EIMS and AM1 study of the fragmentations of 3-coumarinyl Carboxylates :Interpretation from electronic charges of atoms.

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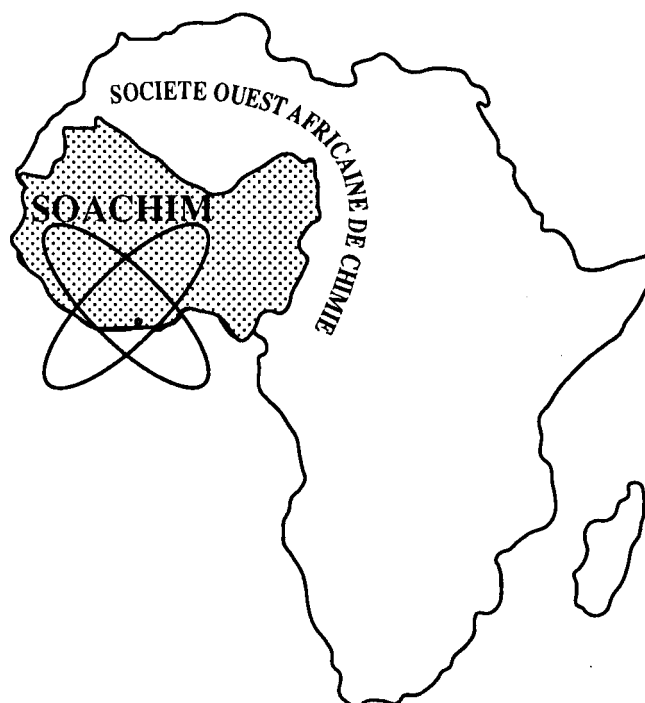**Jules Yoda[1], Abdoulaye Djandé[1], Léopold Kaboré[1], Paul House[2],**

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Abstract: 3-Coumarinyl carboxylates, a new series of organic compounds, are prepared by O-acylation of 3-hydroxycoumarins. We present their electronic impact mass spectra (EIMS), and analyze these with the aid of semi-empirical AM1 method. We demonstrate a good correlation of fragmentation pathways and electronic charges of their constituent atoms.
Keywords: 3-Coumarinyl Carboxylate, AM1, EIMS Fragmentation pathway, Electronic Charge.

Etude par spectrométrie de masse par Impact électronique et par AM1 de la fragmentation des carboxylates de 3-coumarinyle: *Interprétation à partir des charges électroniques des atomes*

Résumé : Les Carboxylates de 3-Coumarinyle, une nouvelle série de composés organiques ont été préparés par O-acylation de la 3-hydroxycoumarine. Nous examinons ici leurs fragmentations en spectrométrie de masse par impact électronique, en nous servant des charges électroniques des atomes calculées par la méthode semi-empirique AM1. Il se dégage une bonne corrélation entre les processus de fragmentation et les charges électroniques.

Mots Clefs : Carboxylate de 3-coumarinyle ; AM1; fragmentation par Impact électronique; Charge électronique.

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1. Introduction

3-coumarinyl carboxylates **2** were prepared in good yield by O-acylation of the corresponding 3-hydroxycoumarin **1** with acid chlorides or acid anhydrides, in the presence of an appropriate base B[1] (scheme 1). As part of our ongoing investigation of these new compounds, we studied their electrons impact mass spectra (EIMS) with particular emphasis on fragmentation pathways. Recent investigations of related compounds by EIMS [3-5] and ESI/MS[6-9] have shown a good correlation between fragmentation pathways and the position of atoms predicted to have high negative charge by a semi-empirical calculation (AM1 Method)[2].The numbering scheme for the atoms of

the 3-coumarinyl carboxyl skeleton is shown in scheme **1a**, augmented by that for the carboxylate substituents in scheme **1b**.

