(25)	(36)	(28)

might be expected to give rise to one more decomposition pathway involving synchronous dissociation of the N–R^2 bond and hydrogen transfer with elimination of alkene molecule and formation of odd-electron ion with *m/z* 143 (**J**). This ion was assigned the structure of 3-methoxy-2-methylsulfanylpyrrole (Scheme 4, channel *3*). In fact, the mass spectra of 1-*sec*-butyl- 1-cyclopentyl-, and 1-cyclohexylpyrroles **IIId**–**IIIf** contained $[M - C_nH_{2n}]^{+\cdot}$ ion peak with relative intensities of 10, 15, and 49%, respectively. Radical cation **I** decomposes in a way similar to decomposition of the molecular ion of pyrrole **IIIa**, leading to ions with *m/z* 128 (**E**, **E′**), 100 (**F**), 84 (**G**), and 67 (**H**).

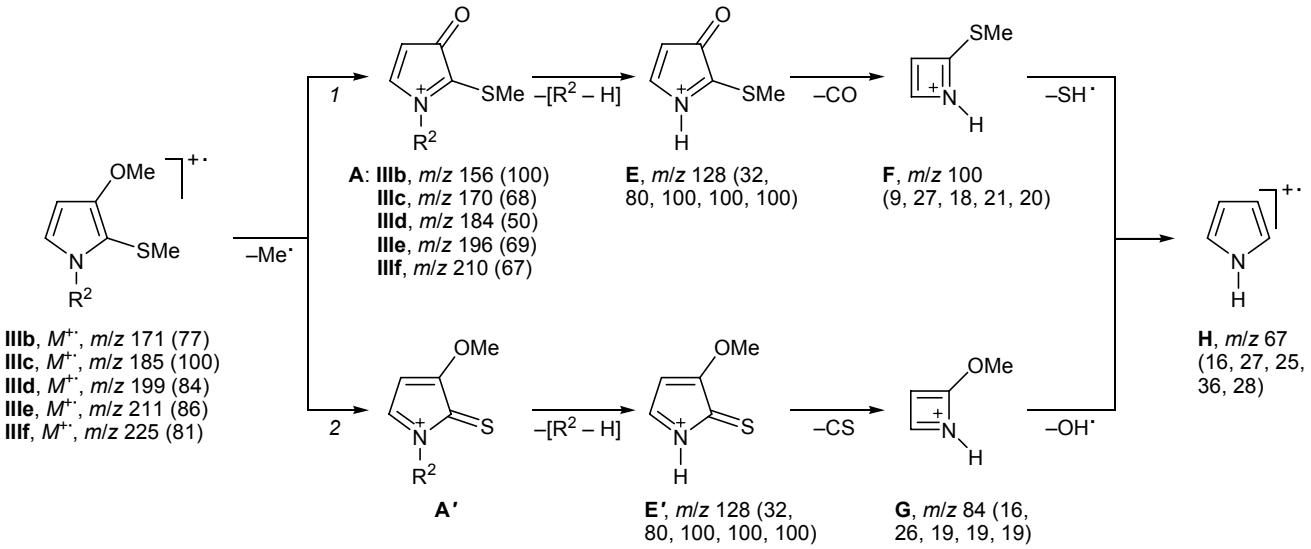
Insofar as the substituents on the oxygen (alkoxy group) and sulfur atom (alkylsulfanyl group) in pyrroles **IIIa**–**IIIf** are similar (Alk = Me), it is difficult to estimate the relative contributions of two possible channels to the formation of $[M - Me]^+$ ion (cleavage of the C–O bond with formation of ion **A** or of the C–S bond with formation of ion **A′**) on the basis of the available experimental data. Taking into account the intensity of peaks from secondary ions **B**, **C**, **F**, and **G** (Table 2), it may be presumed that the contributions to the total ion current of ions **A** and **A′** and those resulting from their further decomposition products are comparable, although the C–S bond in molecular ions is known to be considerably stronger (102 kcal/mol) than the C–O bond (74 kcal/mol) [14]. One should also keep in mind that fragmentation of ion **J** (Scheme 4, channel *3*) also contributes somewhat to the intensity of both **E**/**E′** and **F** and **G** ion peaks.

