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STUDIES IN MASS SPECTROSCOPY—II[1]

MASS SPECTRA OF SUBSTITUTED FURANS

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Abstract—The mass spectra of 29 furans, variously substituted with alkyl, aldehyde, ketone, ester, nitrile and nitro groups are reported and discussed. The spectra are generally quite simple and amenable to analysis. Not only do the characteristic *m/e* values give information as to the type of substituents, but also the operation of certain *ortho*-effects permits conclusions as to the relative location of functional groups. A number of rearrangement processes have been investigated by high resolution measurements and deuterium labelling.

ALTHOUGH the mass spectra of furan,[2,3] some simple alkyl furans,[2,3] and furan-carboxylic acids[4] have been discussed, a detailed investigation of this class of compounds has not hitherto been reported. The purpose of this paper is to point out the relationship between the structure of substituted furans and their fragmentation patterns.

The spectra of 29 substituted furans are reported in the Table and Figs 1, 2 and 3. All ions having an abundance of 5% or more of that of the base peak (100%) are recorded in the Table; in addition, ions of lesser abundance are included if they are of diagnostic value.

Methyl furan-2-carboxylate (I) shows the behaviour anticipated for an aromatic methyl ester, the base peak (*a*, *m/e* 95) corresponding to loss of a methoxyl radical; the only other abundant ion in the spectrum occurs at *m/e* 39 and is associated with the cyclopropenyl cation *b*, which accounts for the base peak in the spectrum of furan itself.[2,3] The introduction of a methyl substituent adjacent to the ester group, as in the isomeric esters II and III, introduces two additional features into the breakdown pattern. First, loss of methanol can now compete with the loss of a methoxyl radical, through the operation of an *ortho*-effect[5] (for example, III → *c*, *m/e* 108). Second, loss of a methyl radical from the ester group occurs to give an M-15 species. Similar behaviour has been observed in pyrroles and it has been proposed[6] that since an

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[1] Part I. J. H. Bowie, D. W. Cameron and D. H. Williams, *J. Amdr. Chem. Soc.* in press. The present paper also constitutes Part III in the series *Studies in Furan Chemistry* Part II: R. Grigg, M. V. Sargent and J. A. Knight, *Tetrahedron Letters* 1381 (1965).

[2] J. Collin, *Bull. Soc. Chim. Belg.* **69**, 449 (1960).

[3] H. Budzikiewicz, C. Djerassi and D. H. Williams, *Interpretation of Mass Spectra of Organic Compounds* pp. 226–229. Holden-Day, San Francisco (1964).

[4] R. I. Reed and W. K. Reid, *J. Chem. Soc.* 5933 (1963).

[5] F. W. McLafferty and R. S. Gohlke, *Analyt. Chem.* **31**, 2076 (1959).

[6] H. Budzikiewicz, C. Djerassi, A. H. Jackson, G. W. Kenner, D. J. Newman and J. M. Wilson, *J. Chem. Soc.* 1949 (1964).

Table 1. Mass spectra of substituted furans

I	*m/e*	126	96	95	39	38	37							
	Abundance (%)	39	9	100	1	13	5							
II	*m/e*	141	140	125	110	109	108	53	52	51	44	39		
	Abundance (%)	6	65	11	11	100	5	70	7	6	7	4		
III	*m/e*	141	140	125	110	109	108	80	53	52	51	50	44	43
	Abundance (%)	6	60	23	8	100	15	8	8	7	9	5	7	19
	m/e	39												
	Abundance (%)	5												
IV	*m/e*	169	168	140	139	127	124	123	122	121	96	95	94	67
	Abundance (%)	9	85	14	70	5	11	100	34	8	7	8	15	8
	m/e	66	65	53	44	43	41	40	39					
	Abundance (%)	9	11	8	18	40	15	5	16					
V	*m/e*	155	154	153	140	139	124	123	122	121	95	94	81	67
	Abundance (%)	10	98	6	7	77	9	100	14	6	12	20	12	5
	m/e	53	52	51	50	43	41	39						
	Abundance (%)	12	7	10	7	80	6	6						
VI	*m/e*	213	212	181	154	153	121	79	59	53	43	39		
	Abundance (%)	5	43	24	10	100	38	7	6	5	18	3		
VII	*m/e*	198	168	167	166	137	113	109	108	107	80	79	59	52
	Abundance (%)	22	7	74	100	15	6	5	18	6	8	6	8	5
	m/e	51	43	39										
	Abundance (%)	7	14	4										
VIII	*m/e*	202	201	200	170	169	168	167	166	138	137	117	112	110
	Abundance (%)	7	12	14	16	62	100	89	7	16	22	8	5	5
	m/e	109	108	107	89	81	80	79	60	53	52	51	50	
	Abundance (%)	20	17	14	6	9	13	10	7	6	10	14	7	
	m/e	46	45	44	43	41	40	39	(d_2, 46%; d_3, 35%; d_4, 19%)					
	Abundance (%)	6	12	12	15	5	8	6						

Table 1. (cont.)

