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Dedicated to Full Member of the Russian Academy of Sciences G.A. Tolstikov on his 75th anniversary

Mass Spectra of New Functionally Substituted Heterocycles: VI.* Fragmentation of 3-Methoxy-7-methyl-2-methylsulfanyl-4,5-dihydro-3*H*-azepine, Its Structural Isomers, 5-Methoxy-2,2-dimethyl-6-methylsulfanyl-2,3-dihydropyridine and 1-Isopropyl-3-methoxy-2-methylsulfanyl-1*H*-pyrrole, and Their Linear Precursors under Electron Impact

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Abstract—Mass spectra of previously unknown isomeric 1-isopropyl-3-methoxy-2-methylsulfanylpyrrole, 5-methoxy-2,2-dimethyl-6-methylsulfanyl-2,3-dihydropyridine, and 3-methoxy-7-methyl-2-methylsulfanyl-4,5-dihydro-3*H*-azepine were studied for the first time. Fragmentation of all heterocyclic compounds under electron impact begins with elimination of methyl radical, and the subsequent decomposition of the $[M - Me]^+$ ion (*m*/z 170) is specific for each isomers, which ensures their reliable identification in reaction mixtures. The corresponding linear precursors, methyl *N*-isopropyl-2-methoxybuta-2,3-dienimidothioate and 2-methoxy-*N*-(1-methylethylidene)-1-methylsulfanylbuta-1,3-dien-1-amine undergo isomerization and decomposition even under very mild temperature conditions, so that their mass spectra could not be recorded.

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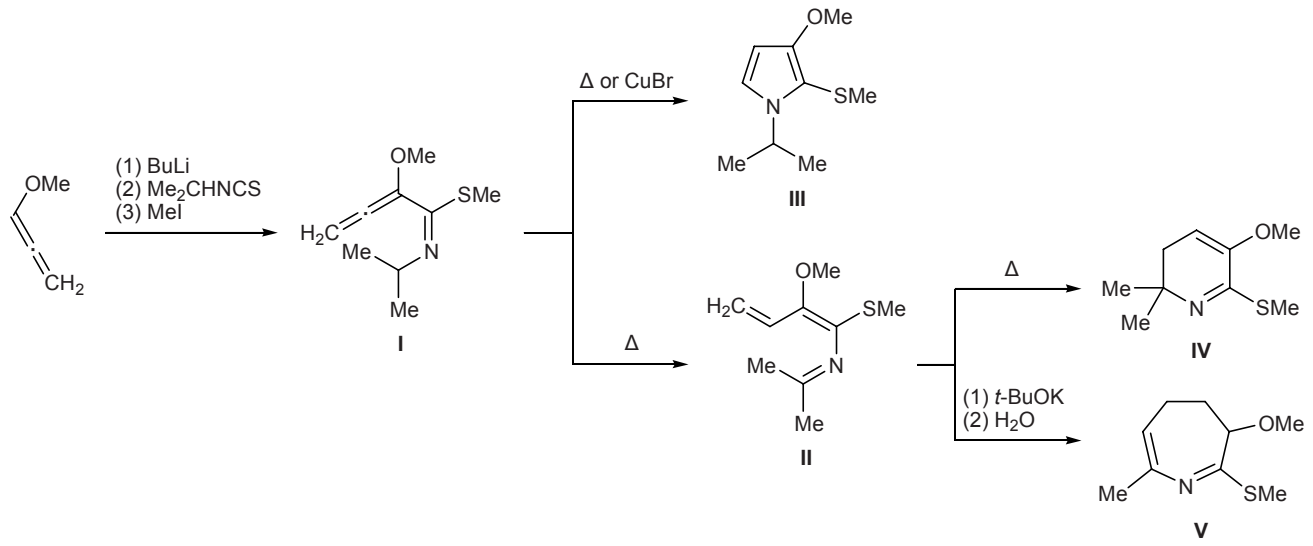
Nitrogen-containing heterocycles, primarily pyrroles, pyridines, azepines, and their partially or exhaustively hydrogenated analogs constitute key structural fragments in many biologically active compounds, both occurring in nature and synthetic, and they play an exceptionally important role in vital activity [2]. These compounds are also important for other practical applications [3]. Therefore, development of novel procedures for their synthesis and comprehensive studies on their properties, including spectral parameters, seem to be fairly urgent.