2. Experimental

The compounds **2** have been identified by their melting points and their ^{1}H and ^{13}C NMR spectra[1]. The EIMS spectra were obtained on a Perkin Elmer Thermo Scientific Trace GC Ultra with DSQ II Mass Spectrometer with auto sampler ; the atomic electronic charges were obtained by AM1 semi empirical method[2-7, 9]. The results were displayed in tables 1 and 2. The EIMS peak heights in table 1 are given as percentages of the highest peak ("base peak").
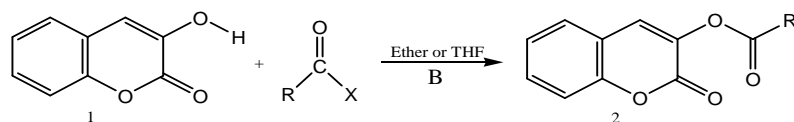
2a : R = CH$_3$; **2b** : R = C$_2$H$_5$; **2c** : R = C$_6$H$_5$; **2d** : R =*p*-ClC$_6$H$_4$; **2e** : R = *p*-FC$_6$H$_4$;
2f : R = *p*-CH$_3$OC$_6$H$_4$; **2g** : R = *p*-(CH$_3$)$_2$NC$_6$H$_4$; **2h** : R = *p*-CNC$_6$H$_4$; **2i** : R = *p*-NO$_2$C$_6$H$_4$.

Scheme 1: Synthesis of compound **2.**
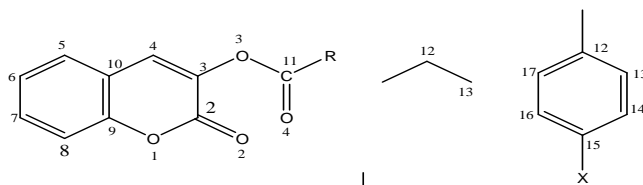
Scheme 1a   **Scheme 1b**

Table 1a: Electronic Impact Mass Spectra of compounds **2**

2a R = CH$_3$		**2b** R = C$_2$H$_5$		**2c** R = C$_6$H$_5$		**2d** R = *p*-ClC$_6$H$_4$		**2e** R = *p*-FC$_6$H$_4$	
m/z	%	m/z	%	m/z	%	m/z	%	m/z	%
204(M)	15	218(M)	11	266(M)	10	302(M)	11	284(M)	4.1
164	2	164	1.5	162	1	300	31	124.2	4.1
163	20	163	11	133	4	173	0.5	122.9	100
162	100	162	100	107	1	142	2	94.8	23.28
135	2	135	1	106	18	141	29	104.9	2.05
134	20	134	9	105	100	139	100	75	12
133	5	133	5	89	1	133	12	63	1
107	2	107	1.5	78	5	111	32	-	-
106	30	106	15	77	70	105	10	-	-
105	20	105	10	-	-	85	2	-	-

Table 1b : Electronic Impact Mass Spectra of compounds **2**

2f R = *p*-NO$_2$C$_6$H$_4$		**2g** R = p-CNC$_6$H$_4$		**2h** R = *p*-MeOC$_6$H$_4$		**2i** R = *p*-(CH$_3$)$_2$NC$_6$H$_4$	
m/z	%	m/z	%	m/z	%	m/z	%
311	100	291	18	296(M)	12	309(M)	8
181	1	162	1	162	1	162	2.5
152	1.5	133	5	137	1	161	11
151	4.5	131	26	136	9	149	14
150	66	130	61	135	100	148	100
133	16	129	100	133	19	133	13.7
120	5	105	9	107	13	131	13
105	10	102	82	92	21	118	10
104	18	89	2	77	36.5	105	32
92	7	77	16	63	10	104	20
77	11	75	13	-	-	78	7.5
76	15	63	4	-	-	77	23
75	5	51	21	-	-	76	15.5
63	2.5	-	-	-	-	62	10.5

