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SHORT COMMUNICATION

AM1 AND ELECTRON IMPACT MASS SPECTROMETRY STUDY OF THE FRAGMENTATION OF 4-ACYL ISOCHROMAN-1,3-DIONES

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ABSTRACT. Recently, in electron impact mass spectrometry (EIMS), it has been found a good correlation between the fragmentation processes of coumarins and the electronic charges of the atoms of their skeleton. In this paper, the same analytical method has been applied to 4-acyl isochroman-1,3-diones, whose mass spectra had been studied earlier and described for the very first time from our laboratory. Results obtained are in good agreement with the last study.

KEY WORDS: 4-Acyl isochroman-1,3-dione, Electron impact mass spectrumetry, AM1, Electronic charges, Fragmentation

INTRODUCTION

4-Acyl isochroman-1,3-diones **1** are very interesting compounds studied in our laboratories. It has been found to have several properties for these compounds. They exhibit fluorescence [1-2], anti-oxidant [3] and anti-bacterial properties [4], among others. Some of their spectral properties, nuclear magnetic resonance (NMR) [5], mass [6], UV-Visible [3], and their reactivity [3, 7-9], have been described. Their crystal structures have also been investigated [10-12]. Recently a new approach of analysis of fragmentation processes of coumarins in electron impact mass spectrometry has been described to give a good correlation with the electronic charges of their atoms [13-15]. It has been found that fragmentation processes in electron impact mass spectrometry (EIMS) takes place mainly at the level of atoms bearing high negative charge. It seems to be possible to predict and explain most of their fragmentations, using electronic charges of atoms. So, as a part of our continuing investigations about 4-acyl isochroman-1,3-diones **1**, the fragmentation processes of these compounds in electron impact mass spectrometry (EIMS) was successfully analyzed by the calculated AM1 electronic charges of atoms. It has been found that the method presents a good reliability. The electronic charges of atoms become a valuable instrument for understanding the fragmentation processes of organic compounds in MS. This study is the second investigation about mass spectra of these compounds but the very first one with both experimental and theoretical investigations.

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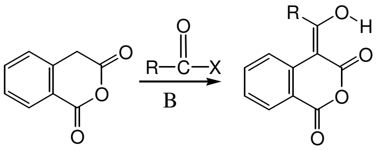
EXPERIMENTAL

The title compounds **1** have been obtained as described in the literature [1], by action of acid chlorides or acid anhydrides on homophthalic anhydride in the presence of a base, as shown below:



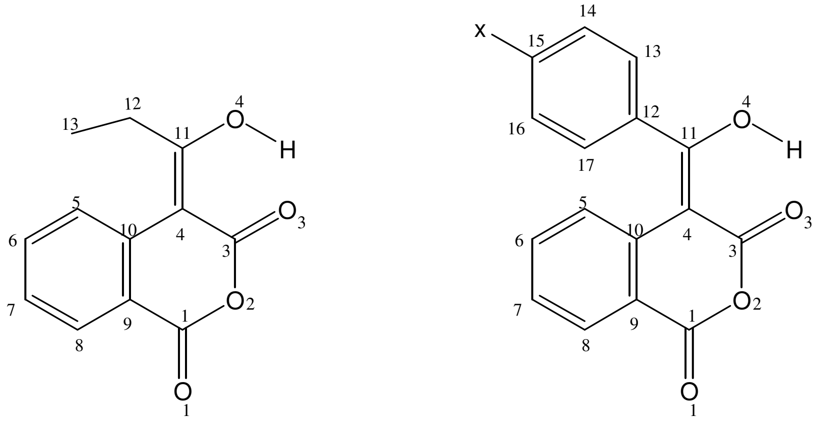
1

X = Cl or OCOR; B = pyridine or triethylamine.
1a: R = CH_3 ; **1b**: R = C_2H_5; **1c**: R = C_6H_5; **1d**: R = *p*-ClC_6H_4; **1e**: R = *p*-$NO_2C_6H_4$.

