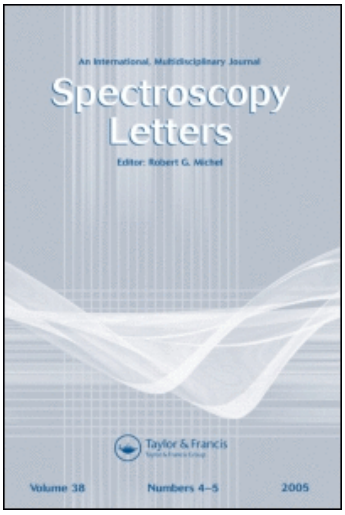

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ELECTRON IMPACT MASS SPECTRA OF SOME UNSATURATED DERIVATIVES OF 2-BENZOTHIAZOLES

KEY WORDS: Mass spectra, styryl-2-benzothiazoles, (4-phenyl-butadienyl)-2-benzothiazoles

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ABSTRACT

The electron impact mass spectra of some p-substituted styryl-2-benzothiazoles **1-6** and p-substituted phenyl-butadienyl-2-benzothiazoles **7** and **8** have been recorded and the identity of various ions in the mass spectra established.

The compounds **1-6** exibit one main fragmentation route which include the formation of M-1 ion as the base peak, and after elimination of p-substituted phenylacetylene molecule, the formation of benzothiazole cation.

Compounds **7** and **8** show the fragmentation pathway which include the formation of butadienyl-2-benzothiazole ion as the base peak.

INTRODUCTION

Our interest in the synthesis, photochemistry, spectroscopy and mass spectrometry of some unsaturated furan and thiophene compounds[1-5] as well as benzothiazoles[6-10] prompted us to investigate some substituted styryl- and [(p-substituted)-4-phenyl-butadienyl]-2-benzothiazoles prepared earlier[11-13].

Although the benzothyazole itself show the fragmentation pathway described by Millard and Temple[14] as well as, by Corn and Massot[15] which include the loss of neutral molecule of hydrogen cyanide and/or carbon monosulfide from the molecular ion, there are a number of fragmentation modes, that are specific to the structure of the compounds examined.

In this work we examined the fragmentation pathway of the following compounds which all bear an unsaturated chain in its structure: styryl-2-benzothyazole **1**, [1-(p-dimethylamino-phenyl)-2-ethenyl]-2-benzothiazole **2**, [1-(p-chloro-phenyl)-2-ethenyl]-2-benzothiazole **3** [1-(p-methoxy-phenyl)-2-ethenyl]-2-benzothiazole **4**, [1-(p-nitro-phenyl)-2-ethenyl]-2-benzothiazole **5**, [1-(α-naphthyl)-2-ethenyl]-2-benzothiazole **6**, (4-phenyl-1-butadienyl)-2-benzothiazole **7** and [4-(p-methoxy-phenyl)-2-butadienyl]-2-benzothiazole **8**.

EXPERIMENTAL

Compounds **1-8** were prepared by the methods described earlier[11-13].

Electron impact (EI) mass spectra were recorded using a Shimadzu QP-5000 GC/MS instrument operated at 70 eV ionizing energy. Samples were introduced using a direct inlet system with a source temperature of 300°C

RESULTS AND DISCUSSION

Plausible fragmentation pathway, which are consistent with the spectral data, together with structure which are suggested for the fragment ion, are shown in Figure1 and 2. Significant peaks in EI mass spectra of the compounds examined are reported in the Table 1 and 2.

