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Mass Spectra of New Heterocycles: VIII.* Fragmentation of 6-Alkoxy- and 6-Aryl(hetaryl)-3*H*-azepines under Electron Impact

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Abstract—The electron impact mass spectra of previously unknown 2-alkyl-6-alkoxy-, 2,3-trimethylene-6-alkoxy- and 2-alkyl-6-aryl(hetaryl)-3*H*-azepines were studied. All compounds give rise to stable molecular ions (I_{rel} = 44–100%) whose fragmentation pattern is determined mainly by the substituent on C^6. Decomposition of the molecular ions derived from 6-alkoxy derivatives (R^1 = MeO, EtO, *i*-PrO) follows general relations typical of alkyl ethers. The main characteristic peaks in the mass spectra of 2-methyl-6-aryl- and 2-methyl-6-hetaryl-3*H*-azepines (R^1 = Ph, 1*H*-pyrrol-1-yl, 5-methylthiophen-2-yl) belong to even-electron rearrangement ions $[M - H]^+$ and $[M - Me]^+$, which have conjugated bi- and tricyclic structures, and products of their subsequent decomposition. Substituents in positions *2* (R^2) and *3* (R^4) [R^4 = H, R^2 = Me, Et; $R^2R^4 = (CH_2)_3$] bring some specificity to the fragmentation pattern, but their contribution is not crucial.

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Azepines and their derivatives constitute structural fragments of many biologically active compounds of both natural and synthetic origin and are widely used both in chemistry (including industrial applications, e.g., in the manufacture of nylon) and in medicine and pharmacology (as drugs for the treatment of various psychic disorders, oncological diseases, and AIDS) [2]. In addition, compounds of the azepine series are convenient models for studying various theoretical problems, in particular those related to stereochemistry [3], valence isomerism [4], aromaticity/antiatiaromaticity [5], etc. Therefore, all aspects of the chemistry of seven-membered nitrogen-containing heterocycles, including their synthesis, structure, properties, and applications, attract increased interest of specialists working in different fields of science [2–5].

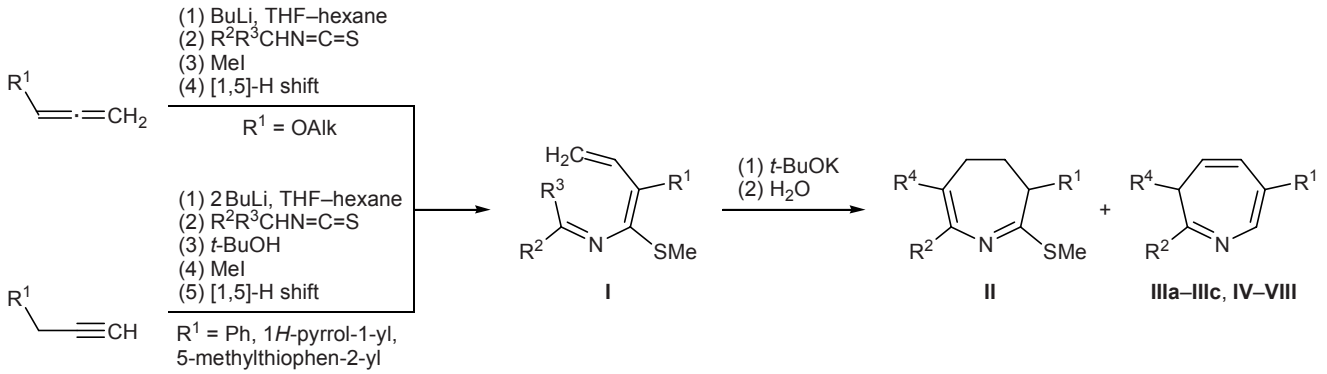
While performing systematic studies on reactions of unsaturated carbanions with heterocumulenes as a new strategy for building up C–C, C–N, C–O, and C–S bonds [6], we recently proposed a novel approach ensuring simple and convenient assembly of nitrogen-containing heterocycles from accessible allenes or alkynes and isothiocyanates. 2-Aza-1,3,5-trienes **I**, which are readily prepared from allenic or acetylenic carbanions and aliphatic isothiocyanates, were found to undergo smooth transformation by the action of potassium *tert*-butoxide into previously unknown (and inaccessible by other methods) 7-methylsulfanyl-4,5-dihydro-3*H*-azepines **II** and 6-alkoxy-, 6-phenyl-, 6-(1*H*-pyrrol-1-yl)-, or 6-(5-methylthiophen-2-yl)-3*H*-azepines **III**–**VIII**, whose ratio depended on the structure of the linear precursor and reaction conditions (Scheme 1) [7]. Compounds **II**–**VIII** were isolated as individual substances by column chromatography and were characterized by IR and NMR spectra.

In the preceding communication [1] we reported for the first time on the mass spectra of a representative series of previously inaccessible 3,7-di- and 3,6,7-trisubstituted 2-methylsulfanyl-4,5-dihydro-3*H*-azepines **II** which were synthesized according to Scheme 1. We found that the fragmentation pattern of the examined 4,5-dihydro-3*H*-azepines under electron impact is determined mainly by the nature of substituent (OAlk, Ph, 1*H*-pyrrol-1-yl) in position *3* of the azepine ring.

Analysis of published data showed that almost no systematic studies on the mass spectra of azepines

* For communication VII, see [1].

Scheme 1.



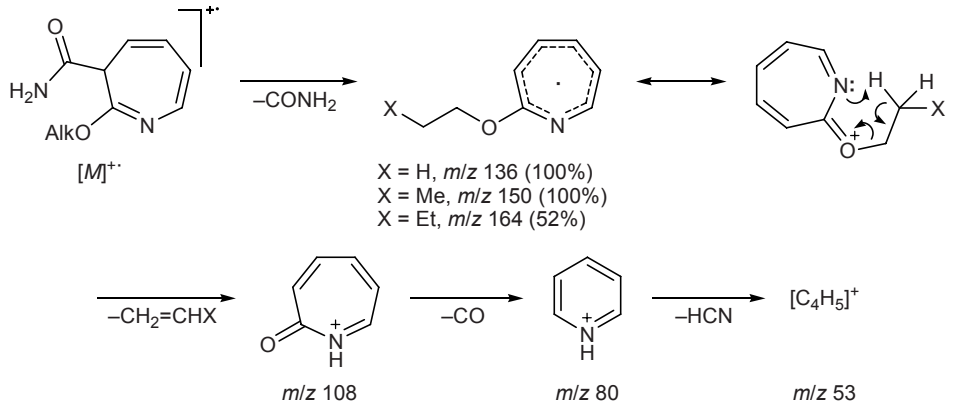
III, R^1 = OMe, R^4 = H, R^2 = Me (**a**), Et (**b**), $R^2R^4 = (CH_2)_3$ (**c**); **IV**–**VIII**, R^2 = Me, R^4 = H; **IV**, R^1 = EtO; **V**, R^1 = *i*-PrO; **VI**, R^1 = Ph; **VII**, R^1 = 1*H*-pyrrol-1-yl; **VIII**, R^1 = 5-methylthiophen-2-yl.

were performed. The available data are very scanty, and they are concerned mainly with 1*H*-azepines [8]. NIST/EPA/NIH Mass Spectral Database contains the spectra of 2-methoxy- and 2-(2,2-dimethylpropoxy)-3*H*-azepines. Fragmentation of the molecular ions of 2-alkoxy-3*H*-azepine-3-carboxamides (Alk = Me, Et, Pr, Bu) under electron impact was briefly noted in [9]. According to [9], the main fragmentation channel involves loss of carbamoyl radical with formation of azatropylium ions which are the most abundant in the spectra of ethoxy and propoxy derivatives (Scheme 2). The subsequent elimination of alkene gives common ion with *m*/*z* 108 and is accompanied by successive expulsion of carbon(II) oxide and hydrogen cyanide molecules. The mass spectrum of 2-methoxy-3*H*-azepine-3-carboxamide differed from the spectra of other alkoxy derivatives. Obviously, the reason is that elimination of CH_2 species is unfavorable from the energy viewpoint. Instead, expulsion of CO molecule directly from the azatropylium ion (*m*/*z* 122) is observed. The standard mass spectrum of 2-methoxy-3*H*-azepine (Mass Spectral Database) includes the following ion peaks, *m*/*z*: 123 $[M]^{+\cdot}$ (base peak), 108 $[M - Me]^+$, 122 $[M - H]^+$, 80 $[M - Me - CO]^+$, 53 $[C_4H_5]^+$. The most abundant ion in the mass spectrum of 2-(2,2-dimethylpropoxy)-3*H*-azepine is $[M - C_5H_{10}]^{+\cdot}$ (*m*/*z* 109); this ion then loses CO molecule to give ion with *m*/*z* 81.