Azatriene systems like **I** (1-aza-1,3,4-triene) and **II** (2-aza-1,3,5-triene) that are readily available from lithiated allenes and aliphatic isothiocyanates turned out to be universal precursors of isomeric five-, six-, and seven-membered nitrogen-containing heterocycles (Scheme 1) [4–9]. As a rule, heterocyclizations of the above azatrienes are highly selective. However, in some cases, depending on the conditions and 1-aza-1,3,4-triene structure, mixtures of two and more possible heterocyclic products are formed. For example, 1-aza-1,3,4-triene **I**, S-alkylated adduct of 1-lithio-1-methoxyallene and isopropyl isothiocyanate [4], undergoes cyclization in the presence of a catalytic amount of CuBr to give exclusively pyrrole **III**, while in the absence of a catalyst (on heating or even on storage in a freezing chamber) it gives rise to a mixture of pyrrole **III** and isomeric 2,3-dihydropyridine **IV**, the latter considerably prevailing (up to 85%) [4, 8]. Thermally induced [1,5]-sigmatropic rearrangement of 1-aza-1,3,4-triene **I** leads to formation of 2-aza-1,3,5-triene **II** which is readily transformed into previously unknown and inaccessible by other methods 4,5-dihydro-3*H*-azepine (**V**) by the action of potassium *tert*-butox-

* For communication V, see [1].

Scheme 1.



ide [9]. However, it was still impossible to completely suppress concurrent intramolecular [1,5]-cyclization of 1-aza-1,3,4-triene **I** to pyrrole **III** and [1,6]-electrocyclization of 2-aza-1,3,5-triene **II** to 2,3-dihydropyridine **IV**.

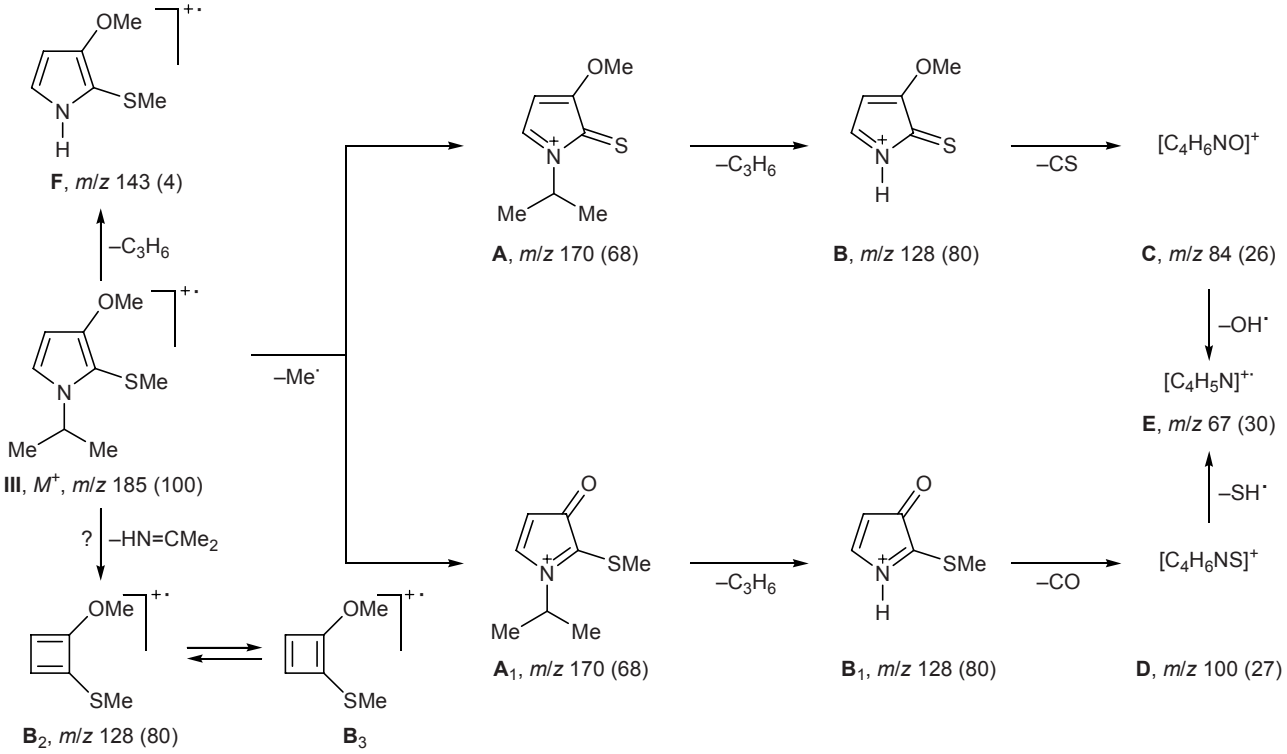
In this case, a simple and convenient express method ensuring fast and reliable identification of structural isomers, both cyclic and open-chain, is necessary for efficient monitoring of the reaction course with a view to optimize conditions for the preparation of a target product, e.g., 4,5-dihydro-3*H*-azepine **V**. The use of mass spectrometry (together with NMR) seems to be especially attractive. However, a necessary condition for its successful application is that the fragmentation patterns of isomeric heterocycles and their linear precursors under electron impact should be essentially different, i.e., fragment ions should be specific for each particular structure. Taking into account that no mass spectra of alkoxy- and alkylsulfanyl-substituted pyrroles, dihydropyridines, and dihydroazepines have been reported so far, their examination was of independent scientific interest.