X	*m/e*	209	208	207	206	205	176	175	174	173	168	167	148	147
	Abundance (%)	5	14	30	18	26	7	94	8	100	5	5	6	6
	m/e	146	119	117	96	95	66	53	44	40	39	38	37	
	Abundance (%)	5	15	17	5	8	9	5	11	8	4	26	10	
		(d_1, 55%; d_2, 35%; d_3, 10%)												
XI	*m/e*	253	252	222	221	194	165	128	127	94	66	54	53	39
	Abundance (%)	8	100	6	78	5·5	9·5	2	4	6	5	2	3	4
	m/e	38	37											
	Abundance (%)	18	5·5											
XIV	*m/e*	174	145	143	140	139	111	108	80	79	52	51	39	
	Abundance (%)	19	7	20	10	100	6	8	8	13	10	11	1	
XV	*m/e*	190	188	154	153	145	144	143	125	109	108	95	81	80
	Abundance (%)	8	22	11·5	100	11	5	32	39	7·5	8·5	5	5	8
	m/e	79	52	51	39									
	Abundance (%)	9	12	12·5	2									
XVI	*m/e*	111	110	109	81	53	51	50	43	39				
	Abundance (%)	7	100	84	7	32	6	6	7	7				
XVII	*m/e*	176	175	174	173	119	117	66	44	39	38			
	Abundance (%)	91	100	95	98	16	17	7	8·5	50	40			
XVIII	*m/e*	222	221	165	127	39	38	37						
	Abundance (%)	100	36	12	5	16	13	5						
XIX	*m/e*	173	172	171	144	116	115	106	105	95	78	77	72	51
	Abundance (%)	12	100	8	11	7	10	8	100	60	5	55	5	20
	m/e	50	39											
	Abundance (%)	7	12											
XX	*m/e*	253	252	251	250	249	175	173	171	115	106	105	77	51
	Abundance (%)	6	48	11	49	5	14	16	22	13	8	100	48	16
	m/e	50	39	38										
		6	3	6										

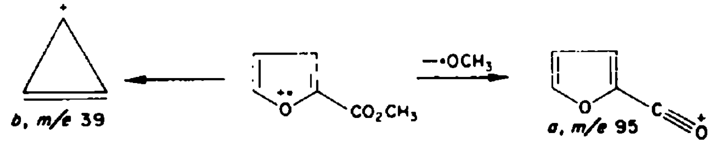
Table 1. (cont.)

XXI	*m/e*	299	298	221	171	115	106	105	78	77	51	50	44	39
	Abundance (%)	15	100	24	10	16	8	80	5	40	18	7	5	5
	m/e	38												
	Abundance (%)	12												
XXII	*m/e*	110	96	95	68	43	39							
	Abundance (%)	50	7	100	4	15	15							
XXIII	*m/e*	190	96	95	40	39	38							
	Abundance (%)	15	8	100	6	20	5							
XXIV	*m/e*	182	151	150	124	110	109	108	53	52	44	43	39	
	Abundance (%)	16	6	17	19	8	100	18	8	5	24	5	5	
XXV	*m/e*	196	151	150	124	110	109	53	45	44	43	39		
	Abundance (%)	17	5	6	12	8	100	9	8	10	10	2		
XXVI	*m/e*	124	96	95	79	77	67	66	65	63	53	52	51	50
	Abundance (%)	19	8	100	7	8	26	7	14	6	11	5	13	7
	m/e	41	40	39	38									
	Abundance (%)	40	7	40	6									
XXVII	*m/e*	138	124	123	95	93	91	79	78	77	67	65	63	55
	Abundacne (%)	10	9	100	14	5	9	16	6	19	22	10	6	16
	m/e	53	52	51	50	43	41	40	39	38				
	Abundance (%)	22	9	21	10	7	38	7	45	6				
XXVIII	*m/e*	174	173	172	171	122	120	119	117	65	64	63	38	37
	Abundance (%)	7	98	8	100	11	11	13	14	5	75	9	11	22
XXIX	*m/e*	192	191	190	189	175	173	171	119	117	105	77	66	65
	Abundance (%)	5	21	5	22	25	42	19	8	8	5	5	5	9
	m/e	64	44	43	41	39	38	37						
	Abundance (%)	33	100	4	5	19	21	15						
XXX	*m/e*	94	93	65	64	39	38	37						
	Abundance (%)	7	100	19	42	16	20	12						

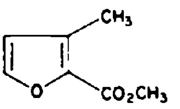
TABLE 1. (cont.)

