Mass Spectral Fragmentation Patterns of 2,5-bis(*p*-R_2-Phenyl)-(3,4)-R_1-furans [1]

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The electron impact mass spectrometric fragmentation pathways for several 2,5-bis(*p*-R_2-phenyl)-(3,4)-R_1-furans, I, were investigated. Our investigation of the mass spectra of these compounds revealed interesting relationships between substitution pattern in the framework of I and the fragmentation patterns.

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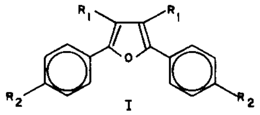
2,5-Diphenylfuran and their derivatives have been widely used as starting materials for the synthesis of various biologically interesting heterocycles *i.e.* 2,5-bis(4-guanylphenyl)furans [4]. In connection with these we have focused our attention on the analysis by electron impact mass spectrometry of these furans with special emphasis on the influence of the 3,4 and *para* substituents.

In the present paper we wish to report the mass spectral fragmentations of 2,5-bis(*p*-R_2-phenyl)-(3,4)R_1-furans, I, (Scheme 1). For the compounds formulated in Scheme 1 the relative abundances of the ions are shown in the Tables 1 to 4 and the proposed fragmentation patterns in Schemes 2 to 5. With few exceptions the latter have been justified by the existence of metastable ions and by comparison with the fragmentation patterns of known compounds.



I

Group	R_1	R_2
Ia	H	Me, Cl, Br
Ib	Me	Me, Cl, Br
Ic	CH_2Br	Me, Cl, Br
Id	Br	Me, Cl, Br

SCHEME 1

I. Fragmentation Pattern of 2,5-bis(*p*-R_2-phenyl)furans, (**1, 2, 3**), Ia.

The major cleavages of Ia upon electron impact may be plausibly represented by Scheme 2. All compounds Ia are very stable under electron impact due to their heteroaromaticity which favors the molecular ion to be observed as base peak (see Table 1) and the subsequent fragmentation is nicely formulated *via* an intermediate **1** which is similar to those of substituted furans [5]. The *para*-R_2 group is lost in the well-known manner [6] as in Scheme 2. This lead to the ion **2**, m/e (M^+-R_2), whose relative intensity is small in all the cases. Fragmentation of ion **2** proceeds along two pathways. One pathway results in the loss of the second *para*-R_2 substituent to give the ion **3** of m/e (M^+-$2R_2$); while the other results in the loss of carbon monoxide to give the ion **2a**, of m/e [M^+-(R_2 + CO)], which further loses the *para*-R_2 substituent with a hydrogen (-HR_2) and ion **2b** of m/e 189 is obtained. The ion **4** of m/e (114 + R_2) can be formed by α-cleavage of the cyclopropene carbonyl function in the molecular ion and the resulting ion loses a *p*-R_2-substituent to give ion **5** of m/e 114. On the other hand, ion **6** of m/e M^+-HR_2 is obtained when the molecular ion loses HR_2. A similar fragmentation has been reported for substituted furans [7].

As expected the benzoyl cation **7** of m/e (104 + R_2) is a pronounced peak in all spectra [8]. It arising from **1** by α-cleavage with respect to the carbonyl function. This ion then loses carbon monoxide resulting in m/e (76 + R_2), ion **8**, (It is possible that some of **8** may originate from the intact furan molecular ion). Fragmentation of this last ion is dependent on the *para*-R_2 substituents.