We were the first to record and analyze mass spectra of five structural isomers, two linear: methyl *N*-isopropyl-2-methoxybuta-2,3-dienimidothioate (**I**) and 2-methoxy-*N*-(1-methylethylidene)-1-methylsulfanylbuta-1,3-dien-1-amine (**II**), and three cyclic: 1-isopropyl-3-methoxy-2-methylsulfanyl-1*H*-pyrrole (**III**), 5-methoxy-2,2-dimethyl-6-methylsulfanyl-2,3-dihydropyridine (**IV**), and 3-methoxy-7-methyl-2-methylsulfanyl-4,5-dihydro-3*H*-azepine (**V**). The mass spectra were obtained under electron impact (70 eV) [10].

As we showed previously [11], the most general decomposition pathway under electron impact of 1-alkyl-2-alkylsulfanylpyrroles having no substituent in the 3-position involves initial abstraction of the alkyl radical. The positive charge in their molecular ions is localized mainly on the sulfur rather than nitrogen atom, so that the alkyl group is abstracted from the exocyclic heteroatom. Analogous process with pyrrole **III** leads to formation of an $[M - Me]^+$ ion with *m*/*z* 170 (Scheme 2); this ion may have alternative structures resulting from abstraction of methyl radical from both methylsulfanyl (**A**) and methoxy group ($\mathbf{A}_1$). Unlike 2-alkylsulfanylpyrroles having no substituent on C^3 [11, 12] (their fragmentation under electron impact is accompanied by rearrangements of the molecular and fragment ions with ring expansion), the subsequent decomposition of the $[M - Me]^+$ ion leads to ion **B** or $\mathbf{B}_1$ with *m*/*z* 128 via elimination of C_3H_6 molecule (propene or cyclopropane). Expulsion of CS or CO from **B** or $\mathbf{B}_1$ gives ions **C** (*m*/*z* 84) and **D** (*m*/*z* 100), respectively, and the latter lose OH or CN radical to give ion **E** (*m*/*z* 67) (Scheme 2).

Two other primary decomposition processes typical of molecular ions derived from 1-alkyl-2-alkylsulfanylpyrroles (where the alkyl group is longer than methyl) [11], namely loss of C_3H_6 molecule (ion **F**) and NR fragment (ion $\mathbf{B}_2$ or $\mathbf{B}_3$), are likely to contribute little to the total ion current, or they do not occur at all. For example, expulsion from the molecular ion of pyrrole **III** of propan-2-imine molecule or its structural isomers of the general formula C_3H_7N could formally produce an ion with *m*/*z* 128 (80%); however, this channel is hardly operative, for no ions that might

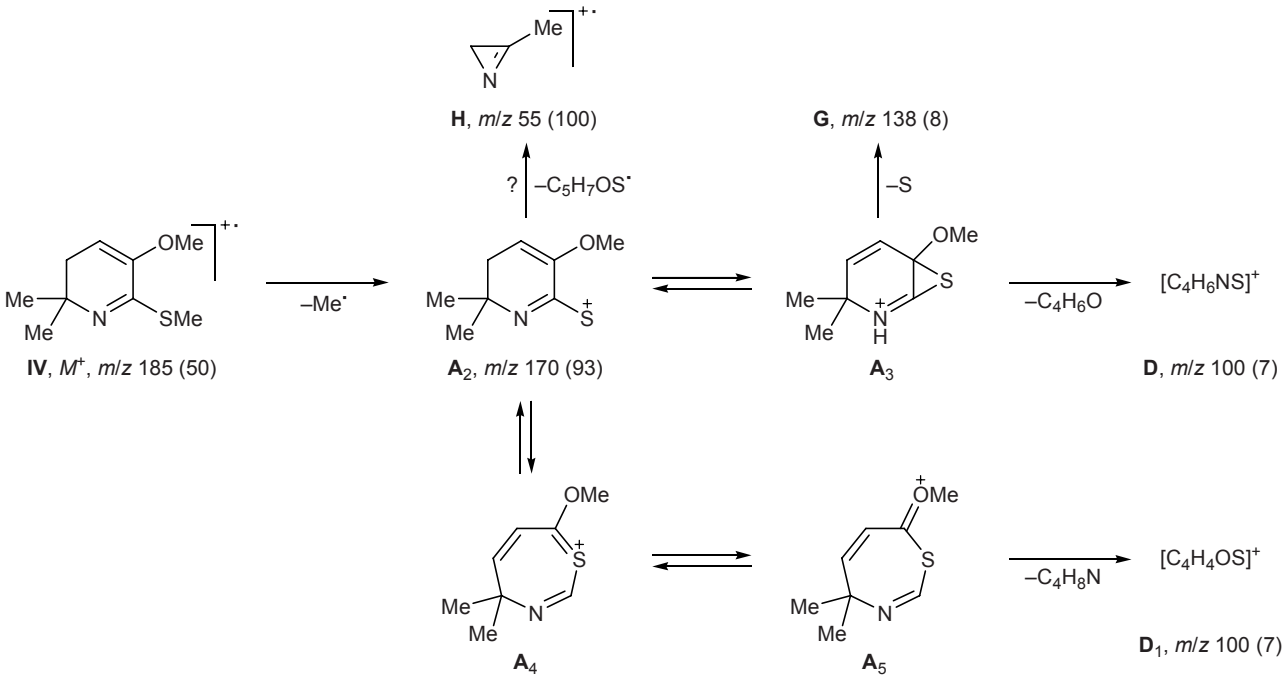
Scheme 2.