Scheme 1. Synthesis of 4-acyl isochroman-1,3-diones **1**.

RESULTS AND DISCUSSION

The acylated isochroman-1,3-diones **1** have been obtained with more than 70% yield [1]. They have been identified by their melting points and by their ^1H, ^{13}C and ^{17}O NMR spectra [3, 5].



Scheme 2. Structure of 4-acyl isochroman-1,3-diones **1**.

Mass spectra. All the mass spectra were obtained by electron impact mass spectrometry (EIMS) on a CPG-JSM AX505 apparatus at 70 eV and the data are given in Table 1.

AM1 calculation of electronic charges of atoms. The electronic charges of atoms were performed by Austin Model 1 (AM1) semi empirical method [16] using “Chem3D Ultra8” software on a Pentium 4 Computer. Results are given in Table 2.

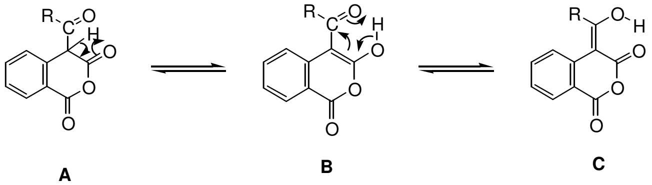
Table 1. Mass spectra (EIMS) of compounds **1**.

R = CH_3 (**1a**)		R = C_2H_5 (**1b**)		R = C_6H_5 (**1c**)		R = *p*-ClC_6H_4 (**1d**)		R = *p*-$NO_2C_6H_4$ (**1e**)	
m/z	%	m/z	%	m/z	%	m/z	%	m/z	%
204	45	218	4	266	35	302	10	311	75
186	100	200	15	249	1	300	14	294	4
176	17	189	6	238	8	287	9	283	8
162	50	162	8	222	10	285	6	267	27
145	4	145	5	194	9	272	5	238	14
134	90	135	27	165	10	256	22	237	13
118	18	134	14	144	0.8	228	16	221	2
105	34	118	100	118	14	209	2	209	6
89	19	105	6	105	100	195	1.8	165	12
77	15	89	12	89	4	158	28	150	100
63	10	77	12	77	32	156	70	133	6
51	6	57	48	51	5	141	32	118	12
43	33	51	1	-	-	139	100	104	25
39	3	39	2	-	-	118	2	76	11
28	2	29	8	-	-	111	38	63	4
-	-	-	-	-	-	37	1	39	1

Table 2. Electronic charges of atoms of compounds **1**.

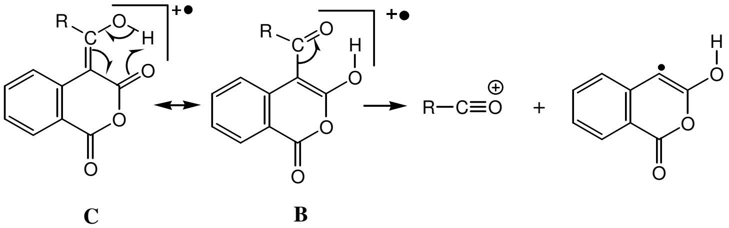
Atoms	R = CH_3 (**1a**)	R = C_2H_5 (**1b**)	R = C_6H_5 (**1c**)	R = *p*-ClC_6H_4 (**1d**)	R = *p*-$NO_2C_6H_4$ (**1e**)
C_1	0.414	0.414	0.402	0.413	0.395
C_3	0.426	0.425	0.417	0.424	0.410
C_4	-0.321	-0.319	-0.309	-0.299	-0.231
C_5	-0.207	-0.206	-0.200	-0.200	-0.138
C_6	-0.149	-0.145	-0.154	-0.149	-0.183
C_7	-0.209	-0.211	-0.216	-0.209	-0.183
C_8	-0.109	-0.110	-0.107	-0.113	-0.118
C_9	-0.175	-0.175	-0.175	-0.177	-0.126
C_{10}	0.050	0.045	0.035	0.045	-0.034
C_{11}	0.215	0.211	0.269	0.254	0.346
C_{12}	-0.351	-0.254	-0.113	-0.109	-0.157
C_{13}	-	-0.349	-0.136	-0135	-0.080
C_{14}	-	-	-0.206	-0.185	-0.149
C_{15}	-	-	-0.162	-0.065	-0.103
C_{16}	-	-	-0.215	-0.184	-0.150
C_{17}	-	-	-0.139	-0.138	-0.148
O_1	-0.301	-0.300	-0.313	-0.300	-0.208
O_2	-0.285	-0.286	-0.249	-0.249	-0.247
O_3	-0.355	-0.354	-0.365	-0.355	-0.292
O_4	-0.307	-0.307	-0.323	-0.298	-0.248
Cl				-0.0036	
NO_2					N: 0.522 O: -0.302 O: -0.294

