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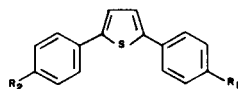
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The mass spectra of a series of 2,5-bis(*p*-R-phenyl)thiophenes are reported and discussed. The fragmentation patterns and mechanisms postulated have been confirmed by the determination of the metastable peaks. All the compounds possess the molecular ion as the base peak.

J. Heterocyclic Chem., **19**, 447 (1982).

A recent paper reported antitrypanosomal activity for a series of 2,5-bis(4-quanyphenyl)thiophenes and its "cyclic amidines" analogues (3). These thiophene compounds were envisioned as potential antiprotozoal agents based upon structural analogy with biologically active aryldi-amidines, and upon their potential interaction with DNA as their bioreceptor (4). This led us to carry out the synthesis and mass spectrometry studies of a series of these types of compounds, which have the general structure I.

In this paper we wish to report the mass spectral fragmentation patterns of substituted 2,5-bis(*p*-R-phenyl)thiophenes I (Scheme I $R_1 = R_2$, H, Br, CN, Cl, NO₂, NH₂, OMe, Me; $R_1 = H$ and $R_2 = CN, NO_2, NH_2$; $R_1 = Br$ and $R_2 = CN$).



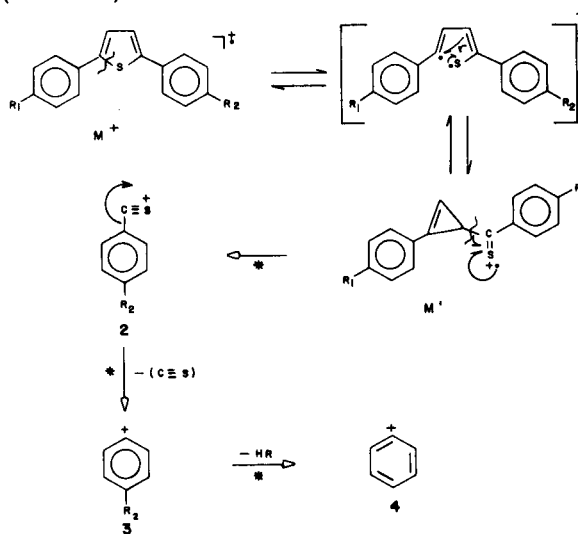
$R_1 = R_2 = H, Br, CN, Cl, NO_2, NH_2, OMe, Me.$
 $R_1 = H$ and $R_2 = CN, NO_2, NH_2.$
 $R_1 = Br$ and $R_2 = CN.$

Scheme 1

The relative abundances of these ions are shown in Table 1 and the proposed fragmentation pattern in Scheme 2 to 5.

All compounds I, are very stable under electron impact due to their heteroaromaticity, which favors the molecular ion to be observed as base peak (see Table 1). The forma-

tion of ion 2 is one of the most important, arising from cleavage of the heterocyclic C-S bond to form the thioketene M^+ ; which undergoes α -cleavage with respect to the C=S group to form 2. This ion loses the thiocarbonyl (C=S) group and then forms ion 3, which loses the R-substituent with a hydrogen (-HR) and ion 4 is obtained (Scheme 2).

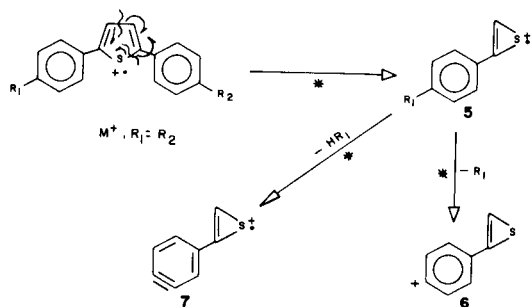


Scheme 2

Table 1
 Relative Abundance of Principal Fragments
 (Number in parentheses indicate the nature of the ions)
 Substituents on R_2, R_1

