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Mass Spectra of New Heterocycles: XII.* Main Fragmentation Pathways of the Molecular Ions of 5-Methylsulfanyl-1-vinyl-1*H*-pyrrol-2-amines under Electron Impact and Chemical Ionization

L. V. Klyba, N. A. Nedolya, O. A. Tarasova, and E. R. Sanzheeva

Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: klyba@irioch.irk.ru

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Abstract—Fragmentation patterns of 5-methylsulfanyl-1-vinyl-1*H*-pyrrol-2-amines under electron impact (70 eV) and chemical ionization (methane as reactant gas) were studied for the first time. The electron impact mass spectra of all the examined compounds contained a strong peak of molecular ion which decomposed along four pathways. Two pathways involved cleavage of the C–S bonds with elimination of methyl (major) and MeS radicals (minor), and the two others, decomposition of the pyrrole ring. The chemical ionization mass spectra displayed strong molecular, $[M + H]^+$, and odd-electron $[M + H - SMe]^+$ ion peaks. *N*,*N*-Dimethyl-5-methylsulfanyl-4-phenyl-1-vinyl-1*H*-pyrrol-2-amine under chemical ionization with methane as reactant gas characteristically decomposed with formation of $[M - C_4H_9N]^+$ as the only fragment ion.

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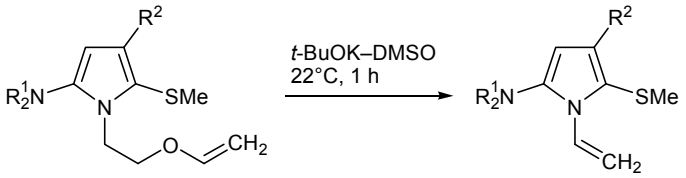
Due to extensive and diverse applications of pyrrole derivatives [2], including 1-vinylpyrroles [3–6], in organic synthesis, medicine, pharmacology, materials science, supramolecular chemistry, optoelectronics, etc., development of new efficient procedures for the preparation of these compounds, especially of those containing rare substituents, and studies of their properties still remain important [4–6]. One of the simplest and most effective methods for the synthesis of 1-vinylpyrrole derivatives is based on the reaction of ketoximes with alkynes in superbasic system (Trofimov reaction) [5]. Up to now, new versions of the Trofimov reaction have been proposed, which ensure one-pot synthesis of 1-vinylpyrroles directly from ketones and acetylene (through the corresponding oximes) [6]. Another synthetically attractive general approach allowing simultaneous construction and functionalization of pyrrole ring to be accomplished in one preparative step is based on reactions of allenic and acetylenic carbanions with isothiocyanates [7]. When 2-(vinyloxy)ethyl isothiocyanate is used as starting compound, the products are 2-alkylsulfanyl-1-[2-(vinyloxy)ethyl]pyrroles [7, 8]; treatment of the latter with *t*-BuOK–DMSO at room or slightly elevated temperature smoothly produces 2,3-di-, 2,5-di-, and 2,3,5-tri- or 2,4,5-trihetero-substituted 1-vinylpyrroles [9] which are difficult to obtain by other methods.

In the preceding communication [1] we described the synthesis of 5-methylsulfanyl-1-[2-(vinyloxy)-ethyl]-1*H*-pyrrol-2-amines and fragmentation of their molecular ions under electron impact and chemical ionization. The present work continues our systematic studies on the mass spectra of heterocycles [1, 10] obtained from allyl isothiocyanate [11] or other isothiocyanates and allenic or acetylenic compounds [7, 8, 12]. We now report for the first time on the fragmentation of molecular ions of 5-methylsulfanyl-1-vinyl-1*H*-pyrrol-2-amines **I**–**VII** under electron impact (70 eV) and chemical ionization (using methane as reactant gas).

5-Methylsulfanyl-1-vinyl-1*H*-pyrrol-2-amines **I**–**VII** were synthesized in 86–97% yield from readily accessible 5-methylsulfanyl-1-[2-(vinyloxy)ethyl]-1*H*-pyrrol-2-amines **VIII**–**XIV** via cleavage of the 2-(vinyloxy)ethyl group by the action of *t*-BuOK–

* For communication XI, see [1].

Scheme 1.



VIII–XIV **I–VII**

I, **VI**, **VII**, R^1 = Me; **II**, R^1 = Et; **III**, R^1 = Pr; **IV**, R^1_2N = pyrrolidin-1-yl; **V**, R^1_2N = piperidin-1-yl; **I–V**, R^2 = H; **VI**, R^2 = Ph; **VII**, R^2 = H_2C=C(Me).

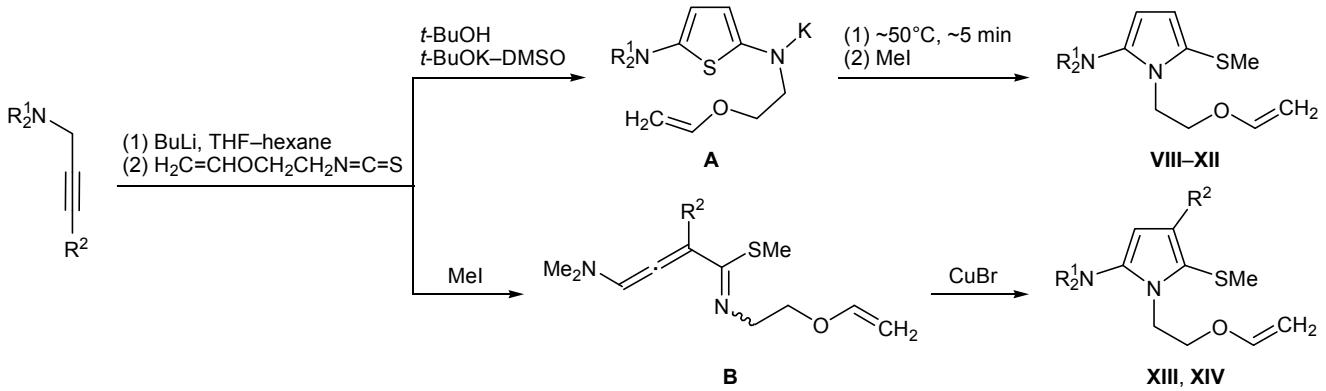
DMSO, which was accompanied by elimination of allyl alcohol (Scheme 1) [9]. Compounds **VIII–XII** were prepared in turn from monolithiated propargylamines and 2-(vinyloxy)ethyl isothiocyanate (through recyclization of intermediate thienylamide anion **A**) in one preparative step (yield 77–84%) according to the procedure developed by us previously [13] (Scheme 2). 4-Substituted 1-[2-(vinyloxy)ethyl]pyrrol-2-amines **XIII** and **XIV** (precursors of **VI** and **VII**) were synthesized in 52 and 59% yield from 2-(vinyloxy)ethyl isothiocyanate and lithiated *N*,*N*-dimethyl-3-phenylprop-2-yn-1-amine and *N*,*N*,4-trimethylpent-4-en-2-yn-1-amine, respectively, through allenyl imidothioate **B** which was subjected to cyclization catalyzed by copper(I) salts (Scheme 2) [14, 15].