II. Fragmentation Pattern of 2,5-bis(*p*-R_2-Phenyl)-3,4-dimethylfurans (**4, 5, 6**), Ib.

Table 1

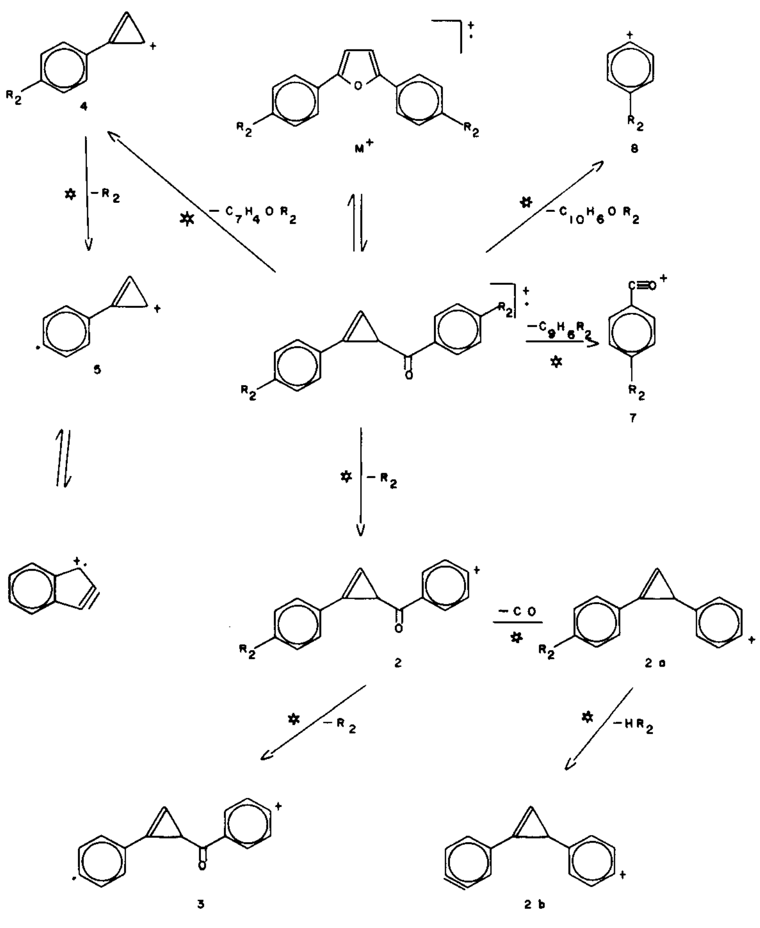
Relative Abundance of Principal Fragments for Compounds Ia (Figures in parentheses indicate the nature of the ions)

Compound No.	R_1	R_2	M^+ (1)	M^+-R_2 (2)	M^+-(R_2+CO) (2a)	187+$2R_1$ (2b)	m/e M^+-$2R_2$ (3)	M^+-(104+R_2) (4)	114 (5)	M^+-HR_2 (6)	(104+R_2) (7)	(76+R_2) (8)
1	H	Me	100.0	1.07	4.30	3.20	1.00	14.40	1.00	1.0	12.90	16.12
2	H	Cl	100.0	1.09	12.30	9. 89	3.29	36.25	3.50	1.0	26.37	30.76
3	H	Br	100.0	1.20	8.80	37.97	12.65	20.0	22.85	1.0	48.10	26.58

Table 2

Relative Abundance of Principal Fragments for Compounds Ib
(Figures in parentheses indicate the nature of the ions)

Compound No.	R_1	R_2	m/e														
			M^+ (1)	M^+-R_2 (2)	M^+-(R_2+CO) (2a)	$187+2R_1$ (2b)	$203+R_2$ (2c)	M^+-$2R_2$ (3)	218 (3a)	M^+-$(104+R_2)$ (4)	M^+-HR_2 (6)	$217+R_2$ (6a)	$202+R_2$ (6b)	245 (6c)	$76+R_2$ (8)	$104+R_2$ (7)	141 (9)
4	Me	Me	100.0	3.79	5.1	5.06	2.88	3.8	2.88	28.84	1.50	2.88	2.4	1.0	10.12	7.60	9.6
5	Me	Cl	100.0	3.80	1.0	3.20	2.59	1.63	3.89	53.89	2.59	1.50	1.0	1.0	23.91	16.30	21.42
6	Me	Br	100.0	3.00	1.0	7.00	1.00	1.50	8.42	28.78	2.02	1.00	1.0	1.0	12.0	15.0	12.0



