A New Approach to the Synthesis of Strained Cyclic Systems: II.* Mass Spectrometric Study of 2-Dialkylamino-3-phenyl-thiophenes and Their Structural Isomers, Iminothietanes and Iminocyclobutenes

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Abstract—Triads of isomeric *N*-alkyl-*N*-methyl-3-phenylthiophen-2-amines, *N*-methyl-3-alkyl-4-methylidene-3-phenylthietan-2-imines, and *N*-methyl-4-alkylsulfanyl-2-phenylcyclobut-2-en-1-imines (Alk = Me, Et, Bu) were synthesized from 1,3-dilithio-3-phenylpropyne, methyl isothiocyanate, and alkyl halides, and their fragmentation under electron impact was studied. Primary decomposition of the molecular ions of 2-aminothiophenes is determined by the localization of a radical cation center on the nitrogen atom, and it follows a path typical of alkyl(aryl)amines with elimination of hydrogen atom or methyl or propyl radical from the α-carbon atom in the *N*-alkyl substituent. Fragmentation of the iminothietanes involves cleavage of the four-membered ring in half to give neutral MeNCS molecule and 1-alkyl-1-phenylallene radical cation. Alkylsulfanyl(imino)cyclobutenes undergo cleavage at the sulfur-containing side chain according to general relations holding in the fragmentation of alkyl sulfides.

We recently [2] reported on an unusual reaction of 1,3-dilithiated 3-phenylpropyne with isothiocyanates, which lead to the formation of four-membered iminothietanes and iminocyclobutenes instead of the expected 2-aminothiophenes and 2-alkylsulfanylpyrroles [3]. In the first communication of this series [1] we described in detail the synthesis of structural isomer triads, previously unknown *N*-alkyl-*N*-methyl-3-phenylthiophen-2-amines **Ia–Ic**, 3-alkyl-4-methylidene-2-methylimino-3-phenylthietanes **IIa–IIc**, and *N*-methyl-4-alkylsulfanylcyclobut-2-en-1-imines **IIIa–IIIc**. The isomers were formed from the same precursor, 1,3-dilithio-3-phenylpropyne adduct with methyl isothiocyanate, which was treated in succession with a proton

Scheme 1.

RX = MeI (**a**), EtI (**b**), BuBr (**c**).
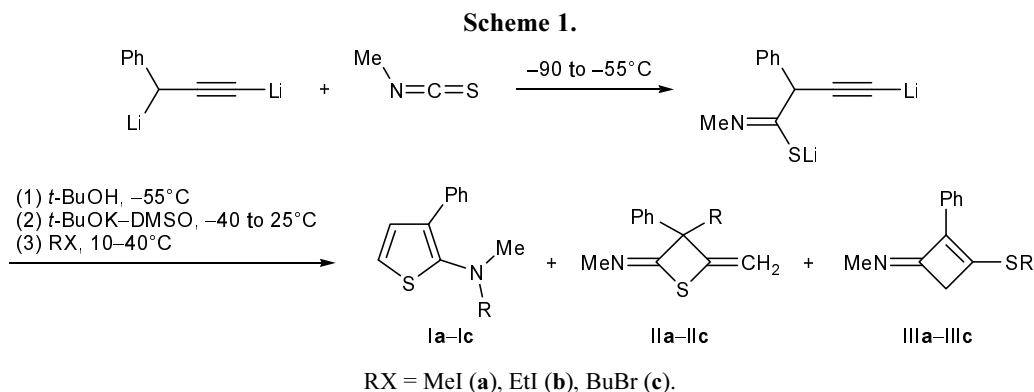
* For communication I, see [1].

donor (*t*-BuOH), base (*t*-BuOK–DMSO), and alkyl halide (MeI, EtI, or BuBr) (Scheme 1).
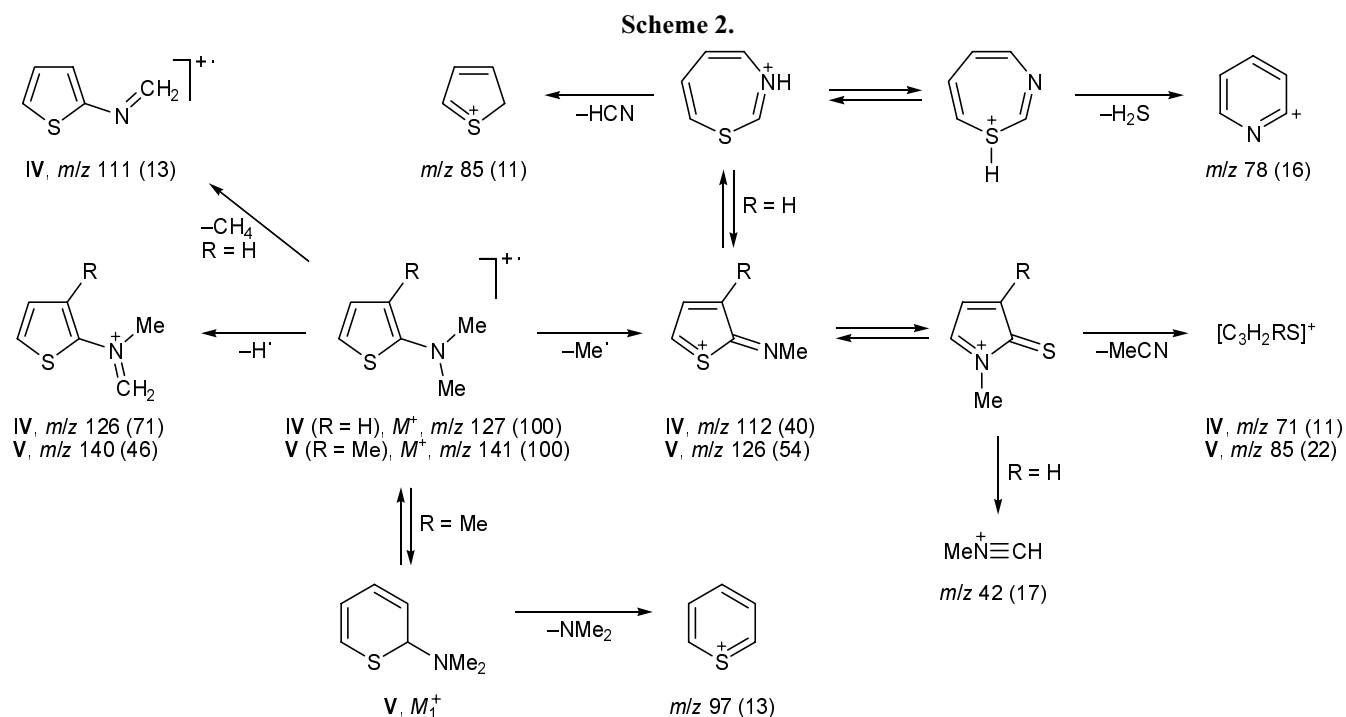
The goal of the present study was to obtain first information on the reactivity of these compounds in the gas phase by mass spectrometry, in continuation of our systematic mass spectrometric studies on hetero- and carbocyclic structures resulting from reactions of unsaturated carbanions with isothiocyanates [4–6].
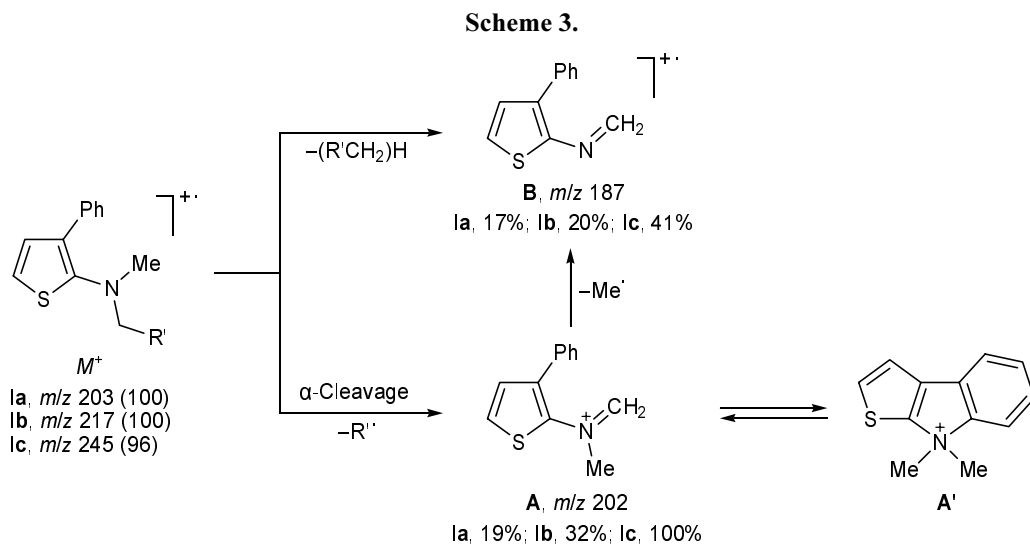
The molecular ions derived from the compounds under study have three centers favorable for localization of positive charge and unpaired electron. These are the nitrogen and sulfur atoms possessing lone electron pairs and π system of the aromatic ring. Therefore, primary fragmentation of the molecular ions may involve cleavage of the C–H, C–C, and C–N bonds in the nitrogen-containing substituent (amine fission), C–S bond (sulfide fission), or four-membered ring (in half; with charge localization on the aromatic fragment). It was necessary to elucidate which of the above decomposition channels will predominate in each case. In addition, we hoped that comparative analysis of the electron-impact mass spectra of structural isomers **I–III** (Tables 1–3) will be useful for understanding mechanisms of their formation.