The electron impact mass spectra of **I–VII**, as well as the spectra of 1-(2-vinyloxy)ethyl precursors **VIII–XIII** [1] and **XIV** (Table 1; $[M^1]^{+\cdot}$, I_{rel} 53–100%), displayed intense molecular ion peaks (I_{rel} 56–100%); however, there is no similarity in the variation of the molecular ion stabilities in the series **I–VII** and **VIII–XIV**. In particular, the abundance of the molecular ions of 1-vinylpyrroles **I**, **II**, and **VI** increased from 53–97% for compounds **VIII**, **IX**, and **XIII** [1] to 100%, whereas the intensity of the molecular ion peaks of **IV** and **V** decreased from 78 and 94% for **XI** and **XII** [1] to 66 and 56%, respectively. The complete lists of ion peaks in the mass spectra of 5-methylsulfanyl-1-vinyl-1*H*-pyrrol-2-amines **I–VII** and 4-isopropenyl-*N*,*N*-dimethyl-5-methylsulfanyl-1-[2-(vinyloxy)ethyl]-1*H*-pyrrol-2-amine (**XIV**) (which was not described in [1]) are given in Table 1.

Another essential feature that makes compounds **I–VII** different from **VIII–XIV** is the character of fragmentation of their molecular ions under electron impact. The molecular ions of 1-[2-(vinyloxy)ethyl]-pyrrol-2-amines decompose according to three main pathways: (1) elimination of EtS radical, (2) expulsion of methyl radical from the MeS group, and (3) cleavage of the C–N and/or C–C bonds, which is accompanied by rearrangement processes [1]. The intensity of the resulting $[M - EtS]^+$, $[M - Me]^+$, and $[M - C_4H_7O]^+$ ion peaks ranges within 96–100, 23–53, and 6–13%, respectively.

The electron ionization mass spectra of 1-vinylpyrrol-2-amines **I–VII** revealed formation of several ion series. Primary decomposition of the molecular ion $[M^1]^{+\cdot}$ involves cleavage of both C–S bonds (Me–S and C^5–S) with elimination of Me and MeS radicals, respectively, and formation of $[M - Me]^+$ (**C**–**C″**) and

Scheme 2.



VIII, **XIII**, **XIV**, R^1 = Me; **IX**, R^1 = Et; **X**, R^1 = Pr; **XI**, R^1_2N = pyrrolidin-1-yl; **XII**, R^1_2N = piperidin-1-yl; **VIII–XII**, R^2 = H; **XIII**, R^2 = Ph; **XIV**, R^2 = H_2C=C(Me).

$[M - MeS]^+$ (**D**, **D′**) ions (Scheme 3, Table 2). Unlike 1-[2-(vinyloxy)ethyl]pyrrol-2-amines, the formation of $[M - Me]^+$ ions is the major fragmentation pathway of 1-vinylpyrrole derivatives. The abundance of the $[M - Me]^+$ ions ranges from 74 to 100% against 23–53% for 1-[2-(vinyloxy)ethyl] analogs [1]. The two other ion series which were not observed in the mass spectra of 1-[2-(vinyloxy)ethyl]pyrrol-2-amines [1] originate from decomposition of the pyrrole ring, leading to ions **E** and **F** and products of their further fragmentation (Scheme 4, Table 2). In addition, there are three decomposition channels, most probably related to rearranged molecular ion $[M^2]^{+\cdot}$; cleavage of the C–N bonds in the latter gives rise to odd-electron

Scheme 3.

