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THE MASS SPECTRA OF FURAN CHALCONE ANALOGUES

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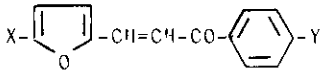
Abstract - The electron impact mass spectra of 14 furan chalcone analogues ($5\text{-}X\text{-}C_4H_2O\text{-}CH{=}CH\text{-}CO\text{-}C_6H_4\text{-}\underline{p}Y$, X = H, Me; Y = OMe, Me, H, F, Cl, CN, NO_2) are reported and the fragmentation pattern is discussed and compared to those of chalcones and their thiophene analogues.

The mass spectral behaviour of α,β-unsaturated cycloketones[1,2], styrylketones[3], benzalacetones[4] and substituted benzalacetophenones[4-6] has been investigated. The mass spectrum of benzalacetophenone was first recorded by Beynon[7]: the major fragmentations of this compound were rationalised and found to be characteristic. Following recent studies on the mass spectra of some substituted thiophene chalcone analogues[8], we here report the electron impact mass spectra at 70 eV of 14 substituted furan chalcone analogues (series 1 and 2).

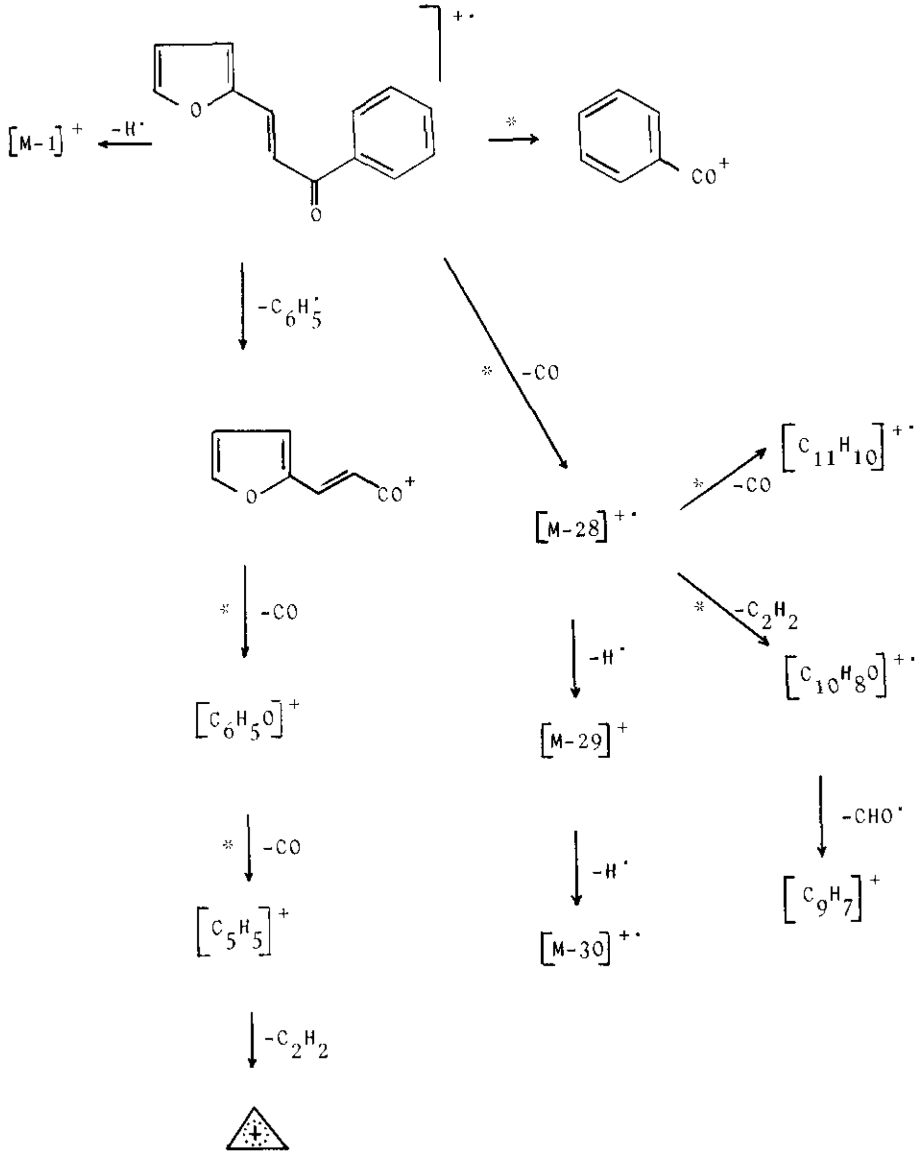


Series	X substituent
1	H
2	CH_3

Y Substituent :	OCH_3	CH_3	H	F	Cl	CN	NO_2
Designation :	a	b	c	d	e	f	g

The effect of the heteroatom and of X and Y substituents on ^{13}C chemical shifts of the terms in series 1 and 2 have been discussed[9]. Their ^{13}C NMR and IR spectra showed that the above compounds exist in the trans isomeric form[9].