Prior to our studies [4, 5], there were almost no available published data on the ionization of 2-amino-thiophenes under electron impact. We were the first to examine in detail the mass spectra of unsubstituted [4] and 3- and 5-alkyl-substituted [5] *N*-alkyl-, *N*-phenyl-,

N,N-dialkyl-, and *N*-alkyl-*N*-phenylthiophen-2-amines. The results showed that decomposition of their molecular ions involves competing fragmentation of the heteroaromatic ring (mainly with cleavage of the C^2–S bond) and side chains (alkyl and aminoalkyl). The fragmentation pattern of the side chain depended on its nature and position in the thiophene ring. Primary decomposition of 3-methyl- and 5-methylthiophen-2-amines may be interpreted in terms of both thiophene and isomeric thiopyran structure of the molecular ion [5]. For the sake of convenience, Scheme 2 shows typical fragmentation pathways of *N,N*-dimethylthio-phen-2-amine (**IV**) [4] and *N,N*,3-trimethylthiophen-2-amine (**V**) which are structurally related to 3-phenyl-thiophen-2-amines **Ia–Ic** [5].

Comparison of the mass spectra of model compounds **IV** and **V** [4, 5] (Scheme 2) and 3-phenyl derivatives **Ia–Ic** (Schemes 3–5, Table 1) revealed both common fragmentation pathways and specific features of dissociative ionization of the latter, resulting from the presence of a phenyl group in the thiophene ring. Like aminothiophenes described in [4, 5], the mass spectra of 3-phenylthiophenes **Ia–Ic** contain strong peaks from the molecular ions whose decomposition begins with cleavage of different bonds in the amino group to give common fragment ions with *m/z* 202 (**A**, $[M - R']^+$) and *m/z* 187 (**B**, $[M - RH]^{+\cdot}$ or $[M - R' - Me]^{+\cdot}$); their relative intensity varies from 17 to 100% (Scheme 3). The ion with *m/z* 202 is formed

Scheme 2.

IV, *m/z* 111 (13)   *m/z* 85 (11)   *m/z* 78 (16)

IV, *m/z* 126 (71)   IV (R = H), M^+, *m/z* 127 (100)   IV, *m/z* 112 (40)   IV, *m/z* 71 (11)
V, *m/z* 140 (46)   V (R = Me), M^+, *m/z* 141 (100)   V, *m/z* 126 (54)   V, *m/z* 85 (22)

$MeN^+\equiv CH$
m/z 42 (17)

V, M_1^+ *m/z* 97 (13)

Scheme 3.

via α-cleavage typical of aliphatic amines [7]. Taking into account that it has the same structure (and hence the same stability) for all the examined thiophenes, the observed difference in the peak intensities in the mass spectra of **Ia–Ic** is likely to originate from different strengths of the bonds whose cleavage gives rise to the above ion. As a rule, more abundant are those ions which arise from elimination of heavier radicals [7].

Ion **B** (m/z 187) may be formed via both successive expulsion of R' and CH_3 radicals and elimination of the corresponding alkane (RH) from the molecular ion. The latter process was observed previously in the fragmentation of only dimethylaminothiophene **IV** [4]

(Scheme 2). If both channels leading to ion **B** are operative, the ratio of their contributions should likely to be responsible for the abundance of that ion.
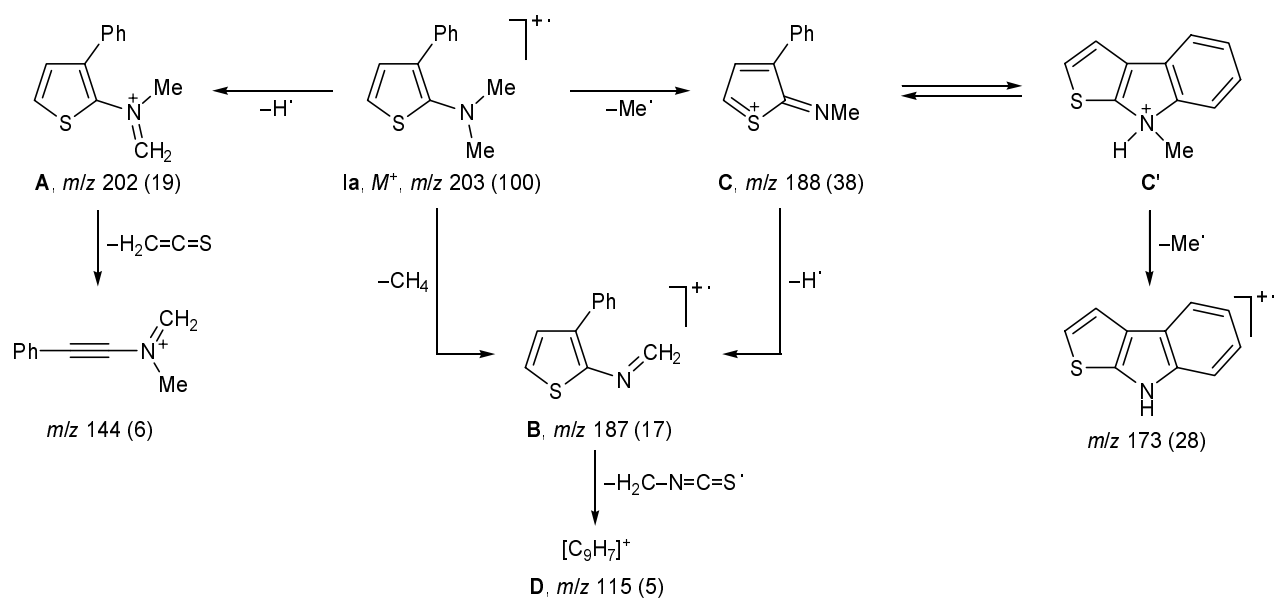
Dissociation of the molecular ions derived from thiophenes **I** is characterized by formation of fragments which can be stabilized via isomerization to polyconjugated tricyclic systems. In the case of ion m/z 202, such a system may be 8,8-dimethyl-8H-thieno-[2,3-b]indol-8-ium ion **A'**. Analysis of the mass spectra of **Ib** and **Ic** recorded at 12 eV confirms the above assumption. These spectra contain a strong ion peak with m/z 202 (I_{rel} 19 and 72%, respectively), indicating that this ion is formed as a result of rearrangement.