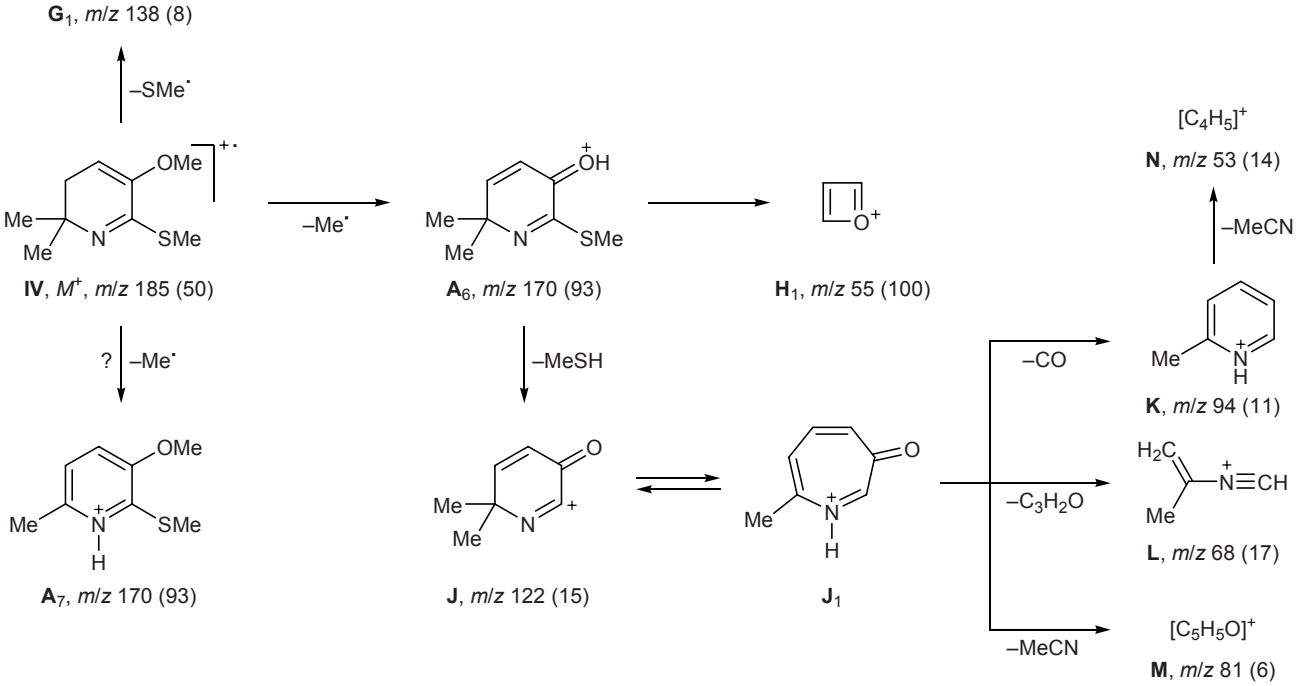
be expected from subsequent decomposition of $\mathbf{B}_2$ and $\mathbf{B}_3$ were detected in the mass spectra.

Prior to our studies, no mass spectrometric data for 2,3-dihydropyridines have been reported [1]. The lack of aromatic π system in 2,3-dihydropyridine **IV** is likely to be responsible for the twice as low intensity of its molecular ion peak [$M^{+\cdot}$, *m*/*z* 185 (50%)] as that of pyrrole isomer **III**) [$M^{+\cdot}$, *m*/*z* 185 (100%)]. In this case, [M – Me]$^+$ ion [*m*/*z* 170 (93%)], which is common for all the examined compounds and is one of the

Scheme 3.



