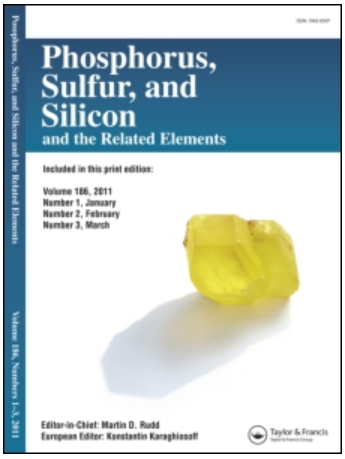

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THE MASS SPECTRA OF SOME (E)- AND (Z)-α-(PHENYL)-β-(2-THIENYL) ACRYLAMIDES

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THE MASS SPECTRA OF SOME (E)- AND (Z)-α-(PHENYL)-β-(2-THIENYL)ACRYLAMIDES

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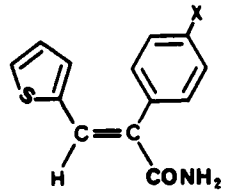
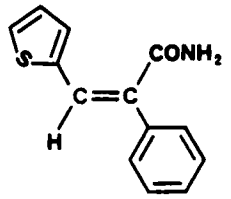
Mass spectra of some (E)- and (Z)-α-(4-X-phenyl)-β-(2-thienyl) acrylamides at 70 eV are reported. The stereoisomeric compounds do not show significant differences. The mass spectra show a four centre reaction scheme with NH_2 migration to the β-carbon atom and subsequent fission of C_α—C_β bond.

Following the research work on mass spectra of thiophene compounds,[1–8] we report here the electron impact mass spectra at 70 eV of some (E)-(I) and (Z)-α-(4-X-phenyl)-β-(2-thienyl)acrylamides (II) with the aim of studying the fragmentations of these stereoisomeric compounds.



I

X = (1) H, (2) F, (3) Cl, (4) Br; (5) NO_2; (6) CH_3; (7) CH_3O



II

X = (8) H; (9) F; (10) Br; (11) CH_3; (12) CH_3O

*Author to whom all correspondence should be addressed.

RESULTS AND DISCUSSION

Compounds I and II are characterized by analogous mass spectral behaviour. In Table 1 are reported only the mass spectra of compounds I. These compounds under electron impact are very stable and the molecular ions are always very intense. The fragmentations of the compounds are reported in Schemes 1–3, where the transitions substantiated by an appropriate metastable peak (directly observed in the 70 eV

TABLE I

Mass spectra at 70 eV of (E)-α-(4-X-phenyl)-β-(2-thienyl)acrylamides (I)

No.	X	$[M]^{+\cdot}$	$[M-H]^+$	$[M-C_6H_4X]^+$	$[M-CONH_2]^+$ (c)	$[c\text{-}X]^{+\cdot}$ (d)	[d-CHS]	$[e]^+$	$[A+H]^{+\cdot}$
1	H	229	228	152	185	184	139	112	118
		(100)	(11)	(13)	(28)	(48)	(8)	(83)	(20)
2	F	247	246	152	203	184	139	112	136
		(99)	(14)	-	(39)	-	(7)	(100)	(22)
		265			221				154
3	Cl	(55)	262	152	(16)	184	139	112	(20)
		263	(25)	(75)	219	(91)	(59)	(100)	152
		(89)			(44)				(75)
		309			265				198
4	Br	(97)	306	152	(19)	184	139	112	(24)
		307	(12)	(26)	263	(96)	(47)	(100)	196
		(93)			(19)				(28)
5	NO_2	274	273	152	230	184	139	112	163
		(100)	(20)	(14)	(22)	(44)	(28)	(99)	—
6	CH_3	243	242	152	199	184	139	112	132
		(100)	(7)	(9)	(18)	(37)	(7)	(69)	(52)
7	CH_3O	259	258	152	215	184	139	112	148
		(97)	(16)	(5)	(45)	(39)	(19)	(100)	(99)

Remaining peaks

1 H 231(6) 230(14) 211(3) 186(7) 183(5) 153(4) 141(7) 115(8) 114(5) 113(6) 106(4) 102(4) 92(6) 89(3) 85(4) 77(6) 63(4) 51(5) 45(4)