Table 2a: electronic charges of atoms of compound **2**

R	Comp.	C$_2$	C$_3$	C$_4$	C$_5$	C$_6$	C$_7$	C$_8$	C$_9$	C$_{10}$
CH$_3$	**2a**	0.3933	-0.0326	-0.0796	-0.1250	-0.2184	-0.1455	-0.2012	0.1090	-0.1481
CH$_3$CH$_2$	**2b**	0.3915	-0.0287	-0.0819	-0.1256	-0.2184	-0.1457	-0.2014	0.1087	-0.1474
C$_6$H$_5$	**2c**	0.3940	-0.0394	-0.0956	-0.1270	-0.2172	-0.1455	-0.2002	0.107	-0.0956
p-ClC$_6$H$_4$	**2d**	0.3880	-0.0498	-0.0843	-0.1244	-0.2167	-0.1431	-0.2003	0.107	-0.1514
p-FC$_6$H$_4$	**2e**	0.4009	-0.0406	-0.0953	-0.1254	-0.2173	-0.1479	-0.1996	0.1004	-0.1421
p-NO$_2$C$_6$H$_4$	**2f**	0.3395	0.1613	-0.1276	-0.1283	-0.1931	-0.0404	-0.2282	0.1677	-0.074
p-CNC$_6$H$_4$	**2g**	0.3919	-0.0350	-0.0768	-0.1238	-0.2180	-0.1442	0.2121	0.1099	-0.1510
p-MeOC$_6$H$_4$	**2h**	0.3922	-0.0269	-0.0817	-0.1254	-0.219	-0.1460	-0.2017	0.1099	-0.1483
p-(CH$_3$)$_2$NC$_6$H$_4$	**2i**	0.3831	-0.0214	-0.1210	-0.1298	-0.2153	-0.1463	-0.2005	0.1055	-0.1333

Table 2b: electronic charges of atoms of compounds **2**

R	Comp.	C$_{11}$	C$_{12}$	C$_{13}$	C$_{14}$	C$_{15}$	C$_{16}$	C$_{17}$	X
CH$_3$	**2a**	0.3518	-0.3631	**-**		**-**	**-**	**-**	-
CH$_3$CH$_2$	**2b**	0.3533	-0.2643	-0.3502	-	-	-		
C$_6$H$_5$	**2c**	0.4077	-0.1640	-0.1216	-0.1981	-0.1634	-0.1973	-0.1255	
p-ClC$_6$H$_4$	**2d**	0.4031	-0.1657	-0.1430	-0.1807	-0.056	-0.1854	-0.1354	-
p-FC$_6$H$_4$	**2e**	0.4132	-0.1565	-0.1025	-0.0930	0.1278	-0.2447	-0.2446	-
p-NO$_2$C$_6$H$_4$	**2f**	0.4282	-0.1246	-0.1240	-0.1434	-0.0734	-0.1420	-0.1267	-
p-CNC$_6$H$_4$	**2g**	0.4055	-0.1111	-0.1345	-0.1669	0.0178	-0.1687	-0.1300	C:-0.068N:-0.063
p-MeOC$_6$H$_4$	**2h**	0.4141	-0.1728	0.0860	-0.2843	0.1202	-0.2342	0.0896	
p(CH$_3$)$_2$NC$_6$H$_4$	**2i**	0.3985	-0.1593	-0.2691	-0.1080	0.0639	-0.0905	-0.2385	-

Table 2c : electronic charges of atoms of compounds **2**

Comp.	R	O_1	O_2	O_3	O_4	Substituant X					
						C	N	O	O	Cl	F
2a	CH_3	-0.2278	-0.3033	-0.2639	-0.3537	-	-	-	-	-	-
2b	CH_3CH_2	-0.2273	-0.3041	-0.2673	-0.3497	-	-	-	-	-	
2c	C_6H_5	-0.2299	-0.2984	-0.2497	-0.3686	-	-	-	-	-	-
2d	p-ClC_6H_4	-0.2276	-0.3073	-0.2295	-0.2916	-	-	-	-	-	
2e	p-FC_6H_4	-0.2281	-0.3001	-0.2583	-0.3572	-	-	-	-	-	-
2f	p-$NO_2C_6H_4$	-0.1816	-0.1682	-0.2441	-0.2636	-	0.5190	-0.3118	-0.3178	-	-
2g	p-CNC_6H_4	-0.2771	-0.2497	-0.2201	-0.3275	-0.0725	-0.072	-	-	-	
2h	p-$MeOC_6H_4$	-0.2291	-0.2999	-0.2621	-0.3623	-0.2095	-	0.2456	-	-	-
2i	p-$(CH_3)_2NC_6H_4$	-0.1990	-0.3037	-0.2212	-0.3668	0.2325 -0.2457	-0.302	-	-	-	-