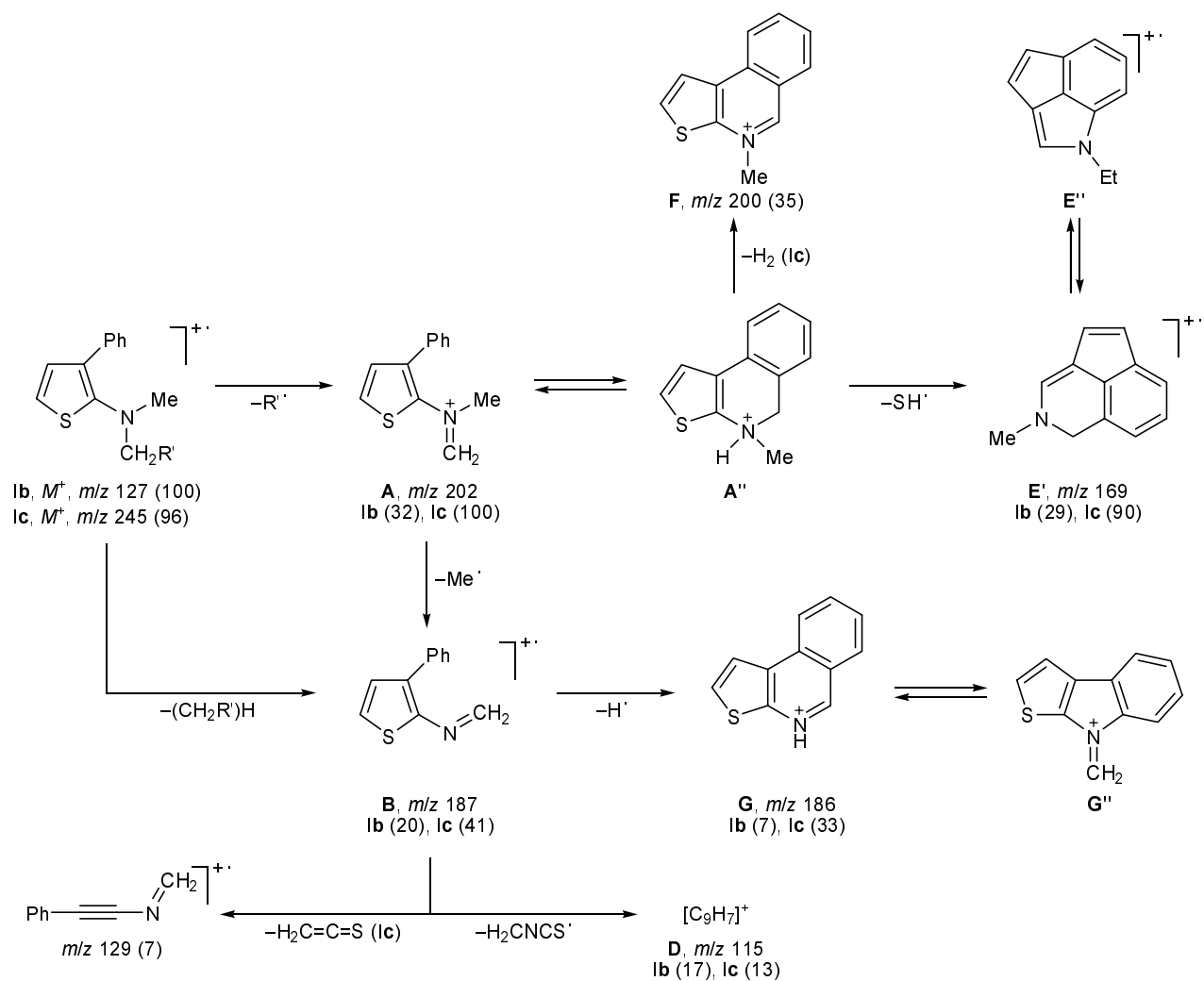**Table 1.** Mass spectra of N,N-dialkyl-3-phenylthiophen-2-amines **Ia–Ic** (60 eV)

Ion	Relative intensity, I_{rel}, %			Ion	Relative intensity, I_{rel}, %		
	Ia	**Ib**	**Ic**[a]		**Ia**	**Ib**	**Ic**[a]
$M^{+\cdot}$	100 (m/z 203)	100 (m/z 217)	96 (m/z 245)	m/z 173 $[M – Me – R]^{+\cdot}$	28	–	14
				m/z 172	–	–	7
A, m/z 202 $[M – R' (H, Me, Pr)]^+$	19	32	100	m/z 168	–	–	14
				m/z 147 $[C_9H_7S]^+$	–	3	6
B, m/z 187 $[M – RH]^{+\cdot}$ or $[A – Me]^{+\cdot}$	17	20	41	m/z 144 $[A – H_2C=C=S]^+$	6	–	–
				m/z 130	6	–	–
C, m/z 188 $[M – R]^+$	38	–	–	m/z 129 $[B – H_2C=C=S]^+$	–	–	7
D, m/z 115 $[B – H_2CNCS]^+$	5	17	13	m/z 100	–	–	18
E, m/z 169 $[A – SH]^{+\cdot}$	2	29	90	m/z 93	–	–	14
F, m/z 200 $[A – H_2]^+$	2	–	35	m/z 89 $[D – C_2H_2]^+$	–	7	–
G, m/z 186 $[B – H]^+$ or $[A – MeH]^+$	5	7	33	m/z 84	–	–	6
				m/z 77 $[C_6H_5]^+$	2	–	9
H, m/z 103 $[C_8H_7]^+$	3	12	6	m/z 45 $[HCS]^+$	2	5	33

[a] 70 eV.

Scheme 4.

A, *m/z* 202 (19)

Ia, *M*⁺, *m/z* 203 (100)

C, *m/z* 188 (38)

C'

−H˙

−Me˙

−H˙

−CH₄

−H˙

−Me˙

−H₂C=C=S

m/z 144 (6)

B, *m/z* 187 (17)

m/z 173 (28)

−H₂C−N=C=S˙

[C₉H₇]⁺

D, *m/z* 115 (5)

Scheme 5.