In continuation of our systematic studies on the mass spectra of new heterocycles prepared from lithiated allenes or alkynes and isothiocyanates [1, 10, 11], in the present work we examined for the first time the behavior of a wide series of previously unknown 6-alkoxy-, 6-phenyl-, 6-(1*H*-pyrrol-1-yl)-, and 6-(5-methylthiophen-2-yl)-3*H*-azepines **III**–**VIII** under electron impact (70 eV).

The molecular ions of 3*H*-azepines **III**–**VIII** possess two possible centers for localization of positive charge and unpaired electron. One of these is the nitrogen atom in the azepine ring, and the other is π-electron system and/or heteroatom in the substituent on C^6, i.e., oxygen atom in the alkoxy group of **IIIa**–**IIIc**, **IV**, and **V** or phenyl, pyrrolyl, or thienyl ring in com-

Scheme 2.



Scheme 3.

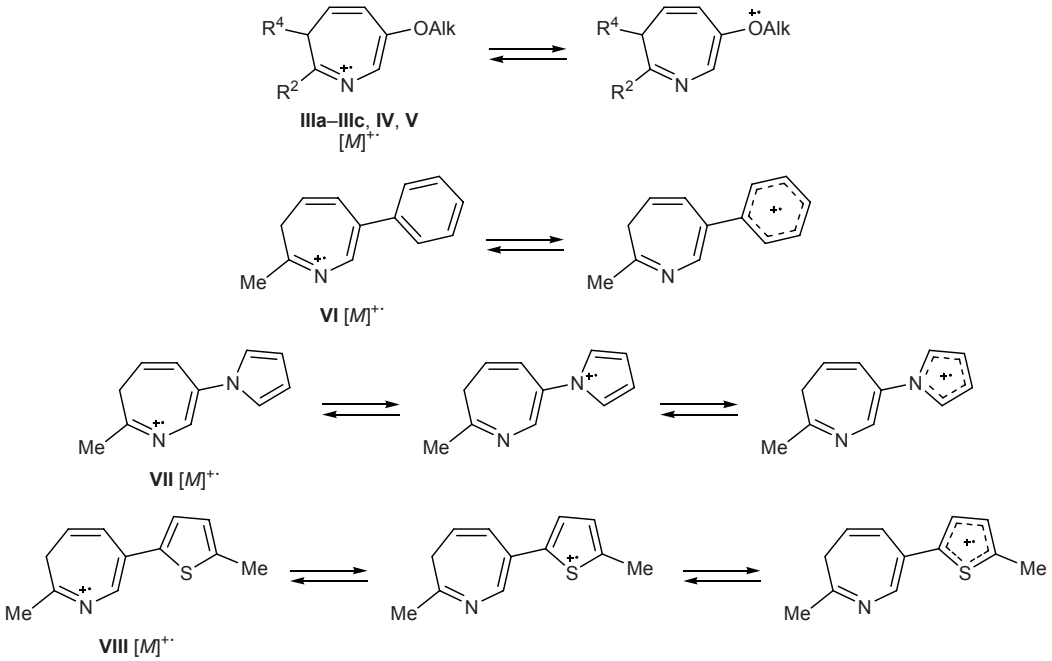
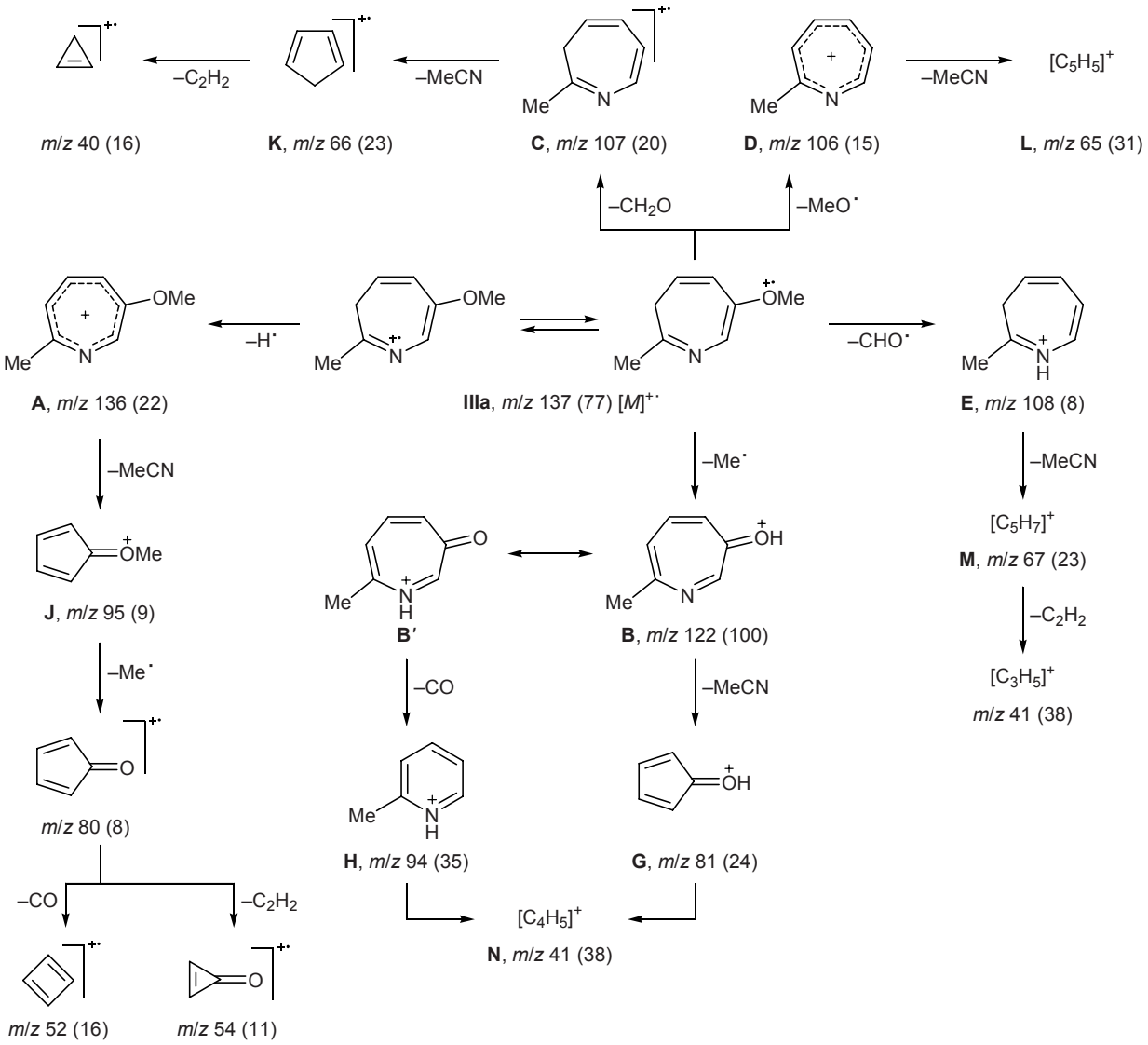


Table 1. Characteristic ions in the mass spectra of 6-alkoxy-3*H*-azepines **IIIa**–**IIIc**, **IV**, and **V**