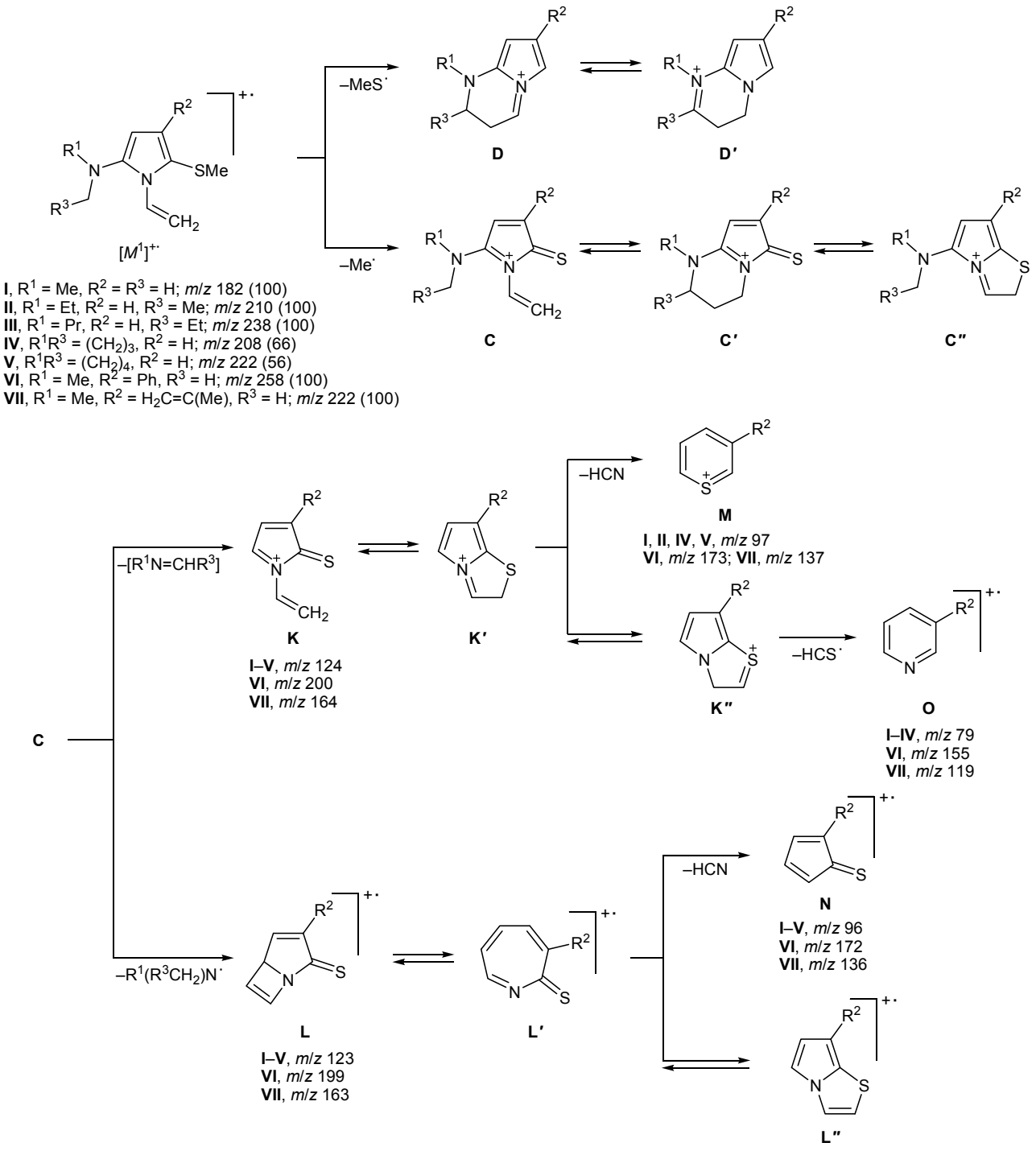


Table 1. Electron impact (70 eV) mass spectra of 5-methylsulfanyl-1-vinyl-1*H*-pyrrol-2-amines **I–VII** and 4-isopropenyl-*N*,*N*-dimethyl-5-methylsulfanyl-1-[2-(vinyloxy)ethyl]-1*H*-pyrrol-2-amine (**XIV**)