## 3. Discussion.

3.1. Formation of the molecular ion.

The process of the formation of the molecular ion by EIMS is described below (**Scheme 2**). The radical - cation $M^{+\cdot}$ is able to present the forms according to **scheme 3.** Experimentally, forms A and B are the most commonly observed ones for carbonylated compounds like esters or lactones, as shown in Scheme 3. Noticealso that the electronic charges of oxygen atoms O_2 and O_4 are the highest negative charges among all the atoms of oxygen. So, the two most probable molecular ions are A and B and fragmentations of compounds **2** must take place from these molecular ions.
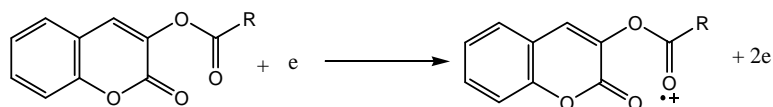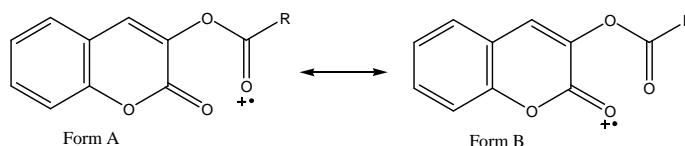

2a : R = CH_3 (m/z = 204) ; 2**b** : R = C_2H_5 (m/z = 218) ; 2**c** : R = C_6H_5 (m/z = 266) ;
2d : R = p-ClC_6H_4 (m/z 300-302) ; **2e** : R = p-FC_6H_4 (m/z = 284) ;
2f : R = p-$NO_2C_6H_4$ (m/z = 311) ; **2g** : R = p-CNC_6H_4 (m/z = 291) ;
2h : R = p-$MeOC_6H_4$ (m/z = 296) ; **2i** : R = p-$(CH_3)_2NC_6H_4$ (m/z = 309) .

Scheme 2 : Formation of molecular ion $M^{\cdot+}$.
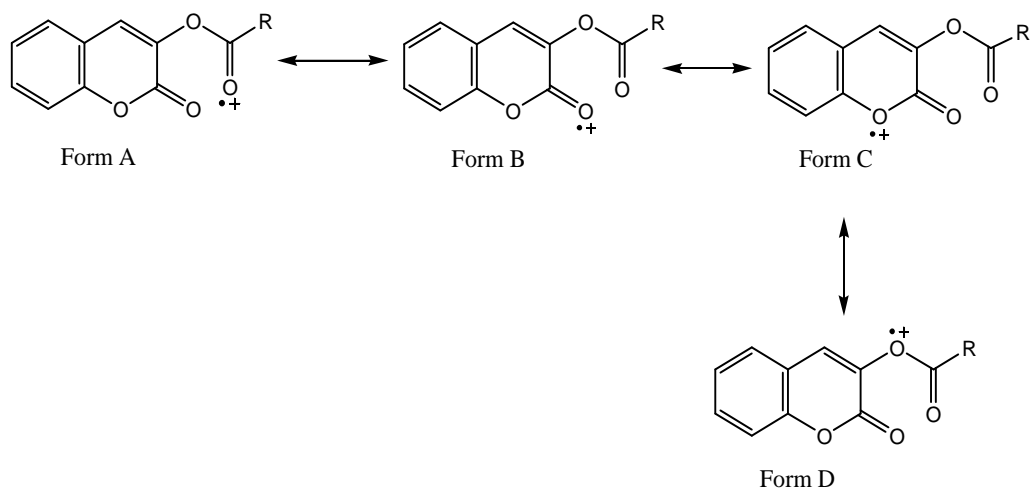
Scheme 3 : possible forms of molecular ion.

Scheme 4 : A and B forms of the molecular ion.

3.2. Common Fragmentations

3.2.1. Formation of acylium ion

One common fragmentation of all compounds **2**, lead to the formation of acylium ion (R-CO$^+$). The fragmentation takes place from form A of molecular ion. This fragmentation, which is present in all spectra, is obtained by homolytic process. In most cases, this fragment is the base peak (100%), except in the spectrum of compound **2a**. The Scheme below explains this fragmentation.