F, *m/z* 200 (35)

E''

−H₂ (Ic)

−SH˙

Ib, *M*⁺, *m/z* 127 (100)
Ic, *M*⁺, *m/z* 245 (96)

−R˙

A, *m/z* 202
Ib (32), **Ic** (100)

A''

E', *m/z* 169
Ib (29), **Ic** (90)

−(CH₂R')H

−Me˙

B, *m/z* 187
Ib (20), **Ic** (41)

−H˙

G, *m/z* 186
Ib (7), **Ic** (33)

G''

m/z 129 (7)

−H₂C=C=S (Ic)

−H₂CNCS˙

[C₉H₇]⁺

D, *m/z* 115
Ib (17), **Ic** (13)

According to the mass spectra recorded at 60 eV, the most stable among the examined compounds is **Ia**: its molecular ion peak, as in the spectra of $N,N,3$-trimethylthiophen-2-amine (**V**) [5] and N,N-dimethylthiophen-2-amine (**IV**) [4], has the maximal intensity (Scheme 4, Table 1). Probably, the same factor is responsible for the absence of clearly predominating channel in the decomposition of the molecular ion of compound **Ia**. Its main fragmentation pathways fully coincide with those typical of unsubstituted and 3-methyl-substituted analogs **IV** [4] and **V** [5] (Schemes 2, 4). Primarily, these include cleavage of the C–H and C–N bonds in the NMe$_2$ substituent, which is accompanied by elimination of H· and Me· to give ions **A**, m/z 202 $[M - H]^+$ and **C**, m/z 188 $[M - Me]^+$, respectively, as well as expulsion of methane molecule from the molecular ion or hydrogen atom from ion **C**, leading to radical cation **B**, m/z 187 $[M - MeH]^{+\cdot}$ or $[C - H]^{+\cdot}$ (Scheme 4).

However, the contribution of each of the above pathways to the overall fragmentation pattern of the molecular ion of **Ia** strongly differs from the corresponding contributions found for both compounds **IV** and **V** [4, 5] and 3-phenylthiophen-2-amines **Ib** and **Ic**. In the series of 3-phenylthiophen-2-amines **I**, $[M - H]^+$ ion peak was identified only in the mass spectrum of **Ia**, and its intensity (19%) was smaller by factors of ~2.4 and ~3.7 than the intensity of analogous ions in the spectra of $N,N,3$-trimethylthiophen-2-amine (**V**) (46%) [5] and N,N-dimethylthiophen-2-amine (**IV**) (71%) [4], respectively. It should be noted that $[M - H]^+$ is the base peak in the mass spectrum of N,N-dimethylaniline (100%) and that the intensity of the molecular ion peak is ~70% (the intensities of the molecular ion peaks of N-methyl-N-ethyl-, N-methyl-N-propyl-, and N-methyl-N-butylanilines are even smaller, ~30, 25, and 10%, respectively) [8]. In addition, the mass spectrum of N,N-dimethylaniline contains peaks from the following ions: $[M - Me]^+$ (m/z 106, ~20%), $[M - MeH]^{+\cdot}$ (m/z 105, ~20%), $[C_7H_7]^+$ (m/z 91, ~5%), $[C_6H_5]^+$ (m/z 77, ~30%), $[C_4H_3]^+$ (m/z 51, ~18%). Thus it is obvious that N,N-dimethyl-3-phenylthiophen-2-amine (**Ia**) under electron impact behaves as a typical dialkyl(aryl)amine. On the other hand, replacement of the phenyl radical in the latter by thienyl and especially 3-phenylthienyl group sharply enhances the stability of the molecular ion (it is known that molecular ion peaks in the mass spectra of amines rarely have a strong intensity, though they are quite distinguishable) [7].
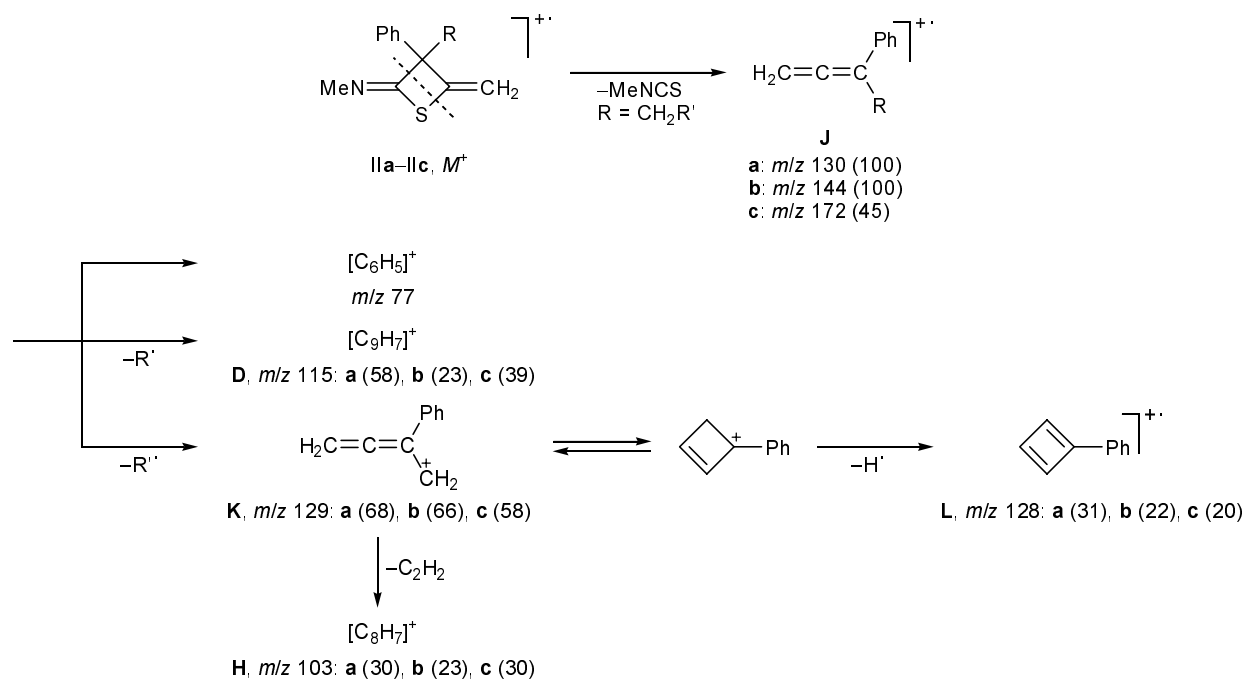
The formation of odd-electron 8H-thieno[2,3-b]indole radical cation (m/z 173, Scheme 4) was observed by us previously in the dissociative ionization of N-phenyl- and N-alkyl-N-phenylthiophen-2-amines [4, 5]; in the fragmentation of compounds **I**, this ion is formed via elimination of methyl group from the $[M - Me]^+$ ion with m/z 188. Although processes leading to $[M - Me]^+$ (m/z 188) and $[M - Me - Me]^{+\cdot}$ ions (m/z 173) are characteristic of fragmentation of 2-aminothiophene molecular ions [4, 5], they should likely to be regarded as untypical (cleavage of the C–N bond with formation of nitrogen-containing cation) [7] or even forbidden (expulsion of a radical from a cation to give a radical ion) [9]; on the other hand, it is difficult to find another reasonable explanation for the appearance of these and many other ions discussed in the present work and in [4–6]. Presumably, the driving force of the concurrent dissociation of the N–Me bond in the decomposition of N,N-dimethylthiophen-2-amine molecluar ions is formation of stable 2-alkylimino-2H-thiophenium ions (Schemes 2, 4).