Ion		*m/z* (I_{rel}, %)				
		IIIa	**IIIb**	**IIIc**	**IV**	**V**
	$[M]^{+\cdot}$	137 (77)	151 (46)	163 (77)	151 (44)	165 (51)
A	$[M - H]^+$	136 (22)	150 (18)	162 (100)	–	–
B	$[M - Alk]^+$	122 (100)	136 (100)	148 (71)	122 (48)	122 (40)
C	$[M - C_nH_{2n}O]^{+\cdot}$	107 (20)	121 (18)	133 (11)	107 (15)	107 (12)
D	$[M - AlkO]^+$	106 (15)	120 (9)	132 (38)	–	–
E	$[M - C_nH_{2n-1}O]^+$	108 (8)	122 (9)	134 (12)	108 (9)	108 (21)
F	$[M - C_nH_{2n}]^{+\cdot}$	–	123 (34)	135 (17)[a]	123 (15)	123 (98)
G	$[\mathbf{B} - R^2CN]^+$, *m/z* 81	(24)	(7)[b]	–	(23)[c]	(47)[c]
H	$[\mathbf{B} - CO]^+$	94 (35)	108 (31)[d]	120 (28)[e]	94 (69)[f]	94 (100)[f]
J	$[\mathbf{A} - R^2CN]^+$, *m/z* 95	(9)	(16)	–	(18)[g]	(56)[g]
K	$[\mathbf{C} - R^2CN]^{+\cdot}$, *m/z* 66	(23)	(14)	(8)[h]	(15)	(15)
L	$[\mathbf{D} - R^2CN]^+$, *m/z* 65	(31)	(27)	(29)[h,i]	(29)[g]	(40)[g]
M	$[\mathbf{E} - R^2CN]^+$, *m/z* 67	(23)	(41)	(23)[h]	(20)[j]	(23)[j]
N	$[\mathbf{H} - R^2CN]^+$ or $[\mathbf{G} - CO]^+$, *m/z* 53	(89)	(27)[b]	(13)[h]	(71)	(70)

[a] This ion may originate from decomposition of both heteroring and carbocycle (Scheme 6, ions **O** and **F**).
[b] The other ways of formation of this ion are shown in Scheme 5.
[c] Odd-electron ion $[\mathbf{C} - C_2H_2]^{+\cdot}$ (2-methylpyrrole) has the same *m/z* value (Scheme 7).
[d] Ion with *m/z* 108 is formed via successive elimination of C_2H_4 and Me$^{\cdot}$ (or vice versa) from $[M]^{+\cdot}$ (Scheme 5, ions $\mathbf{B}_1$ and $\mathbf{B}'_1$).
[e] The other ways of formation of ions with *m/z* 120 are shown in Scheme 6.
[f] Ion $[\mathbf{F} - CHO]^+$ has the same *m/z* value (Scheme 7).
[g] Taking into account that no ions **A** and **D** are present in the spectra of compounds **IV** and **V**, ions with *m/z* 95 and 65 may result from fragmentation of odd-electron ion **F** (Scheme 7).
[h] This ion has a different origin.
[i] Theoretically possible ways of formation of ions with *m/z* 65 are shown in Scheme 6.
[j] Ions $[\mathbf{H} - HCN]^+$ and $[\mathbf{F} - CO - C_2H_4]^{+\cdot}$ have the same *m/z* value (Scheme 7).

Scheme 4.



pounds **VI**–**VIII**, respectively (Scheme 3). Therefore, decomposition of the molecular ions $[M]^{+\cdot}$ of **III**–**VIII** may follow general relations typical of both azacycloheptatrienes and ethers or aromatic and heteroaromatic compounds. Moreover, quite different fragmentation patterns cannot be ruled out.

As in our previous study on the mass spectra of substituted 4,5-dihydro-3*H*-azepines **II** [1], we initially examined how the substituents in positions *2* (R^2) and *3* (R^4) affect decomposition of 6-methoxy-3*H*-azepines **IIIa**–**IIIc**. Compounds **IIIa**–**IIIc** give rise to fairly stable molecular ions (I_{rel} 46–77%) whose subsequent fragmentation follows five competing pathways with formation of even-electron ions $[M - H]^+$, $[M - Me]^+$, $[M - MeO]^+$, and $[M - CHO]^+$ and odd-electron ion $[M - CH_2O]^{+\cdot}$ (Table 1, Schemes 4–6; the complete mass spectra of these compounds are given in Table 2). Obviously, the fragmentation patterns of **IIIa**–**IIIc** are typical of ethers [12], indicating that the positive charge and unpaired electron are localized mainly on the ether oxygen atom. Among fragmentation pathways typical of azepine structures, only elimination of hydrogen to give ion **A** was observed. The main fragmentation pathway of the molecular ion $[M]^{+\cdot}$ of azepine **IIIa** (Scheme 4) involves expulsion of methyl radical from the methoxy group with formation of ion **B** with *m*/*z* 122 (100%); the latter can exist in the keto form (**B′**), as follows from its further decomposition via elimination of MeCN and CO molecules, leading to ions **G**, **H**, and **N**. In addition, the mass spectrum of

IIIa contained fairly intense ion peaks arising from both cleavage of the C–H and C^6–O bonds (azatropylium ions **A** and **D**, respectively) and rearrangement processes (ions **C** and **E**). The subsequent decomposition of ions **A** and **C**–**E** follows a common pathway involving elimination of MeCN and C_2H_2 molecules (Scheme 4; Tables 1, 2).

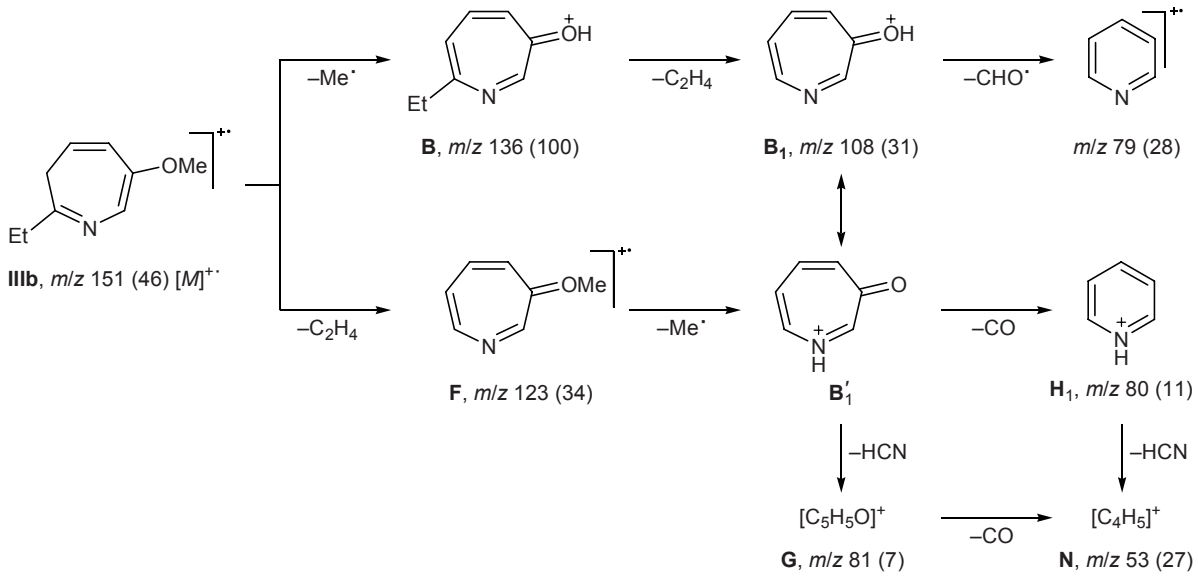
Replacement of the methyl group on C^2 by ethyl does not affect the general fragmentation pattern, except for the appearance of additional decomposition channels typical of alkyl-substituted compounds with an alkyl group longer than methyl [12] (Scheme 5; Tables 1, 2). Thus the mass spectrum of **IIIb** contains peaks of ions resulting from elimination of ethylene molecule from both molecular ion (**F**, *m*/*z* 123) and primary fragment ion **B** (**B**$_1$, *m*/*z* 108). Nevertheless, the main fragmentation channel of the molecular ion of azepine **IIIb** is cleavage of the O–Me bond, leading to ion **B** with *m*/*z* 136 (100%) (Table 1).