XXXI	m/e	194	193	192	191	135	133	119	117	109	107	105	96	82
	Abundance (%)	6	97	6	100	74	76	47	47	5	18	14	40	6
	m/e	80	68	54	52	51	44	39	38	37				
	Abundance (%)	5	14	8	8	5	17	5	100	31				

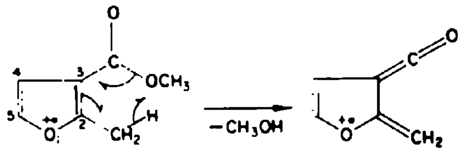
isolated ester will not decompose appreciably by loss of an alkyl radical, that an *ortho*-effect is also operative here (IIIa → *d*, *m/e* 125). The evidence which indicates that the methyl group lost in the fragmentation of II and III comes from the ester rather than the nuclear methyl group is unequivocal. Thus the spectrum of the ester (IV) exhibits a very pronounced M—C_2H_5 fragment, but an almost negligible (~ 2% of base peak) M—CH_3 ion.



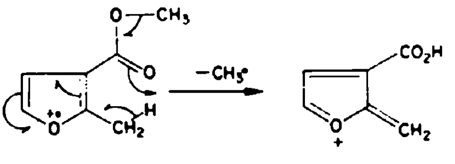
I

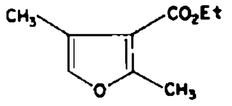


II



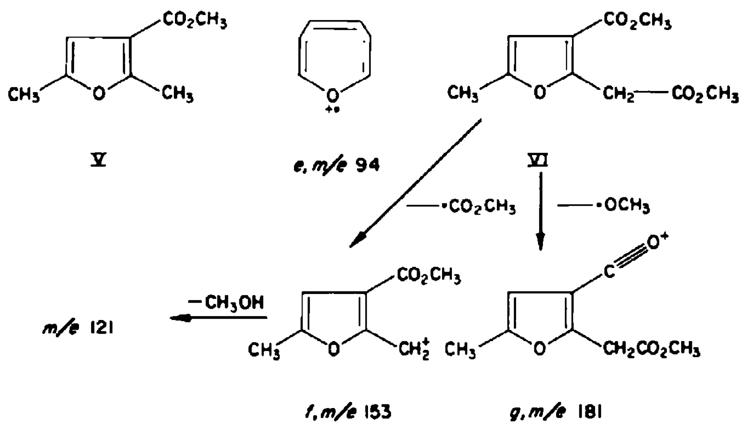
III c, m/e 108





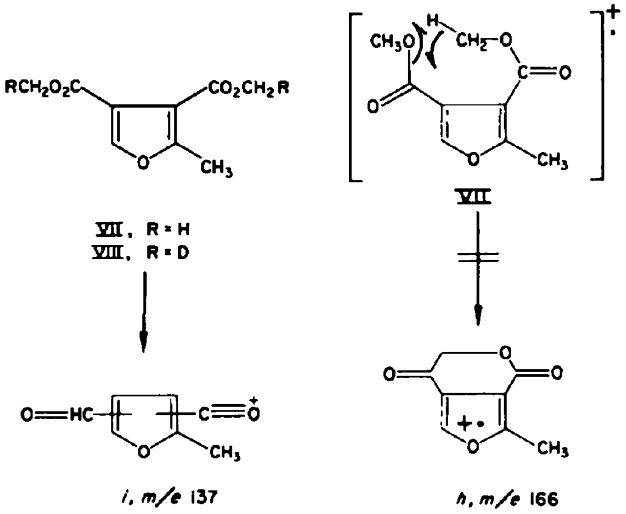
IIIa d, m/e 125 IV

Although the spectra of II and III are very similar the compounds can in fact be differentiated by the prominent *m/e* 43 ion present only in the spectrum of the latter and corresponding to the acetyl cation (CH_3—C—O+) formed by cleavage of the 2–3 and 1–5 bonds (see III). As might be expected, the acetyl ion (*m/e* 43) is also prominent in the spectrum of the ethyl ester (IV) as is also an M—C_2H_5OH peak (*ortho*-effect). The *m/e* 43 ion is most pronounced in the presence of two α-methyl groups and attains 80% of the base peak in the spectrum of methyl 2,5-dimethylfuran-3-carboxylate (V). The spectra of IV and V are notable for the presence of peaks (15% and 19%, respectively) at *m/e* 94 which may be associated with the oxepin ion *e*; both compounds contain the two nuclear methyl groups necessary for a double ring expansion to the seven-membered ring.



If an ester group is present as part of a furyl acetate ester moiety, as in VI, then the favourable nature of β-cleavage adjacent to an aromatic ring leads to loss of a carbomethoxyl radical (VI → *f*, *m/e* 153, base peak). Rather surprisingly, *f* then decomposes further by elimination of methanol to afford *m/e* 121 as evidenced by an appropriate metastable ion at *m/e* 95·8 (calc. 95·7). The loss of a methoxyl radical, presumably mainly from the conjugated ester group, leads to *m/e* 181 (*g*).