2 F 249(8) 248(21) 204(7) 202(71) 201(7) 183(5) 171(4) 170(14) 159(12) 157(11) 133(10) 124(9) 120(7) 114(7) 113(11) 108(5) 101(10) 85(6) 75(5) 69(5) 45(7) 44(9) 39(6)

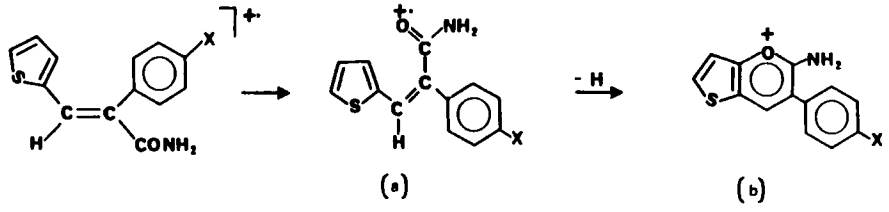
3 Cl 267(5) 266(14) 264(46) 247(5) 246(5) 245(5) 230(5) 220(22) 218(42) 204(5) 202(5) 199(5) 186(19) 185(35) 183(30) 182(13) 175(8) 173(10) 167(6) 160(4) 158(5) 155(6) 153(11) 151(17) 150(10) 149(11) 142(4) 141(6) 140(24) 138(15) 137(8) 136(13) 127(7) 126(10) 125(9) 124(6) 123(5) 115(7) 114(28) 113(37) 111(8) 110(5) 109(6) 108(8) 105(4) 101(9) 100(5) 99(13) 98(6) 97(5) 93(5) 92(14) 91(5) 89(9) 88(7) 87(10) 86(8) 85(15) 84(7) 82(6) 79(5) 77(5) 76(5) 75(22) 74(12) 73(4) 69(13) 63(17) 62(8) 58(7) 51(12) 50(10) 48(7) 45(17) 44(23) 39(14)

4 Br 411(4) 410(6) 408(7) 311(7) 310(24) 308(31) 291(3) 264(17) 262(15) 227(5) 199(6) 195(7) 186(12) 185(26) 183(19) 182(12) 180(3) 171(3) 167(4) 158(4) 153(3) 151(7) 150(6) 141(4) 140(11) 138(7) 137(3) 128(9) 126(9) 125(7) 115(6) 114(33) 113(28) 108(6) 105(4) 101(7) 100(4) 99(6) 98(4) 92(11) 91(6) 89(6) 87(6) 86(4) 85(12) 84(4) 82(4) 79(5) 77(4) 76(5) 75(11) 74(7) 69(7) 63(9) 62(5) 51(6) 50(7) 45(9) 44(11) 39(8)

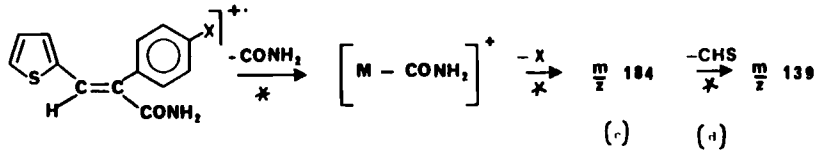
5 NO_2 276(10) 275(27) 272(3) 258(4) 241(4) 231(3) 229(11) 227(5) 199(5) 186(3) 185(9) 183(16) 182(5) 171(8) 158(3) 151(5) 140(6) 128(4) 115(5) 114(10) 113(13) 108(7) 99(4) 92(3) 91(5) 89(5) 87(4) 85(6) 84(6) 77(3) 75(5) 74(4) 69(5) 63(7) 51(5) 50(4) 45(8) 43(5) 39(6)

6 CH_3 245(7) 244(16) 200(4) 198(9) 197(10) 185(58) 171(3) 165(10) 153(4) 152(9) 133(5) 120(4) 116(3) 115(11) 114(4) 113(5) 104(4) 99(3) 97(3) 91(5) 89(5) 87(4) 77(5) 76(3) 69(3) 65(5) 63(6) 51(3) 45(4) 39(6)