On the whole, the fragmentation pattern of tetrahydrocyclopenta[*b*]azepine **IIIc** under electron impact is analogous to those observed for compounds **IIIa** and **IIIb** (Tables 1, 2), though the base peak in the mass spectrum of **IIIc** belongs to azatropylium ion $[M - H]^+$

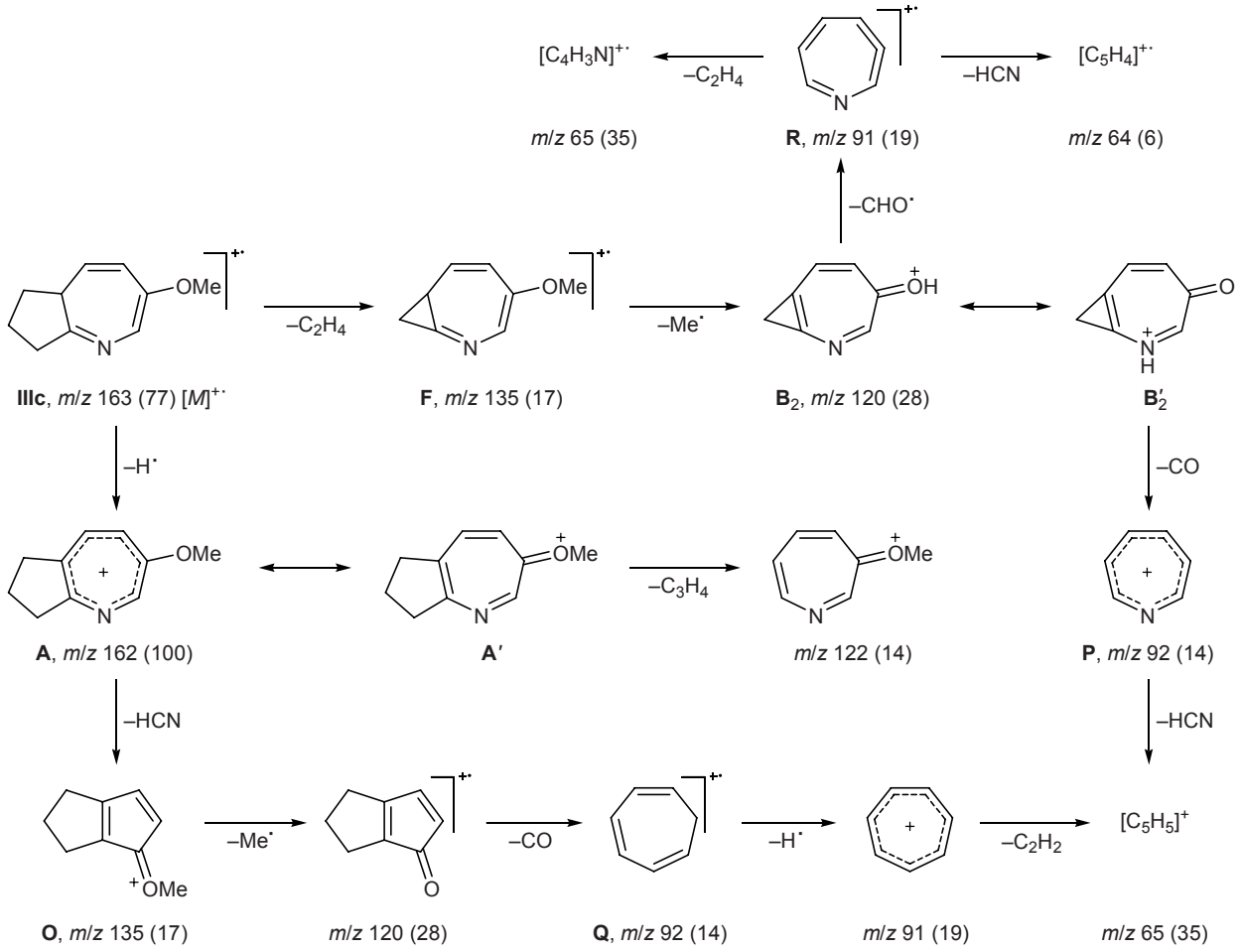
Table 2. Complete mass spectra (electron impact, 70 eV) of 3*H*-azepines **III**–**X**

Compound no.	*m*/*z* (I_{rel}, %)
IIIa	137 (77), 136 (22), 122 (100), 109 (3), 108 (8), 107 (20), 106 (14), 95 (9), 94 (30), 93 (8), 92 (16), 81 (24), 80 (8), 79 (11), 78 (11), 77 (7), 68 (7), 67 (23), 66 (23), 65 (31), 64 (5), 63 (9), 55 (7), 54 (11), 53 (89), 52 (16), 51 (17), 50 (8), 43 (17), 42 (22), 41 (38), 40 (16), 39 (73)
IIIb	151 (46), 150 (18), 137 (15), 136 (100), 126 (6), 124 (6), 123 (34), 122 (9), 121 (18), 120 (9), 109 (10), 108 (31), 107 (11), 106 (24), 95 (16), 94 (12), 93 (13), 92 (7), 91 (7), 81 (7), 80 (11), 79 (28), 78 (10), 77 (22), 71 (12), 68 (8), 67 (41), 66 (14), 65 (27), 63 (6), 58 (10), 57 (7), 56 (20), 55 (16), 54 (11), 53 (27), 52 (18), 51 (24), 50 (10), 44 (17), 43 (53), 42 (21), 41 (59), 40 (15), 39 (50)
IIIc	163 (77), 162 (100), 149 (7), 148 (71), 147 (13), 136 (5), 135 (17), 134 (12), 133 (11), 132 (38), 122 (14), 120 (28), 119 (7), 118 (19), 117 (9), 109 (5), 93 (7), 92 (14), 91 (19), 79 (9), 78 (10), 77 (21), 66 (8), 65 (35), 64 (6), 63 (11), 59 (6), 53 (13), 52 (12), 51 (20), 50 (8), 42 (7), 41 (19), 40 (8), 39 (47)
IV	151 (44), 136 (11), 123 (15), 122 (48), 108 (9), 107 (15), 95 (18), 94 (69), 92 (6), 82 (32), 81 (23), 80 (10), 79 (5), 78 (12), 68 (6), 67 (20), 66 (15), 65 (29), 64 (5), 63 (8), 55 (17), 54 (24), 53 (71), 52 (16), 51 (17), 44 (5), 43 (18), 42 (35), 41 (46), 40 (21), 39 (100)
V	165 (51), 124 (15), 123 (98), 122 (40), 108 (21), 107 (12), 96 (9), 95 (58), 94 (100), 83 (6), 82 (82), 81 (47), 80 (24), 79 (5), 78 (12), 77 (8), 68 (16), 67 (23), 66 (15), 65 (40), 64 (6), 63 (10), 55 (30), 54 (58), 53 (70), 52 (19), 51 (19), 50 (7), 43 (70), 42 (71), 41 (89), 40 (29), 39 (96)
VI	183 (100), 182 (74), 181 (9), 168 (36), 167 (20), 142 (24), 141 (93), 139 (9), 116 (7), 115 (53), 102 (6), 91 (16), 89 (9), 83 (7), 77 (10), 76 (8), 70 (20), 65 (9), 63 (16), 57 (10), 51 (17), 50 (8), 39 (21)
VII	172 (100), 171 (34), 170 (10), 169 (7), 157 (27), 156 (18), 155 (6), 145 (9), 144 (13), 131 (10), 130 (30), 118 (6), 117 (8), 106 (11), 105 (6), 104 (7), 103 (10), 97 (6), 96 (5), 95 (5), 94 (6), 93 (9), 92 (6), 91 (7), 85 (14), 83 (8), 81 (7), 80 (16), 79 (14), 78 (18), 77 (24), 73 (9), 71 (18), 70 (7), 69 (9), 68 (5), 67 (24), 66 (9), 65 (38), 64 (10), 63 (12), 57 (36), 56 (8), 55 (16), 53 (10), 52 (21), 51 (25), 50 (12), 48 (40), 47 (50), 45 (28), 44 (15), 43 (30), 42 (15), 41 (47), 40 (15), 39 (72)
VIII	203 (100), 202 (73), 189 (5), 188 (28), 187 (11), 173 (8), 170 (6), 162 (6), 161 (20), 147 (11), 144 (5), 135 (6), 134 (6), 129 (8), 128 (22), 127 (6), 121 (10), 115 (11), 111 (6), 101 (20), 97 (6), 91 (10), 79 (6), 78 (7), 77 (16), 74 (6), 71 (8), 69 (12), 67 (5), 65 (9), 63 (12), 59 (16), 57 (5), 53 (9), 52 (5), 51 (19), 50 (7), 45 (24), 42 (10), 41 (11), 39 (36)
IX	139 (100), 138 (8), 124 (53), 106 (14), 98 (22), 97 (44), 93 (26), 92 (30), 80 (24), 79 (4), 67 (20), 66 (10), 65 (47), 53 (19), 45 (30), 39 (75)
X	153 (100), 152 (7), 138 (18), 137 (8), 136 (5), 122 (10), 120 (14), 112 (16), 111 (8), 107 (16), 106 (19), 105 (6), 104 (7), 99 (8), 98 (8), 97 (74), 96 (5), 95 (7), 94 (14), 91 (6), 85 (14), 83 (10), 81 (9), 80 (11), 79 (21), 78 (11), 77 (18), 74 (10), 71 (30), 70 (12), 69 (21), 67 (16), 66 (13), 65 (53), 64 (9), 63 (15), 58 (7), 57 (47), 56 (14), 55 (22), 53 (24), 52 (9), 51 (15), 50 (9), 48 (37), 47 (47), 46 (9), 45 (46), 44 (13), 43 (47), 42 (18), 41 (52), 40 (11), 39 (82)