By contrast, processes involving decomposition of the thiophene ring are not typical of compound **Ia**. For example, the intensity of ion peaks with m/z 144 and 115 (**D**) (which may arise from expulsion of thioketene molecule from ion **A** (m/z 202) or of H$_2$CNCS· radical from ion **B** (m/z 187) is as low as 6 and 5%, respectively (Scheme 4).

Increase in the length of the substituent on the nitrogen atom in going to aminothiophenes **Ib** and **Ic** leads mainly to redistribution of the contributions of the main channels to the overall fragmentation pattern (Schemes 3–5, Table 1). Unlike their analogs described in [4, 5] and N,N-dialkylanilines [8], structural variations in compounds **Ia**–**Ic** almost do not affect intensities of their molecular ion peaks.

Another specific feature of the decomposition of compounds **Ib** and **Ic** is the absence in their mass spectra of $[M - H]^+$ ion peak, which makes them closer to N-alkyl-N-methylanilines. The $[M - H]^+$ ion was detected in the mass spectra of all unsubstituted and methyl-substituted 2-aminothiophenes examined previously [4, 5], and the intensity of the $[M - H]^+$ ion peak was the largest in the spectra of methyl derivatives (32–73%) [5]. The intensity of that peak in the mass spectra of unsubstituted 2-aminothiophenes [4] was considerably smaller, 2–22% on the average (except for aminothiophene **IV**, I_{rel} 71%). Analogous ion peak is present in the spectrum of N-methyl-N-ethylaniline but is very weak ($I_{rel} < 8$%), while the most abundant

Scheme 6.

IIa–IIc, M^+

$-MeNCS$
$R = CH_2R'$

J
a: m/z 130 (100)
b: m/z 144 (100)
c: m/z 172 (45)

$[C_6H_5]^+$
m/z 77

$[C_9H_7]^+$
D, m/z 115: a (58), b (23), c (39)

$-R^\cdot$

$-R'^\cdot$

K, m/z 129: a (68), b (66), c (58)

$-C_2H_2$

$[C_8H_7]^+$
H, m/z 103: a (30), b (23), c (30)

L, m/z 128: a (31), b (22), c (20)

$-H^\cdot$

ion is $[M - Me]^+$ (I_{rel} 100%) [8]. No $[M - H]^+$ ion peak is present in the mass spectra of N-methyl-N-butyl-aniline and aminothiophene **Ic**; in both cases, the base ion is $[M - Pr]^+$ [8]. To some extent, these data are consistent with the known fact that the energy of dissociation of C–C bond decreases more rapidly than the energy of dissociation of C–H bond as the length of the alkyl chain increases [7].

Like aminothiophene **Ia**, the molecular ions of its homologs **Ib** and **Ic** decompose with formation of a stable ion with m/z 202 (Scheme 5). However, the intensity of the $[M - Me]^+$ ion peak (m/z 202) in the mass spectrum of **Ib** was fairly small (32%), in contrast to the molecular ions derived from N-ethyl- and N,N-diethylthiophen-2-amines [4] and N-ethyl-N-methylaniline [8]; the latter undergo quantitative decomposition at the α-carbon atom in the N-ethyl group with loss of methyl radical and formation of ion giving the maximal peak in the spectrum.

Elimination of propyl radical in the dissociation of aminothiophene **Ic** molecular ion and formation of ion with m/z 202 as the most abundant one are quite reasonable and consistent with the rule implying preferential elimination of a larger alkyl radical and with the strong ability of an aminoalkyl unit to undergo cleavage at the α-carbon atom [7] (the resulting cation is well stabilized due to the presence of lone electron pair on the nitrogen atom). The same factor is responsible for the α-cleavage of aminothiophenes **Ia** and **Ib**.

An alternative fragmentation pathway of ions with m/z 202 derived from compounds **Ia–Ic** (except for that leading to ions with m/z 187) is expulsion of sulfanyl radical with formation of ion with m/z 169; the latter was assumed to have the structure of 2-methyl-1,2-dihydrocyclopenta[de]isoquinoline radical ion (**E'**) or 1-ethyl-1H-cyclopenta[cd]indole (**E''**) (Scheme 5). The mass spectra of both aminothiophenes **Ia** and **Ic** contain a common ion with m/z 200 which may be 4-methylthieno[2,3-c]isoquinolin-4-ium (**F**) arising from elimination of hydrogen molecule from the $[M - R']^+$ ion (m/z 202; Scheme 5) (dehydrogenation processes are known to be typical of such structures [7]). However, in the spectrum of aminotiophene **Ia** the intensity of the corresponding ion peaks does not exceed 2% (Table 1).

The mass spectra of aminothiophenes **Ia–Ic** contain a common ion peak with m/z 186; most probably, this ion has the structure of 4-methylthieno[2,3-c]isoquinolin-4-ium (**G'**) or 8-methylidene-8H-thieno[2,3-b]indol-8-ium (**Zh''**) and is formed via elimination of hydrogen atom from the ion with m/z 187 or of methane molecule from the ion with m/z 202 (Scheme 5).

We can conclude that the fragmentation of molecular ions derived from 2-amino-3-phenylthiophenes **I** follows mainly the path typical of amines (with localization of charge and unpaired electron on the nitrogen atom) and that some differences between the mass

spectra of compounds **Ia–Ic** are determined by the length of the *N*-alkyl radical.

Unlike 2-aminothiophenes **I**, their structural isomers, iminothietanes **IIa–IIc** having a strained four-membered heteroring, show no molecular ion in the mass spectrum (Scheme 6, Table 2). It is known [9] that fragmentation of thietane and its methyl derivative under electron impact involves cleavage of the four-membered ring in half with charge localization on the sulfur-containing fragment. In fact, ions with the largest *m/z* values result from thietanes **IIa–IIc** via cleavage of the C^2–C^3 and C^4–S bonds with formation of methyl isothiocyanate as neutral species, while the positive charge is localized on 1-alkyl-1-phenylallene fragment **J** which is stabilized by conjugation between the π systems of the aromatic ring and cumulene moiety. Further decomposition of 1-alkyl-1-phenylallene radical cations gives ions **K** (*m/z* 129), **L** (*m/z* 128), and **D** (*m/z* 115) as a result of expulsion of R′, H, and R radicals, respectively; the corresponding ion peaks were present in the mass spectra of all iminothietanes **IIa–IIc** (Scheme 6).