Scheme 4.



most abundant ions in the mass spectrum of 2,3-dihydropyridine **IV**, can be formed along three pathways. The first of these involves elimination of methyl radical from the sulfur atom (see above the data for pyrrole **III**) with formation of bicyclic ion $\mathbf{A}_2$; formalistically, the latter can be stabilized via isomerization into thiirenopyridine ion $\mathbf{A}_3$ and 1,3-thiazepine structure $\mathbf{A}_4$ or $\mathbf{A}_5$ with localization of the positive charge on the nitrogen, sulfur, or oxygen atom, respectively (Scheme 3). The subsequent decomposition of that ion with expulsion of C_4H_6O or C_4H_8N molecule leads to an even-electron ion with *m*/*z* 100 (**D** or $\mathbf{D}_1$), while elimination of sulfur gives ion **G** with *m*/*z* 138. However, the base peak in the mass spectrum has an *m*/*z* value of 55; the corresponding ion is also formed by fragmentation of $[M - Me]^+$ (*m*/*z* 170) and is likely to have the structure of 3-methyl-2*H*-azirene (radical cation **H**).

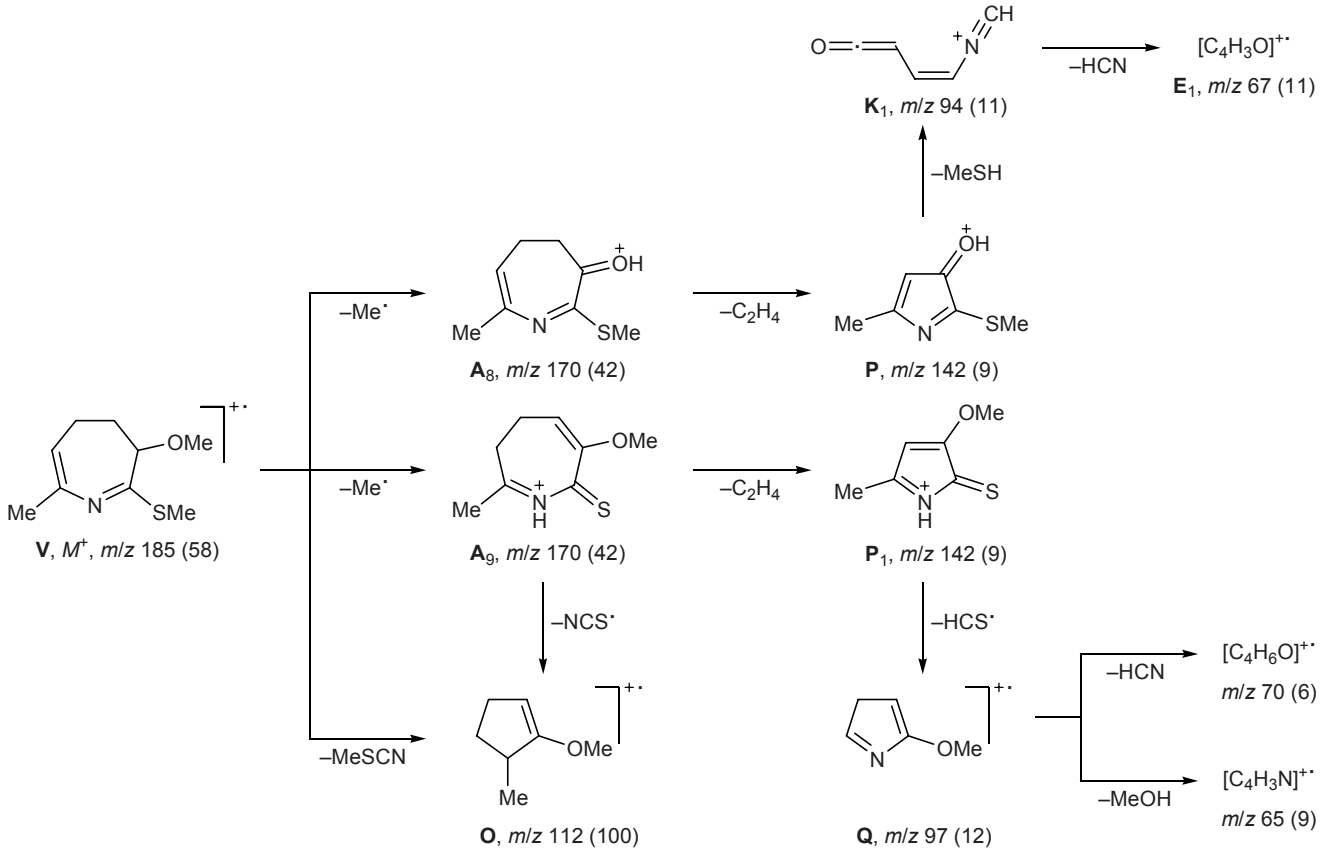
As in the fragmentation of pyrrole **III**, a comparable contribution to the decomposition of 2,3-dihydropyridine molecular ion is provided by abstraction of methyl radical from the methoxy group; the positive charge in ion $\mathbf{A}_6$ thus formed is localized on the oxygen atom (Scheme 4). This follows from the presence in the mass spectrum of peaks belonging to ions **J**–**N**, which result from fragmentation of $[M - Me]^+$ (*m*/*z* 170). Presumably, elimination of MeSH molecule (ion **J**, *m*/*z* 122), which was not observed previously in the fragmentation of 2,3-dihydropyridines [1], is favored by the presence of a labile hydrogen atom on the oxygen in $\mathbf{A}_6$. Further decomposition of ion **J** (*m*/*z* 122) involves extrusion of CO (ion **K**), C_3H_2O (ion **L**), or MeCN molecule (ion **M**), indicating that azepine structure $\mathbf{I}_1$ of the ion with *m*/*z* 122 is most probable.