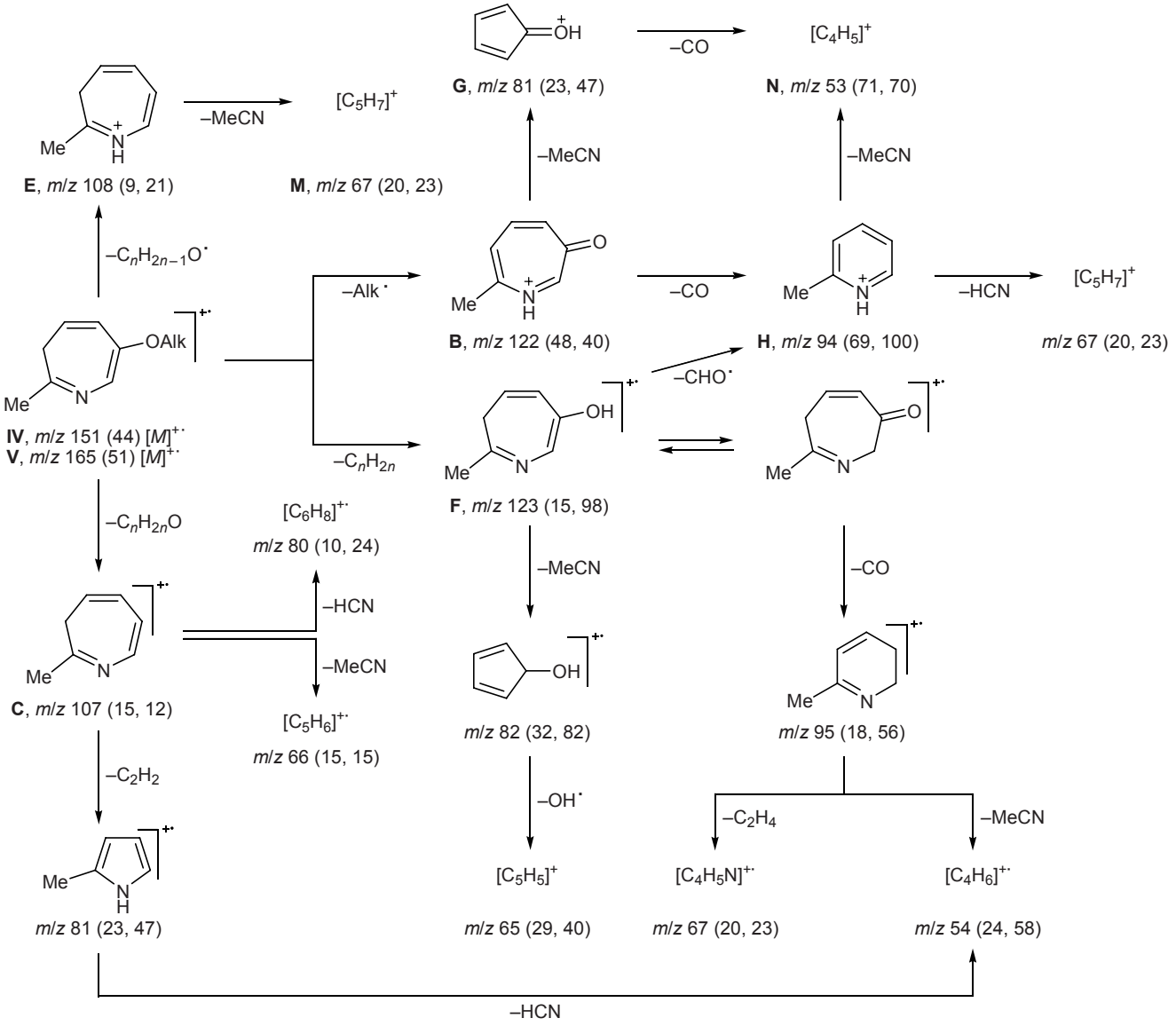
Scheme 5.



Scheme 6.



Scheme 7.



(**A**) (Scheme 6) rather than to **B**. Ion **A** then decomposes via contraction of the azepine ring through elimination of HCN molecule (**O**, *m*/*z* 135) and elimination of C_3H_4 molecule from the cyclopentane fragment to give methoxyazatropylium ion with *m*/*z* 122. Ion **F** with *m*/*z* 135 results from elimination of ethylene from $[M]^{+\cdot}$ due to decomposition of the carbocycle. Successive expulsion of methyl radical and CO molecule from ions **F** and **O** (*m*/*z* 135) leads to azatropylium ion **P** and cycloheptatriene radical cation **Q**, respectively (*m*/*z* 92). The latter is transformed into tropylium ion (*m*/*z* 91) via elimination of hydrogen atom. Both tropylium and azatropylium ions decompose along characteristic channels to give common ion $[C_5H_5]^+$ with *m*/*z* 65 (Scheme 6) [13]. Loss of acetylene molecule by the latter leads to ion $[C_3H_3]^+$ with *m*/*z* 39 (47%). Strong peaks (21–100%) of ions with *m*/*z* 39 were present in the mass spectra of all the examined azepine derivatives.