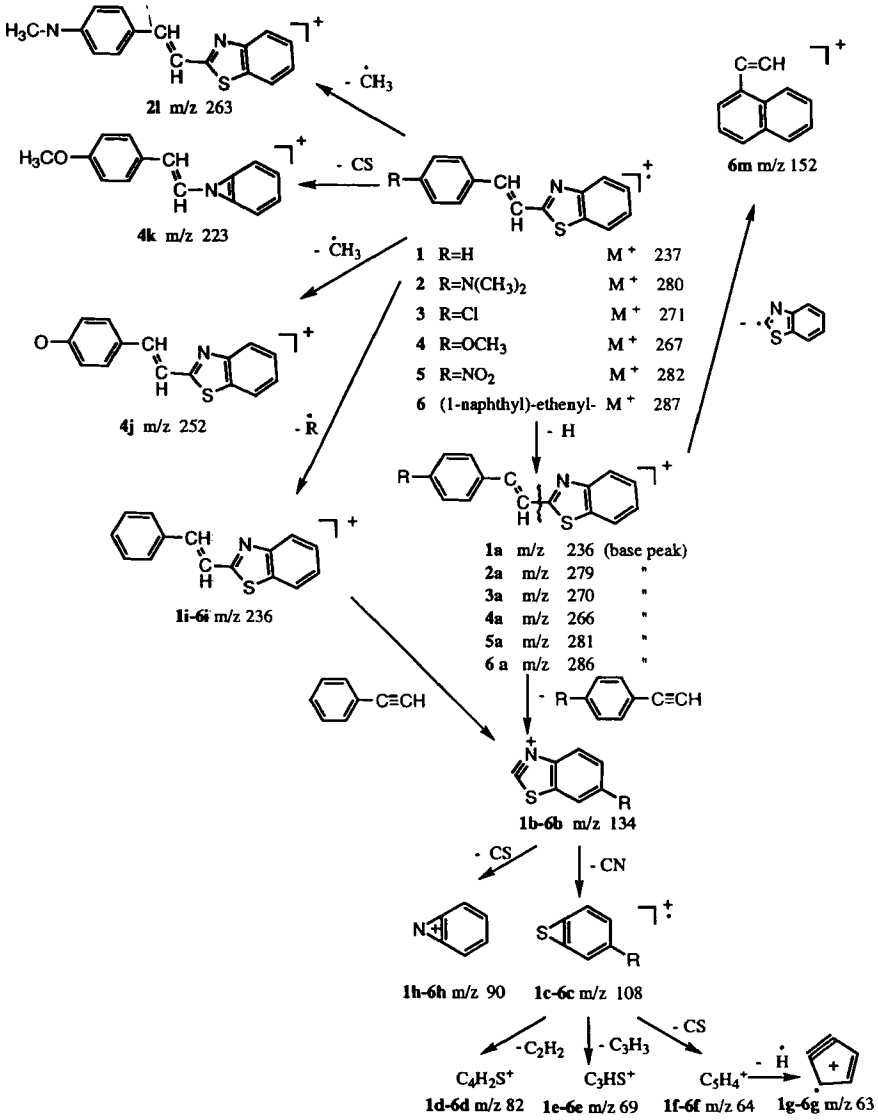

Fig. 1

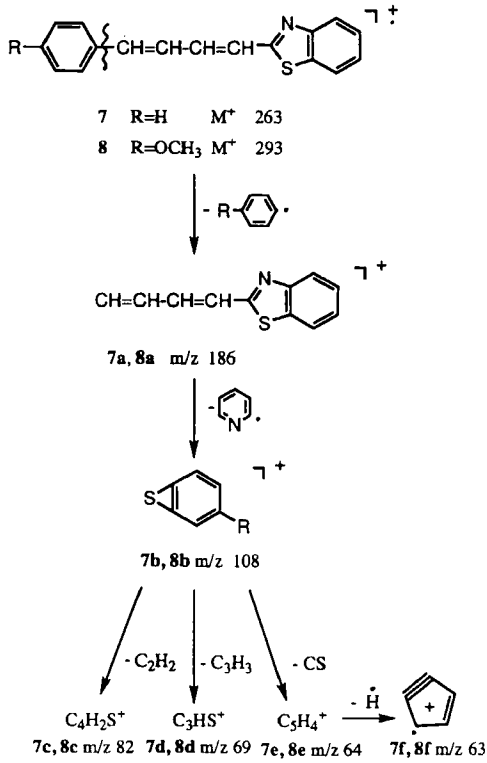

Fig. 2

The molecular ions of the compounds **1-6** are always abundant between 30.9-63.4, but in the compounds **7** and **8** between 11.8 and 16.5.

The main fragmentation route of the compounds **1-6** include the cleavage of the hydrogen radical, and the formation of M-1 ions as the base peaks, namely **1a** $C_{15}H_9NS^{+}$ m/z 236, **2a** $C_{17}H_{14}N_2S^{+}$ m/z 279, **3a** $C_{15}H_8ClNS^{+}$ m/z 270, **4a** $C_{16}H_{11}NOS^{+}$ m/z , **5a** $C_{15}H_8N_2O_2S^{+}$ m/z 281 and **6a** $C_{11}H_{13}NS^{+}$ m/z 287. Benzothiazolyl cation **1b-6b** $C_7H_4NS^{+}$ m/z 134 is formed by the elimination of R-phenyl-acetylene molecule from **1a-6a** ions. Further fragmentation pathway include the fragmentation which is characteristic for benzothiazole molecule[14, 15]