*Tautomery of compounds **1***. The three tautomeric forms **A**, **B**, **C** (Scheme 3) had been suspected and described as possible structures for these compounds [8, 9] but the only one form **C** has been really observed both in solution [5] and in crystalline form [10-12].



Scheme 3. Tautomeric forms of **1**.

Formation of molecular ion. In all the precedents descriptions of the structure of compounds **1** using NMR [5] or crystallographic methods [10-12], only the tautomeric form **C** had been found, whatever the nature of R (aliphatic or aromatic). AM1 calculation of heat of formation (ΔH) of **1** gave positive values also the same results [5]. The behaviour of these compounds in mass spectrometry has been reported for the very first time since a few years [6]. It had been observed only the two enolic forms, **B** and **C**, of this tautomery. Nevertheless, this tautomery takes place only after formation of molecular ion. According to the above theory, the molecular ion must take place at the level of O_4 and/or O_3, as oxygen bearing the highest negative charges. Fragmentations must then take place at the level of C_4, C_5, C_6, C_7, C_8, C_9, C_{12} and oxygen atoms (O_1, O_2, O_3 and O_4). So, formation of the resulting molecular ion, its tautomery and the subsequent fragmentations shown below, were induced by O_3, O_4 and C_4 atoms. These atoms are bearer of the highest negative charges. The tautomery can take place after ionisation because the values of the charges of C_4, O_3 and O_4 are very close to themselves. The formation of R-CO or Ar-CO fragments take place for every molecule with a significant percentage ($32 \leq \% \leq 100$). Only this tautomery can explain the formation of the R-CO or Ar-CO fragments, observed in all the spectra.

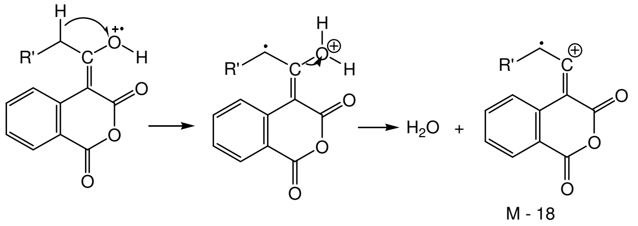


R = CH_3, m/z = 43 (33%); R = C_2H_5, m/z = 57; R = C_6H_5, m/z = 105; R = *p*-ClC_6H_4, m/z = 139 and 141; R = *p*-$NO_2C_6H_4$, m/z = 150.

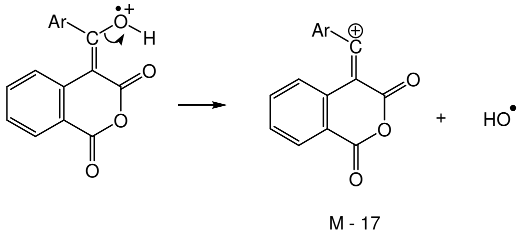
Scheme 4. Formation of molecular ion and of fragments R-CO^+ or Ar-CO^+.