This fragmentation is oriented by both the atoms O$_3$ and O$_4$. Each of these atoms bears an important negative electronic charge. The lack of this fragment is noticeable in the spectrum of compound **2a**.This abnormal behavior of **2a** can be explained via electronic charges of carbon C$_{12}$. This charge is the highest negative charge of the compound **2a** (q =- 0.3631) and seemed to supplant O$_2$ and O$_3$ for the direction of this fragmentation. This is why compound **2a** leads to the formation of another new fragment, shown in scheme 6 with m/z = 162, as

100 % peak. The same fragmentation is observed for **2b**, but does not lead to 100 % peak because of the negative charge of C$_{12}$ is weaker for **2b** (q = -0.2643) than for **2a** (-0.3631).

3.2.2. Loss of the carbonyl group (CO) from acylium cation.

The loss of the carbonyl group (CO) is observed in the most carbonyl compounds. The acylium cation (R-CO$^+$) loses the carbonyl group, leading to the fragment R$^+$ or Ar$^+$. It is always guided by the oxygen atom of the carbonyl group (scheme 7).

When the substituent R is a para substituted aromatic moiety, with X as substituent, the acylium cation can be fragmented in two other ways, according to the nature of the para substituent X : loss of the carbonyl group and loss of the substituent X.

The fragmentation of scheme 8 is the more usual. When X is a nitro group or a dimethylamino one, its
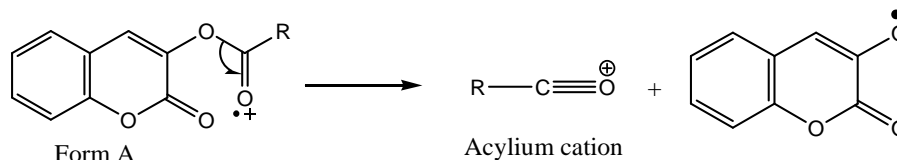
2b : R = C$_2$H$_5$; m/z = 57 (82%) ; **2c** : R = C$_6$H$_5$,m/z = 105(100%) ; **2d** : R = *p*-ClC$_6$H$_4$ (m/z = 139-141 (100%) ; **2e** : R = *p*-FC$_6$H$_4$ (m/z = 123) ; **2f** : R = *p*-NO$_2$C$_6$H$_4$ (m/z = 150 ; **2g** : R = *p*-CNC$_6$H$_4$ (m/z = 130 100%) ; **2h** : R = *p*-CH$_3$OC$_6$H$_4$: m/z = 135 (100%) ; **2h** : R = *p*-MeOC$_6$H$_4$(m/z = 135) ; **2i** : R = *p*-(CH$_3$)$_2$NC$_6$H$_4$ (m/z = 148 (100%)

Scheme 5: formation of acylium cation.
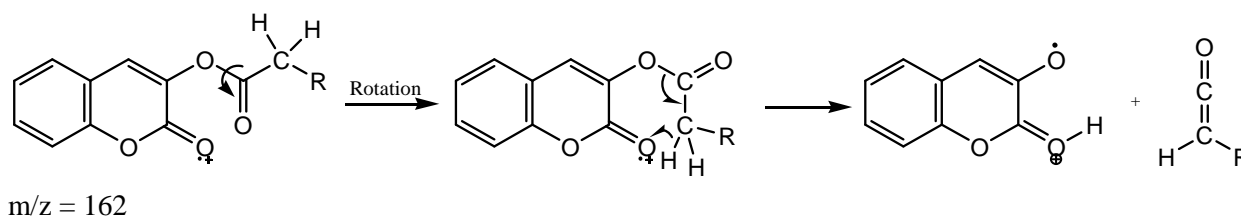
m/z = 162

Scheme 6 : Formation of fragment m/z = 162 for **2a** (R = H) and **2b** (R = CH$_3$).

loss leads to the fragment m/z = 104. The negative charge of oxygen of nitro group in **2f** (q = -0.31) and for methyl groups (q = -0,24) in dimethylamino one in **2i** (table 2c) can drive this fragmentation. It produces a dicationic fragment, not usually observed.