SCHEME 2

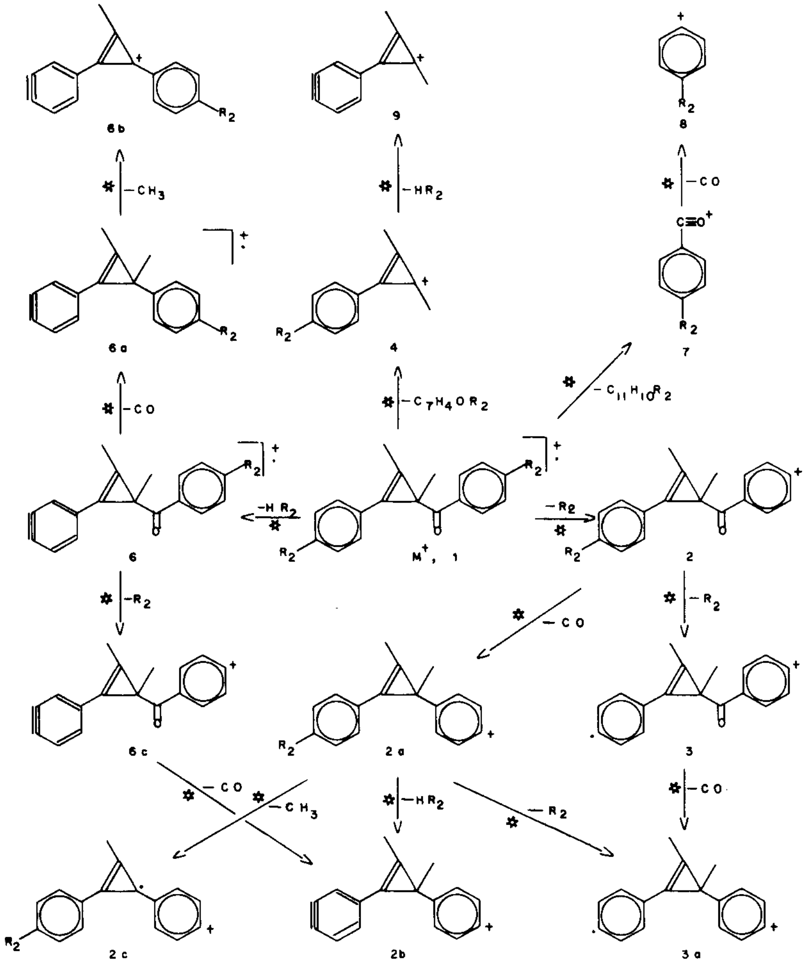
3,5-Dimethylfurans Ib (see Table 2) are also relatively stable under electron impact and as expected the most intense peak in their spectrum is due to the molecular ion **1**. Their characteristic fragmentation pattern (Scheme 3) follows that of the analogous Ia and show the loss of *para*-R_2-substituent to give ion **2** which in turn loses another molecule of R_2-substituent to produce the ion **3** of small intensity. The latter then loses carbon monoxide to give **3a** of m/e 218. This ion can be also formed by the loss of *para*-R_2-substituent from ion **2a**, which was formed from **2** by the loss of carbon monoxide. The ion **2a** further dissociates to **2b** by loss of HR_2 and to **2c**, m/e (203 + R_2) by loss of a methyl radical.

Consistent with the behavior of furans Ia, the molecular ion of Ib compounds undergoes expected α-cleavages to yield **4** and **7** ions as shown in Scheme 3. The ion **4** then loses a molecule of HR_2 to give **9**, m/e 141. Another interesting fragmentation pathway of 3,5-dimethylfurans Ib is the elimination of a HR_2 unit from the molecular ion giving rise to a fragment at m/e (M^+-HR_2), **6**. Fragmentation

Table 3

Relative Abundance of Principal Fragments for Compounds Ic
(Figures in parentheses indicate the nature of the ions)

Compound No.	R_1	R_2	m/e M^+ (1)	$104+R_2$ (7)	$76+R_2$ (8)	M^+-Br (10)	M^+-2Br (11)	$244+R_2$ (12)	244 (12a)	$216+R_2$ (12b)	216 (12c)	202 (12d)	M^+-159 (13)	$243+R_2$ (14)	$215+R_2$ (15)	215 (16)
7	CH_2Br	Me	17.50	32.5	30.0	100.0	17.50	31.25	10.0	17.5	20.0	3.75	11.25	12.50	35.3	25.0
8	CH_2Br	Cl	5.0	100.0	87.8	38.75	3.75	15.00	67.7	7.5	30.0	6.25	2.5	5.0	—	25.0
9	CH_2Br	Br	2.5	42.5	80.6	10.0	17.50	7.50	100.00	2.5	20.0	55.00	—	—	—	42.5

