Mass spectra of new groups of functionalized heterocycles
3.* 3-Alkyl- and 5-alkyl-2-thienylamines

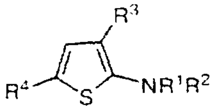
L. V. Klyba,[a*] *V. N. Bochkarev,*[b†] *L. Brandsma,*[c] *O. A. Tarasova,*[a]
N. A. Nedolya,[a] *and B. A. Trofimov*[a]

[a]*Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences,*
1 ul. Favorskogo, 664033 Irkutsk, Russian Federation.
Fax: + 7 (395 2) 39 6046. E-mail: admin@ irioch.irk.ru
[b]*State Research Center of the Russian Federation*
"State Research Institute of Chemistry and Technology of Elementoorganic Compounds,"
38 sh. Entuziastov, 111123 Moscow, Russian Federation
[c]*Department of Preparative Organic Chemistry, Debye Institute, University of Utrecht,*
Padualaan 8, 3584 CH Utrecht, The Netherlands.
E-mail: l.brandsma@chem.ruu.nl

The influence of the position and nature of the substituent in the thiophene ring on the fragmentation of 3-alkyl- and 5-alkyl-2-thienylamines under electron impact was studied. The derivatives containing the ethyl group in position 3 decompose due to both the elimination of the fragments from the substituents and thiophene ring rupture. In the case of the compounds with the *tert*-butyl group in position 5, the last process is not observed. The fragmentation of the 3- and 5-methyl-substituted derivatives occurs mainly from the isomeric thiopyran form of the molecular ion.

Key words: *C*-alkyl-2-thienylamines, mass spectra, fragmentation, rearrangement, electron impact.

We have previously[2] described the general regularities of the mass spectrometric fragmentation of secondary and tertiary 2-thienylamines containing no substituent in positions 3—5 of the thiophene ring. With the purpose of revealing the influence of the nature and position of an alkyl substituent in the thiophene ring on the decomposition of molecular ions of 2-thienylamines, in this report, we analyzed the mass spectra of secondary and tertiary 3-alkyl- and 5-alkyl-2-thienylamines **1—9**.



1—9

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
R^1	H	H	Me	Me	Me	Me	H	H	Me
R^2	Me	Ph	Me	Me	Me	Ph	Me	Ph	Me
R^3	H	H	H	Me	Et	H	H	H	H
R^4	Me	Me	Me	H	H	Me	Bu^t	Bu^t	Bu^t

Alkyl substituents in any of the considered positions of the thiophene ring generate new decomposition channels and noticeably decrease the contribution of processes characteristic of nonsubstituted compounds ($R^3 = R^4 = H$).[2] The *tert*-butyl group in position 5 exerts the strongest effect. In this case, fragmentation with the decomposition of the heterocyclic system does not occur, and the main process of the decomposition of molecular ions of compounds **7—9** is the elimination of the methyl radical to form ions stabilized due to conjugation, whose peaks are maximal in the mass spectra (Scheme 1).

The $[M - Me]^+$ and $[M - 2\ Me]^{+\cdot}$ ions are formed due to both the elimination of the methyl groups from the *tert*-butyl substituent (see Scheme 1) and N—Me bond cleavage, especially in the case of dimethylamino-substituted derivative **9**, whose mass spectrum exhibits an intensity of the peak of the $[M - 2\ Me]^{+\cdot}$ ion almost fourfold higher than that for compound **8** containing the phenylamino group.

In the mass spectrum of dimethyl(3-ethyl-2-thienyl)-amine (**5**), along with the peaks corresponding to the $M^{+\cdot}$, $[M - Me]^+$, and $[M - 2\ Me]^{+\cdot}$ ions, the peaks of the ions that appeared due to the fragmentation of the thiophene ring have a high intensity. These processes are identical to those observed by us previously[2] for alkyl(aryl)(2-thienyl)amines ($R^3 = R^4 = H$). The cleavage of the S(1)—C(2) and C(4)—C(5) bonds results (Scheme 2, I_{rel} (%) are given in parentheses) in ions with m/z 45 and 110, and the cleavage of the S(1)—C(2) and C(2)—C(3) bonds in ion **A** affords ions with m/z 42 and 99. The thiopyrilium cation with m/z 97 is formed upon extension of the five-membered cycle.[3]

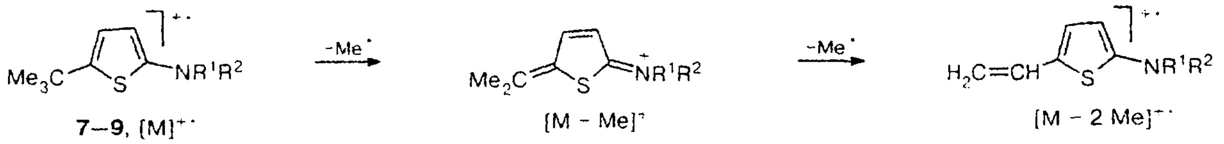
---

[*] For Part 2, see Ref. 1.