The base peak (*m*/*z* 55; Scheme 3) in the mass spectrum of 2,3-dihydropyridine **IV** may also result from decomposition of ion $\mathbf{A}_6$ which is formed by cleavage of the C–O bond in the molecular ion (Scheme 4). In this case, the ion with *m*/*z* 55 may have structure $\mathbf{H}_1$ (elimination of 2,2-dimethyl-3-methylsulfanyl-2*H*-azirene molecule from $\mathbf{A}_6$).

Also, the formation of ion with *m*/*z* 170 via abstraction of methyl radical from the heteroring (ion $\mathbf{A}_7$) cannot be ruled out. The driving force of that fragmentation pathway of the molecular ion of 2,3-dihydropyridine **IV** may be aromatization of the heteroring. However, no ions that could be formed via decomposition of $\mathbf{A}_7$ were detected in the mass spectrum. A probable reason is either high stability of $\mathbf{A}_7$ which is quite natural or its low concentration; in both cases, the contribution of this fragmentation pathway to the total ion current is insignificant.

Apart from the above ions, the mass spectrum of **IV** contained low-intensity peaks corresponding to $[M - OMe]^+$ (*m*/*z* 154, 1%) and probably $[M - SMe]^+$ ions ($\mathbf{G}_1$, *m*/*z* 138, 8%). As we already noted, ion **G**

Scheme 5.

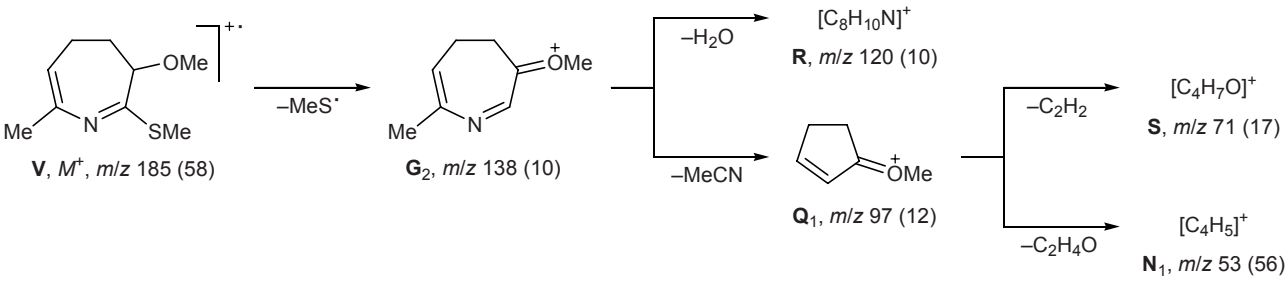


with *m*/*z* 138 may result from expulsion of sulfur from ion $\mathbf{A}_3$ (*m*/*z* 170) as shown in Scheme 3).

It should be noted that fragmentation of the molecular ion of 5-(1-ethoxyethoxy)-6-methylsulfanyl-2-methoxy-2,3-dihydropyridine having an acetal moiety [OCH(Me)OEt] on C^5 instead of methoxy group at ionization energies of 12 and 60 eV (temperature range 50 to 250°C) includes two main pathways: (1) dissociation of the C–O bonds in the acetal fragment, leading to oxonium ions with *m*/*z* 73, and (2) unexpectedly easy MacLafferty rearrangement with elimination of ethoxyethene molecule (neither dihydropyridines nor acetals were reported previously to undergo fragmentation along that pathway), leading to a ion with *m*/*z* 173. Above 170°C, elimination of methanol molecule from the molecular ion of 5-(1-ethoxyethoxy)-2,3-dihydropyridine gives rise to aromatic pyridine structure [1].