*Other fragmentations processes of 4-acyl isochroman-1,3-diones **1**.*

Formation of M-18 and M-17 fragments. It has been observed that compounds **1**, with an aliphatic R, loose one molecule of water (M-18) while the compounds with arylic R loose simply the OH radical, as shown in the below Scheme 5. This fragmentation is initiated and guided by the two atoms, O_4 and C_{12}.



R' = H : **1a** m/z 186; R' = CH_3 : **1b** m/z = 200.

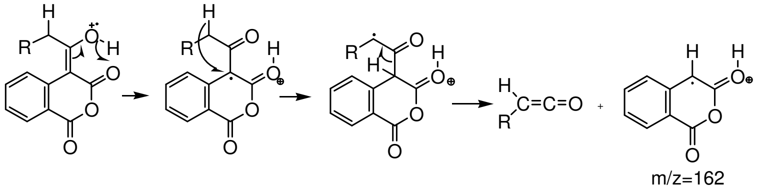


Ar = C_6H_5 : **1c**, m/z = 249; Ar = *p*ClC_6H_4 : **1d**, m/z = 285 and 287; Ar = *p*$NO_2C_6H_4$: **1e** m/z = 294.

Scheme 5. Formation of M-18 and M-17 fragments.

The M-18 fragmentation takes place after transposition of aliphatic hydrogen from C_{12} onto O_4 atom, to produce water. The M-17 fragmentation takes place by direct lost of the hydroxyl group, when R is an aromatic moiety. In this case, there is no hydrogen on C_{12} to remove from this aromatic group. It must be noticed that for compounds **1a** and **1b**, atoms C_{12} and O_4 exhibit high negative charges.

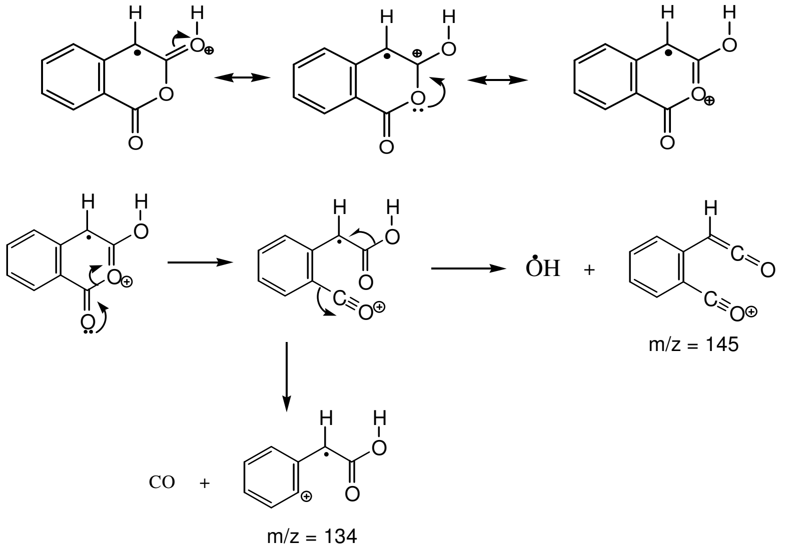
Formation of the fragments m/z = 162, 145 and 134. Due to the proximity of the charges values of C_4 and O_4, the transposition of aliphatic hydrogen described above in the formation of water, can also take place onto C_4, leading to another type of fragmentation shown below. It is then obtained the fragments m/z = 162 (Scheme 6), 145 and 134 (Scheme 7). The following mechanism had been described to explain the formation of these fragments, obtained exclusively when R is an aliphatic moiety (R = CH_3 or C_2H_5). However, the difference of stability of this fragment m/z = 162, 50% for **1a** and only 8% for **1b**, can be explained by the difference between the charges value of their C_{12} atom: -0.351 for **1a** and -0.254 for **1b**. So, the transfer of the aliphatic hydrogen from this C_{12} onto C_4 is less favoured for **1b** than for **1a**.