[†] Deceased.

Published in *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 9, pp. 1560—1563, September, 2000.

Scheme 1

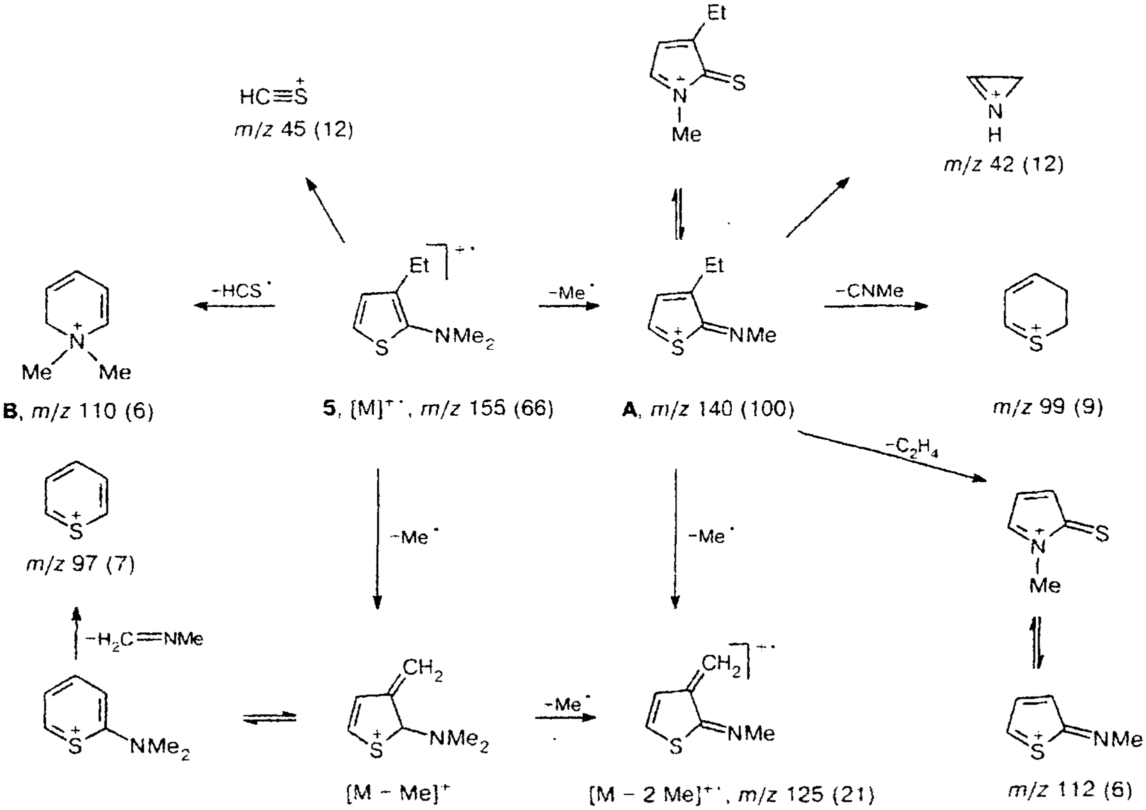


	m/z (I_{rel} (%))		
7	169 (85)	154 (100)	139 (14)
8	231 (33)	216 (100)	201 (9)
9	183 (64)	168 (100)	153 (35)