The mass spectrum of 4,5-dihydro-3*H*-azepine **V** sharply differs from those typical of compounds **III** and **IV**. The base peak in the spectrum of **V** belongs to an odd-electron ion with *m*/*z* 112 (**O**) which may arise from both expulsion of NCS radical from $[M - Me]^+$ (*m*/*z* 170) and elimination of MeSCN molecule directly from the molecular ion (Scheme 5). No corresponding ion peak was detected in the mass spectra of pyrrole **III** and dihydropyridine **IV**. The $[M - Me]^+$ ion (which is common for all isomeric compounds **III**–**V**) in the spectrum of **V** is less abundant [$\mathbf{A}_8$ or $\mathbf{A}_9$, *m*/*z* 170 (46%)] than those derived from its five- and six-membered analogs. Abstraction of methyl radical from the methoxy group gives ion $\mathbf{A}_8$ having a labile hydrogen atom, but no $[\mathbf{A}_8 - MeSH]^+$ ion peak with *m*/*z* 122, which is typical of 2,3-dihydropyridine **IV**, was present in the mass spectrum of 4,5-dihydro-3*H*-azepine **V**. Elimination of ethylene molecule is thermodynamically more favorable [13] than expulsion of MeSH. Therefore, the subsequent transformation of $[M - Me]^+$, apart from elimination of NCS radical with formation of ion **O**, involves contraction of the seven-membered ring to five-membered (ions **P** and $\mathbf{P}_1$ with *m*/*z* 142). It is interesting that, unlike seven-membered ion $\mathbf{A}_8$, five-membered ion **P** having a labile hydrogen atom on the oxygen decomposes via elimination of methanethiol molecule (ion $\mathbf{K}_1$). The *m*/*z* values and relative intensities (%) of the other fragment ions are given in Scheme 5.

Scheme 6.



A pathway involving dissociation of the C–SMe bond in the molecular ion with elimination of methylsulfanyl radical should also be noted (Scheme 6). Ion $\mathbf{G}_2$ (*m*/*z* 138) thus formed and products of its subsequent decomposition (ions $\mathbf{N}_1$, $\mathbf{Q}_1$, **R**, and **S**) provide a considerable contribution to the total ion current, in contrast to fragmentation of the molecular ion derived from 2,3-dihydropyridine **IV**, where analogous contribution is insignificant. No such fragmentation pathway was found for pyrrole **III** and pyrroles studied previously [11, 12].

Thus we have found that the fragmentation patterns of molecular ions derived from isomeric heterocyclic compounds **III**–**V** under electron impact strongly differ from each other and that neither molecular nor fragment ions undergo isomerization. The primary decomposition of all isomers involves abstraction of methyl radical, and the subsequent fragmentation of the $[M - \mathrm{Me}]^+$ ions with *m*/*z* 170 is specific for each isomer, which ensures reliable mass spectrometric identification of compounds **III**–**V**.

There are no published data on electron-impact ionization of azatriene systems like **I** and **II**. We were the first to obtain the mass spectra of linear precursors of pyrrole **III**, 2,3-dihydropyridine **IV**, and 4,5-dihydro-3*H*-azepine **V**, i.e., highly reactive isomeric 1-aza-1,3,4-triene **I** and 2-aza-1,3,5-triene **II**. Insofar as 1-aza-1,3,4-triene **I** readily undergoes isomerization (see above) into both pyrrole **III** and 2-aza-1,3,5-triene **II** and electrocyclization of the latter gives 2,3-dihydropyridine **IV** (Scheme 1), GC–MS analysis of thermally unstable compound **I** was performed under as mild temperature conditions as possible (injector and ion source temperature 70–80°C, gas inlet pressure 280 kPa). However, even under these conditions, four peaks were present on the chromatogram with an intensity ratio of 21 : 16 : 30 : 33. The mass spectra of the first two components (retention times 19.9 and 21.7 min) resembled each other and contained no molecular ion peak, while the number of fragment ion peaks was very small. In the mass spectrum of the first component we observed only 4 main ion peaks with *m*/*z* 116 (35%), 74 (100%), 43 (17%), and 41 (15%). Ion peaks with the same *m*/*z* values and approximately similar intensities [*m*/*z* 116 (39%), 74 (100%), 43 (15%), and 41 (14%)] were observed in the mass spectrum of the second component. In addition, a weak ion peak with *m*/*z* 163 (3%) was present in the mass spectrum of the first compound; while the second one displayed a weak $[M - \mathrm{H}]^+$ ion peak with *m*/*z* 184 (2%) and a fairly strong ion peak with *m*/*z* 83 (48%). The mass spectrum of the third component (retention time 27.0 min) completely coincided with the spectrum of 2,3-dihydropyridine **IV** (for details, see above). The fourth component of the mixture of thermolysis products of 1-aza-1,3,4-triene **I** (retention time 27.3 min) showed in the mass spectra ion peaks with *m*/*z* values of 185 (9%) and lower [*m*/*z* 39 (20%), 41 (28%), 43 (39%), 55 (16%), 65 (8%), 74 (100%), 97 (56%), 116 (48%), 170 (14%)], as well as two peaks whose *m*/*z* values exceeded 185 [*m*/*z* 198 (2%) and 213 (3%)], indicating that a reaction occurred between the thermolysis products.