3-Butyl-substituted homolog **IIc** gives rise to additional fragmentation pathways of radical ion **J**, which include elimination of ethylene and propylene molecules. As a result, the intensity of the ion peak with *m/z* 172 decreases to 45%, and the most abundant ion has an *m/z* value of 130 (Scheme 7). The formation of an ion with *m/z* 147 from thietanes **II** is difficult to rationalize without involving skeletal rearrangement which precedes decomposition of the molecular ion (Scheme 8). Presumably, electron impact promotes isomerization of $M^{+\cdot}$ into thione form $M_3^{+\cdot}$ with separated cationic and radical centers. The occurrence of such transformation of the molecular ion follows from the presence in the mass spectra of thietanes **IIb** and **IIc** of $[C_7H_7]^+$ ion peak with *m/z* 91. The driving force of this rearrangement may be elimination of MeNCR˙ radical with formation of a cation with *m/z* 147 which is stabilized due to effect of the phenyl group or heteroatom [10], e.g., 3-phenylthietium

Scheme 7.
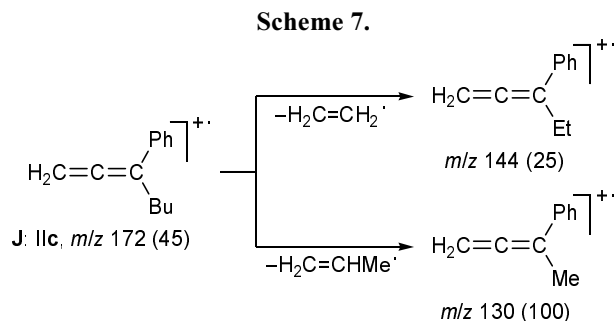
**Table 2.** Mass spectra of *N*-methyl-3-alkyl-4-methylidene-3-phenylthietan-2-imines **IIa–IIc** (60 eV)

Ion	Relative intensity, I_{rel}, %		
	IIa	**IIb**	**IIc**
$M^{\cdot}$	–	–	–
D, *m/z* 115 $[J - R]^+$	58	23	39
H, *m/z* 103 $[K - C_2H_2]^+$	30	23	30
J $[M - \text{MeNCS}]^{+\cdot}$	100 (*m/z* 130)	100 (*m/z* 144)	45 (*m/z* 172)
K, *m/z* 129 $[J - R']^+$	68	66	58
L, *m/z* 128 $[K - N]^{+\cdot}$ or $[J - R'N]^{+\cdot}$	31	22	20
M, *m/z* 147 $[M_3 - \text{MeNCR}]^+$	35	17	14
m/z 160	11	–	6
m/z 145 $[M - H_2C=C=S]^{+\cdot}$	12	–	–
m/z 144 $[J - H_2C=CH_2]^{+\cdot}$	–	a	25
m/z 143	–	23	–
m/z 131	25	–	–
m/z 130 $[J - H_2C=CHMe]^{+\cdot}$	a	–	100
m/z 116	8	–	–
m/z 91 $[C_7H_7]^+$	–	3	6
m/z 89 $[C_7H_5]^+$	2	–	–
m/z 77 $[C_6H_5]^+$	16	8	7
m/z 63 $[C_5H_3]^+$	2	–	–
m/z 51 $[C_4H_3]^+$	8	–	–
m/z 42 $[\text{MeN}\equiv\text{CH}]^+$	2	2	3

a Overlapped by the radical ion **J** peak.

ion **M**. An additional fragmentation channel implying cleavage of the C^2–S and C^3–C^4 bonds to give $[M - H_2C=C=S]^{+\cdot}$ radical cation (*m/z* 145) is observed only for thietane **IIa** (Scheme 9).

Thus dissociative ionization of iminothietanes **IIa–IIc** is characterized by both cleavage of the four-membered ring in half to produce neutral methyl isothiocyanate molecule and 1-alkyl-1-phenylallene radical cation in which the charge and unpaired electron are localized on the conjugated π system (main fragmentation pathway) and skeletal rearrangement of the molecular ion to thione form with separated cationic and radical centers, which is followed by elimination of MeNCR˙ radical (concurrent fragmentation pathway).

Carbocyclic isomers of thietanes **IIa–IIc**, *N*-methyl-4-alkylsulfanyl-2-phenylcyclobut-2-en-1-imines **IIIa–IIIc**, turned out to be quite stable compounds, both thermally and under electron impact. These com-
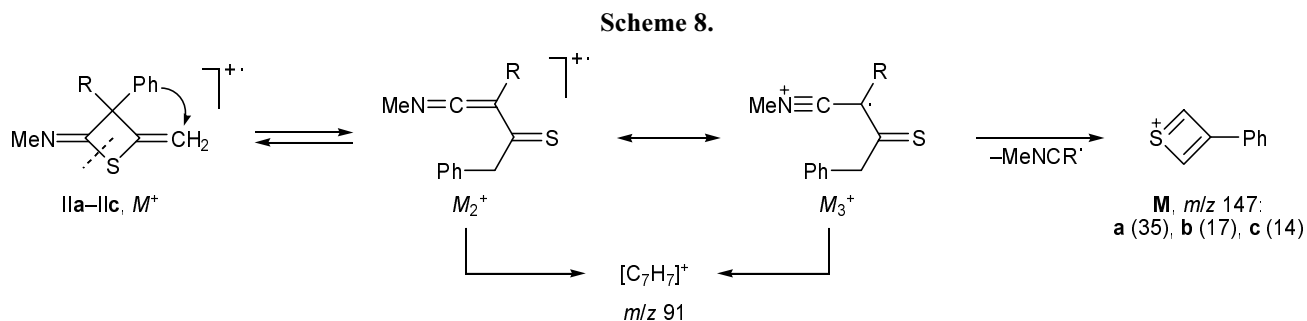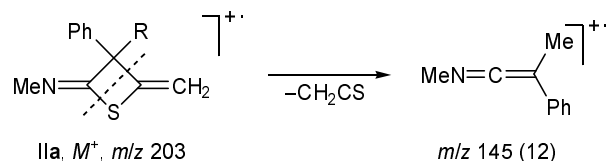
Scheme 8.

pounds can be purified by vacuum distillation without appreciable isomerization, despite fairly high boiling points (100–160°C at 0.1–0.2 mm) [1], and their mass spectra contain the molecular ion peaks whose intensity varies from 87 to 25% (Scheme 10, Table 3). However, the most obvious and convincing proof for the greater thermodynamic stability of the cyclobutene ring relative to thietane (in compounds **III** and **II**, respectively) is that cyclobutenethiolate ion was ex-

Table 3. Mass spectra of N-methyl-4-alkilsulfanyl-2-phenyl-cyclobut-2-en-1-imines **IIIa–IIIc** (60 eV)

Ion	Relative intensity, I_{rel}, %		
	IIIa	**IIIb**	**IIIc**
$M^{+\cdot}$	87 (m/z 203)	81 (m/z 217)	25 (m/z 245)
D, m/z 115 [**N** – MeCN]$^+$ or [M – MeNCSR]$^+$	100	100	100
H, m/z 103	6	39	21
M, m/z 147 [M – MeNCR]$^+$ or [**O** – MeCN]$^+$	3	23	10
N, m/z 156 [M – SR]$^+$ or [**P** – CH]$^+$	49	61	27
O, m/z 188 [M – R]$^+$	–	34	69
P, m/z 189 [M – C$_n$H$_{2n}$]$^{+\cdot}$	–	26	48
Q [M – H]$^+$	10 (m/z 202)	26 (m/z 216)	–
m/z 134	–	6	–
m/z 116	–	36	–
m/z 89 [C$_7$H$_5$]$^+$	10	25	6
m/z 77 [C$_6$H$_5$]$^+$	–	11	–
m/z 69	–	2	–
m/z 63 [C$_5$H$_3$]$^+$	2	12	–
m/z 57	–	–	20
m/z 51 [C$_4$H$_3$]$^+$	–	4	–
m/z 45 [HCS]$^+$	–	2	–
m/z 41	–	–	9
m/z 39	–	3	

perimentally shown to be formed via rearrangement of thietanylamide ion under fairly mild conditions, on heating at ~45–50°C for a short time (no longer than for 30 min) [11].