TABLE 1. Characteristic peaks for the compounds **1-6**

No	Fragment ions m/z (%)													
	M^+	a	b	c	d	e	f	g	h	i	j	k	l	m
1	237 (30.9)	236 (100)	134 (1.9)	108 (9.4)	82 (16.6)	69 (46.2)	64 (10.5)	63 (23.7)	90 (2.2)	236 (-)				
2	280 (85.4)	279 (100)	134 (1.0)	108 (2.2)	82 (2.7)	69 (7.0)	64 (1.2)	63 (4.9)	90 (-)	236 (11.1)	(-) (-)	(-) (-)	263 (27.8)	(-) (-)
3	271 (40.1)	270 (100)	134 (-)	108 (7.1)	82 (8.9)	69 (21.0)	64 (2.2)	63 (9.8)	90 (-)	236 (13.5)				
4	267 (57.2)	266 (100)	134 (6.6)	108 (3.2)	82 (4.2)	69 (11.1)	64 (2.7)	63 (10.8)	90 (2.7)	236 (4.4)	252 (10.7)	223 (34.2)	(-) (-)	(-) (-)
5	282 (64.3)	281 (100)	134 (1.3)	108 (7.5)	82 (7.9)	69 (18.7)	64 (2.7)	63 (12.5)	90 (1.7)	236 (30.8)				
6	287 (42.5)	286 (100)	134 (-)	108 (-)	82 (6.6)	69 (17.3)	64 (3.0)	63 (10.6)	90 (-)	236 (-)	(-) (-)	(-) (-)	(-) (-)	152 (18.3)

TABLE 2. Characteristic peaks for the compounds **7** and **8**

No	Fragment ions m/z (%)						
	M^+	a	b	c	d	e	f
7	236 (11.8)	186 (100)	108 (3.2)	82 (2.1)	69 (6.1)	64 (-)	63 (3.6)
8	293 (16.5)	186 (100)	108 (1.9)	82 (1.3)	69 (3.2)	64 (-)	63 (3.0)

and the formation of ions **1c-6c** $C_6H_4S^{\cdot+}$ m/z 108 and **1h-6h** $C_6H_4N^{\cdot+}$ m/z 90 which are formed by loss of CN radical or CS respectively from **1b-6b**. Fragment ions **1d-6d** $C_4H_2S^{\cdot+}$ m/z 82 are than formed from **1c-6c** by elimination of C_2H_2, the cleavage characteristic for the benzene nucleus, while ion **1e-6e** $C_3HS^{\cdot+}$ m/z 69 are formed from **1c-6c** by elimination of C_3H_3. Fragment ion **1f-6f** $C_5H_4^{\cdot+}$ m/z 64 are formed from **1e-6e** by elimination of CS. Finaly, fragmentation ions **1g-6g** $C_5H_3^{+}$ m/z 63 are formed with moderate abundance, by elimination of one hydrogen radical.

Compounds **2-6** follow an additional fragmentation pathway in which fragment ions **2i-6i** $C_{15}H_{11}NS^{+}$ m/z 236 are formed, by elimination of substituent on the benzene nucleus from the molecular ion.

Compound **4** show two additional specific fragmentation pathways followed with the formation **4j** $C_{15}H_{11}NOS^{+}$ m/z 252 cation, which give rise by the elimination of CH_3 radical from the methoxy group in the p-position of the benzene nucleus, and **4k** $C_{15}H_{13}NO^{+}$ m/z 223 which give rise with the moderate intensity, from the molecular ion **4**, by the elimination of CS.

Compound **2**, show additional fragmentation pathway, namely the formation of **2l** $C_{16}H_{13}N_2^{+}$ m/z 263 ion which give rise, with the moderate intensity , by the elimination of CH_3 radical from the dimethylamino group substituted in the benzene nucleus.

Compound **6** show also **6m** $C_{12}H_7^{+}$ m/z ion, which is formed by the elimination of benzothiazolyl radical from the **6a** fragment ion.

Phenyl-butadienyl substituted 2-benzothiazoles **7** and **8** show a different fragmentation pathway then the compounds **1-6**, namely the main fragmentation pathway include the elimination of phenyl or substituted phenyl radical from the molecular ions and the formation of 2-butadienyl-benzothiazole cation **7a** and **8a** $C_{11}H_8NS^{+}$ m/z 186 as base peak. Further fragmentation pathway include the formation of **7b** and **8b** $C_6H_4S^{+}$ m/z 108 which give rise from **7a** and **8a** by the elimination of pyridyl radical.

CONCLUSION

The following generalization can be made from the study by electron impact mass spectrometry of substituted styryl- and phenyl-butadienyl-2-benzothiazoles. Styryl-2-substituted benzothiazoles show specific fragmentation pathway, namely the cleavage of phenyl-acetylene molecule from M-1 ions, while the formation of butadienyl-2-benzothiazole ion **7a** and **8a** can be compared with the formation of the same fragment ion which give rise by the fragmentation of [1-(2-furyl)-2-ethenyl]-2-benzothiazole[8].

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