The spectrum of VII,[7] which contains adjacent carbomethoxyl groups, contains M—CH$_3$OH (*m/e* 166) as the base peak. This represents by far the most pronounced *ortho*-effect observed in the furan series and therefore the possibility arose that the methanol might be eliminated due to some interaction between the methoxyl groups of the esters (e.g., VII → *h*). Isotopically labelled ester, corresponding predominantly to VIII (d_6–VII) was therefore prepared by esterification of the di-acid with diazomethane in the presence of deuterium oxide.[8] The spectrum of VIII shows a negligible



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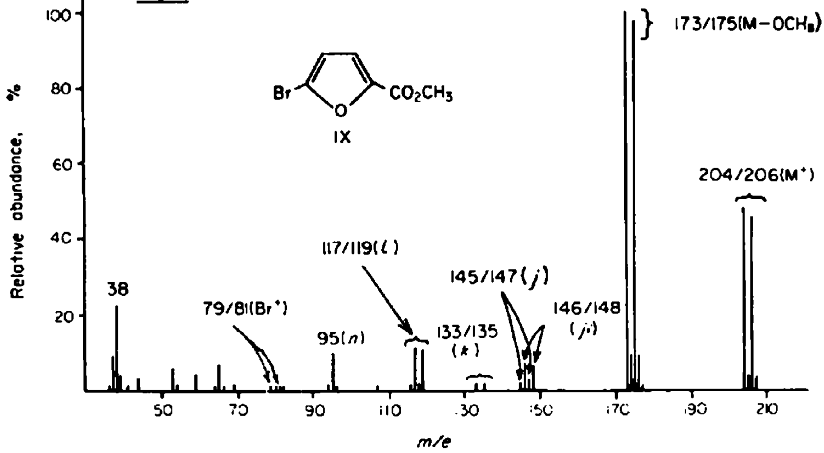
[7] The spectrum of VII reported in the Table is appreciably different from that reported previously,[4] which shows some evidence of thermal decomposition of the compound, e.g., pronounced M-1 and M-2 peaks.

[8] K. J. Van Der Merwe, P. S. Steyn and S. H. Eggers, *Tetrahedron Letters* 3923 (1964).

loss of CH_2DOD and therefore establishes that the *ortho*-effect involves the nuclear methyl group as usual. The spectrum of VIII also establishes that *m/e* 137 arises from elision of both methoxyl groups but with rearrangement of one hydrogen to afford *i*.

The spectra of a number of halo-esters (IX–XV) have been determined. The spectrum (Fig. 1) of methyl 5-bromofuran-2-carboxylate (IX) is open to unambiguous interpretation due to the characteristic isotopic abundances ($\sim$ 1 : 1) of ^{79}Br and ^{81}Br, and with the aid of the spectrum of the d_1-ester (X), prepared by the usual method.[8] The base peak arises from the usual loss of a methoxyl group (*m/e* 173/175 in Fig. 1), but less abundant ions are evident in the high mass region corresponding to loss of the whole ester substituent (*j*, *m/e* 145/147) and loss of the ester substituent with hydrogen rearrangement (*j'*, *m/e* 146/148). The hydrogen rearrangement is confirmed by the spectrum of the d_1-ester (X).[9] The rather small *m/e* 133/135 doublet arises from elimination of C-2 and its ester substituent to give a fragment corresponding to *k*. The peaks at *m/e* 117/119 are due to the bromocyclopropenyl cation (*l*), which decomposes further by loss of a bromine radical to yield *m/e* 38. Generally speaking, the presence of an abundant *m/e* 38 ion is consistent with a furan containing a C-5 substituent which can be lost relatively easily as a radical (e.g., Br, I) and C-3 and C-4 unsubstituted.[10] The peak at *m/e* 95 (*n*) corresponds to elimination of a bromine radical from the M—CH_2O ion (*m/e* 174/176, which is 3·5% of the base peak after correcting for the natural abundance of ^{13}C in the *m/e* 173/175 peak). However, it appears unlikely that the established hydrogen rearrangement from the methoxyl group occurs to give the 2-formyl-5-bromofuran (XVII) molecular ion, since the spectrum of this compound shows virtually no *m/e* 95 ion. Also since there is no direct expulsion of a bromine radical from the molecular ion of IX (to support an (M—Br)—CH_2O sequence), a concerted process (see *m* → *n*) following hydrogen rearrangement to oxygen might be entertained. The 5-iodo-analogue (XI) fragments in a very similar manner; although no ion corresponding to *j* is formed, loss of both substituents leads