Scheme 9.

Enhanced thermal stability of iminocyclobutenes **III** distinguishes them not only from thietanes **II** but also from known cyclobutenes many of which are capable of undergoing spontaneous (under the conditions of their synthesis) [12] or thermally induced (at 120–200°C) [13] electrocyclic ring opening. The transformation of unsubstituted cyclobutene into *cis*-buta-1,3-diene is one of the most thoroughly studied reactions in organic chemistry [14]. Analysis of the mechanism of this reaction in terms of the molecular orbital theory was the earliest example of successful application of the Woodward–Hoffmann rules [15]. Mechanistic details and the activation barrier of the electrocyclic ring opening in cyclobutene radical cation, leading to buta-1,3-diene structure, are the subjects of increased experimental and theoretical interest over a period of more than two decades [16]. However, some issues remain unclear. It is now well established that opening of the four-membered ring in cyclobutene radical cation is faster by many orders of magnitude than in the neutral molecule [16] and that dissociation of isomeric C$_4$H$_6$ radical cations with loss of methyl group involves isomerization to 3-methylcyclopropene structure [17]. Surprisingly, we have found no studies on the mass spectra of these compounds among more than 700 available publications.

Analysis of the mass spectra of iminocyclobutenes **III** showed that the fragmentation of their molecular ions does not include decomposition of the four-mem-

Scheme 10.
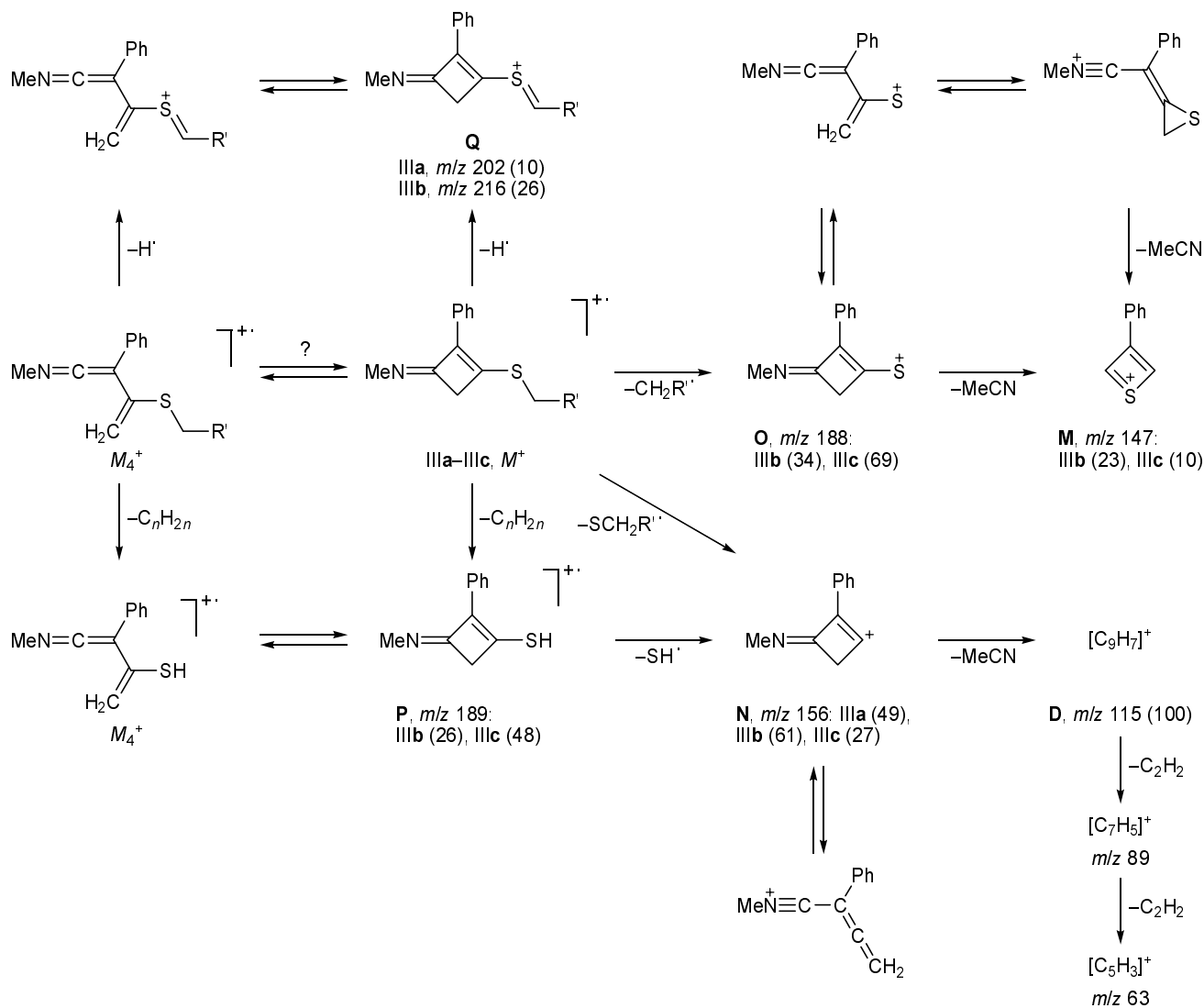
bered ring in half, which is typical of thietanes and their carbocyclic analogs, cyclobutanes [9, 18]. In any case, we identified no alkyl 2-phenylethynyl sulfide ion peaks which would be formed as a result of elimination of *N*-ethenylidenemethanamine. The main fragmentation pathway of the molecular ions derived from compounds **III** is cleavage of the C–S bond (Scheme 10). Analogous processes are typical of dissociative ionization of alkyl cycloalkyl sulfides and alkyl aryl sulfides; therefore, their interpretation involves no specific difficulties [7]. The main problem in the analysis of the mass spectra of aminocyclobutenes **III** was to determine which form of the molecular ion, cyclic $M^{+\cdot}$ or open-chain $M_4^{+\cdot}$ undergoes decomposition, i.e., whether the fragmentation of the molecular ion is preceded by ring opening to give *N*-(3-alkylsulfanyl-2-

phenylbuta-1,3-dien-1-ylidene)methanamine structure. Here, the main difficulty is that in both cases the corresponding fragment ions have similar *m/z* values, and they may be represented by equilibrium structures.

The formation of *N*-(3-alkylsulfanyl-2-phenylbuta-1,3-dien-1-ylidene)amines as key intermediates was postulated in the recently reported thermal (~120°C, 10–30 min) rearrangement of alkyl *N*-alkyl-2-phenyl-buta-2,3-dien-1-imidothioates into cyclobutenes [19] (Scheme 11). However, these intermediates are very reactive (the rate of their cyclization considerably exceeds the rate of their formation), and they cannot be isolated or even detected (e.g., by NMR spectroscopy). Taking the above into account, it is difficult to suppose that such thermodynamically unstable structures could give rise to stable molecular ions.