Replacement of the methyl group on the nitrogen atom (pyrrole **IIIa**) by phenyl (**IIIg**) does not change the fragmentation pattern to a significant extent. As in the mass spectrum of pyrrole **IIIa** (Scheme 2), the main peaks in spectrum of **IIIg** were those corresponding to $[M - Me]^+$ (**A**, **A′**), $[\mathbf{A} - CO]^+$ (**B**), $[\mathbf{A}' - CS]^+$ (**C**), and odd-electron **G** ion (*m/z* 143); the latter is

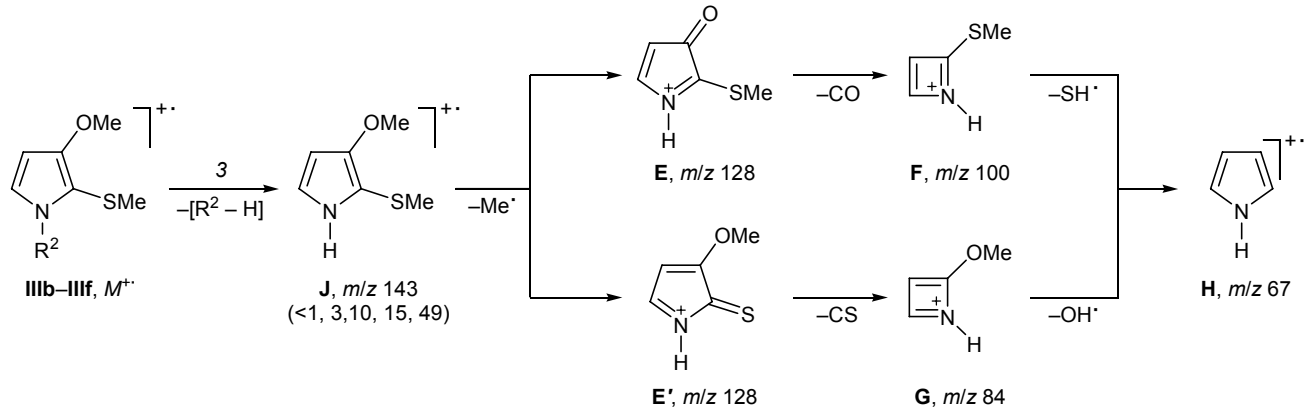
Scheme 2.



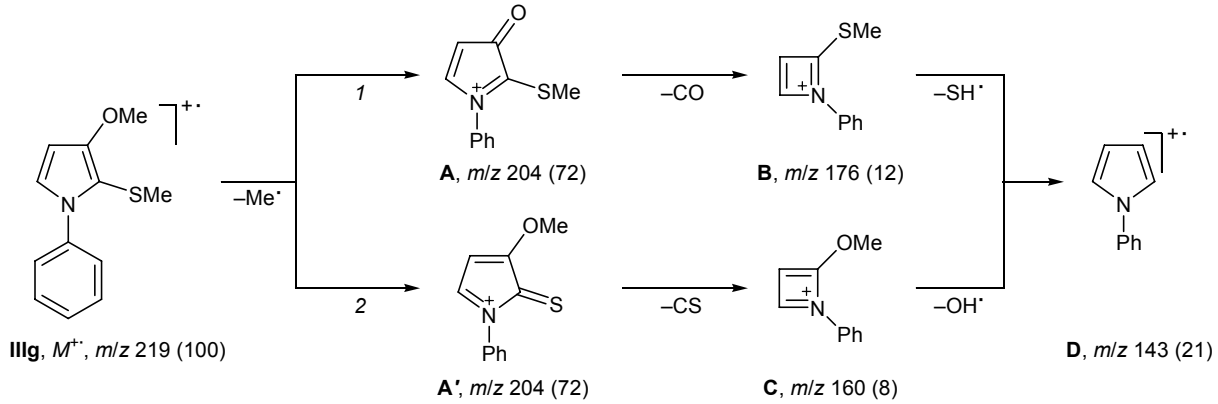
Scheme 3.



Scheme 4.