Fig.1



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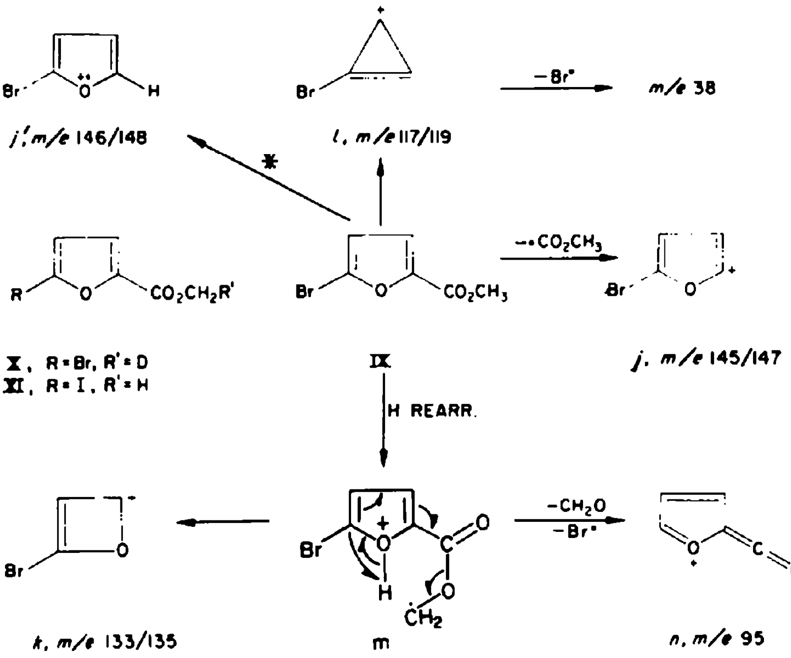
[9] Degradation paths supported by an appropriate metastable peak are indicated by an asterisk.

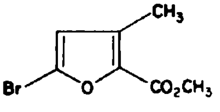
[10] It is quite likely that 3-bromo- and 2-iodo-furans unsubstituted at C-4 and C-5, or 4-bromo- or 4-iodo-furans unsubstituted at C-3 and C-5 will also give rise to corresponding *m/e* 38 ions.

to *m/e* 66. It is noteworthy that whereas *k* decomposes by loss of Br and HBr to give *m/e* 54 and *m/e* 53 in the ratio 1:3, the iodo-analogue of *k* loses I and HI to afford the same ions in the ratio 3:2; the relative abundances of these two processes reflect the relative stabilities of the two halogens as radicals. Similarly, while *m/e* 79/81 (Br^+) and *m/e* 80/82 (HBr^+) are of the same abundance (Fig. 1), *m/e* 127 (I^+) is 2·5 times the abundance of *m/e* 128 (HI^+) in the spectrum of XI.

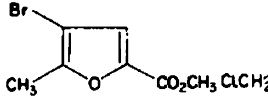
The spectra (Figs. 2 and 3 respectively) of the isomeric furans (XII and XIII) forcibly illustrate how substitution patterns can be deduced and isomers differentiated in this class of compounds. The M—CH_3 and M—CH_3OH peaks present in Fig. 2 and absent in Fig. 3 illustrate that only in XII are the methyl and methoxyl functions adjacent (these peaks are formed by processes analogous to IIIa → *d* and III → *c* respectively). Abundant ions associated with the methylbromocyclopropenyl cation (*m/e* 131/133) in both spectra indicate that the ester substituents must be at C-2 (or C-5) in both XII and XIII. The *m/e* 109 ion (M—CH_2O—Br) in Fig. 2 is formed by



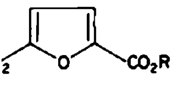
the proposed double hydrogen transfer (see IX → *m* → *n*) characteristic of 2-carbomethoxy-5-halo compounds and the structure of XII is therefore available on mass spectrometric evidence alone. The pronounced *m/e* 43 ion indicates that XIII is an α-methylfuran.



XII



XIII



XIV, R = CH_3
XV, R = C_2H_5

Fig.2

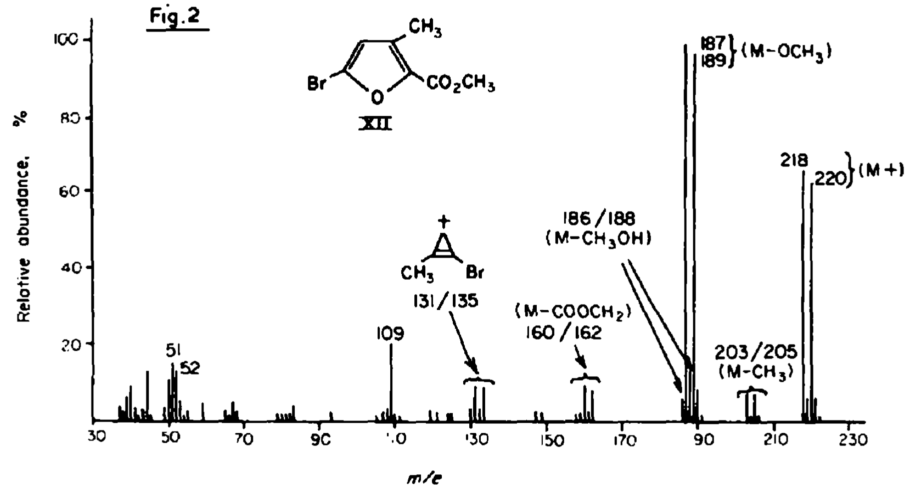
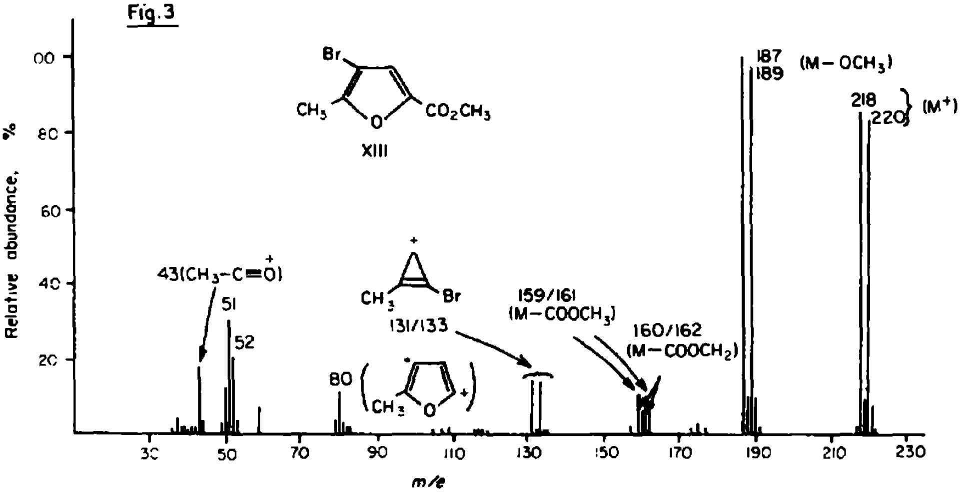