Comp. no.	m/z (I_{rel}, %)[a]
I	182 (100) $[M]^{+\cdot}$, 183 (11), 184 (5), 169 (4), 168 (8), 167 (85), 165 (4), 155 (3), 152 (10), 151 (10), 141 (4), 140 (28), 139 (5), 138 (3), 137 (6), 136 (5), 135 (19), 134 (7), 133 (12), 126 (14), 125 (7), 124 (23), 123 (54), 121 (7), 120 (12), 119 (5), 114 (8), 111 (4), 110 (4), 108 (4), 107 (6), 106 (4), 105 (6), 100 (3), 99 (5), 98 (4), 97 (10), 96 (21), 94 (8), 93 (19), 92 (5), 91 (5), 85 (5), 84 (3), 83 (4), 82 (17), 81 (5), 80 (9), 79 (11), 78 (5), 76 (5), 73 (5), 72 (3), 71 (11), 70 (14), 69 (13), 68 (6), 67 (8), 66 (18), 65 (6), 64 (3), 59 (5), 58 (4), 56 (3), 55 (4), 54 (5), 53 (5), 52 (10), 51 (3), 47 (4), 46 (3), 45 (16), 44 (14).
II	210 (100) $[M]^{+\cdot}$, 211 (16), 212 (5), 197 (4), 196 (8), 195 (74), 181 (4), 180 (8), 168 (9), 167 (9), 166 (34), 165 (10), 164 (5), 163 (16), 162 (6), 161 (3), 154 (13), 153 (5), 152 (6), 151 (21), 149 (3), 148 (4), 147 (7), 141 (4), 140 (25), 139 (6), 138 (8), 137 (19), 136 (7), 135 (7), 134 (28), 133 (14), 132 (3), 128 (3), 126 (22), 125 (5), 124 (19), 123 (6), 121 (4), 119 (6), 118 (3), 112 (7), 111 (3), 110 (8), 108 (8), 107 (7), 106 (12), 105 (16), 100 (15), 99 (8), 98 (4), 97 (8), 96 (22), 94 (4), 93 (5), 86 (4), 85 (6), 84 (3), 82 (5), 81 (3), 80 (12), 79 (34), 78 (7), 73 (4), 72 (5), 71 (6), 70 (11), 69 (7), 68 (4), 67 (3), 66 (3), 65 (3), 61 (3), 59 (9), 58 (4), 56 (14), 55 (3), 54 (8), 53 (9), 52 (16), 47 (4), 45 (14), 44 (5), 42 (10), 41 (8), 40 (3), 39 (11), 38 (3).
III	238 (100) $[M]^{+\cdot}$, 224 (12), 223 (84), 191 (16), 181 (8), 180 (17), 179 (5), 168 (6), 166 (6), 162 (8), 161 (4), 154 (16), 152 (4), 151 (12), 149 (11), 138 (11), 137 (10), 133 (19), 126 (16), 124 (10), 123 (5), 120 (6), 119 (7), 112 (8), 106 (6), 105 (10), 100 (7), 96 (9), 80 (4), 79 (15), 70 (4), 54 (3), 52 (30).
IV	208 (66) $[M]^{+\cdot}$, 209 (8), 210 (4), 195 (5), 194 (12), 193 (100), 191 (3), 178 (6), 166 (9), 165 (13), 161 (11), 160 (10), 159 (9), 153 (3), 152 (4), 151 (6), 150 (3), 149 (14), 147 (5), 138 (4), 137 (4), 136 (3), 134 (4), 133 (4), 132 (5), 131 (3), 126 (4), 125 (4), 124 (29), 123 (5), 119 (4), 118 (4), 112 (3), 110 (3), 108 (7), 107 (5), 106 (8), 105 (10), 104 (3), 100 (3), 98 (5), 97 (13), 96 (23), 94 (3), 93 (5), 92 (3), 85 (4), 83 (4), 81 (4), 80 (12), 79 (22), 78 (5), 71 (9), 70 (19), 69 (8), 68 (4), 67 (3), 66 (5), 65 (4), 61 (3), 59 (8), 58 (3), 56 (3), 55 (16), 54 (8), 53 (10), 52 (14), 51 (4), 47 (5), 46 (3), 45 (18), 43 (4), 42 (9), 41 (26), 40 (6), 39 (25), 38 (4).
V	222 (56) $[M]^{+\cdot}$, 223 (8), 224 (4), 209 (4), 208 (10), 207 (77), 192 (5), 180 (5), 179 (5), 175 (11), 174 (5), 173 (5), 163 (8), 161 (3), 153 (3), 152 (3), 151 (5), 148 (3), 147 (4), 145 (3), 139 (7), 138 (3), 137 (4), 133 (3), 132 (3), 126 (5), 125 (4), 124 (20), 123 (8), 122 (11), 120 (4), 119 (5), 118 (7), 117 (4), 112 (6), 111 (4), 110 (3), 107 (7), 106 (7), 105 (10), 100 (3), 98 (4), 97 (10), 96 (21), 95 (5), 94 (4), 93 (5), 92 (4), 85 (5), 84 (14), 83 (3), 82 (3), 80 (10), 79 (17), 78 (4), 71 (6), 70 (7), 69 (11), 68 (4), 67 (5), 66 (6), 65 (6), 61 (9), 59 (8), 58 (3), 56 (6), 55 (13), 54 (11), 53 (12), 52 (15), 51 (4), 47 (6), 46 (3), 45 (23), 43 (5), 42 (25), 41 (100), 40 (11), 39 (40), 38 (5).
VI	258 (100) $[M]^{+\cdot}$, 259 (16), 260 (6), 252 (4), 245 (5), 244 (20), 243 (93), 241 (3), 231 (3), 229 (3), 228 (11), 227 (9), 217 (3), 216 (12), 215 (3), 213 (4), 212 (14), 211 (51), 210 (15), 209 (8), 202 (5), 201 (7), 200 (18), 199 (24), 198 (8), 197 (6), 196 (8), 195 (20), 191 (3), 190 (20), 187 (4), 186 (10), 185 (9), 184 (24), 183 (22), 182 (11), 181 (36), 180 (3), 174 (7), 173 (11), 172 (11), 171 (8), 170 (6), 169 (18), 168 (20), 167 (25), 166 (5), 160 (4), 159 (8), 158 (14), 157 (4), 156 (6), 155 (6), 154 (10), 153 (5), 147 (10), 146 (7), 145 (7), 144 (5), 143 (7), 142 (9), 141 (8), 140 (23), 139 (4), 134 (14), 130 (4), 129 (15), 128 (34), 127 (17), 121 (10), 117 (3), 116 (11), 115 (43), 114 (8), 113 (6), 110 (3), 108 (3), 105 (3), 104 (4), 103 (8), 102 (56), 101 (17), 100 (8), 99 (12), 98 (4), 95 (10), 94 (5), 93 (5), 91 (6), 90 (6), 89 (11), 88 (18), 87 (4), 86 (4), 82 (4), 81 (4), 80 (4), 79 (8), 78 (8), 77 (26), 76 (15), 75 (12), 74 (11), 73 (6), 72 (5), 71 (11), 70 (9), 69 (12), 68 (7), 67 (5), 66 (3), 65 (8), 64 (6), 63 (17), 62 (8), 61 (5), 59 (15), 58 (7), 56 (7), 55 (5), 54 (7), 53 (3), 52 (12), 51 (25), 50 (12).
VII	222 (100) $[M]^{+\cdot}$, 223 (15), 224 (6), 209 (5), 208 (13), 207 (96), 205 (4), 192 (11), 191 (7), 180 (3), 179 (4), 178 (6), 177 (7), 176 (6), 175 (35), 174 (20), 173 (13), 166 (5), 165 (13), 164 (37), 163 (11), 162 (15), 161 (5), 160 (12), 159 (14), 155 (4), 154 (31), 152 (3), 151 (7), 150 (17), 149 (11), 148 (27), 147 (12), 146 (5), 145 (12), 144 (4), 139 (5), 138 (29), 137 (12), 136 (13), 135 (7), 134 (6), 133 (14), 132 (12), 131 (15), 130 (10), 124 (5), 123 (7), 122 (17), 121 (7), 120 (5), 119 (5), 118 (8), 117 (9), 111 (11), 110 (5), 109 (7), 108 (4), 107 (6), 106 (8), 105 (7), 103 (31), 99 (4), 98 (4), 97 (7), 96 (8), 95 (6), 94 (8), 93 (6), 92 (14), 91 (9), 90 (7), 89 (4), 88 (8), 87 (4), 85 (8), 83 (6), 82 (6), 81 (7), 80 (7), 79 (13), 78 (9), 77 (18), 76 (5), 75 (3), 74 (4), 73 (3), 71 (11), 70 (96), 69 (13), 68 (10), 67 (8), 66 (17), 65 (29), 64 (7), 63 (9), 62 (3), 61 (6), 59 (12), 58 (9), 56 (4), 55 (9), 54 (6), 53 (10), 52 (10), 51 (13), 50 (4), 47 (3), 46 (3), 45 (13), 44 (20).

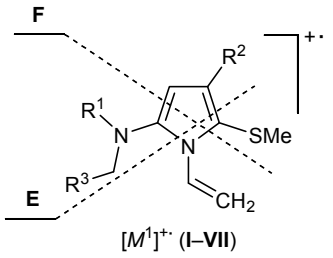
Table 1. (Contd.).