R = CH_3 or C_2H_5.

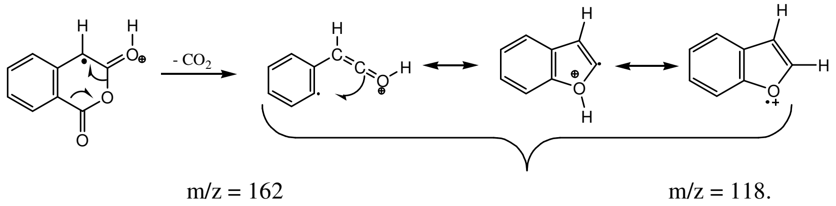
Scheme 6. Formation of fragment m/z = 162.

This fragment presents several mesomeric forms as shown below and lead to the fragments m/z =145 and 134.



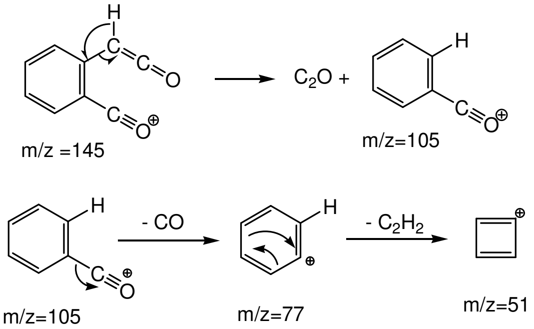
Scheme 7. Formation of fragments m/z = 145 and 134.

In all these last fragmentations, atoms which put a lot into the fragmentations processes are C_9, C_4, C_{12}, O_1, O_2 and O_3. On the other hand, it is then possible to understand why the compound **1b**, (R = CH_3-CH_2), has its base peak at m/z = 118. Its formation take place from the fragment m/z = 162 by the follow mechanism, after losing CO_2 (Scheme 8). It is, once, noticeable that these atoms exhibit high negative electronic charge.



Scheme 8. Formation of base peak of **1b**.

Formation of fragments m/z = 105, 77 and 51. An original behaviour has been signalled the presence of three unusual fragments m/z = 105, 77 and 51 in the spectrum of fused bicyclic heterocyclic compounds. These fragments had been observed both for **1a** and **1b** (R aliphatic) [6]. Usually, these fragments are characteristic of mono substituted phenones and mono substituted derivatives of benzoic acid. If the presence of these fragments has been naturally obtained and described above for the compound **1c** (Ar = C_6H_5), in the present case, this phenomenon has been explained after considering the fragment m/z = 145, as their parent peak because only these two compounds can form these fragments. In this case, the follow process had been described.



Scheme 9. Formation of fragments m/z = 105, 77 and 51.

After a transfer of hydrogen atom from the fragment m/z = 145, the ion with the m/z = 105 is obtained, which leads to other fragments 77 and 51 by the usual process of fragmentation (Scheme 9) [6]. This process is driven by C_4, C_7 and C_9 which are bearers of high negative electronic charges.

CONCLUSIONS

After the application of analysis of fragmentations of three series of coumarins through the electronic charges of their atoms, title compounds had also been investigated by electron impact mass spectrometry, using the electronic charges of atoms obtained by AM1 semi empirical method. The method appeared as a useful one for understanding and explaining the processes of the fragmentations. In this study, it has been found logic and good explanations of most of fragmentations obtained: formation of molecular ions of the compounds and most of their fragments take place mainly at the level of atoms bearing high positive charge. So loss of water (H_2O) or hydroxyl ($OH^{\cdot}$) group and formation of fragments m/z = 162, 145, 134, 105, 77 and 51 can be justified by exploiting electronic charges of atoms. The correlation between charges of atoms and fragmentations processes of these compounds had been found to be very suitable. So, the method seemed to be applicable to every family of organic compounds.

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