Fig.3



In the spectra of methyl and ethyl 5-chloromethyl-2-carboxylates (XIV and XV, respectively), the base peaks arise from the favoured loss of a chlorine radical by β-cleavage. In the thiophene[11] and pyrrole[12] series it has been proposed that the derived carbonium ions (for example *o*, *m/e* 139) undergo ring expansion to the corresponding thiopyrylium and pyridinium ions. Supporting evidence for a similar ring expansion of *o* to the pyrylium ion *p* is found in the breakdown of *m/e* 139 to *m/e* 111 by loss of CO as definitely substantiated by high resolution measurements. This process requires either the ring expansion *o* → *p* followed by loss of carbon monoxide from the pyrylium ring or loss of carbon monoxide from the ester group with an associated methoxyl migration. The former possibility appears more likely, but ^{18}O labelling of the ester function is currently under investigation to settle this point unambiguously. The ion *m/e* 139 (*o* or *p*) then decomposes further as indicated in Scheme 1. On the basis of the plausible ring expansion *o* → *p*, *m/e* 79 would be a

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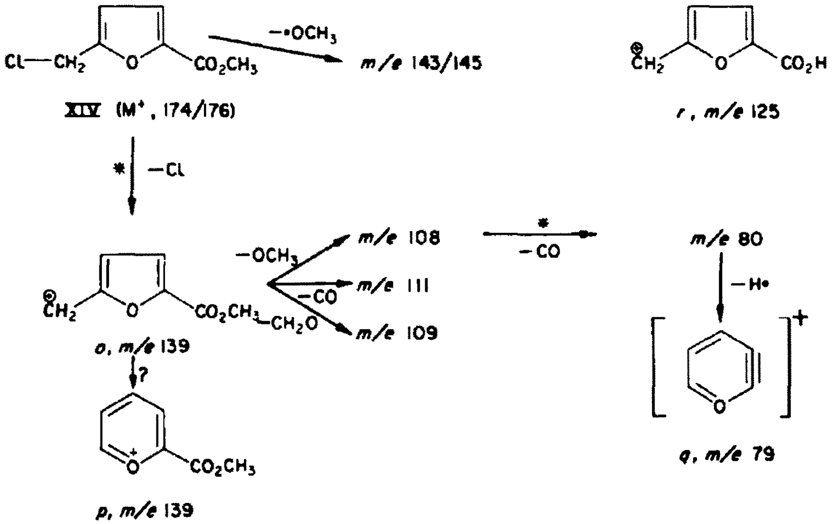
[11] V. Hanuš and V. Čermák, *Coll. Czech. Chem. Comm.* **24**, 1602 (1959).

[12] Ref. 3, pp. 238–239.

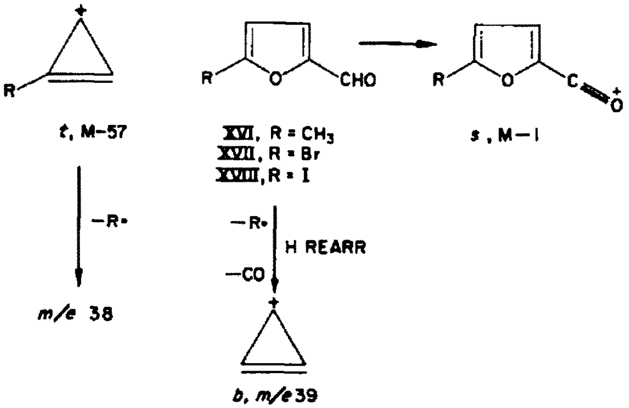
dehydropyrylium ion *q*. The ethyl ester XV behaves very similarly, except that the loss of 28 mass units from the M-Cl ion is much more pronounced and almost certainly is associated with elimination of ethylene from the ethyl group to furnish *r* (*m*/*e* 125) or its pyrylium analogue.

