THE BEHAVIOUR OF SOME LONG-CHAIN 3-SUBSTITUTED FURANS AND THIOPHENES UNDER ELECTRON IMPACT

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The behaviour of 24 long-chain 3-substituted furans (*I*, *II*) and thiophenes (*III*, *IV*) under electron impact, was studied. Different fragmentation pathways were outlined.

Recently[1], we have synthesized a series of new long-chain 3-alkyl- and 3-(alk-1-en-1-yl)-furans *I*, *II* and thiophenes *III*, *IV* by the Wittig reaction between alkyltriphenylphosphonium bromides and the appropriate furan- and thiophene-3-carboxaldehydes. Compound *I* – *IV* could be used as intermediates for a variety of synthetic applications and industrial utilities especially in the field of electropolymerization, formation of Langmuir–Blodgett films[2 – 4] as well as for fabrication of molecular electron devices and chemically modified electrodes[5].

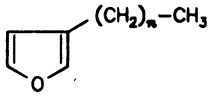
In response to our growing interest concerning heterocyclic compounds[6], we studied the mass spectra of compounds *I* – *IV*. We believe that such unique series of compounds *I* – *IV* possesses constitutional features sufficient to justify their study under electron impact, since the induced decompositions might depend not only on the length of the carbon-chain linked to the 3-position of the ring but also on the heterocyclic ring itself.

EXPERIMENTAL

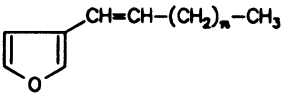
For preparation of compounds *I* – *IV*, cf. ref.[1]. The mass spectra were obtained on a Parkin–Elmer RMU-7 mass spectrometer or a Kratos MS 80 instrument with a DS-55 data systems. Measurements were done at 70 eV. All molecular ion peaks were identified by high resolution mass spectral investigations.

RESULTS AND DISCUSSION

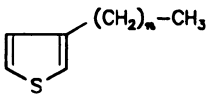
The mass spectra of furans *Ia* – *Ic* show close resemblence to each other. The relatively low intensities of their molecular ion peaks (~ 10%) (Table I) show that they possess relative instability toward electron impact[7,8]. The first conspicuous peak in their spectra appears at *m/z* 124 (Scheme 1). This indicates that the largest alkyl fragment attached to the furan ring in *Ia* – *Ic* incorporates 4 carbon atoms.



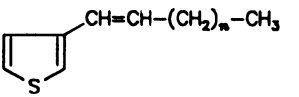
I	*n*
a	15
b	16
c	18



II	*n*
a	13
b	14
c	16



III	*n*
a	12
b	13
c	14
d	15
e	16
f	18



IV	*n*
a	10
b	11
c	12
d	13
e	14
f	16

The molecular ion peak (M^+) of compound *Ib*, taken as a representative example, appears at *m/z* 306 (*A*, 10%) (Scheme 1, Fig. 1). Cleavage of M^+ at site *w* produces cation *a* at *m/z* 67 (13%) while cleavage at site *x* yields the ion at *m/z* 81 (64%). The

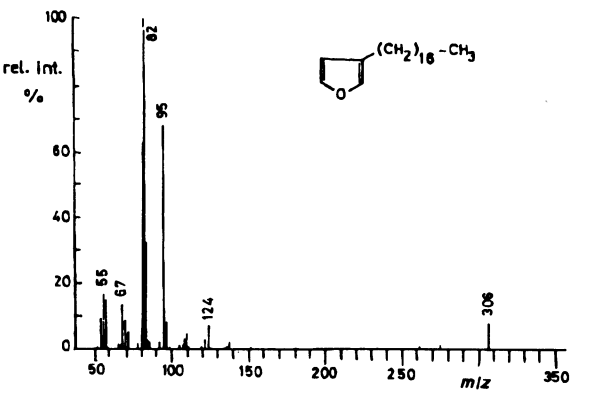


Fig. 1
Mass spectrum of compound *Ib*

SCHEME 1

latter ion is best represented by the pyryllium cation *b* (ref. [7]). In the same sense, cleavage of M^+ at sites *y* and *z* would also produce cations *c* and *d* at *m/z* 95 (68%) and 109 (< 5%), respectively. However, formation of the main fragments in the mass spectrum of *Ib* can be interpreted in terms a priori rearrangement of ion *A* to structure *B*. Subsequent cleavage of structure *B* at site *w* produces ion *e* at *m/z* 82 (100%, base peak). Similarly cleavage of *B* along site *z* produces cation *f* with *m/z* 124 (8%).