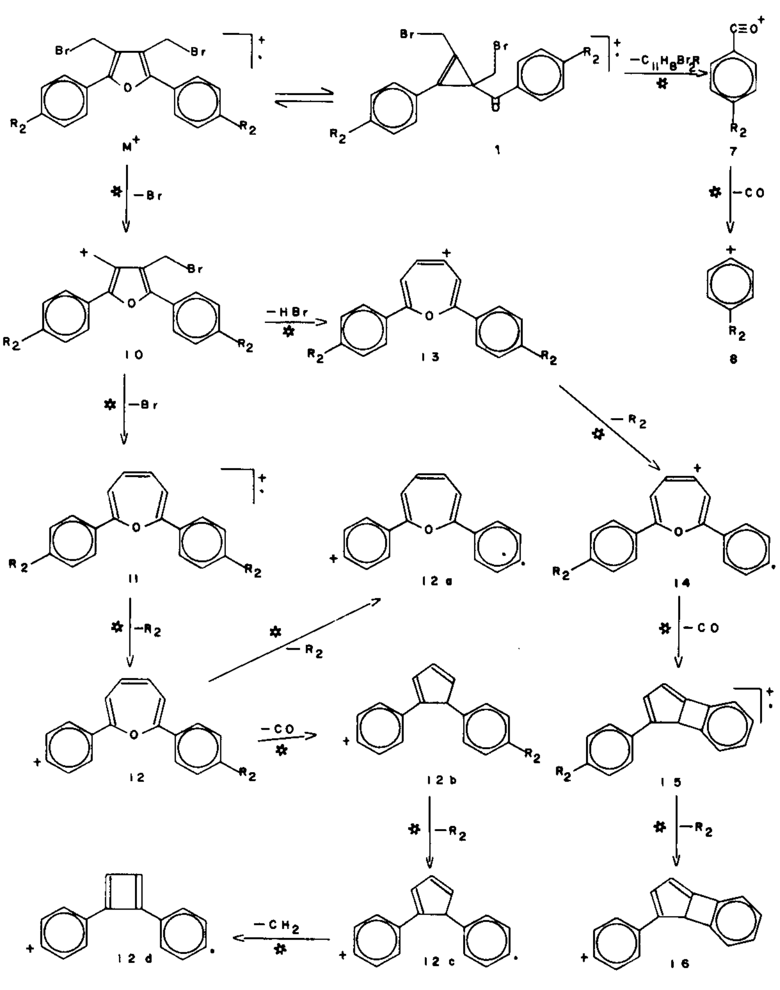


SCHEME 3

of **6** then proceeds along two pathways. One pathway results in the loss of *para*-R_2-substituent to give the ion **6c** of m/e 245; while the other results in the loss of a carbon monoxide unit to give the ion **6a** of m/e (217 + R_2) which further loses a methyl radical to yield **6b** of m/e (202 + R_2).

III. Fragmentation Pattern of 2,5-bis(p-R_2-Phenyl)-3,4-dibromomethylfurans (**7, 8, 9**), Ic.

Substitution of the two hydrogen atoms at C-3 and C-4 position of furans Ia by bromomethyl radicals to give Ic compounds alters the fragmentation to a considerable extent. The molecular ions of these compounds are of low abundance and besides ions which can be explained in terms of the fragmentation modes of Ia compounds *e.g.* fragments **7** and **8**, there are also new prominent peaks at different m/e relations. Based on the metastable ions the principal fragmenation of 3,4-dibromomethylfurans Ic is interpreted as shown in Scheme 4.



S C H E M E 4

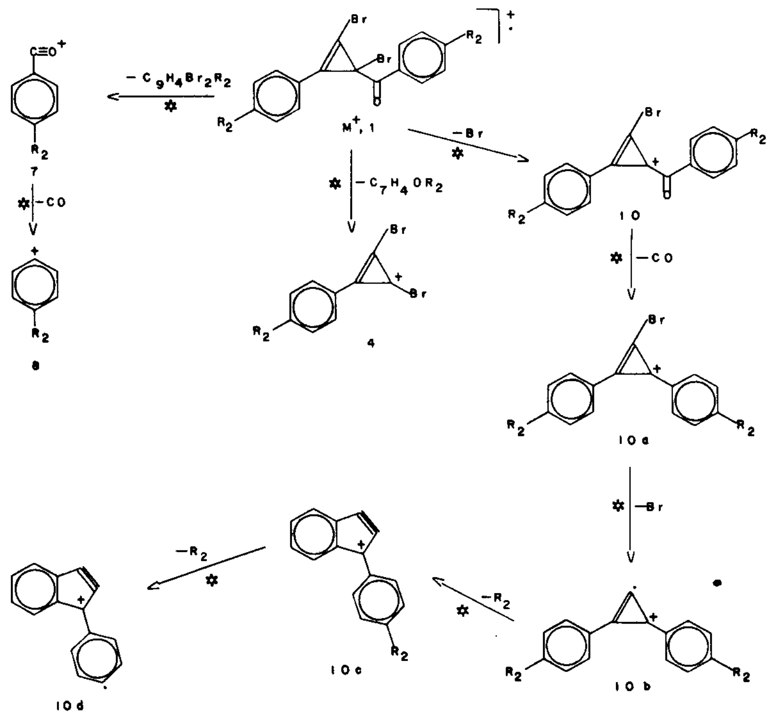
Table 4

Relative Abundance of Principal Fragments for Compounds Id (Figures in parentheses indicate the nature of the ions)