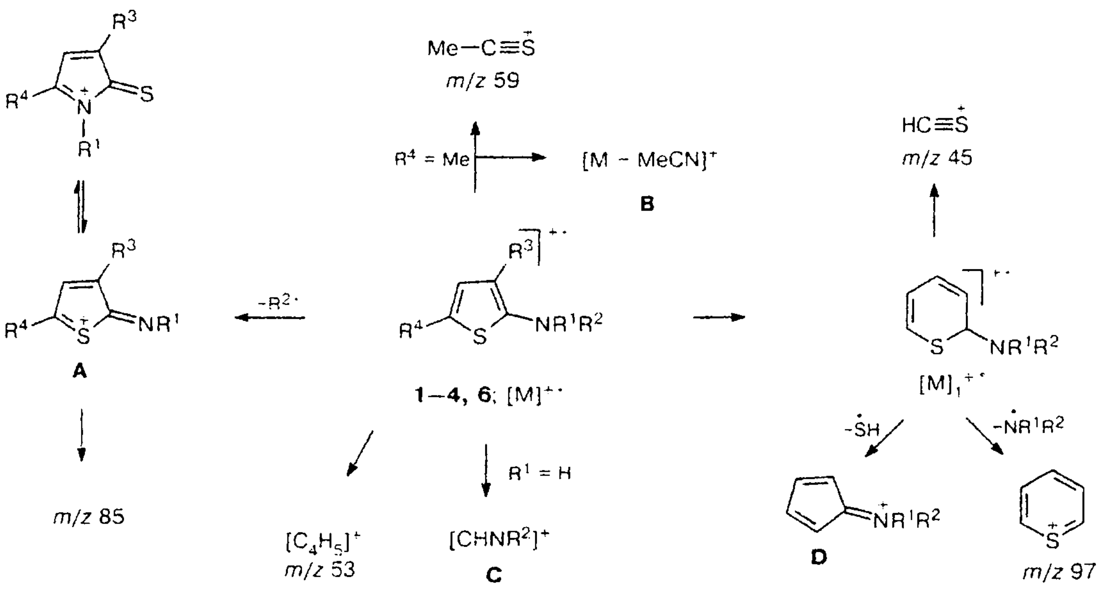
The presence of the major fragmentation ions manifested in the spectra of 3-methyl- (**4**) and 5-methyl-2-thienylamines (**1**—**3**, **6**) is due to extension of the thiophene ring followed by decomposition of the corresponding 2-amino derivatives of thiopyran. This is indicated by the following. First, the mass spectrum of dimethyl(3-methyl-2-thienyl)amine **4** differs sharply from that of homolog **5** containing the 3-ethyl group, but is very close to the mass spectrum of isomeric compound **3** with the methyl group in position 5. Second, the spectra of 3-methyl- (**4**) and 5-methyl-2-thienylamines (**6**) contain the peaks of the $[M - NR^1R^2]^+$ and $[M - SH]^+$ ions (Scheme 3, Table 1), which are not characteristic of nonsubstituted 2-thienylamines ($R^3 = R^4 = H$). Finally, for S(1)—C(2) and C(4)—C(5) bond cleavage typical of thiophene derivatives,[2—4] $[MeC{\equiv}S]^+$ ions with *m/z* 59 and **B** $[M - MeC{\equiv}S]^+$ should appear in the case of 5-methyl-substituted derivatives. In the spectra of compounds **1**—**3** and **6**, the peaks of these ions have a low intensity or are completely absent, but in all cases, a sufficiently intense peak of the $[HC{\equiv}S]^+$ ion with *m/z* 45, which is generated due to S(1)—C(2) and C(5)—C(6) bond cleavage of the thiopyran cycle, was observed. The formation of ion **C** and the ion with *m/z* 85 is possible from both the thiophene and thiopyran structure due to S(1)—C(2) and C(2)—C(3) bond cleavage. The same goes for the ion with *m/z* 53, an analog of the $[C_3H_3]^+$ ion with *m/z* 39 in the spectra of the nonsubstituted compounds.[2] The structures of the listed ions are shown in Scheme 3, and their *m/z* and relative intensities are presented in Table 1.

Despite the aforementioned similarity of the mass spectra of isomeric 3-methyl- and 5-methyl-2-thienyl-

Scheme 2



Scheme 3



amines (**4** and **3**), they demonstrate one substantial distinction: the spectrum of compound **4** does not contain the peak of ion **D** [M − SH]⁺ with *m/z* 108, which is characteristic of compound **3**, but exhibits the peak of the [(M − Me) − CH_4]⁺ ion with *m/z* 110 (5%).

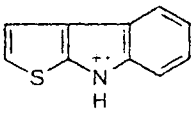
In the case of methyl(5-methyl-2-thienyl)amine **1**, ion **A** eliminates the CS molecule to form an ion with *m/z* 68 (15%), and for 5-methyl-substituted derivative **6**, the sulfhydryl radical transforms into an odd-electron ion with *m/z* 155. Another odd-electron ion with *m/z* 129 (8%) appears due to splitting off of the methyl radical from ion **B**.