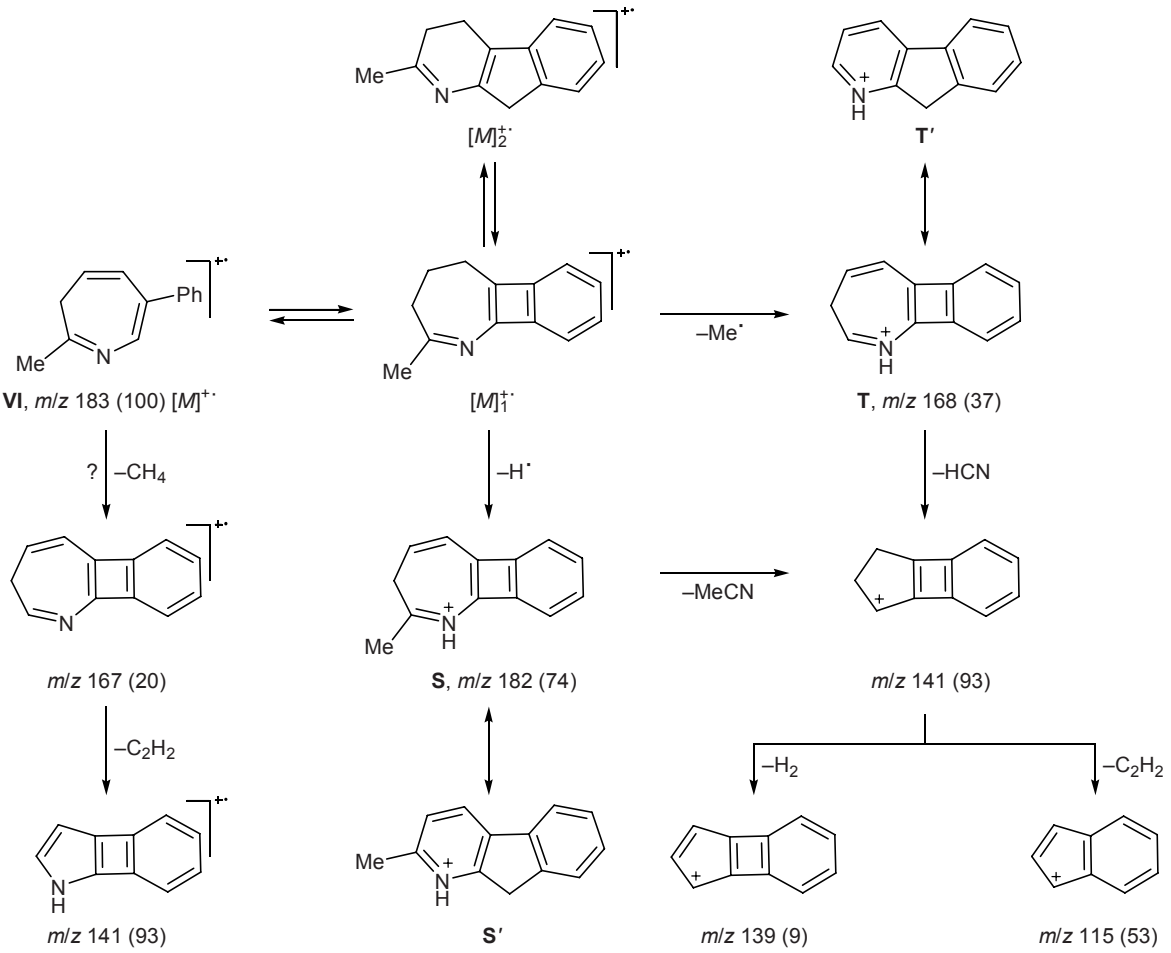
Radical cation **R** is also characterized by an *m*/*z* value of 91 (Scheme 6). It is formed via elimination of CHO radical from $\mathbf{B}_2$. Analogous fragmentation pathway was observed for azepine **IIIb**. Decomposition of **R** via elimination of C_2H_2 and HCN molecules with formation of odd-electron ions $[C_4H_3N]^{+\cdot}$ (*m*/*z* 65) and $[C_5H_4]^{+\cdot}$ (*m*/*z* 64), respectively, is consistent with published data [13].

It follows from the above stated that the fragmentation patterns of the molecular ions of 6-methoxy-3*H*-

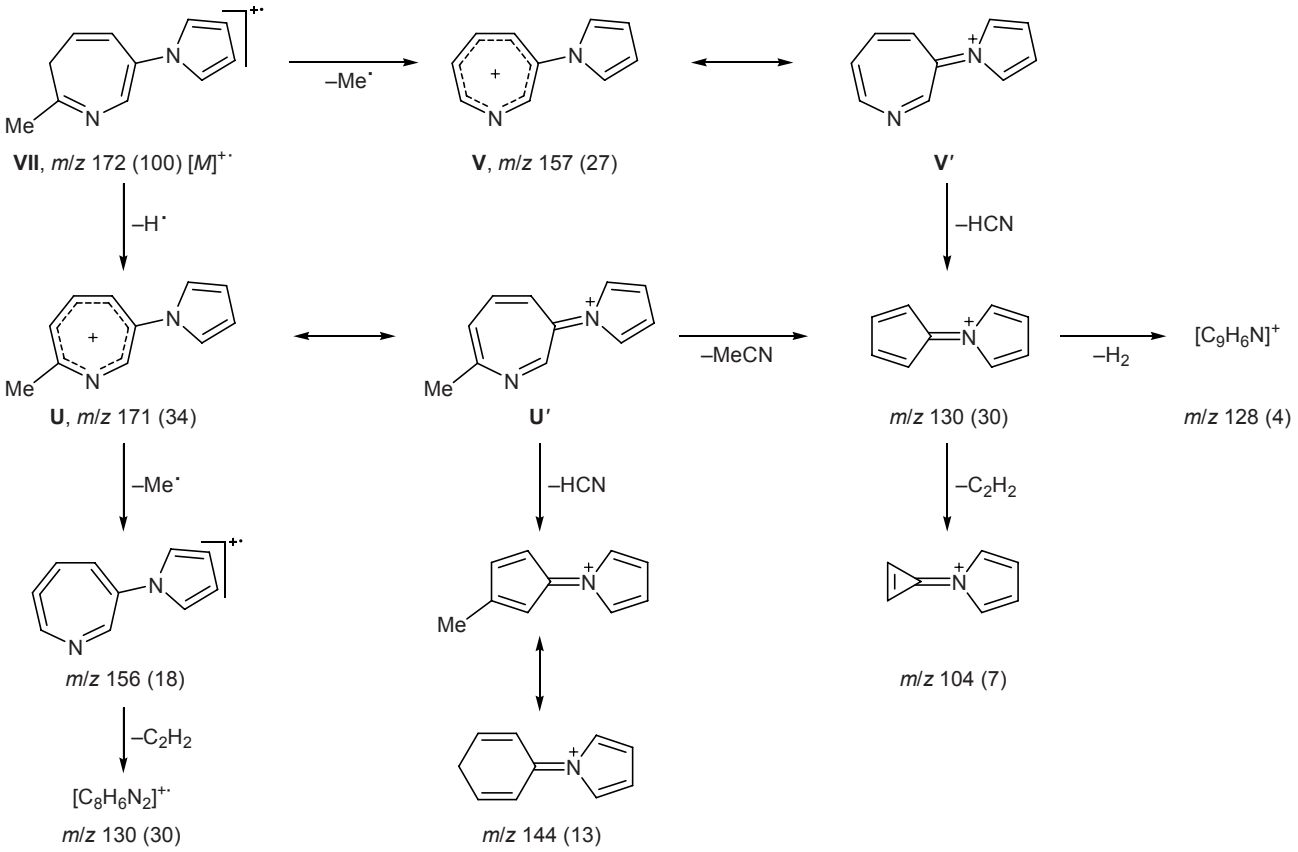
azepines **IIIa**–**IIIc** conform to similar relations and that substituents in positions *2* and *3* of the azepine ring give rise to additional decomposition channels involving primarily elimination of alkene molecules from those substituents (R ≠ Me; Table 1, Schemes 4–6). In addition, the presence of a fused carbocyclic fragment in molecule **IIIc** strongly increases the stability of the corresponding azatropylium ion (**A**) which becomes the most abundant. Fragment ions arising from azatropylium ion **A** give a certain (or even main) contribution to the intensity of ion peaks with the same *m*/*z* values, which are formed along other fragmentation pathways (Scheme 6).

Analysis of the mass spectra of 6-alkoxy-3*H*-azepines **IIIa**–**IIIc**, **IV**, and **V** showed that general relations holding in the decomposition of the molecular ion of 6-methoxy-2-methyl-3*H*-azepine (**IIIa**) are also inherent to 6-ethoxy and 6-isopropoxy analogs **IV** and **V** (Table 1). Fragmentation of the molecular ions derived from compounds **IV** and **V** is also contributed to an appreciable extent by rearrangement processes, though most characteristic fragment ions are formed as a result of simple dissociation of bonds (Scheme 7). As above, elimination of alkyl radical with formation of ion **B** and subsequent loss of CO or MeCN molecule (ions **H** and **G**) constitute the main fragmentation pattern of 6-alkoxy-3*H*-azepines **IV** and **V**. Ion **H** gives the base peak in the mass spectrum of **V**. Increase in the length and size of the alkyl substituent in going from MeO to EtO and *i*-PrO leads to appearance of an additional decomposition channel related to elimination of alkene [9, 12] with formation of odd-electron ion with *m*/*z* 123. The latter is likely to have the structure of 2-methyl-3*H*-azepin-6-ol (**F**, Scheme 7) or its keto tautomer (as follows from the presence of ion peaks with *m*/*z* 95, 82, 67, 65, and 54, which could be formed from ion **F**). Ion **F** is the second abundant in the spectrum of **V** (I_{rel} 98%). On the other hand, pathways leading to ions $[M - H]^+$ (**A**) and $[M - AlkO]^+$ (**D**) are not observed. Presumably, elimination of alkene molecule is energetically more favorable than cleavage of the C–H and C^6–O bonds.

Scheme 8.



Scheme 9.