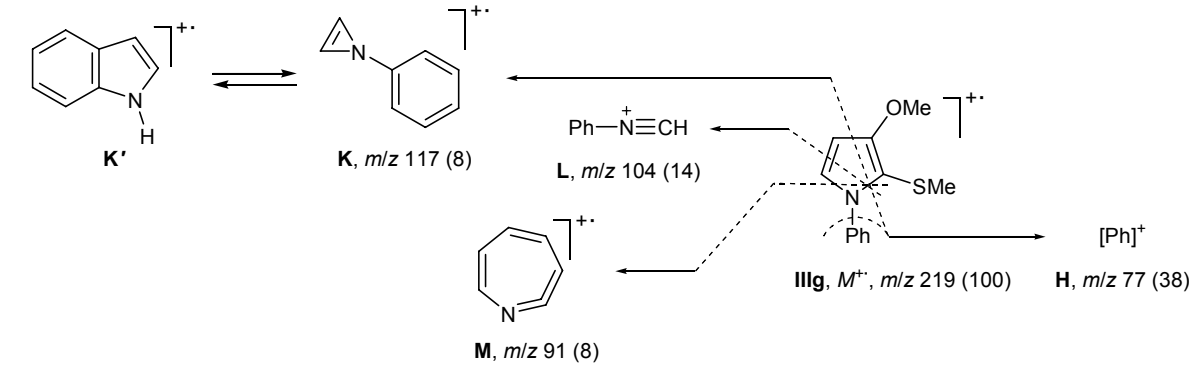


Scheme 5.

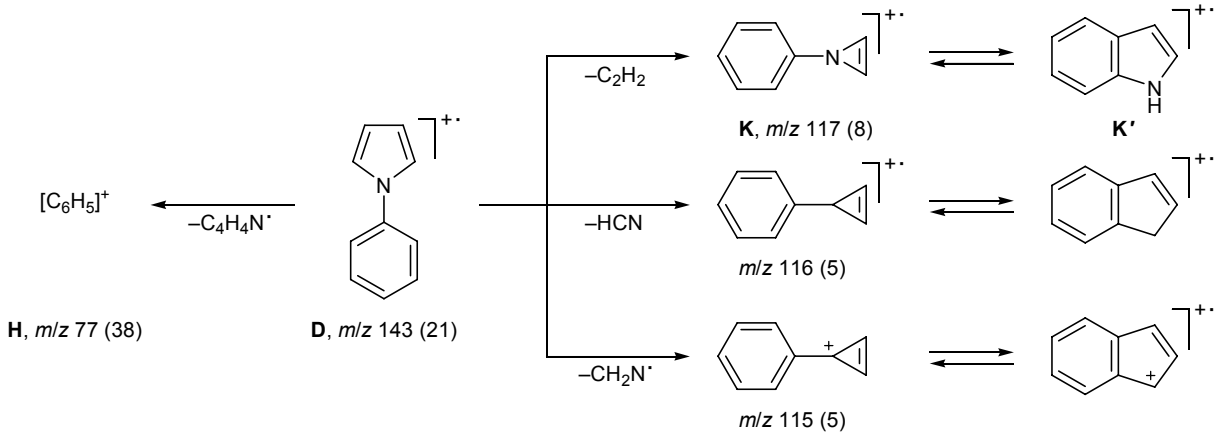


most likely to have the structure of 1-phenylpyrrole (Scheme 5). In addition, peaks belonging to three more series of ions were observed in the mass spectrum of **IIIg**. One of these series results from elimination of sulfur-containing species to produce fragment ions with m/z (I_{rel}, %): 186 (10) $[M - HS]^+$, 170 (22) $[\mathbf{A} - H_2S]^+$, 171 (10) $[\mathbf{A} - HS]^{+\cdot}$. The other series corresponds to decomposition of the pyrrole ring with charge localization on the phenyl-containing fragment (ions **K**–**N** in Scheme 6). The same ions (**K**–**N**) could

Scheme 6.



Scheme 7.