The loss of 26 mass units (CH=CH) frequently observed in the mass spectra of monosubstituted furans (and pyrans)[7] was also noticeable in the spectrum of *Ib*, and accounts for formation of cations *g* (*m/z* 55, 18%), *h* (*m/z* 83, 33%), *i* (*m/z* 97, 8%), *j* (*m/z* 56, 15%) and *k* (*m/z* 84, 5%), respectively.

TABLE I
Mass spectra of 3-alkylfurans *Ia* – *Ic* and 3-alkylthiophenes *IIIa* – *IIIf*

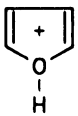
Compound	*m/z* (relative intensity, %)						
	M^+	*a*	*b*	*c*	*d*	*e*	*f*
Ia	292 (10)	67 (23)	81 (70)	95 (70)	109 (< 5)	82 (100)	124 (8)
Ib	306 (10)	67 (13)	81 (64)	95 (68)	109 (< 5)	82 (100)	124 (8)
Ic	334 (10)	67 (6)	81 (25)	95 (32)	109 (< 5)	82 (100)	124 (8)
IIIa	266 (100)	83 (< 5)	97 (23)	111 (11)	125 (< 5)	98 (75)	140 (< 5)
IIIb	280 (28)	83 (< 5)	97 (59)	111 (23)	125 (< 5)	98 (100)	140 (6)
IIIc	294 (4)	83 (5)	97 (32)	111 (12)	125 (< 5)	98 (100)	140 (< 5)
IIId	308 (25)	83 (< 5)	97 (48)	111 (22)	125 (5)	98 (100)	140 (5)
IIIe	322 (80)	83 (5)	97 (78)	111 (48)	125 (5)	98 (100)	140 (18)
IIIf	350 (45)	83 (< 5)	97 (38)	111 (15)	125 (< 5)	98 (100)	140 (5)

$CH_2=CHC\equiv O^+$
$C_3H_3O^+$
g, *m/z* 55, 18%

$C_5H_7O^+$
h, *m/z* 83, 33%

$C_6H_9O^+$
i, *m/z* 97, 8%

$C_3H_4O^+$
j, *m/z* 56, 15%



$C_5H_8O^+$
k, *m/z* 84, 5%

l, *m/z* 69, $C_4H_5O^+$

Presence of an ion at *m/z* 69 in the mass spectrum of *Ib* is attributable to cation *l* which is also observed in the spectra of a number of monosubstituted alkylfurans[7].

The mass spectra of compounds *IIIa – IIIf* (Table I) also possess some unique features. Except for *IIIa*, they show the base peak at *m/z* 98 which stands for cation *e* (X = S, Scheme 1). The intensity of the molecular ion peaks in the spectra of *IIIa – IIIf* is much higher in comparison with those of furan analogues *I*. This shows that thienyl compounds *III* are relatively stable under electron bombardment. Presence of the peak at *m/z* 140 with a considerable intensity (5 – 18%) in the spectra of *IIIa – IIIf* indicates that the longest chain attached to the thiophene nucleus has four carbon atoms. The low intensity of ion *d* (< 5%) in the spectra of *Ia – Ic* and *IIIa – IIIf* indicates that cleavage of their molecular ions (structure *A*) at site *z* is less frequent (Fig. 2).