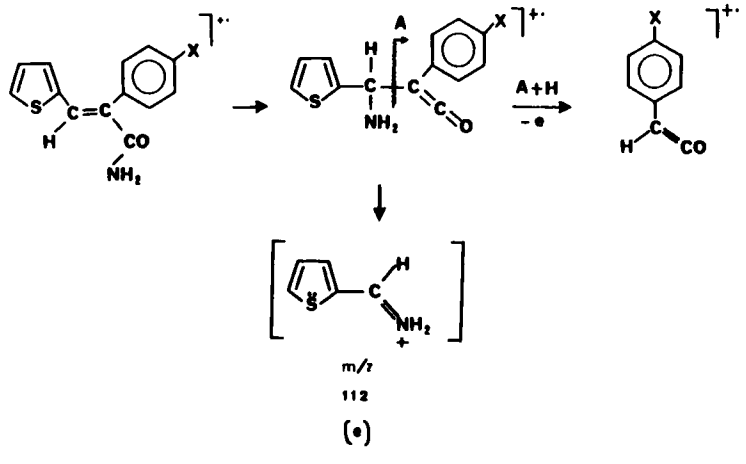
7 CH_3O 261(17) 260(45) 216(9) 214(13) 201(8) 200(36) 199(21) 186(6) 185(10) 183(12) 173(9) 172(34) 171(78) 170(7) 147(6) 146(6) 145(9) 140(4) 136(11) 132(5) 129(4) 128(10) 127(11) 126(5) 121(6) 120(21) 117(4) 115(7) 114(11) 113(17) 108(18) 102(7) 99(5) 97(14) 92(6) 89(12) 87(6) 86(6) 85(13) 77(7) 76(4) 75(7) 74(5) 69(8) 64(4) 63(14) 62(5) 51(7)



SCHEME 1



SCHEME 2



SCHEME 3

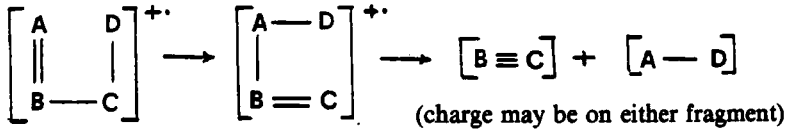
mass spectra) are indicated by an asterisk. The formal structures written for certain fragment ions are simply a convenient mean of representing common types of fission and do not necessary indicate the actual ion structures.

The $[M—H]^+$ fragment ion in the mass spectra of compounds **1–12** results from cyclization to stable oxonium ion (Scheme 1). The expulsion of a hydrogen atom from the styryl ring (a) is a known process in mass spectrometric fragmentation, as was shown in the mass spectra of chalcones.[9]

Compounds **1–12** do not show $[M—2H]^+$ radical ion that is characteristic of the mass spectra of stilbene,[10] 2-styrylthiophene,[11] α-cyanostilbene,[7] and (Z)-α-(phenyl)-β-(2-thienyl)acrylonitryles,[7] nor a $[M—CH_3]^+$ peak as found for the corresponding cyano derivatives.[7] Compounds **1–12** lose NH_2 and $CONH_2$.

The $[M—CONH_2]^+$ ion gives $[M—CONH_2—X]^{+\cdot}$ with m/z 184, that loses the CHS radical with formation of a m/z 139 ion (Scheme 2).

Most of the compounds reported here show a m/z 112 base peak. This can be explained with a formal four-centre reation[12] that has been proposed to generalize the behaviour on electron impact of amides and a wide range of related compounds[13,14] (Scheme 3).



The m/z 112 ion is very stable owing to the presence of the thiophene ring in conjugation with the charged nitrogen atom. This fragmentation has been confirmed by exact mass measurements.

The compounds **1–12** can also lose $\cdot C_6H_4X$ to form the m/z 152 ion, except for the fluoro derivatives (compounds no. **2** and **9**). Compounds no. **3** gives the m/z 152 peak as a doublet owing to the presence of the radical ion $[p\text{-Cl—}C_6H_4CHO]^{+\cdot}$ according to the fragmentation Scheme 3.

EXPERIMENTAL

(E)-α-(4-X-phenyl)-β-(2-thienyl)acrylamides (I) were prepared from the corresponding (E)-acrylic acids with thionyl chloride and ammonia gas in anhydrous ether solution. (E)-α-(4-X-phenyl)-β-(2-thienyl)acrylic acids were obtained with Perkin reaction from thiophene-2-carboxaldeyde and the corresponding para-substituted phenylacetic acid. Most (E)-acrylic acids were known and the analytical data were consistent with the values reported in the literature.[14,15]

(E)-α-(4-F-phenyl)-β-(2-thienyl)acrylic acid: m.p. 188–9°C, anal. calcd. for $C_{13}H_9FSO_2$: C, 62.89; H, 3.65; found: C, 62.97; H, 3.71.