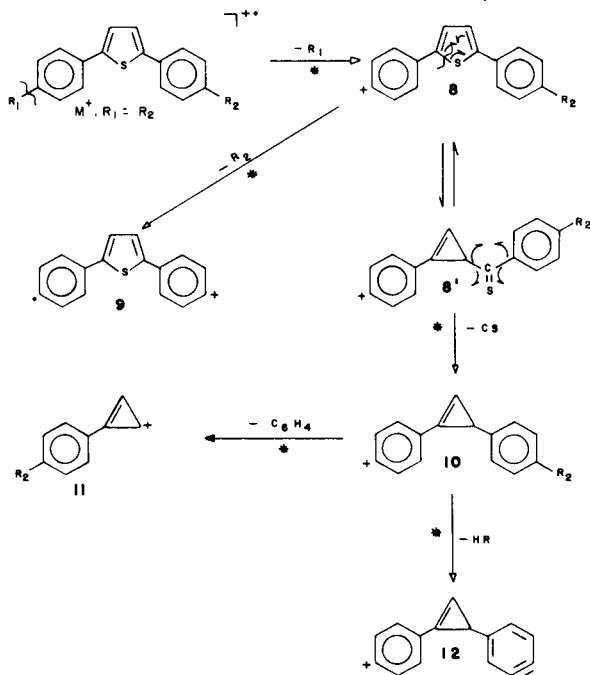
m/z		$R_1 = R_2$							$R_1 \neq R_2$				
		H	Br	CN	Cl	NO ₂	NH ₂	OMe	Me	Br; CN	H; CN	H; NO ₂	H; NH ₂
M^+	(1)	100	100	100	100	100	100	100	100	100	100	100	100
$120 + R$	(2)	15.15	5.26	36.58	27.71	7.01	0.92	2.42	5.34	2.41; 2.06	7.46; 11.64	57.84; 3.07	12.46; 4.67
$76 + R$	(3)	6.36	0.70	8.53	6.32	5.26	3.07		23.44	12.06; 3.7	8.65; 7.46	30.76; 5.23	11.83;
75	(4)	1.81	4.56	3.65	8.73	7.01	0.61	0.60	5.34	7.50	3.58	6.15	2.49
$133 + R$	(5)	6.06	2.45	9.14	8.73			0.60	6.23	0.68; 2.41	2.90;	2.46; 3.07	0.62;
133	(6)	0.60	3.50	0.60	5.42	4.56	0.76	0.45		3.79		0.92	
132	(7)	0.60	0.70	2.74	2.40	3.85	0.92	0.45	7.71	0.51		0.92	
$M^+ - R$	(8)	6.60	1.05	0.91	2.40	5.96	0.61		20.17	3.70;	0.29;	3.07; 10.15	16.51; 0.62
234	(9)	9.39	9.82	0.60	12.04	19.29	0.92	0.60			0.29	39.69	3.42
$190 + R$	(10)	2.42	0.07	0.91	2.40	6.31	9.23	3.03	5.93	; 3.79	; 1.49	30.79; 11.07	6.85; 2.80
$114 + R$	(11)	8.18	2.80	9.75	10.54		6.15		15.13	0.68; 1.37	5.97; 1.19	4.61; 0.61	0.62; 5.29
189	(12)	2.72	8.77	0.76	6.92	33.33	8.61	2.42	8.90	4.48	1.49	24.92	6.23
$M^+ - HR$	(13)	9.09	12.20	1.06	5.42		0.46	0.90	0.44	2.40;	4.47; 0.29	; 0.61	3.73; 3.73
232	(14)	1.21	4.21	0.91	3.91	14.03		0.60	0.29	0.68		5.84	2.49
$201 + R$	(15)	8.78	1.05	0.60	6.92		2.76	0.87	0.59	; 0.34	; 0.59	22.15;	0.46; 12.46

Other interesting fragmentation patterns are the cleavages of the S-C₂ and C₃-C₄ bonds from the molecular ion when it loses R-phenylacetylene to form ion **5**; this ion loses the R-substituent as R or HR to give ions **6** and **7** (Scheme 3).