Compound No.	R_1	R_2	m/e								
			M^+ (1)	$104+R_2$ (7)	$76+R_2$ (8)	M^+-Br (10)	M^+-107 (10a)	$188+2R_2$ (10b)	$188+R_2$ (10c)	188 (10d)	$[M^+-(104+R_2)]$ (4)
10	Br	Me	7.50	100.0	53.35	1.0	5.0	5.0	6.75	2.5	2.0
11	Br	Cl	10.00	100.0	40.30	1.0	5.0	2.5	7.5	2.5	2.0
12	Br	Br	23.07	100.0	40.0	8.0	10.0	10.0	23.07	92.0	5.0

Table 5

Compound No.	R_1	R_2	Mp °C	Yield %	Formula	Calcd./Found C %		Calcd./Found H%	
1	H	Me	132-134	71.4	$C_{18}H_{16}O$	87.09	87.10	6.49	6.51
2	H	Cl	138-139	46.1	$C_{16}H_{10}Cl_2O$	66.45	66.44	3.48	3.49
4	Me	Me	91-92	95.6	$C_{20}H_{20}O$	86.91	86.92	7.29	7.29
5	Me	Cl	121-122	92.1	$C_{18}H_{14}Cl_2O$	68.15	68.13	4.44	4.43
7	CH_2Br	Me	144-145	41.6	$C_{20}H_{18}Br_2O$	55.32	55.31	4.17	4.17
8	CH_2Br	Cl	142-143	42.1	$C_{18}H_{12}Br_2Cl_2O$	45.51	45.53	2.54	2.56
10	Br	Me	140-141	95.0	$C_{18}H_{14}Br_2O$	53.23	53.21	3.47	3.46
11	Br	Cl	141-142	95.0	$C_{16}H_8Br_2Cl_2O$	42.99	43.01	1.80	1.79
12	Br	Br	138-139	95.0	$C_{16}H_8Br_4O$	35.86	35.88	1.50	1.51



S C H E M E 5

The ion **10**, m /e (M^+-Br), base peak for compound **7** ($R_2 = CH_3$), which results from the parent ion by the loss of a bromine radical is considered to lose hydrogen bromide yielding the ion **13**, m/e (M^+-159). Loss of the *para*-R_2-substituent from **13** gives the ion **14** of m/e (243 + R_2) which further loses carbon monoxide to yield **15**, m/e (215 + R_2). The radical ion **15** loses the *para*-R_2-substituent to yield the species of m/e 215, ion **16**.

Ion **10** may also lose bromine to yield **11** of m/e (M^+-2Br) which subsequently loses the *para*-R_2-substituent to give the ion **12** of m/e (244 + R_2). This ion loses the *para*-R_2-substituent and carbon monoxide to form fragment **12a**, m/e 244, base peak for compound **9**, (R_2 = Br), and **12b** of m/e (216 + R_2) respectively. This ion loses the other *para*-R_2-substituent and then forms **12c** ion of m/e 216 which loses 14 amu and ion **12d**, m/e 202, is obtained.

IV. Fragmentation Pattern of 2,5-bis(*p*-R_2-Phenyl)-3,4-dibromofurans (**10, 11, 12**), Id.

Most of the results given previously for compounds **1** to **9** are similar for the 3,4-dibromofurans Id (see Scheme 5). The main fragmentation mechanism can be regarded as a α-cleavage with respect to the carbonyl function of molecular ion **1** yielding ions **4** and **7**, base peak for compounds Id.

These compounds have a second fragmentation pathway of some importance. This is also shown in Scheme 5. In this pathway the molecular ion **1** cleaves to give fragment **10** which appears to undergo a loss of carbon monoxide resulting in **10a**. Ion **10a** then goes on to lose a bromine radical giving **10b** which in turn readily loses the *para*-R_2-substituent giving **10c**. The formation of **10d** involves the elimination of the other *para*-R_2-substituent from **10c** ion.

In conclusion, the compounds **1-12** give characteristic fragments with high intensities under electron impact. These fragments are the diagnostic value and may be of importance for selected ion monitoring assay of biological samples.

EXPERIMENTAL

The compounds have been prepared by modified technique already described in the literature [9-11]. All the compounds investigated gave satisfactory elemental analysis. Some have been reported: **3**, **6** and **9** [4]. The rest are described in Table 5.

The mass spectra were measured on a Hitachi-Perkin-Elmer RMU-7H double focusing mass spectrometer and a Hewlett Packard 59854-A quadropole mass spectrometer using the direct inlet system. The samples were recorded at an ionization chamber temperature of 190° and operating at 70 eV.

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