So, instead of losing the carbonyl group, the

acylium cation loses substituent X. This behavior is a rare phenomenon in EIMS. From the fragment m/z = 104, these two compounds **2f** (R = $O_2NC_6H_4$) and **2i** (R= $(CH_3)_2NC6H4$) in question, give the peak m/z = 76 losing CO, corresponding to another dication fragment, as shown in scheme 10 :
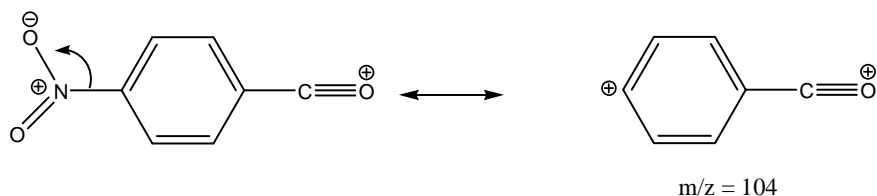
$$Ar-C\equiv\overset{+}{O} \longleftrightarrow Ar-C\equiv\overset{+}{O} \longrightarrow Ar^+ + CO$$
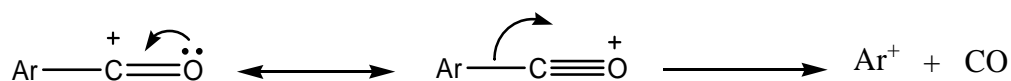
2c : Ar = C_6H_5 (m/z = 77) ; **2d** : Ar = p-ClC_6H_4 (m/z = 111-113) ; **2e** : Ar = p-FC_6H_4 (m/z = 95) ;
2f : Ar = p-$NO_2C_6H_4$ (m/z = 122) ; **2g** : R = p-CNC_6H_4 (m/z = 102) ;
2h : R = p-MeOC_6H_4 (m/z = 107) ; **2i** : R = p-$(CH_3)_2NC_6H_4$ (m/z = 110).

Scheme 7: Formation of fragment Ar^+.
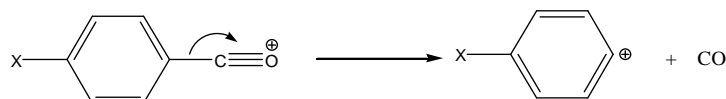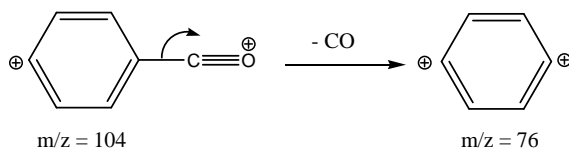
2d : X = Cl (m/z = 111-113) ; **2e** : X = F (m/z = 95) ; **2h** : X = CH_3O, (m/z = 107) ;
2f : X = NO_2 (m/z = 128) ; **2g** : X = CN (m/z = 102) ; **2i** : X = $(CH_3)_2N$ (m/z = 120).

Scheme 8 : Formation of fragment Ar^+ by loss of CO.

m/z = 104

R = $O_2NC_6H_4$ (20%); R = $(CH_3)_2NC_6H_4$ (18.3%)

Schema 9 : Formation of fragment m/z = 104

m/z = 104   m/z = 76

Scheme 10 : Formation of fragment m/z = 76.

3.2.3. Formation of the fragment m/z = 133.

This fragment m/z = 133,is common to all the 3-coumarinyl carboxylates **2**. Its presence is not bound to the nature of R. So, we propose the process below following from molecular ion A. Oxygens O_3 and O_4 could then be initiators of the heterolytic process.

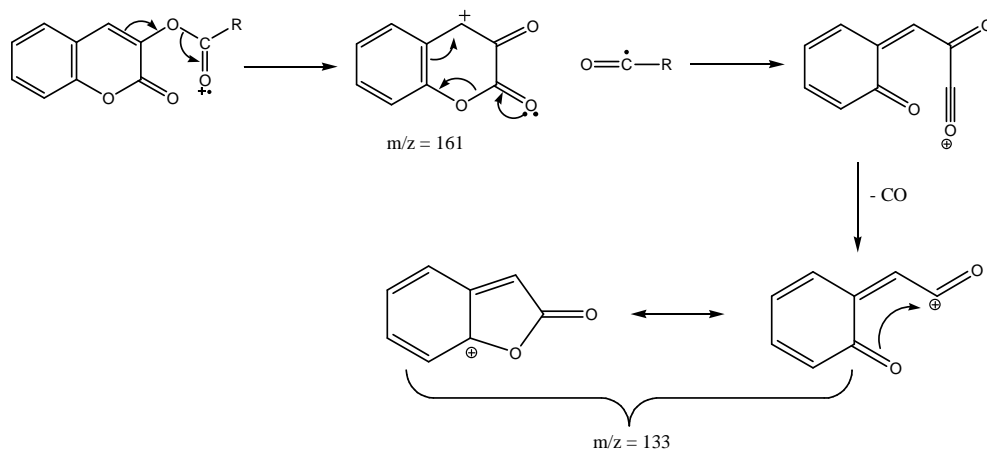### 3.2.4. Formation of fragments m/z = 105 and 77