Comp. no.	m/z (I_{rel}, %)[a]
XIV	266 (100) $[M]^{+\cdot}$, 267 (19), 268 (7), 253 (5), 252 (13), 251 (74), 237 (3), 236 (3), 223 (3), 222 (6), 221 (3), 220 (10), 219(57), 217 (6), 209 (3), 208 (15), 207 (13), 206 (15), 205 (13), 195 (11), 194 (7), 193 (17), 192 (43), 189 (3), 181 (8), 180 (27), 179 (22), 178 (11), 177 (7), 176 (4), 175 (8), 174 (4), 173 (4), 167 (3), 166 (11), 165 (19), 164 (43), 163 (11), 162 (15), 161 (7), 160 (3), 159 (3), 155 (3), 154 (30), 152 (9), 151 (15), 150 (14), 149 (15), 148 (9), 147 (16), 146 (6), 145 (4), 139 (4), 138 (15), 137 (11), 136 (21), 135 (5), 134 (5), 133 (11), 132 (6), 131 (7), 130 (3), 125 (3), 124 (5), 123 (5), 122 (9), 121 (4), 120 (5), 119 (5), 118 (5), 117 (3), 111 (6), 110 (4), 109 (5), 108 (4), 107 (5), 106 (7), 105 (6), 104 (26), 96 (14), 95 (7), 94 (6), 93 (4), 92 (9), 91 (7), 90 (5), 89 (5), 87 (8), 86 (4), 85 (3), 84 (7), 83 (4), 82 (6), 81 (5), 80 (6), 79 (9), 78 (6), 77 (14), 75 (3), 74 (3), 72 (9), 71 (5), 70 (14), 69 (6), 68 (5), 67 (5), 66 (8), 65 (16), 64 (3), 63 (4), 61 (5), 59 (5), 58 (8), 57 (4), 56 (4), 55 (5), 54 (4), 53 (6), 52 (4), 51 (8), 49 (7), 47 (4), 46 (4), 45 (30), 44 (18).

[a] Given are ion peaks with a relative intensity of no less than 3%.

$[M - R^3C_3H_5]^{+\cdot}$ (**G**) and $[M - R^1NH_2]^{+\cdot}$ (**H**) ions and $[M - R^1NH]^+$ ion (**J**), which are common for compounds **I**–**III**, **VI**, and **VII** (Scheme 5, Table 2). Radical cations **G** and **H** are likely to have the structures of 5-methylsulfanyl-2*H*-pyrrol-2-imine and 2-methylsulfanyl-1-(prop-2-yn-1-yl)-1*H*-pyrrole, respectively.

Scheme 4.

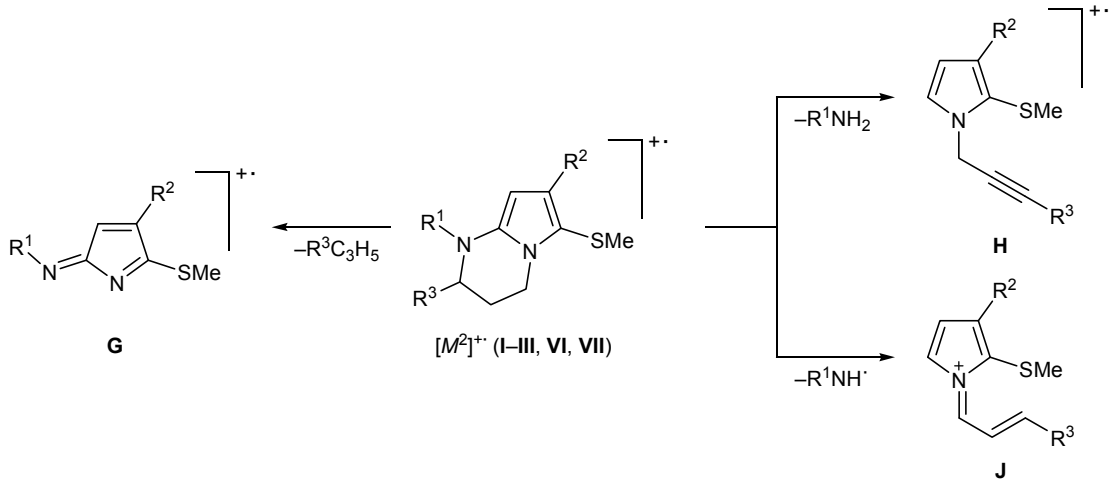


$[M^1]^{+\cdot}$ (**I**–**VII**)

As we already noted, elimination of methyl radical from the molecular ion to form ion **C** is the major primary fragmentation act for all the examined compounds under electron impact. The subsequent decomposition of ion **C** follows two pathways via expulsion of imine molecule or dialkylamine radical to give, respectively, $[\mathbf{C} - R^1N{=}CHR^3]^+$ (possible structures **K**–**K″**) and $[\mathbf{C} - R^1(R^3CH_2)N]^{+\cdot}$ ions (possible structures **L**–**L″**) (Scheme 3). Elimination of HCN molecule or HCS radical from the latter yields ions **M** $[\mathbf{K} - HCN]^+$, **N** $[\mathbf{L} - HCN]^{+\cdot}$, and **O** $[\mathbf{K} - HCS]^{+\cdot}$. The contribution of each of the other common decomposition channels of $[M^1]^{+\cdot}$ to the total ion current is considerably smaller than that of the channel leading to ion **C**; it ranges within 11–51 (**D**), 7–17 (**E**), and 3–30% (**F**) (Schemes 3, 4; Table 2).

The effect of the substituent on the amino nitrogen atom in pyrroles **I**–**VII** on their fragmentation pattern under electron impact was seen most clearly in the molecular ion decomposition pathways involving cleavage of C–N bonds (Scheme 5). In this case, compounds **IV** and **V** containing pyrrolidinyl and piperidinyl substituents behaved differently. This is not

Scheme 5.



$[M^2]^{+\cdot}$ (**I**–**III**, **VI**, **VII**)

Table 2. Characteristic ions in the electron impact (70 eV) mass spectra of 5-methylsulfanyl-1-vinyl-1*H*-pyrrol-2-amines **I**–**VII**