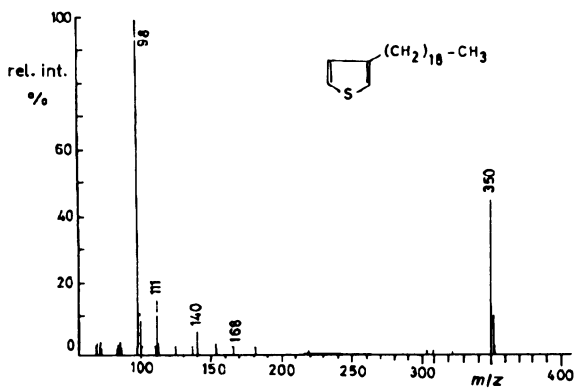
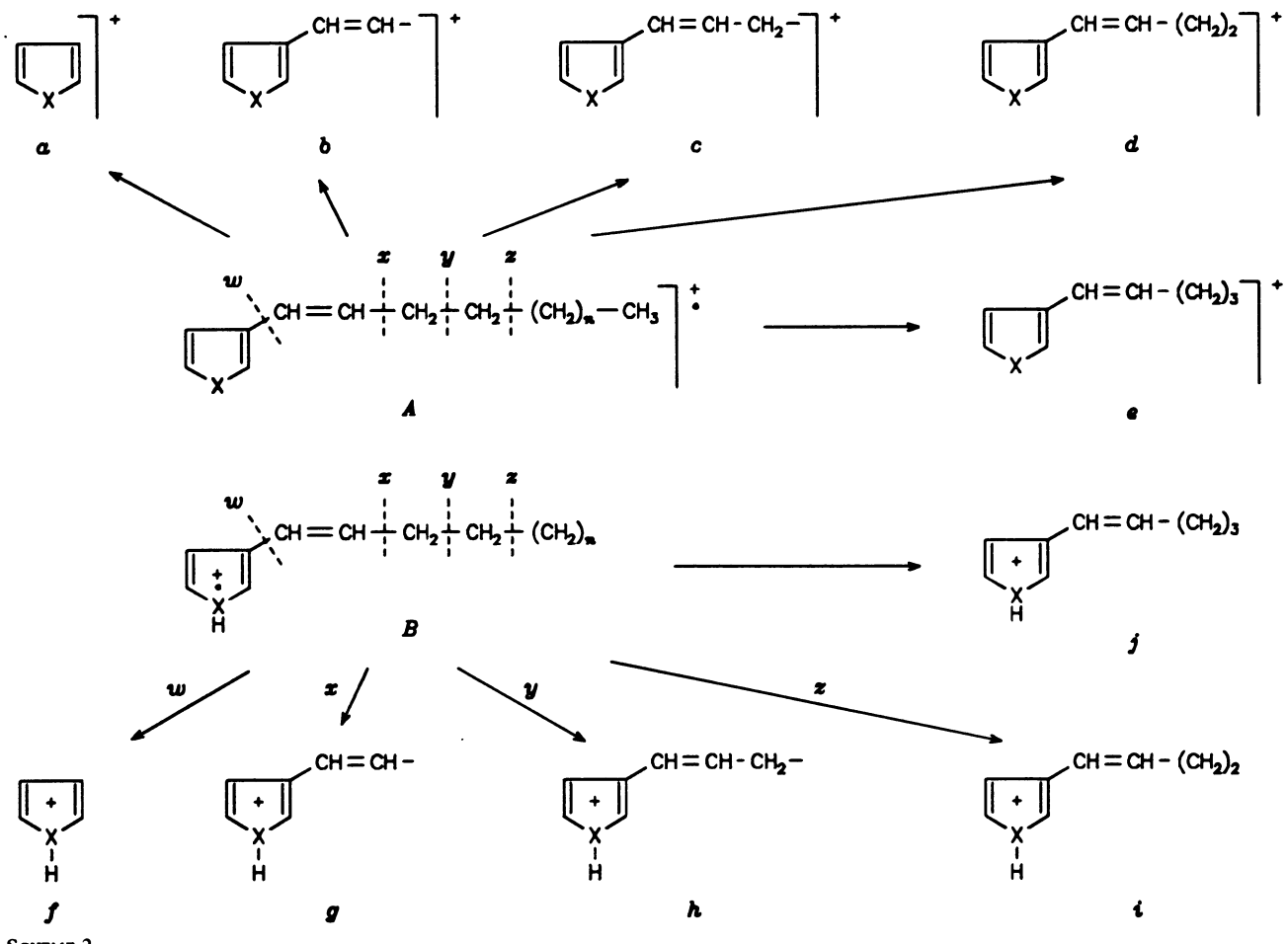