These unusual fragmentations of fused heterocyclic compounds are present in the spectra of all the compounds **2**. We suggest the following process to explain their formation, from molecular ion B.

The whole atoms of oxygen (O_1, O_2 and O_3) and the atoms of carbon C_8 are likely or entire during the fragmentation process producing the m/z = 105 fragment. Their electronic charges are negative and a bit high.

This last fragment m/z = 105 leads naturally to the formation of phenyl cation (m/z = 77) after the loss of carbonyl group.

We specify this kind of fragmentation have been yet observed during our work on mass spectra of other coumarins[2] and the mass spectra of 4-acyl isochroman-1,3-diones[5].
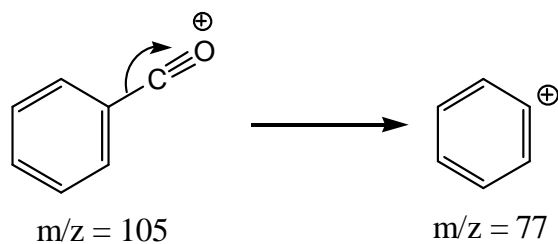

Scheme 11 Formation of fragment m/z = 133
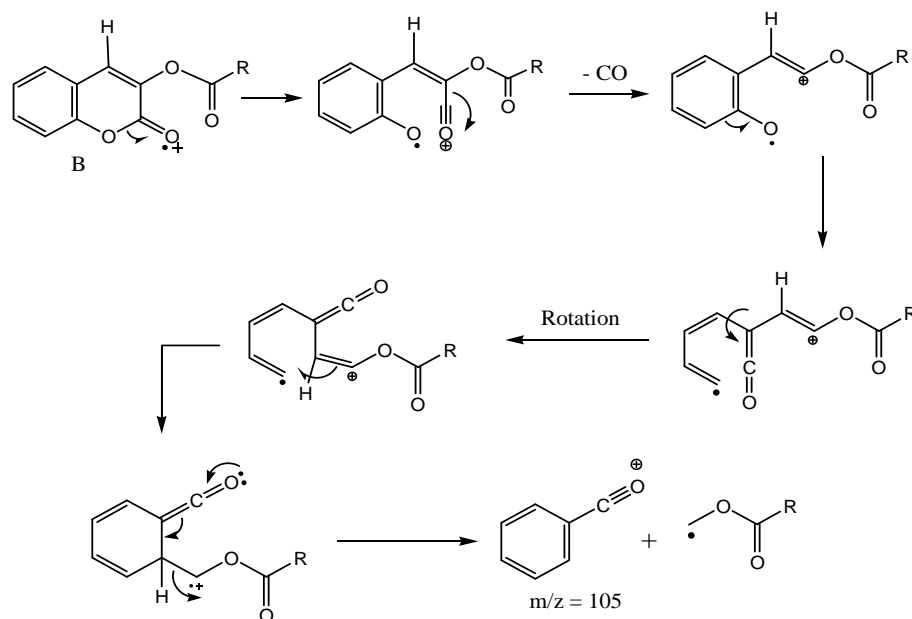
Scheme 12 : Formation of fragment m/z = 105

Scheme 13: Formation of fragment m/z = 77

4. Conclusion.

In this study, we report the synthesis and characterization of a series of 3-coumarinyl carboxylates and explore the electronic impact mass spectra (EIMS) of these new compounds. Their fragmentation pathways are analyzed in detail and we find a good correlation between the orienting effect of certain constituent atoms and their atomic electronic charges as calculated using a semi-empirical method (AM1). This extends our earlier work and supports the proposition that the study of mass spectral fragmentation pathways offers a fruitful meeting ground for experiment and theory.

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