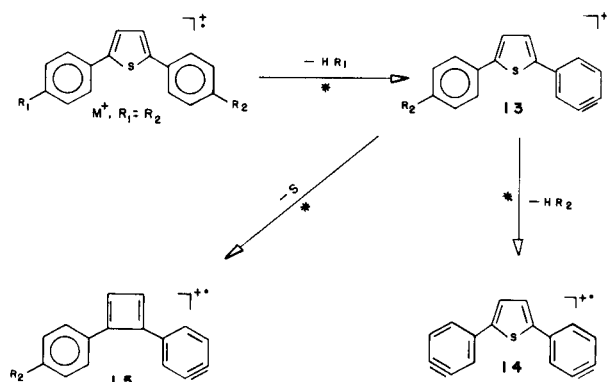
Scheme 3

Ion **8** arises from the molecular ion when it loses the R-substituent; the fragment undergoes a rearrangement and forms the thioketene **8'** which loses the thiocarbonyl group (C=S) and forms ion **10**. This ion loses the phenyl group and HR to form fragments **11** and **12**, respectively. The formation of ion **9** involves the elimination of the other R-substituent from the molecular ion **8** (Scheme 4).



Scheme 4

Ions **13** and **14** are obtained when the molecular ion loses HR and 2HR. Ion **15** arises from ion **13** when this ion loses an atom of sulfur (Scheme 5).



Scheme 5

All fragmentation pathways are supported by the corresponding metastable transitions which are depicted by an asterisk in the figures.

EXPERIMENTAL

The compounds have been prepared by modified techniques already described in the literature (5-8).

All the compounds investigated gave satisfactory elemental analyses. Some have been reported: R₁ = R₂ = H, Br, CN, Cl, NH₂, OMe, Me (8). The rest are described in Table 2.

The mass spectra were measured on a Hitachi-Perkin-Elmer RMU-7H double focusing mass spectrometer and a Hewlett-Packard 5985 A quadrupole mass spectrometer using the direct inlet system. The samples were recorded at an ionization chamber temperature of 190° and operating at 70 eV.

REFERENCES AND NOTES

- (1) To whom correspondence should be addressed.
- (2) Contribution No. 597 from Instituto de Química.
- (3) B. P. Das, D. W. Boykin, *J. Med. Chem.*, **20**, 1219 (1977).
- (4) B. P. Das, D. W. Boykin, *J. Med. Chem.*, **20**, 531 (1977).
- (5) *Org. Synth.*, XI, 88 (1931).
- (6) *Org. Synth.*, Collective Vol. III, 422 (1955).
- (7) J. B. Conent and R. E. Lutz, *J. Am. Chem. Soc.*, **47**, 1303 (1923).
- (8) E. Campaigne and W. O. Foye, *J. Org. Chem.*, **17**, 1405 (1952).

Table 2

Compound	R ₁	Mp °C	Yield %	Formula	Calcd./Found C%		Calcd./Found H%		Calcd./Found N%	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
NO ₂	NO ₂	181	43	C ₁₆ H ₁₂ N ₂ O ₄ S	58.95	58.93	3.71	3.70	8.59	8.61
H	CN	164	21	C ₁₇ H ₁₁ NS	78.23	78.20	4.24	4.24	5.36	5.33
H	NO ₂	74	37	C ₁₆ H ₁₁ NO ₂ S	68.39	68.36	3.94	3.95	4.98	4.94
H	NH ₂	137	20	C ₁₆ H ₁₃ NS	76.56	76.52	5.22	5.22	5.58	5.60
Br	CN	186	38	C ₁₇ H ₁₀ BrNS	60.23	60.21	2.97	2.96	4.13	4.12