The mass spectra of furan chalcone analogues in series 1 and 2 are listed in the Table. These compounds, under electron impact, are very stable being characterized by a high degree of conjugation and the molecular ions are always very intense, as already found for the corresponding thiophene chalcone analogues[8] and for benzalacetophenones[4-6]. The molecular ions for 1a, 1b and 1d perform the base peak, whereas for 1c,1e-1g the base peak is the substituted benzoyl cation $\left[Y-C_6H_4-CO\right]^{+}$. In series 2 the base peak is the $\left[M - CH_3\right]^{+}$ ion, except for 2a where the molecular ion is also the base peak; the benzoyl cation shows lower intensity in this series. Inspection of the spectra reveals analogies with the fragmentation patterns of benzalacetophenones[4-6]. We report below, as an example, the fragmentation pathway of 1c. The transitions substantiated by metastable peaks (directly observed in the 70 eV mass spectra) are indicated by an asterisk.



For substituted styrylketones[3] only one of the two possible α-cleavages with respect to the carbonyl was observed, while in series 1 and 2 both α-cleavages are observed, as found for substituted benzalacetophenones[4-6] and for the corresponding thiophene chalcone analogues[8]. Formation of both $X-C_4H_2O-CH=CH-C{\equiv}O^+$ and $Y-C_6H_4-C{\equiv}O^+$ ions and further CO elimination is observed in all compounds. For the nitro derivatives 1g and 2g the CO elimination from the benzoyl cations is preceded by loss of the nitro substituent. Another feature in the mass spectra of compounds in series 1 and 2 is the presence of $[M-1]^+$ peaks whose intensities are lower than for benzene[4-6] and thiophene[8] derivatives. The mass spectra of benzalacetophenones[5,6] are also characterized by loss of the styryl linked ring whereas this fragmentation is absent in series 1 and 2. All the examined compounds show very weak peaks due to CO elimination from the molecular ion, probably occurring by a rearrangement process analogous to that described by Van de Sande[5]. The CO elimination is followed by loss of two hydrogen atoms as reported for some thiophene derivatives[8].

EXPERIMENTAL

Products - The syntheses and the physical properties of furan chalcone analogues in series 1 and 2 have been reported[9].

Mass spectra - The mass spectra were recorded on a LKB 9000S spectrometer at 70 eV, with ion source temperature 250°C. The samples were introduced using the direct inlet probe technique.

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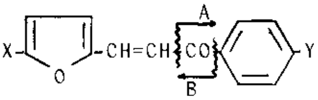
Table Characteristic peaks in the mass spectra of furan and 5-methylfuran chalcone analogues (series 1 and 2)[a].



Comp.	M^+	M-1	M-Y	M-CO	A	A-CO	B	B-CO	M-15
1a	228 (100)	227 (7)	197 (3)	200 (6)	135 (50)	107 (5)	121 (12)	93 (2)	-
1b	212 (100)	211 (9)	197 (6)	184 (8)	119 (71)	91 (35)	121 (23)	93 (2)	-
1c	198 (90)	197 (11)	-	170 (12)	105 (100)	77 (59)	121 (45)	93 (5)	-
1d	216 (100)	215 (13)	197 (1)	188 (9)	123 (83)	95 (34)	121 (24)	93 (4)	-
1e	232 (95) 234 (35)	231 (10) 233 (3)	197 (14)	204 (10) 206 (3)	139 (100) 141 (36)	111 (32) 113 (11)	121 (31)	93 (4)	-
1f	223 (76)	222 (10)	-	195 (13)	130 (100)	102 (28)	121 (25)	93 (4)	-
1g	243 (88)	242 (9)	197 (5)	215 (4)	150 (100)	-	121 (32)	93 (5)	-
2a	242 (100)	241 (2)	211 (3)	214 (4)	135 (23)	107 (12)	135 (23)	107 (12)	227 (85)
2b	226 (81)	225 (2)	211 (100)	198 (3)	119 (6)	91 (12)	135 (11)	107 (2)	211 (100)
2c	212 (84)	211 (2)	-	184 (3)	105 (12)	77 (41)	135 (22)	107 (5)	197 (100)
2d	230 (97)	229 (3)	-	202 (2)	123 (13)	95 (15)	135 (11)	107 (3)	215 (100)
2e	246 (81) 248 (27)	245 (1)	211 (10)	218 (3) 220 (1)	139 (15) 141 (5)	111 (18) 113 (6)	135 (18)	107 (5)	231 (100)
2f	237 (70)	236 (2)	-	209 (3)	130 (8)	102 (15)	135 (14)	107 (4)	222 (100)
2g	257 (89)	-	211 (4)	229 (3)	150 (3)	-	135 (17)	107 (4)	242 (100)

[a] Relative intensities in parentheses.

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