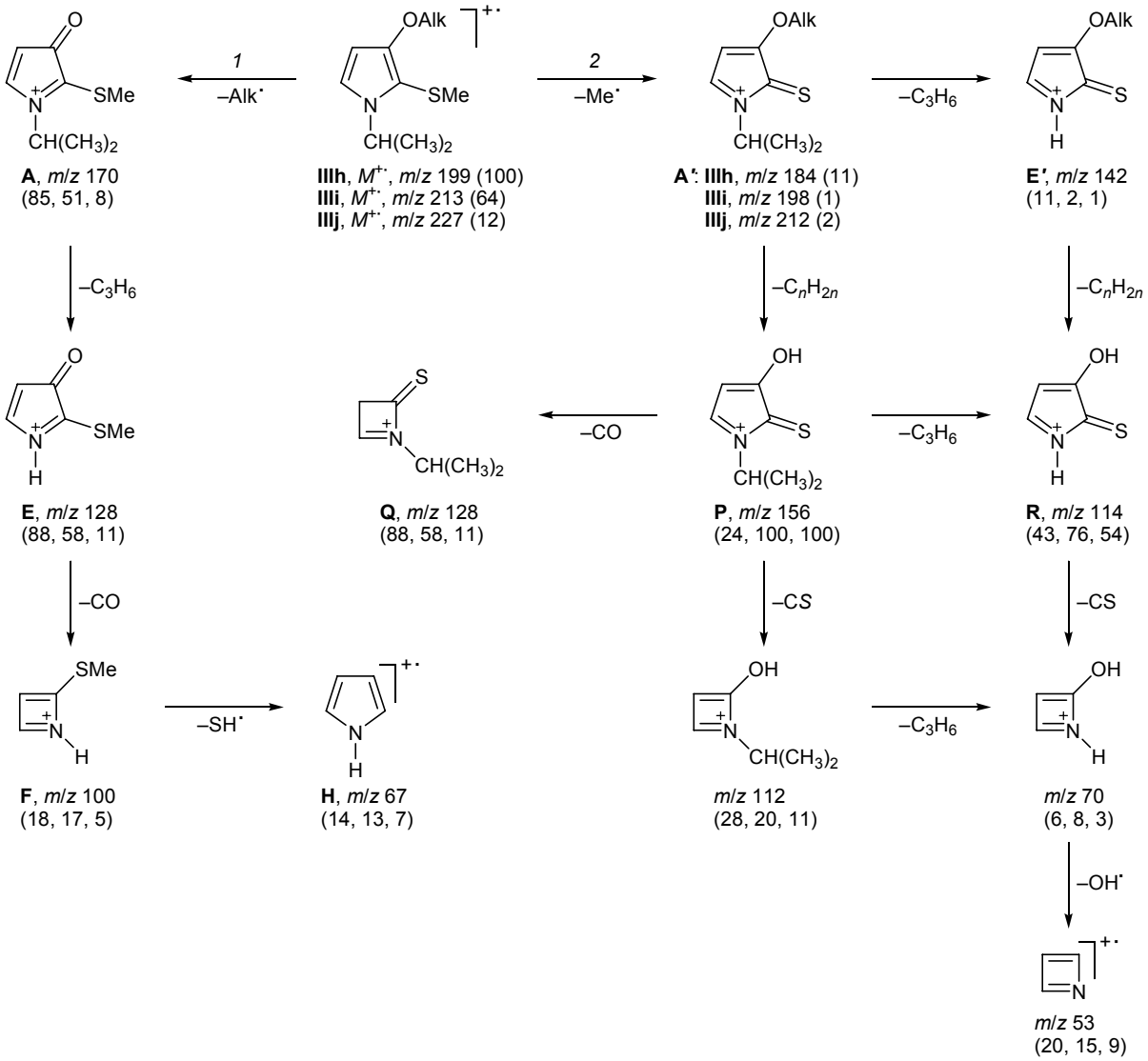
be formed via analogous fragmentation of odd-electron ion **D**. The third ion series (Scheme 7) is typical of decomposition of 1-phenylpyrrole (ion **D**) with loss of acetylene and hydrogen cyanide molecules or $CH_2N^{\cdot}$ and $C_4H_4N^{\cdot}$ radicals [6, 13].

Using 1-isopropyl-2-methylsulfanyl-1*H*-pyrroles **IIIc** and **IIIh**–**IIIj** as examples we examined the effect of stereoelectronic parameters of the 3-alkoxy substituent. Increase in length and size of the alkyl group (Me < Et < *i*-Pr < *t*-Bu) favors decomposition of the C–O bond, so that the intensity of the molecular ion peak sharply decreases. For example, the molecular ions of pyrroles **IIIc** and **IIIh** are the most abundant (I_{rel} 100%) in their mass spectra, while the relative intensities of the molecular ion peaks in the spectra of **IIIi** and **IIIj** are 64 and 12%, respectively (Table 1, Schemes 8, 9). Unlike 3-methoxy-2-methylsulfanyl-1*H*-pyrroles **IIIa**–**IIIg**, the substituents on the oxygen and sulfur atoms in compounds **IIIh**–**IIIj** are different, so that the relative contributions of the corresponding fragmentation channels of the molecular ions can be estimated, though fairly arbitrarily (Scheme 8).