Fig. 2
Mass spectrum of compound *IIIf*

The behaviour of 3-(alk-1-en-1-yl)furans *IIa – IIc* under electron impact resembles that of thiophene analogues *IVa – IVf*. Fragmentation of M^+ in both groups of compounds (*II*, *IV*) can be interpreted in terms of its existence in the radical cation structure *A* and *B* (Scheme 2). In the case of the mass spectra of *IIc* (Fig. 3) and *IVf*, taken as representative examples, cleavage at the site *w* in both structures (*A* or *B*) is rather inefficient and produces hardly conspicuous (< 5%) ion peaks *a* and *f*. Cleavage at site *x*, however, is much obvious in structure *B* which produces ion *g*. Allylic cleavage of M^+ (*A* or *B*) at site *y* produces cations *c* and *h* and accounts for the formation of the base peak in the spectra of *IVf* and of all other thiophene derivatives (Fig. 4). Cleavage at site *z* is noticeable only in structure *A* and gives rise to ion *d*. Cleavage further than site

TABLE II
Mass spectra of 3(alk-1-en-1-yl)furans (*IIa – IIc*) and 3(alk-1-en-1-yl)thiophenes (*IVa – IVf*)

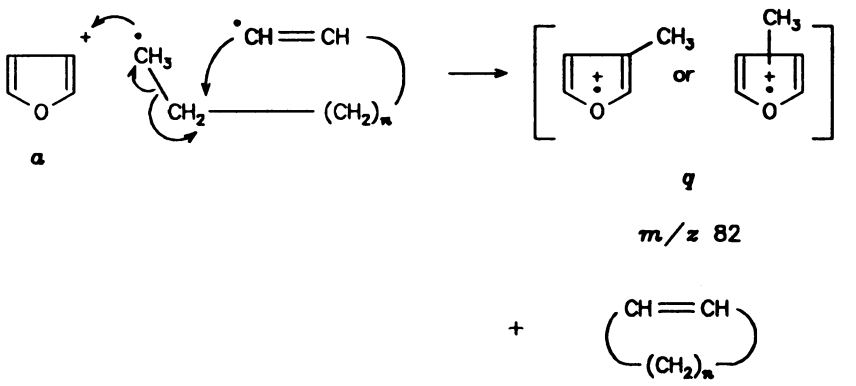
Compound	*m/z* (relative intensity, %)										
	M^+	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*
IIa	290 (23)	67 (18)	93 (12)	107 (80)	121 (40)	135 (20)	68 (7)	94 (77)	108 (70)	122 (8)	136 (< 5)
IIb	304 (19)	67 (18)	93 (10)	107 (73)	121 (35)	135 (17)	68 (12)	94 (73)	108 (75)	122 (7)	136 (< 5)
IIc	332 (37)	67 (5)	93 (5)	107 (85)	121 (35)	135 (28)	68 (6)	94 (68)	108 (75)	122 (10)	136 (6)
IVa	264 (48)	83 (< 5)	109 (< 5)	123 (100)	137 (18)	151 (15)	84 (5)	110 (38)	124 (24)	138 (5)	152 (< 5)
IVb	278 (45)	83 (5)	109 (5)	123 (100)	137 (18)	151 (14)	84 (5)	110 (48)	124 (22)	138 (< 5)	152 (< 5)
IVc	292 (35)	83 (5)	109 (< 5)	123 (100)	137 (17)	151 (13)	84 (6)	110 (48)	124 (22)	138 (<5)	152 (< 5)
IVd	306 (70)	83 (< 5)	109 (68)	123 (100)	137 (38)	151 (30)	84 (< 5)	110 (70)	124 (55)	138 (35)	152 (< 5)
IVe	320 (53)	83 (5)	109 (60)	123 (100)	137 (18)	151 (12)	84 (7)	110 (60)	124 (32)	138 (< 5)	152 (< 5)
IVf	348 (95)	83 (5)	109 (5)	123 (100)	137 (19)	151 (18)	84 (7)	110 (40)	124 (25)	138 (6)	152 (7)