Ion	*m/z* (I_{rel}, %)						
	I	**II**	**III**	**IV**	**V**	**VI**	**VII**
$[M]^{+\cdot}$	182 (100)	210 (100)	238 (100)	208 (66)	222 (56)	258 (100)	222 (100)
$[M - Me]^+$, **C**	167 (85)	195 (74)	223 (84)	193 (100)	207 (77)	243 (93)	207 (96)
$[M - MeS]^+$, **D**	135 (19)	163 (16)	191 (16)	161 (11)	175 (11)	211 (51)	175 (35)
$[M - C_2H_3NCSMe]^+$, **E**	82 (17)	110 (8)	138 (11)	108 (7)	122 (11)	158 (14)	122 (17)
$[M - R^2C_3SMe]^+$, **F**	98 (4)	126 (22)	154 (16)	124 (30)	138 (3)	98 (4)	98 (4)
$[M - R^3C_3H_5]^{+\cdot}$, **G**	140 (28)	154 (14)	168 (6)	–	–	216 (12)	180 (3)
$[M - R^1NH_2]^{+\cdot}$, **H**	151 (10)	165 (11)	179 (5)	–	–	227 (9)	191 (7)
$[M - R^1NH]^+$, **J**	152 (10)	166 (34)	180 (17)	–	–	228 (11)	192 (11)
$[C - R^1N{=}CHR^3]^+$, **K**	124 (23)	124 (19)	124 (10)	124[a] (30)	124 (20)	200 (18)	164 (37)
$[C - R^1NCH_2R^3]^{+\cdot}$, **L**	123 (54)	123 (6)	123 (5)	123 (5)	123 (8)	199 (24)	163 (11)
$[K - HCN]^+$, **M**	97 (10)	97 (8)	–	97 (13)	97 (10)	173 (11)	137 (12)
$[L - HCN]^{+\cdot}$, **N**	96 (21)	96 (22)	96 (9)	96 (23)	96 (21)	172 (11)	136 (13)
$[K - HCS]^{+\cdot}$, **O**	79 (11)	79 (34)	79 (15)	79 (22)	79 (17)	155 (6)	119 (5)

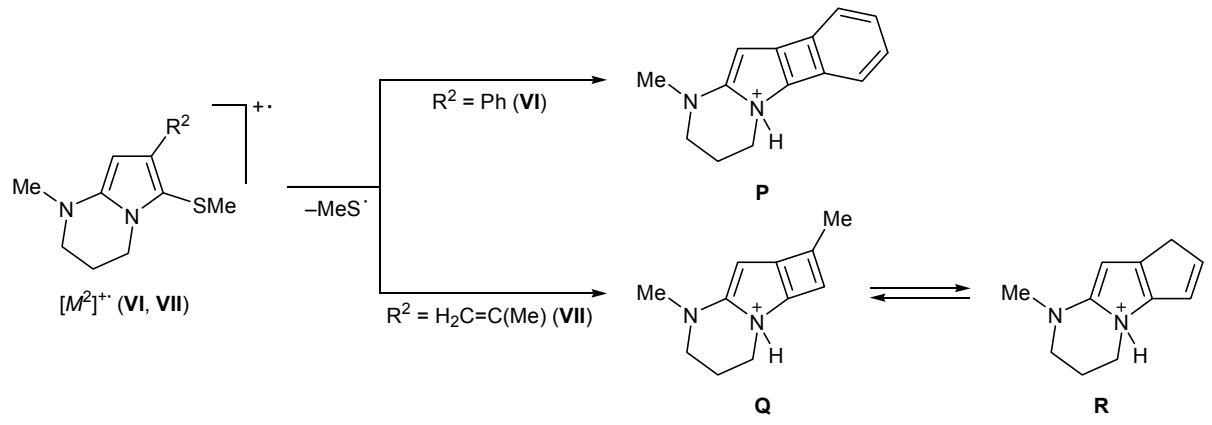
[a] Coincides with ion **F** in *m/z* value.

surprising, taking into account the absence of separate R^1 and R^3 substituents in their molecules. Therefore, no $[M - R^3C_3H_5]^{+\cdot}$, $[M - R^1NH_2]^{+\cdot}$, or $[M - R^1NH]^+$ ion can be formed from fused polycyclic rearranged molecular ions of **IV** and **V**.

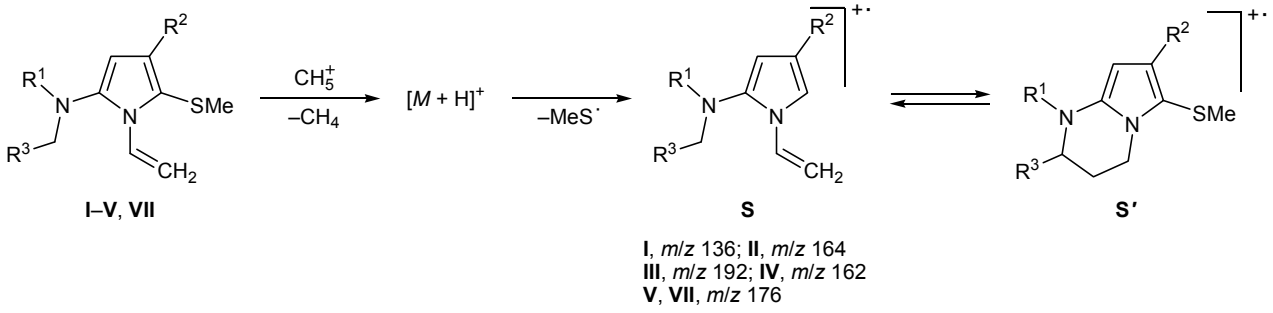
The substituent in the amino group also has an appreciable effect on the stability of all ions observed in the mass spectra; however, no any distinct relation can be found (Table 2). The presence of a phenyl or isopropenyl substituent on C^4 (**VI**, **VII**) did not affect the general fragmentation pattern, but in some cases appreciable stabilization of fragment ions was observed. In the mass spectra of **VI** and **VII**, the $[M - MeS]^+$ ion peak has the maximum intensity (51 and 35%, respectively), whereas the intensity of the corresponding ion peak in the spectra of **I**–**V** does not exceed 19% (Table 2). Presumably, stabilizing effect of these substituents is determined by the formation of polycyclic conjugated structures like 1-methyl-1,2,3,4-tetrahydrobenzo[3′,4′]cyclobuta[1′,2′:4,5]pyrrolo[1,2-*a*]pyrimidin-5-ium (**P**) and 1,7-dimethyl-1,2,3,4-tetrahydrocyclobuta[4,5]pyrrolo[1,2-*a*]pyrimidin-5-ium (**Q**) or 1-methyl-1,3,4,8-tetrahydro-2*H*-cyclopenta[4,5]pyrrolo[1,2-*a*]pyrimidin-5-ium (**R**) as a result of loss of methylsulfanyl radical (Scheme 6).

Like their precursors **VIII**–**XIV** [1], chemical ionization of compounds **I**–**VII** using methane as reactant gas involves protonation and charge exchange processes. As a result, the molecular ions (I_{rel} 97–100%) and $[M + H]^+$ ions (I_{rel} 62–100%) are generally

Scheme 6.