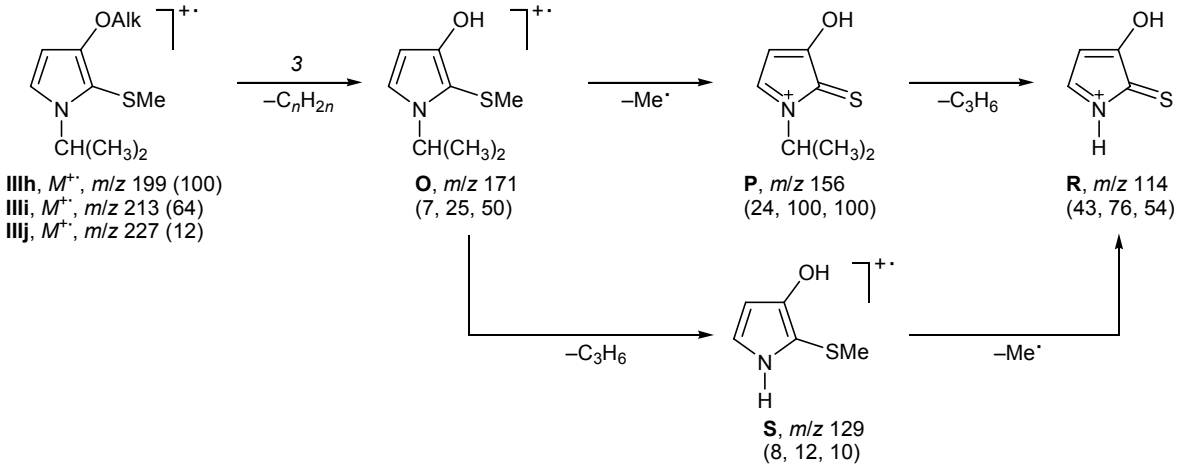
Comparison of the mass spectra of pyrroles **IIIh**–**IIIj** clearly shows that α-decomposition of the alkoxy group with formation of $[M - Alk]^+$ ion (**A**) and products of its subsequent fragmentation (ions **E**, **F**, and **H**; Scheme 8) predominates in the fragmentation of 3-ethoxy and 3-isopropoxy derivatives **IIIh** and **IIIi**. By contrast, the main fragmentation path of 3-*tert*-butoxypyrrole **IIIj** is rearrangement leading to $[M - C_nH_{2n}]^{+\cdot}$ ion with *m*/*z* 171 (**O**), (Table 1; Schemes 8, 9). Further decomposition of ion **O** suggests that it has the structure of 1-isopropyl-2-(methylsulfanyl)pyrrol-3-ol (Scheme 9) [1].

Judging by the intensity of ion peak **A′** (1–11%), the contribution of the sulfide path (channel *2*) to the total ion current in the mass spectra of pyrroles **IIIh**–**IIIj** seems to be relatively small, whereas the intensity of peaks belonging to fragment ion peaks **P** (*m*/*z* 156), **Q** (*m*/*z* 128) and **R** (*m*/*z* 114) formed via decomposition of ion **A′** is quite significant (24–100, 11–88, and 43–76%, respectively). Therefore, we must speak about low stability of $[M - Me]^+$ ion (**A′**) rather than about minor contribution of channel *2*. Ions with

Scheme 8.



Scheme 9.