a
b
c
d
e
A
B
f
g
h
i
j
w
x
y
z
CH=CH-
CH=CH-CH2-
CH=CH-(CH2)2
CH=CH-(CH2)3
CH=CH-CH2-
CH=CH-(CH2)2
CH=CH-(CH2)3
CH=CH-CH2-CH2-(CH2)m-CH3
CH=CH-CH2-CH2-(CH2)m

SCHEME 2

z, more remote from heterocyclic ring, is observed only in structure *A* whereby ion *e* is produced (Scheme 2, Table II).

The base peak in the mass spectra of the furan derivatives *IIa – IIc*, appears at *m/z* 82 (Fig. 3). This might be explained in terms of initial formation of cation *a* via ejection of the alkenyl radical. The latter can eject a methyl radical to give the neutral cycloalkenyl species *p*. Combination of the CH_3 radical with cation *a* produces then the radical cation at *m/z* 82 (*q*, 100%, Scheme 3).



SCHEME 3

It is evident that the long-chain 3-alkylfurans *Ia – Ic* give rise to the molecular ion peaks in ca 10% intensity under electron impact. The analogous thiophenes *IIIa – IIIf* give molecular ions which vary in intensities between 4% and 100%, differing thus from the behaviour of the short-chain analogues (e.g. 2-ethylthiophene)[9]. Also, it has to

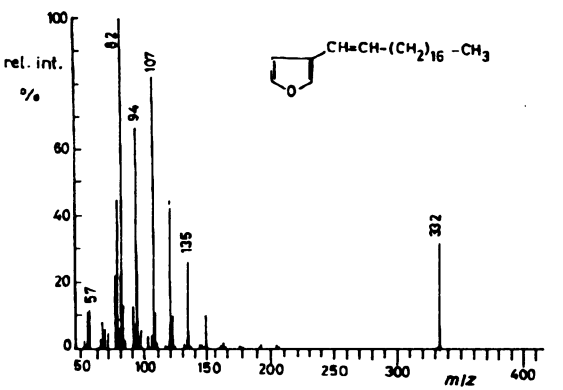


Fig. 3
Mass spectrum of compound *IIc*

be stated that the first conspicuous peak in the mass spectra of both furans *I* and thiophenes *III* bears 4 carbon atoms in the side chain regardless of the length of this chain. On the other hand, 3-(alk-1-en-1-yl)furans and/or thiophenes show almost the same fragmentation pattern but differ in the identity of the base peak which appears at *m/z* 82 in the spectra of the furans *I* while it is shown at *m/z* 123 in the thiophene analogues *III*.

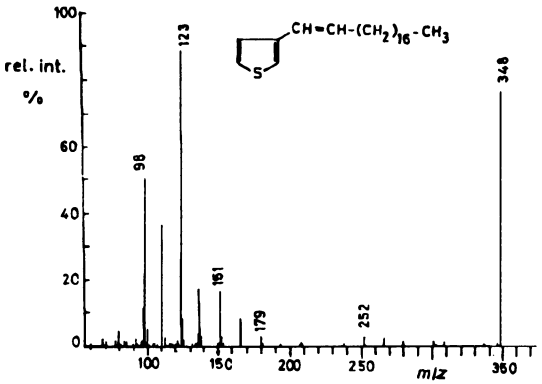


Fig. 4
Mass spectrum of compound *IVf*

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