Scheme 11.
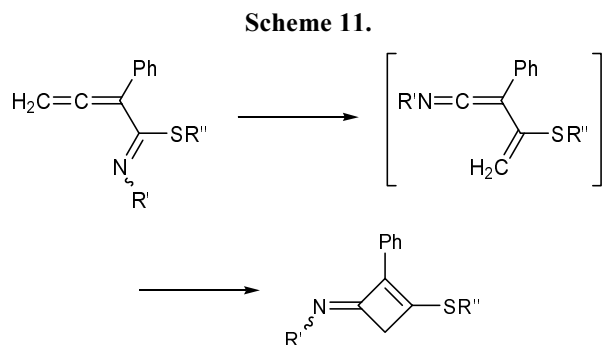
Presumably, cleavage of one C–S bond in the molecular ion is accompanied by elimination of alkylsulfanyl radical and ion **N** (m/z 156) thus formed loses MeCN molecule to give stable phenylallenyl or phenylcyclopropenyl cation **D** (m/z 115, I_{rel} 100%). Fragmentation of the latter occurs via expulsion of acetylene molecule. Cleavage of the other C–S bond, which is accompanied by elimination of a radical or olefin and is typical of long-chain alkyl aryl sulfides [7], is observed in the mass spectra of ethylsulfanyl and butylsulfanyl derivatives **IIIb** and **IIIc**. Analogous fragmentation pathway is not inherent to compound **IIIa**. The $[M - R]^+$ ion peak (m/z 188) arising from homolytic dissociation of the S–R bond has a fairly large intensity in the mass spectra of cyclobutenes **IIIb** and **IIIc** (34 and 69%, respectively). Further decomposition of that ion can follow two pathways: (1) with elimination of sulfanyl radical and formation of fragment ion **N** (m/z 156) or (2) with elimination of neutral MeCN molecule and formation of ion **M** (m/z 147). Elimination of olefin is an energetically favorable process of decomposition of iminocyclobutenes **IIIb** and **IIIc**; this follows from the low-energy spectra of these compounds, where radical cation **P** $[M - C_nH_{2n}]^{+\cdot}$ (m/z 189) gives peaks with a relative intensity of 100 (**IIIc**) and 14% (**IIIb**).

Compound **IIIa** displays in the mass spectrum an ion peak with m/z 147 (3%); its intensity is considerably lower than in the spectra of cyclobutenes **IIIb** and **IIIc**. This ion cannot be formed according to the pathway shown in Scheme 10 since the key fragment $[M - Me]^+$ is absent. We believe that the molecular ion of **IIIa** initially undergoes rearrangement into structure $M_5^{+\cdot}$ with separated cationic and radical centers and that the subsequent elimination of MeNCMe$^{\cdot}$ radical gives fragment ion with m/z 147 (Scheme 12). It is quite probable that the pathway shown in Scheme 12 somewhat contributes to the formation of the ion with m/z 147 in the decomposition of the molecular ions of **IIIb** and **IIIc**. An analogous skeletal rearrangement of

molecular ions was observed in the mass spectra of isomeric thietanes (Scheme 8).

Scheme 12.
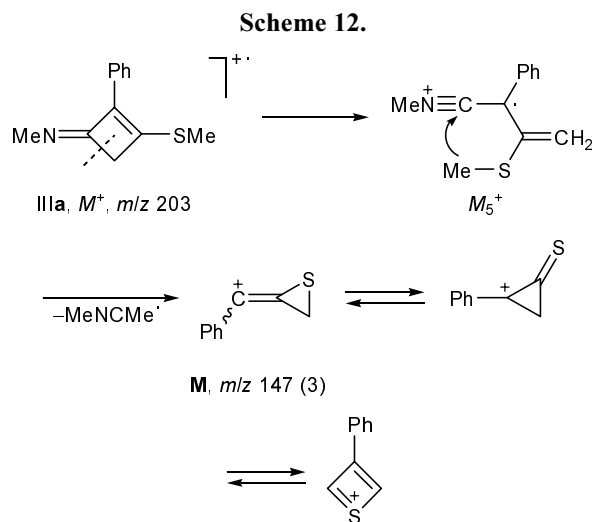
It should be emphasized that α-cleavage of molecular ions, which is typical of alkyl sulfides and alkylamines (including 2-aminothiophenes **Ia–Ic**) was revealed only in the mass spectra of cyclobutenes **IIIa** and **IIIb**, where it was accompanied by elimination of hydrogen atom. The mass spectra of these compounds contained no $[M - Me]^+$ ion peaks, indicating that the S–Me and C–Me bonds are stronger than the C–H bond. Presumably, the S–Bu bond in iminocyclobutene **IIIc** radical cation is the weakest; this is confirmed by the high intensity of the ion peak arising from cleavage of that bond. On the other hand, no $[M - H]^+$ and $[M - Pr]^+$ ion peaks were present in the spectrum of compound **IIIc**.

We can conclude that the fragmentation pattern of the molecular ions derived from iminocyclobutenes **III** is determined by charge localization on the sulfur atom and that it follows general relations holding in the decomposition of alkyl cycloalkyl sulfides and alkyl aryl sulfides. As concerns ring opening before fragmentation of the molecular ion with formation of N-(3-alkylsulfanyl-2-phenyl-1,3-butadienylidene)-methanamine, this problem requires additional studies, including quantum-chemical calculations.

Thus comparative analysis of the behavior of structural isomers **I–III** under electron impact revealed two important aspects: (1) each isomeric structure is characterized by its own fragmentation pattern of the molecular ion, which is determined by localization of the radical and cationic centers (the mass spectrum ensures reliable identification of the structure); and

(2) decomposition of molecular ions derived from isomeric compounds gives no common intermediates. These data indicate that five- and four-membered rings are formed as a result of kinetically and thermodynamically controlled anionic rearrangements of the 1,3-dilithio-3-phenylpropyne–methyl isothiocyanate adduct in the system *t*-BuOH–*t*-BuOK–DMSO (Scheme 1). Neutralization of the N- (thienylamide), C- (thietanyl), and S-centered anions (cyclobutenyl-sulfide) thus formed via reaction with alkyl halide leads to stable aminothiophenes **Ia–Ic**, iminothietanes **IIa–IIc**, and iminocyclobutenes **IIIa–IIIc**.

EXPERIMENTAL

The mass spectra (electron impact, 12 and 60 eV) were recorded on an LKB-2091 GC–MS system; samples were introduced into the ion source either directly (cyclobutenes) or through a chromatographic column (cyclobutenes, tiophenes, thietanes). The temperature of the direct inlet probe was selected in such a way that thermal decomposition of a sample be avoided and a well resolved spectrum be obtained. The ion source temperature was varied from 150 to 200°C. An SE-54 capillary column, 30 m × 0.25 mm was used (carrier gas helium, oven temperature programming from 50 to 240°C at a rate of 8 deg/min, injector temperature 250°C). The mass spectrum of thiophene **Ic** was recorded on a GCMS-QP5050A system (injector temperature 220°C; carrier gas helium, flow rate 0.7 ml/min; detector temperature 230°C; quadrupole mass analyzer; electron impact, 70 eV; ion source temperature 200°C; a.m.u range 34–650). Total ion urrent chromatograms were recorded. The synthesis of compounds **Ia–Ic**, **IIa–IIc**, and **IIIa–IIIc** was described previously [1].

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