Table 1. Mass spectra of 3-methyl- and 5-methyl-2-thienylamines **1—4** and **6** (at 60 V)

Ion	*m/z* (I_{rel} (%))*				
	1	**2**	**3**	**4**	**6**
[M]⁺·	127 (100)	189 (100)	141 (100)	141 (100)	203 (100)
[M − H]⁺	126 (73)	188 (68)	140 (65)	140 (46)	202 (32)
A	112 (27)	112 (2)	126 (43)	126 (54)	188 (23)
B	68 (7)	—	82 (4)	—	144 (5)
C	42 (7)	104 (2)	—	—	—
D	94 (16)	156 (14)	108 (12)	—	—
Ion with *m/z*					
173	—	(5)	—	—	(21)
104	—	—	—	—	(7)
93	—	(6)	—	—	—
97	(10)	(19)	(17)	(13)	(5)
85	(20)	(7)	(18)	(22)	(9)
77	—	(20)	—	—	(25)
53	(9)	(7)	(8)	(7)	(4)
51	—	(16)	—	—	(15)
45	(17)	(8)	(19)	(19)	(12)

* The *m/z* values (I_{rel} (%)) for **8**: 93 (13), 77 (15), 51 (7); for **9**: 140 (6).

The ion of 8*H*-thieno[2,3-*b*]indole with *m/z* 173 has previously[2] been observed in the mass spectrum of 2-thienylphenylamine. The peaks of this ion are also observed in the mass spectra of phenylamines **2** and **6**.



m/z 173

Thus, the comparative analysis of the mass spectra of 2-thienylamines bearing alkyl groups in positions 3 or 5 of the thiophene ring and the corresponding unsubstituted compounds showed that the presence of the ethyl substituent in position 3 weakly affects the decomposition of the molecule, which occurs due to both the elimination of the fragments from the ethyl and NR¹R² groups and the destruction of the thiophene ring. At the same time, the 5-*tert*-butyl-substituted derivatives are not characterized by the processes related to the decomposition of the heterocyclic system, and the fragmentation of 3-methyl- and 5-methyl-2-thienylamines mainly proceeds from the isomeric thiopyran form of the molecular ion.

Experimental

Mass spectra were recorded at ionizing voltages of 12 and 60 V on an LKB-2091 GC-MS spectrometer using both the system of chromatographic introduction (glass capillary column

38 m long with the SE-54 phase, temperature of the evaporator 250 °C, velocity of the temperature rise from 70 to 250 °C 10 deg min^{-1}) and the system of direct introduction of the sample into the ion source (temperature of the source 240 °C). The synthesis of compounds **1—9** has been described previously.[5,6]

This work was financially supported by the Russian Foundation for Basic Research (Project No. 98-03-32941a).

References

1. L. V. Klyba, V. N. Bochkarev, L. Brandsma, N. A. Nedolya, and B. A. Trofimov, *Zh. Obshch. Khim.*, 1999, **69**, 1885 [*Russ. J. Gen. Chem.*, 1999, **69** (Engl. Transl.)].
2. L. V. Klyba, V. N. Bochkarev, L. Brandsma, O. A. Tarasova, V. Yu. Vvedenskii, N. A. Nedolya, and B. A. Trofimov, *Zh. Obshch. Khim.*, 1999, **69**, 1881 [*Russ. J. Gen. Chem.*, 1999, **69** (Engl. Transl.)].
3. A. A. Polyakova and R. K. Khmel'nitskii, *Mass-spektrometriya v organicheskoi khimii* [*Mass Spectrometry in Organic Chemistry*], Khimiya, Leningrad, 1972, 367 pp. (in Russian).
4. N. S. Vul'fson, V. G. Zaikin, and A. I. Mikaya, *Mass-spektrometriya organicheskikh soedinenii* [*Mass Spectrometry of Organic Compounds*], Khimiya, Leningrad, 1986, 312 pp. (in Russian).
5. L. Brandsma, N. A. Nedolya, O. A. Tarasova, L. V. Klyba, L. M. Sinegovskaya, and B. A. Trofimov, *Dokl. Akad. Nauk*, 1997, **357**, 350 [*Dokl. Chem.*, 1997 (Engl. Transl.)].
6. O. A. Tarasova, L. V. Klyba, V. Yu. Vvedensky, N. A. Nedolya, B. A. Trofimov, L. Brandsma, and H. D. Verkruijsse, *Eur. J. Org. Chem.*, 1998, 253.

Received December 6, 1999;
in revised form March 27, 2000