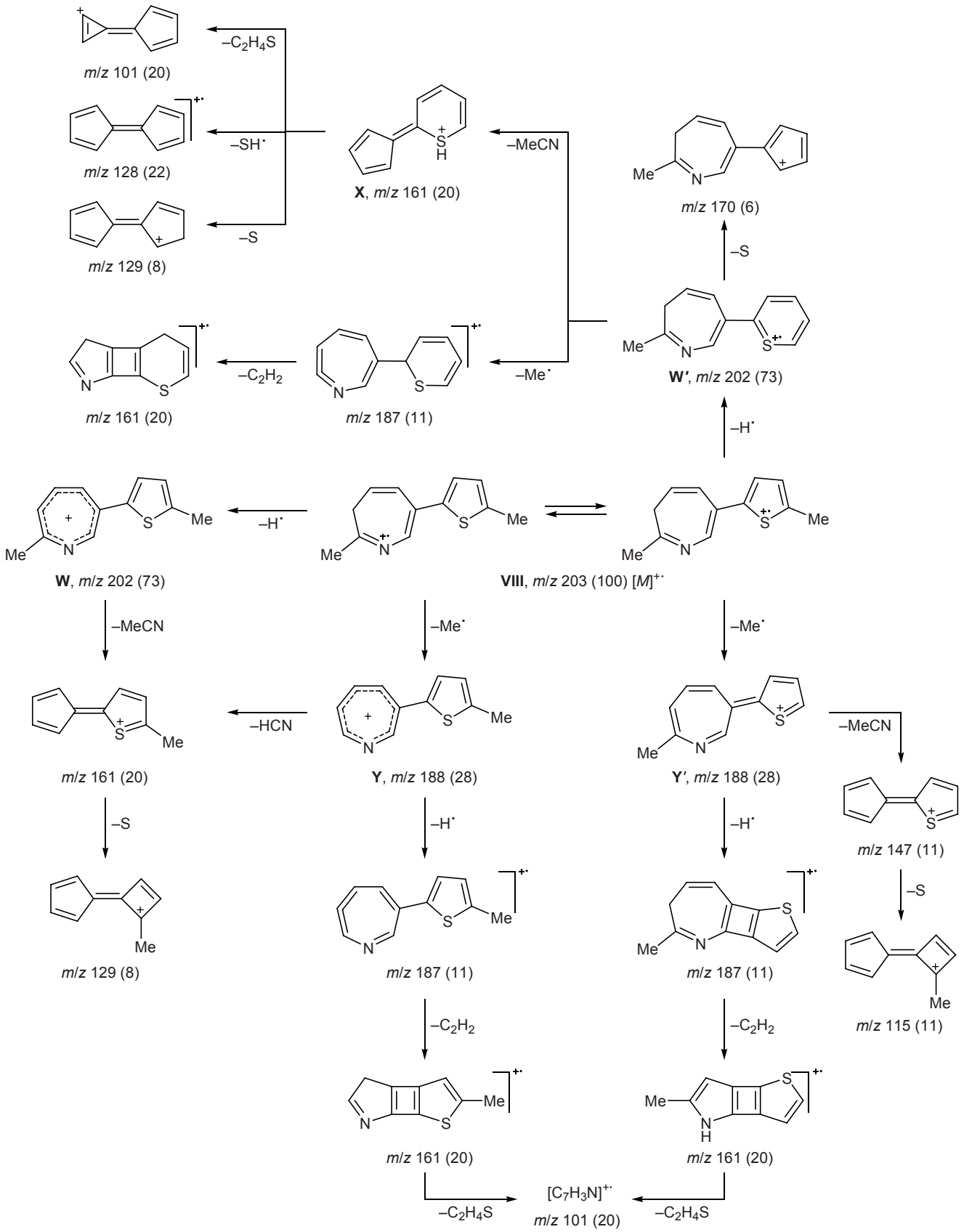
Introduction of an aromatic or heteroaromatic substituent instead of alkoxy group into the 6-position of 2-methyl-3*H*-azepine favors stabilization of positive charge in the corresponding radical cation. As a result, the molecular ion peaks in the mass spectra of 6-phenyl-, 6-(1*H*-pyrrol-1-yl)-, and 6-(5-methylthiophen-2-yl)-2-methyl-3*H*-azepines **VI**–**VIII** have the maximal intensity, and their main fragmentation pathways include elimination of hydrogen atom and methyl radical (Schemes 8–10).

Ionization of phenyl-substituted azepine **VI** is likely to be accompanied by isomerization of the molecular ion into 2-methyl-4,5-dihydro-3*H*-benzo[3,4]-cyclobuta[1,2-*b*]azepine ($[M_1]^{+\cdot}$) and/or 2-methyl-4,9-dihydro-3*H*-indeno[2,1-*b*]pyridine radical cations ($[M_2]^{+\cdot}$), whose fragmentation leads to even-electron 3*H*-benzo[3,4]cyclobuta[1,2-*b*]azepinium (**S** and **T**, respectively) and/or 9*H*-indeno[2,1-*b*]pyridinium ions (**S′** and **T′**) and products of their subsequent decomposition (Scheme 8). Stable conjugated tricyclic structures can also be formed as a result of fragmentation of the unisomerized molecular ion ($[M]^{+\cdot}$) [13].

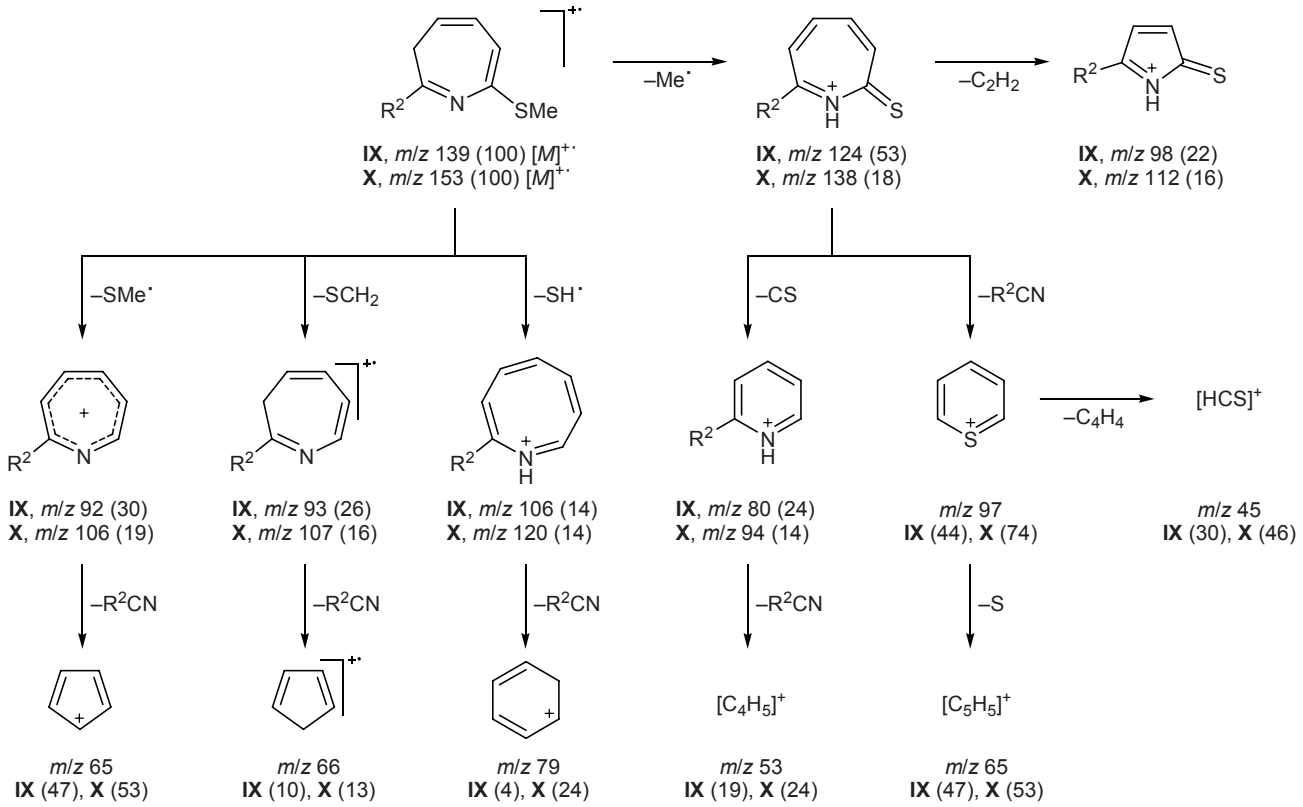
The fragmentation pattern of 2-methyl-6-(1*H*-pyrrol-1-yl)-3*H*-azepine (**VII**) under electron impact is similar to that observed for phenyl-substituted analog **VI** (Scheme 9). In this case, stabilizing effect is exerted by the pyrrole ring which is capable of localizing positive charge on the nitrogen atom to give pyrrolium ion. Analysis of the mass spectrum of thienyl-substituted azepine **VIII** shows that both possible forms of its molecular ion, which charge localization on the nitrogen and sulfur atoms, contribute to the overall fragmentation pattern, i.e., the decomposition of **VIII** fits general relations typical of both azepines and thiophenes (Scheme 10).