Scheme 1



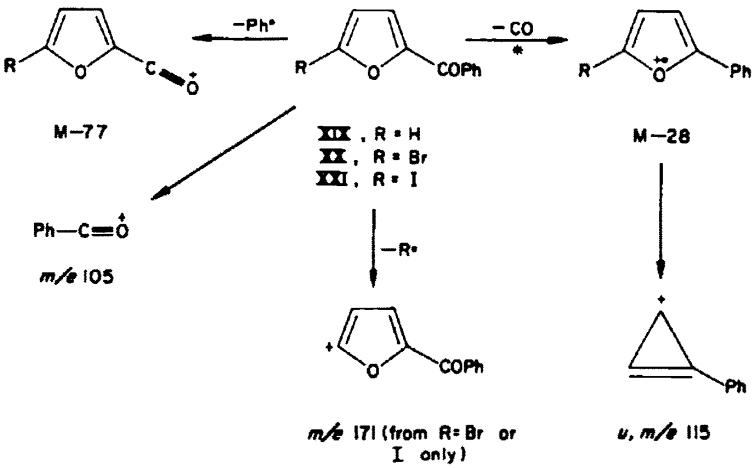
The spectra of three aldehydes containing C-5 methyl (XVI), bromine (XVII) and iodine (XVIII) substituents have been measured and all show abundant M-1 fragments due to the formation of a species *s* (Scheme 2), although loss of a hydrogen atom from the methyl group of XVI may be a contributing factor in that compound. Substituted cyclopropenyl ions (*t*) are also common to all three spectra and give rise to *m*/*e* 38 by loss of the substituent. However, these substituted 2-formylfurans differ from the substituted methyl furan-2-carboxylates discussed previously inasmuch as the *m*/*e* 38 ions are accompanied by *m*/*e* 39 species of slightly greater abundance. Evidently the cyclopropenyl cation *b* may be formed by elimination of R and CO with associated migration of the aldehyde hydrogen to the charged moiety.

Scheme 2



The decomposition modes of the three phenyl ketones (XIX, XX and XXI) are indicated in Scheme 3 and for the most part follow the principles previously outlined. However, the bromo- and iodo-compounds (XX and XXI) undergo a small but significant loss of carbon monoxide from the molecular ion and in furyl phenyl ketone (XIX) the M—CO peak is quite large (11 % of the base peak). The presence of a peak at *m/e* 115 due to the phenylcyclopropenyl cation *u* in all three spectra establishes the migration of the phenyl group to the furan nucleus in this process. All three spectra exhibit ions associated with the benzoyl ion (*m/e* 105 and its characteristic decomposition products *m/e* 77 (the phenyl cation) and *m/e* 51. Finally, the spectra of XX and XXI contain the anticipated *m/e* 38 ions, whereas that of XIX shows an abundant *m/e* 39 species.

Scheme 3



The spectra of 2-acetylfuran (XXII) and furil (XXIII) require little comment except to note that the spectrum of XXII shows no M—CO peak, an observation which supports the reasonable conclusion that phenyl has a greater migrating aptitude than methyl upon electron impact in these cases.

The β-ketoesters XXIV and XXV behave very similarly insomuch as both decompose to a greater extent by elimination of ROH (methanol and ethanol, respectively) than by loss of ·OR; ethyl acetoacetate breaks down in exactly the same manner[18] and presumably the alcohol fragment is lost via a cyclic transition state involving the enol form of the molecular ion *v* (Scheme 4). Loss of the COOR groups occurs almost exclusively with hydrogen rearrangement to the charged fragment, probably to afford *w* (*m/e* 124). In each case the base peak arises from β-cleavage to give *m/e* 109 (*x*), although it is interesting to note that when the substituents are adjacent in XXIV an appreciable (18 %) *m/e* 108 ion appears; this fragment can arise by loss of methyl acetate as indicated in XXIV → *y*(*m/e* 108).

The spectra of the alkyl furans XXVI and XXVII are unexceptional, the respective M—C_2H_5 and M—CH_3 base peaks, arising from β-cleavage, indicating maximum chain lengths of 3 and 2 carbon atoms in the alkyl substituents of these compounds.

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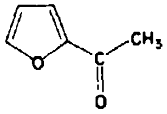
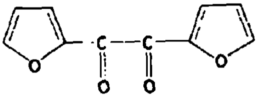
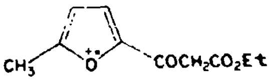
[18] J. H. Bowie, S.-O. Lawesson, P. Madsen, G. Schroll and D. H. Williams, unpublished work.