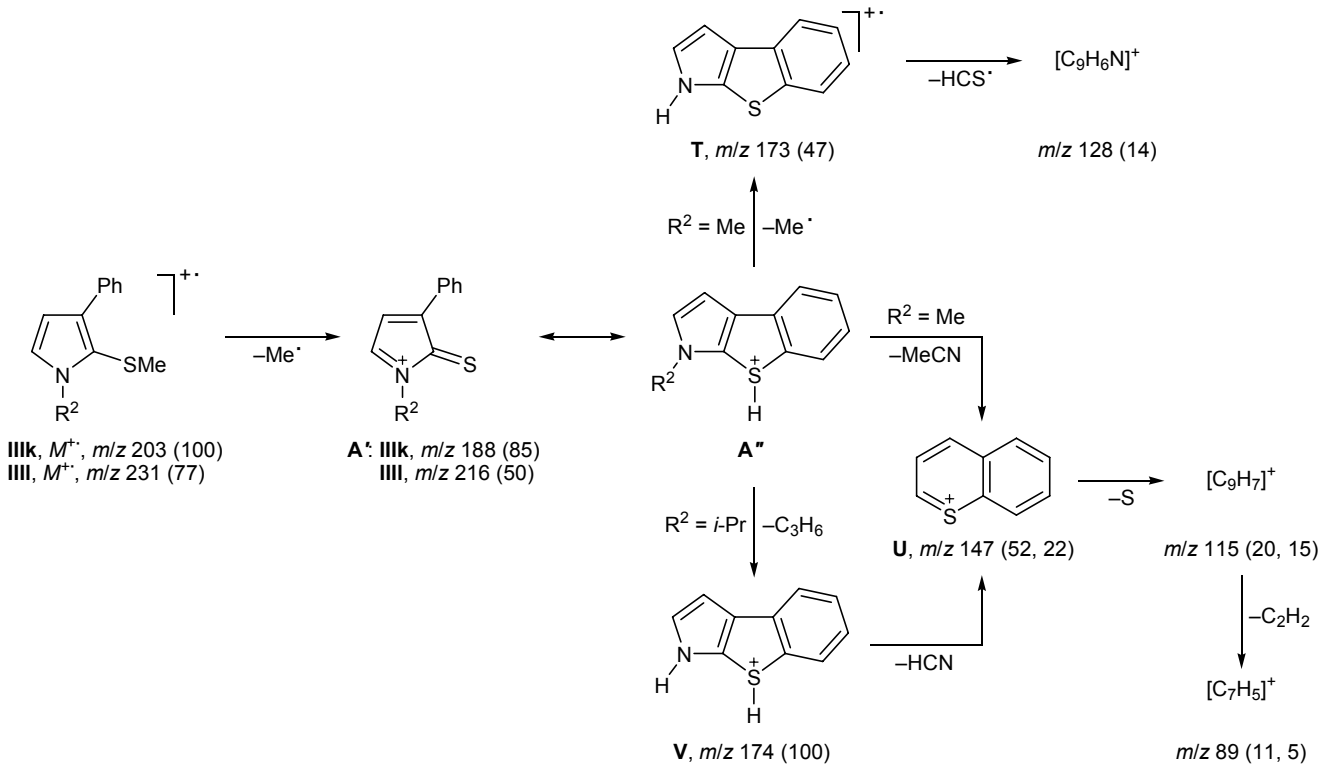


m/*z* 156 and 114 can also be formed according to channel *3*, i.e., as a result of fragmentation of ion **O** (Scheme 9), though this path is not determining, at least for pyrroles **IIIh** and **IIIi**. Decomposition of ion **A** could also give rise to ion **E** with *m*/*z* 128 (**D**) (Scheme 8, channel *1*).

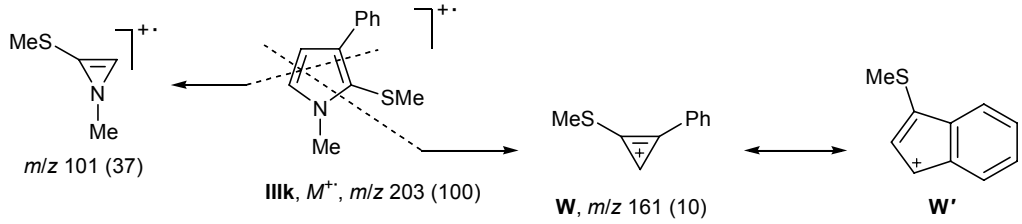
Thus it is obvious that the diversity of possible paths for formation of key fragment ions in the decomposition of 3-alkoxypyrroles under electron impact does not allow us to draw unambiguous conclusion on the relative contributions of the main fragmentation channels to the total ion current.