Increase of the injector and ion source temperature to 250°C and reduction of the carrier gas pressure to 100 kPa leads to appearance of 11 peaks on the chromatogram. This means that 1-aza-1,3,4-triene **I** or its isomer, as well as their thermolysis products, undergo profound thermal decomposition. The relative intensity of the first two peaks on the chromatogram decreased to 8 and 2%, respectively, while the fraction of dihydropyridine **IV** increased to 43%. The overall intensity of chromatographic peaks corresponding to the other thermolysis products was 47%.

In no case pyrrole **III** was detected among the thermolysis products. Therefore, we presumed that under chromatographic conditions 1-aza-1,3,4-triene **I** undergoes fast and quantitative isomerization into azatriene **II** and that the mass spectrum of product leaving the column first is not the spectrum of **I**. Our previous

experimental data [4] confirm that the rate of [1,5]-sigmatropic rearrangement of compound **I** into **II** considerably exceeds the rate of its concurrent cyclization to pyrrole **III**. Evacuation of 1-aza-1,3,4-triene **I** for 3 min at 60°C (bath temperature) gave a mixture of products containing ~70% of 2-aza-1,3,5-triene **II**, ~30% of unisomerized 1-aza-1,3,4-triene **I**, and only traces of pyrrole **III**. By heating compound **I** for 5 min at the same temperature we obtained 2-aza-1,3,5-triene **II** containing 11% of pyrrole **III** (according to the NMR data). Quick heating of 1-aza-1,3,4-triene **I** to ~145°C was accompanied by exothermic electrocyclization (the temperature rose to ~190°C) with formation of a mixture of dihydropyridine **IV** and pyrrole **III** at a ratio of ~85 : 15.

The formation of dihydropyridine **IV** in the injector while recording mass spectrum of 1-aza-1,3,4-triene **I** may be regarded as a necessary but insufficient proof for the assumption that one of the first two chromatographic peaks belongs to 2-aza-1,3,5-triene **II**. Gas chromatographic–mass spectrometric analysis of an authentic sample of 2-aza-1,3,5-triene **II** under analogous conditions did not allowed us to unambiguously determine whether its peak was present on the chromatogram or not. It should be noted that both the chromatogram containing 4 peaks and the corresponding mass spectra were identical to those observed for 1-aza-1,3,4-triene **I**. First of all, these findings indicate the absence of 1-aza-1,3,4-triene **I** peak on the chromatogram obtained from compound **I**. Second, all the above thermolysis products are most likely to result from thermally induced transformations of 2-aza-1,3,5-triene **II** (formed via isomerization of **I**) rather than from 1-aza-1,3,4-triene **I** itself. We can conclude that special conditions should be found to record the mass spectra of azatriene systems like **I** and **II** provided that this is possible at all.

EXPERIMENTAL

Methyl *N*-isopropyl-2-methoxybuta-2,3-dienimidothioate (**I**), 2-methoxy-*N*-(1-methylethylidene)-1-methylsulfanylbuta-1,3-dien-1-amine (**II**), 1-isopropyl-3-methoxy-2-methylsulfanylpyrrole (**III**), 5-methoxy-2,2-dimethyl-6-methylsulfanyl-2,3-dihydropyridine (**IV**), and 3-methoxy-7-methyl-2-methylsulfanyl-4,5-dihydro-3*H*-azepine (**V**) were synthesized according to the procedures described in [4, 8, 9].

The mass spectra (electron impact, 70 eV) of compounds **I**–**V** were recorded on a Shimadzu GCMS-QP5050A instrument (quadrupole mass analyzer, a.m.u. range 34–650). Chromatographic 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, split ratio 1 : 2; injection volume 1 μl. The temperature conditions were varied, depending on the sample: 1-aza-1,3,4-triene **I** and 2-aza-1,3,5-triene **II**: injector and ion source temperature 70–80°C, gas inlet pressure 280 kPa, oven temperature programming from 40 to 80°C at a rate of 5 deg/min; pyrrole **III**, 2,3-dihydropyridine **IV**, and 4,5-dihydro-3*H*-azepine **V**: injector and ion source temperature 120–130°C; gas inlet pressure 280 kPa, oven temperature programming from 60 to 130°C at a rate of 10 deg/min.

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