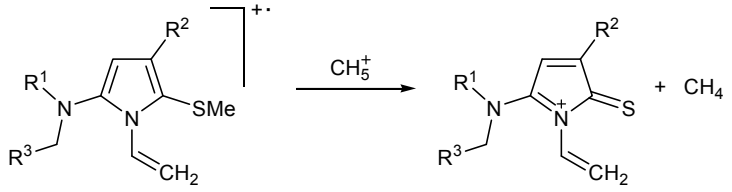
Scheme 7.



I–V, **VII**

I, *m*/*z* 136; **II**, *m*/*z* 164
III, *m*/*z* 192; **IV**, *m*/*z* 162
V, **VII**, *m*/*z* 176

Scheme 8.



$[M^1]^{+\cdot}$ (**I–V**, **VII**) **C**

most abundant (Table 3). The main fragment ion (**S** or **S′**, I_{rel} 37–95%) is formed via elimination of MeS radical from protonated molecular ion $[M + H]^+$ (Scheme 7). The $[M + C_2H_5]^+$ ion generated by electrophilic addition also ejects MeS radical, but the contribution of this fragmentation pathway is relatively small (I_{rel} 6–11%; Scheme 7).

Unlike electron ionization, the formation of $[M – Me]^+$ ion (I_{rel} 11–14%) under chemical ionization is not the main fragmentation pathway of pyrroles **I–VII** (Scheme 8, Table 3).

Further decomposition of the $[M + H – MeS]^+$ ion (**S**) generated from **I–III** and **VII** follows the amine pattern. Expulsion of R^1N molecule (as imine) from ion **S** gives radical cation **T**, while elimination of alkyl radicals or propene (cyclopropane) molecule yields ions **U**, **W**, and **Y** (Scheme 9). The charge in ions **U** may be localized on either amine or pyrrole nitrogen atom. Ions **W** derived from compounds **I** and **VII** have the same *m*/*z* values as those of ions **T**; in the spectrum of **III**, the *m*/*z* values of ions **U** and **W** coincide with each other.

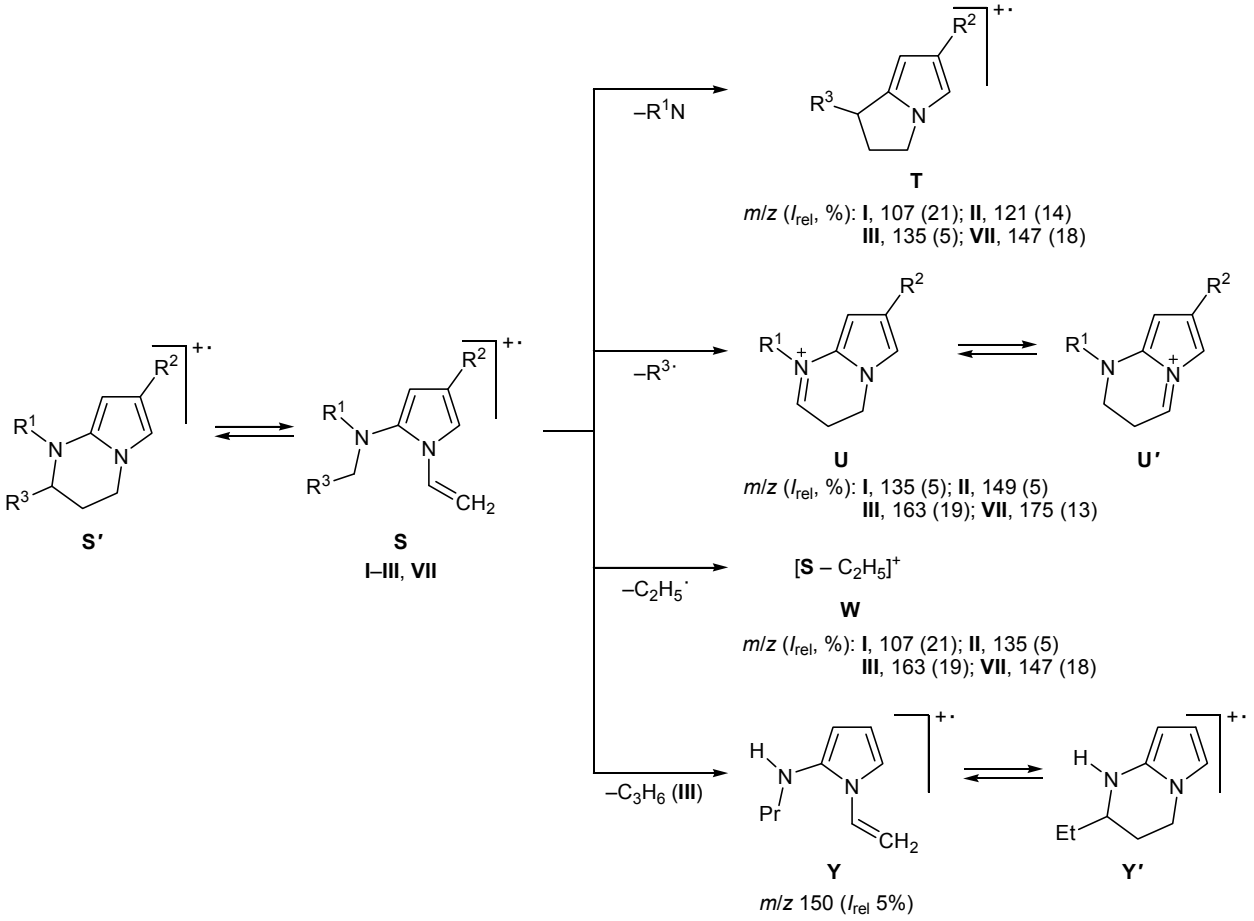
The most essential difference of the chemical ionization mass spectrum of **VII** from the spectra of **I–V** is the presence in the former of a strong ion peak with *m*/*z* 177 (I_{rel} 79%), $[M – HCS]^+$, (**Z**). Ion **Z** is likely to result from rearrangement of the molecular ion of **VII** into bicyclic structure $[M^3]^{+\cdot}$ with participation of the methylsulfanyl group and isopropenyl substituent in position *4* of the pyrrole ring (Scheme 10).