XXII

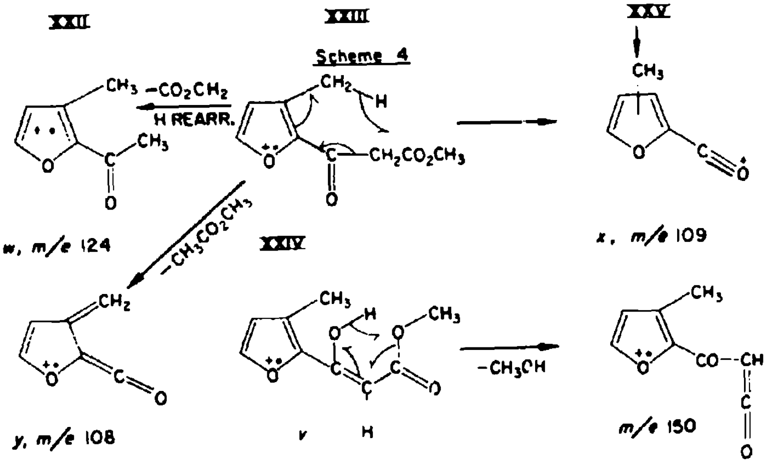


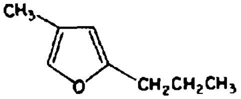
XXIII



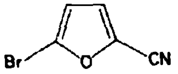
XXV

Scheme 4

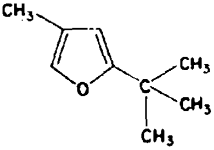




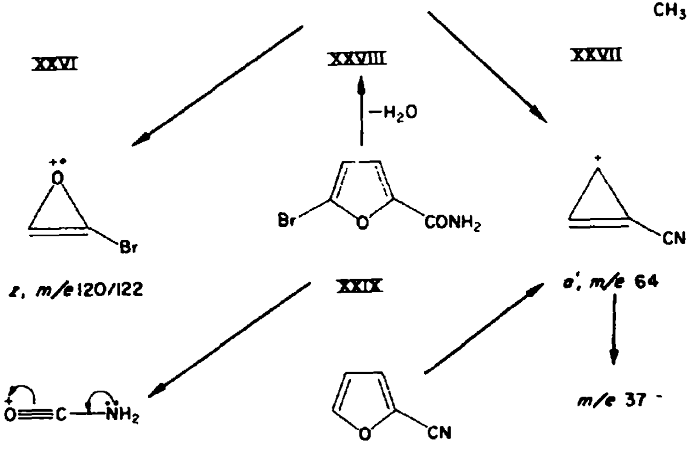
XXVI

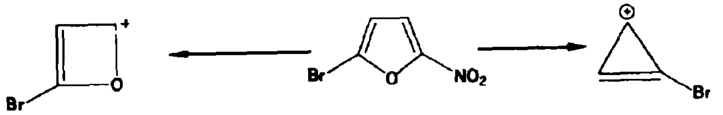


XXVIII



XXVII





The bromo-amide XXIX undergoes the loss of 16 mass units (—NH_2), characteristic of primary amides,[14] from the molecular ion. The recorded spectra of aromatic amides[14] do not exhibit M-18 peaks and it appears likely that the M-18 peak in the spectrum of XXIX is due to thermal dehydration of XXIX to nitrile XXVIII. The spectra of both XXVIII and XXIV contain peaks corresponding to *z* (*m/e* 120/122) and the cyanocyclopropenyl cation *a'* (*m/e* 64); the latter decomposes to the rather remarkable C_3H^+ (*m/e* 37) ion, the obvious driving force being the elimination of the very favourable neutral particle HCN. 2-Cyanofuran (XXX) fragments normally, while the nitrofuran XXXI behaves slightly differently from nitrobenzenes[15] in that the M—NO_2 (*m/e* 147/149) is relatively small and only of comparable abundance to the M—NO (*m/e* 151/153) peak; the most abundant fragment ions are *k* (*m/e* 133/135) and *l* (*m/e* 117/119) and its characteristic decomposition product (*m/e* 38). The *m/e* 96 ion is due to an M—OBr species, but the mechanism of its formation is not obvious.

In summary, it can be said that the mass spectra of substituted furans indicate very selective breakdown patterns upon electron impact. The formation of characteristic ions and the operation of predictable rearrangement processes (e.g., *ortho*-effects) indicate both the nature and relative orientation of substituents in many cases. Hence mass spectrometry, used in conjunction with IR[16] and NMR spectroscopy, should greatly facilitate structure elucidation in this class of compounds.

EXPERIMENTAL

All mass spectra were determined on an AEI MS 9 mass spectrometer using a heated inlet system operating at approximately 150°. The energy of the electron beam was 70eV. The preparation of hitherto unreported furans will be published in a subsequent paper.

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[14] G. Spiteller, *Monatsh.* **92**, 1147 (1961).

[15] J. H. Beynon, R. A. Saunders and A. E. Williams, *Ind. Chim. Belg.* **4**, 311 (1964).

[16] R. Grigg, M. V. Sargent and J. A. Knight, *Tetrahedron Letters* 1381 (1965).