Unlike 1-phenylpyrrole **IIIg**, introduction of a phenyl group into position *3* of the pyrrole ring (instead of alkoxy group) makes the sulfide path the main process in the fragmentation of 1-methyl- and 1-isopropyl-2-methylsulfanyl-3-phenyl-1*H*-pyrroles **IIIk** and **IIIl**. This path involves initial formation of 3-phenyl-2-thioxo-2*H*-pyrrolium ion **A′** (Scheme 10, Table 1), which is likely to be stabilized via rearrangement into 1*H*-[1]benzothieno[2,3-*b*]pyrrol-8-ium **A″**. The subsequent decomposition pattern of the latter depends on the substituent on the nitrogen atom. Fragmentation of ions **A′** and **A″** derived from 1-methylpyrrole **IIIk** follows two main pathways: (1) expulsion of methyl radical with formation of odd-electron ion with *m*/*z* 173 (**T**) which is likely to have 1*H*-[1]benzothieno[2,3-*b*]pyrrole structure and (2) elimination of acetonitrile molecule with formation of ion **U** with *m*/*z* 147 (presumably with thiochromenium structure); the corresponding ion peaks are characterized by comparable intensities. The main fragmentation path of ions **A′** and **A″** generated from 1-isopropylpyrrole **IIIl** is rearrangement through elimination of cyclopropene molecule. Ion **V** thus formed, *m*/*z* 174, is the most

Scheme 10.



Scheme 11.



abundant in the spectrum (100%). Elimination of hydrogen cyanide molecule from ion **V** could also give rise to ion **U** (Scheme 10).

In addition, the mass spectrum of pyrrole **IIIk** contains ion peaks indicating decomposition of the pyrrole ring. Presumably, phenyl-containing fragment ion with *m*/*z* 161 has the structure of 1-methylsulfanyl-2-phenylcyclopropenium (**W**) or 3-(methylsulfanyl)-1*H*-indenium (**W′**) where the positive charge is stabilized by the benzene ring. Nitrogen-containing fragment with *m*/*z* 101 is likely to be a radical cation species (Scheme 11).

Comparison of the spectra of two pyrrole series, i.e., those containing similar substituents on the nitrogen atom (R^2 = Me, *i*-Pr) but different substituents in position *3* of the pyrrole ring (OMe, Ph) revealed unusual effect of all substituents on both stability of the molecular and/or fragment ions and selectivity of their fragmentation. Replacement of the 3-methoxy group in *N*-isopropylpyrrole **IIIc** by phenyl (**IIIl**) destabilizes the molecular and fragment ions, and the relative intensities of the $[M]^{+\cdot}$ and $[M - Me]^+$ ion peaks decrease, respectively, from 100 to 77% and from 68 to 50%. Analogous replacement in *N*-methylpyrrole **IIIa** exerts no effect (pyrrole **IIIk**) or the effect is the opposite. In both cases, the molecular ion peak $[M]^{+\cdot}$ is the base peak in the spectrum 100%, and $[M - Me]^+$ ion derived from **IIIk** (*m*/*z* 188, 85%) is even more stable than analogous ion (*m*/*z* 142, 62%) in the spectrum of **IIIa**. On the other hand, comparison of the spectra of 3-methoxypyrroles **IIIa** and **IIIc** with those of 3-phenylpyrroles **IIIk** and **IIIl** shows that the spectra of *N*-methyl derivatives **IIIa** and **IIIk** are richer and more complex than the spectra of *N*-isopropyl-substituted analogs **IIIc** and **IIIl**, though the reverse pattern could be expected taking into account the ability of long and/or branched alkyl chains to undergo various rearrangements and diversity of possible bond cleavage modes therein.

On the whole, fragmentation of the molecular ions of the examined pyrroles begins with decomposition of heteroatom-containing substituents on C^2 or C^3 with formation of oxygen- and sulfur-centered radical cations (from 3-alkoxypyrroles **IIIa**–**IIIg**) or only sulfur-centered radical cation species (from 3-phenylpyrroles **IIIk** and **IIIl**). The fragmentation pattern (simple dissociation of carbon–heteroatom bond or rearrangement process) is determined by stereoelectronic parameters of the alkyl group. The effect of substituent on the nitrogen atom is generally reflected in subsequent decomposition of the primary fragment ions. *sec*-Butyl, cycloalkyl, and phenyl substituents on the nitrogen atom (**IIId**–**IIIg**) give rise to additional fragmentation channels of the molecular ion.

EXPERIMENTAL

Compounds **IIIa**–**IIIl** were synthesized according to the procedures reported in [12]. The mass spectra (electron impact, 70 eV) were recorded on a Shimadzu GCMS-QP5050A instrument (quadrupole mass analyzer, a.m.u. range 34–650; SPB-5 capillary column, 60 m × 0.25 mm × 0.25 μm; carrier gas helium, flow rate 0.7 ml/min; injector and ion source temperature 250°C; gas inlet pressure 250 kPa; oven temperature programming from 60 to 250°C at 10 deg/min).

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