Like 6-phenylazepine **VI**, the main fragmentation pathway of the molecular ion of 2-methyl-6-(5-methylthiophen-2-yl)-3*H*-azepine (**VIII**) is elimination of hydrogen atom (Scheme 10). However, apart from hydrogen abstraction from the azepine ring with formation of azatropylium ion **W**, ring expansion rearrangement process typical of alkylthiophenes to give stable thiopyrylium ion **W′** is possible [14]. Elimination of MeCN molecule from **W′** leads to ion **X** with *m*/*z* 161, which can decompose via expulsion of C_2H_4S molecule, sulfur atom, and/or SH radical. In the latter case, odd-electron ion $[C_{10}H_8]^{+\cdot}$ with *m*/*z* 128 is formed. Probably, it has the structure of 1,1′-bi(cyclopenta-2,4-

Scheme 10.


m/z 101 (20)
–C2H4S
m/z 128 (22)
–SH•
m/z 129 (8)
–S
X, m/z 161 (20)
–MeCN
m/z 170 (6)
–S
W′, m/z 202 (73)
–Me•
–H•
m/z 161 (20)
–C2H2
m/z 187 (11)
W, m/z 202 (73)
–H•
VIII, m/z 203 (100) [M]+•
–MeCN
–Me•
–Me•
m/z 161 (20)
–HCN
Y, m/z 188 (28)
Y′, m/z 188 (28)
–MeCN
m/z 147 (11)
–S
–S
–H•
–H•
m/z 129 (8)
m/z 187 (11)
m/z 187 (11)
m/z 115 (11)
–C2H2
–C2H2
m/z 161 (20)
m/z 161 (20)
–C2H4S
[C7H3N]+•
m/z 101 (20)
–C2H4S

Scheme 11.



dien-1-ylidene). Successive elimination of acetonitrile molecule and sulfur atom from ion **W** also leads to ions with *m*/*z* 161 and 129.

Another fragmentation pathway of the molecular ion of 3*H*-azepine **VIII** implies expulsion of methyl radical with formation of ion with *m*/*z* 188 whose subsequent decomposition can follow two competing channels with abstraction of methyl radical from the azepine ring to give azatropylium ion **Y** and from the thiophene ring to produce 2*H*-thiophenium ion **Y′**. Further decomposition of ion **Y′** via successive elimination of MeCN molecule and sulfur atom gives ions with *m*/*z* 147 and 115. In addition, the mass spectrum of **VIII** contains a strong peak from odd-electron ion with *m*/*z* 187, which is likely to have 3-(5-methylthiophen-2-yl)-1-aza-1,3,5,6-cycloheptatetraene, 3-[(2*H*)-thiopyran-2-yl]-1-aza-1,3,5,6-cycloheptatetraene, or 7-methyl-6*H*-thieno[3′,2′:3,4]cyclobuta[1,2-*b*]-azepine structure. This ion arises from abstraction of methyl radical from $[M - H]^+$ or of hydrogen atom from $[M - Me]^+$. Expulsion of acetylene molecule from the ion *m*/*z* 187 leads to stable radical cation with *m*/*z* 161. The latter may be assigned the structure of 5-methyl-4*H*-thieno[2′,3′:3,4]cyclobuta[1,2-*b*]pyrrole, 2-methyl-4*H*-thieno[3′,2′ : 3,4]cyclobuta[1,2-*b*]pyrrole, or 4,5-dihydrothiopyrano[3′,2′:3,4]cyclobuta[1,2-*b*]-pyrrole.

In the mass spectra of azepines **VI**–**VIII** we also observed peaks from ions with *m*/*z* 142 (24), 131 (10), and 162 (6), respectively, which may be formed along the third fragmentation channel, i.e., decomposition of the azepine ring via elimination of MeCN molecule (Table 2). The intensity of the corresponding peak in the spectrum of **VIII** is considerably lower than in the spectrum of **VI**, presumably due to concurrent thiophene-like fragmentation of the molecular ion. Judging by the intensities of fragment ion peaks, the contribution of this pathway to the total ion current is at least comparable with the contribution of the azepine-like fragmentation pathway.

We can conclude that the fragmentation pattern of 3*H*-azepines **III**–**VIII** under electron impact is determined mainly by the nature of substituent on C[6]. The most probable cationic center in the molecular ions of 6-alkoxy-substituted 3*H*-azepines **IIIa**–**IIIc**, **IV**, and **V** is the alkoxy oxygen atom, and their decomposition conforms to general relations typical of alkyl ethers. Aromatic or heteroaromatic substituent in position *6* of the azepine ring favors stabilization of positive charge in the corresponding molecular ions, and their frag-

mentation involves mainly formation of rearrangement ions having conjugated bi- and tricyclic structures. However, unlike 6-phenyl and 6-(1*H*-pyrrol-1-yl) derivatives **VI** and **VII** in which the radical cation center is localized on the azepine nitrogen atom, decomposition of 6-(5-methylthiophen-2-yl)-substituted analog **VIII** is contributed by two forms of the molecular ion with charge localization on both nitrogen and sulfur atoms. As a result, the fragmentation of **VIII** takes pathways typical of both azepines and thiophenes. The effect of substituent in position *2* of the azepine ring is not crucial.

Replacement of the 6-methoxy group by 3-methylsulfanyl strongly increases the stability of molecular ion [1]. For example, the molecular ion peaks in the electron-impact mass spectra of 7-methylsulfanyl-3*H*-azepine (**IX**, R^2 = H) and 2-methyl-7-methylsulfanyl-3*H*-azepine (**X**, R^2 = Me) have the maximal intensity (Scheme 11). Primary decomposition of the molecular ions of both compounds includes elimination of methylsulfanyl radical or its fragments with formation of $[M - MeS]^+$ (azatropylium ion), $[M - CH_2S]^{+\cdot}$, $[M - SH]^+$, and $[M - Me]^+$ ions which then lose R^2CN, C_2H_2, C_4H_4, or CS molecule or sulfur atom. It is obvious that the fragmentation patterns of the molecular ions of azepines **IX** and **X** completely conform to general relations typical of alkyl sulfides [15]. This indicates that the positive charge in the molecular ions of **IX** and **X** is localized on the sulfur atom. Unlike azepines **III** and **VI**–**VIII**, the azatropylium ion peak $[M - H]^+$ in the mass spectra of 7-methylsulfanyl-3*H*-azepines **IX** and **X** has low intensity (7–8%; Table 2).

EXPERIMENTAL

3*H*-Azepines **III**–**VIII** were synthesized according to the procedure described in [7]. 7-Methylsulfanyl-3*H*-azepines **IX** and **X** were formed as a result of elimination of methanol molecule from the corresponding 3-methoxy-2-methylsulfanyl-4,5-dihydro-3*H*-azepines during chromatographic introduction into ion source of mass spectrometer [1].

The electron impact mass spectra (70 eV) of compounds **IIIa**–**IIIc** and **IV**–**X** were measured on a Shimadzu GCMS-QP5050A instrument (quadrupole mass analyzer, a.m.u. range 34–650 Da; SPB-5 capillary column, 60 m × 0.25 mm × 0.25 μm; carrier gas helium, flow rate 0.7 ml/min; ion source and injector temperature 150°C, inlet pressure 300 kPa, oven temperature programming from 60 to 150°C at a rate of 10 deg/min.

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