(E)-α-(4-Br-phenyl)-β-(2-thienyl)acrylic acid: m.p. 238–9°C; anal. calcd. for $C_{13}H_9BrSO_2$: C, 50.50; H, 3.93; found: C, 50.78; H, 3.97.

TABLE II

Physical properties and analytical data of the (E)-(I) and (Z)-acrylamides (II)

No.	X	M.p. (°C)	Molecular formula	Analysis Found (%) C	H	N	Required (%) C	H	N	λ_{max} (nm)	log ξ	Chemical shift H_{α} (δ, ppm)
1	(E)H	124–25	$C_{13}H_{11}NOS$	68.21	4.91	6.17	68.08	4.83	6.11	312	4.17	8.11
2	F	189–90	$C_{13}H_{10}FNOS$	63.19	4.12	5.74	63.14	4.07	5.66	312	4.24	7.99
3	Cl	150–51	$C_{13}H_{10}ClNOS$	59.31	3.88	5.37	59.20	3.82	5.31	312	4.20	7.98
4	Br	163–4	$C_{13}H_{10}BrNOS$	50.71	3.21	4.60	50.66	3.27	4.54	311	4.25	8.12
5	NO_2	223–24	$C_{13}H_{10}N_2O_3S$	56.88	3.72	10.31	56.92	3.67	10.21	295	4.21	8.14
6	CH_3	163–4	$C_{14}H_{13}NOS$	69.21	5.47	5.82	69.10	5.38	5.75	312	4.34	8.07
7	CH_3O	153–54	$C_{14}H_{13}NO_2S$	64.93	5.11	5.48	64.84	5.05	5.40	310	4.21	8.12
8	(Z)H	170–71	$C_{13}H_{11}NOS$	68.18	4.92	6.18	68.08	4.83	6.11	317	4.20	7.32
9	F	171–72	$C_{13}H_{10}FNOS$	63.20	4.14	5.72	63.14	4.07	5.66	337	4.26	7.40
10	Br	176–77	$C_{13}H_{10}BrNOS$	50.74	3.33	4.62	50.66	3.27	4.54	325	4.27	7.47
11	CH_3	158–59	$C_{14}H_{13}NOS$	69.20	5.45	5.83	69.10	5.38	5.75	320	4.39	7.47
12	CH_3O	167–68	$C_{14}H_{13}NO_2S$	64.94	5.13	5.51	64.84	5.05	5.40	328	4.25	7.52

All the acids were recrystallized from EtOH.

(Z)-α-(4-X-phenyl)-β-(2-thienyl)acrylamides (**II**) were prepared refluxing the corresponding (Z)-acrylonitriles (1 g)[16,17] 30 hrs with 1 g KOH in 8 ml 80% EtOH. The solution was then evaporated and stirred with 200 ml H_2O giving the (Z)-acrylamides.

The assignment of the configuration of the amides I and II have been accomplished by the position of the olefinic proton in the NMR spectrum. As previously observed for the α, β-di-(2-thienyl)acrylic acids,[18] α-phenyl-β-(2-thienyl),[14] β-(2-furyl)[19] and α-phenyl-β-[2-(*N*-methyl) nitropyrrolyl] acrylic acids[20] the resonance lines of ethylene proton in the (Z)-compounds lie at higher fields compared with the corresponding proton in the (E)-isomers. (E) and (Z) isomers were recrystallized from ethanol.

NMR spectra were performed on 4% solutions with ca. 1% of TMS as internal standard. A Brucker WP 80 spectrometer was used. $CDCl_3$ of commercial quality was employed as solvent. U.V. spectra were obtained with a Hitachi Perkin-Elmer EPS-3T spectrometer, using 5×10^{-5} M solutions in 95% ethanol. Mass spectra at low resolution were recorded on LKB 9000S instrument at nominal 70 eV. The temperature of the ion source was 250°C and the samples were introduced via the direct inlet probe, at room temperature. High resolution mass spectra were determined with a double focusing Kratos MS 50S instrument at 10000 resolving power. Perfluorokerosene (PFK) was used for computer calibration; the ion source was maintained at 200°C. The spectra were obtained at 70 eV.

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