The behavior of 1-vinylpyrrol-2-amine **VI** under chemical ionization deviates from the general pattern observed for compounds **I–VII**. It is characterized by charge exchange involving the phenyl and methyl-

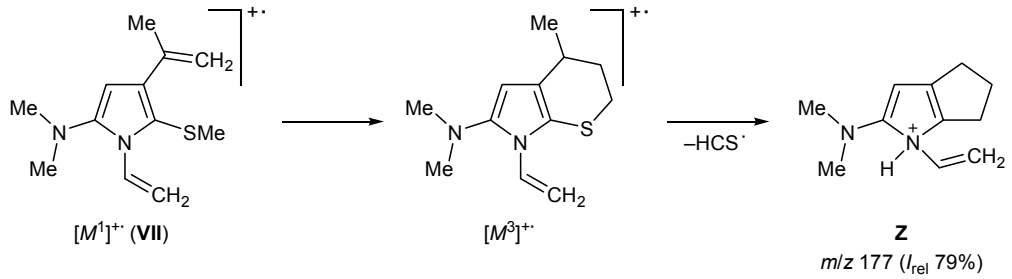
Table 3. Characteristic ions in the chemical ionization (reactant gas methane) mass spectra of 5-methylsulfanyl-1-vinyl-1*H*-pyrrol-2-amines **I–V** and **VII**

Ion	*m*/*z* (I_{rel}, %)					
	I	**II**	**III**	**IV**	**V**	**VII**
$[M]^{+\cdot}$	182 (100)	210 (100)	238 (97)	208 (100)	222 (100)	222 (100)
$[M + H]^+$	183 (62)	211 (68)	239 (100)	209 (63)	223 (86)	223 (88)
$[M – Me]^+$, **C**	167 (11)	195 (12)	223 (12)	193 (14)	207 (11)	207 (14)
$[M + N – MeS]^{+\cdot}$, **S**	136 (95)	164 (37)	192 (40)	162 (64)	176 (64)	176 (92)
$[M + C_2H_5]^+$	211 (2)	239 (4)	267 (7)	237 (2)	251 (5)	251 (4)
$[M + C_2H_5 – MeS]^{+\cdot}$	164 (11)	192 (6)	220 (6)	190 (8)	204 (9)	204 (8)

Scheme 9.



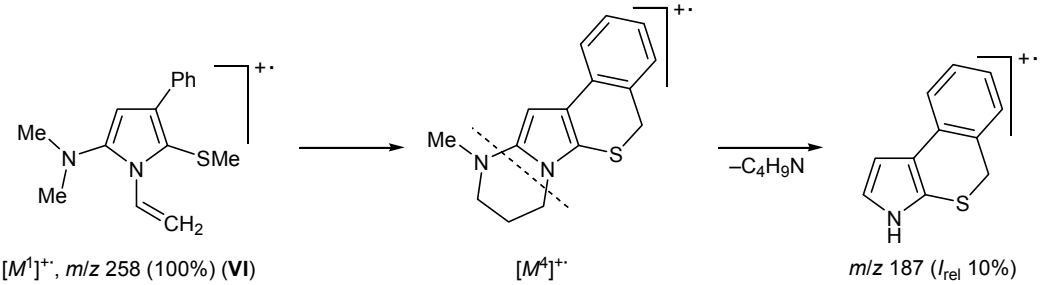
Scheme 10.



sulfanyl substituents. Obviously, the formation of the only fragment ion $[M - C_4H_9N]^{+\cdot}$ with *m*/*z* 187 (assumingly having the structure of 3,5-dihydroisothiochromeno[3,4-*b*]pyrrole) is possible only from rearranged molecular ion $[M^4]^{+\cdot}$ with a probable structure of 11-methyl-4a,8,9,10,11,12b-hexahydro-5*H*-isothiochromeno[4′,3′:4,5]pyrrolo[1,2-*a*]pyrimidine (Scheme 11). By contrast, the precursor of **VI**, 1-[2-(vinyloxy)ethyl]pyrrol-2-amine **XIII**, revealed no specific behavior under chemical ionization, i.e., the presence of a phenyl group in molecule **XIII** did not affect the general fragmentation pattern [1].

To conclude, the fragmentation patterns of the molecular ions of 5-methylsulfanyl-1-vinyl-1*H*-pyrrol-2-amines **I**–**VII** under both electron impact and chemical ionization radically differ from the decomposition pathways of the corresponding 1-[2-(vinyloxy)ethyl]-pyrrol-2-amines [1]. Electron ionization of **I**–**VII** gives rise to seven ion series. The two major series result from elimination of Me and MeS radicals from the molecular ions. The other two series are related to decomposition of the pyrrole ring. Three more ion series observed in the mass spectra of **I**–**III**, **VI**, and **VII** reflect cleavage of C–N bonds. The nature of the

Scheme 11.



$[M^1]^{+\cdot}$, *m*/*z* 258 (100%) (**VI**) $[M^4]^{+\cdot}$ *m*/*z* 187 (I_{rel} 10%)

substituent on C^4 [R^2 = H, Ph, H_2C=C(Me)] almost does not affect the fragmentation pattern of **I**–**VII** under electron impact.

Chemical ionization of **I**–**VII** is accompanied by protonation, charge exchange, and electrophilic addition processes. The major fragment ions are formed via elimination of MeS radical from $[M + H]^+$ and $[M + C_2H_5]^+$ ions and of Me radical from $[M^1]^{+\cdot}$. Unlike electron ionization, the fragmentation pattern of **I**–**VII** under chemical ionization with methane strongly depends on the nature of the R^2 substituent. In particular, compound **VII** [R^2 = H_2C=C(Me)] revealed an additional fragmentation pathway leading to $[M – HCS]^+$ ion, and 4-phenyl derivative **VI** (R^2 = Ph) gave only one fragment ion $[M – C_4H_9N]^{+\cdot}$.

EXPERIMENTAL

Compounds **I**–**VII** were synthesized according to the procedures described in [9, 13–15].

The electron impact mass spectra (70 eV) were recorded on a Shimadzu GCMS-QP5050A instrument (quadrupole mass analyzer, a.m.u. range 34–650) with direct sample admission into the ion source (DI-50 direct inlet probe). The ion source and direct inlet probe temperatures were selected so that to ensure recording of high-quality spectra and minimize thermal decomposition of samples.

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

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