

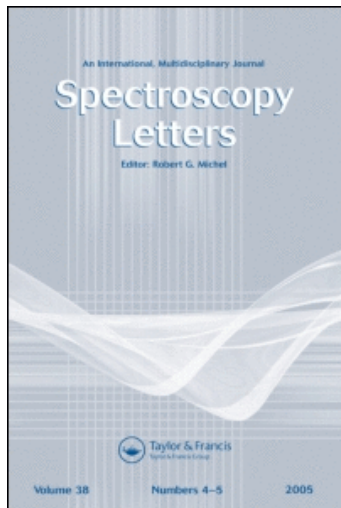
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Spectroscopy Letters

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597299>

Mass Spectrometry of Some Benzylidene Imidazolidinediones and Thiazolidinediones. II- chlorobenzyl imidazolidinedione and Fluoro or Chlorobenzyl Thiazolidinedione Compounds

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To cite this Article Galdino, Suely L. , Lima, Maria C. A. , Góes, Alexandre J. S. , Pitta, Ivan R. and Luu-Duc, Cuong(1991) 'Mass Spectrometry of Some Benzylidene Imidazolidinediones and Thiazolidinediones. II- chlorobenzyl imidazolidinedione and Fluoro or Chlorobenzyl Thiazolidinedione Compounds', *Spectroscopy Letters*, 24: 7, 1013 — 1021

To link to this Article: DOI: 10.1080/00387019108020679

URL: <http://dx.doi.org/10.1080/00387019108020679>

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**MASS SPECTROMETRY OF SOME BENZYLIDENE
IMIDAZOLIDINEDIONES AND THIAZOLIDINEDIONES.
II- CHLOROBENZYL IMIDAZOLIDINEDIONE AND FLUORO OR
CHLOROBENZYL THIAZOLIDINEDIONE COMPOUNDS**

Key Words: Mass Spectra, chlorobenzyl benzylidene
imidazolidinediones, fluoro or chlorobenzyl
benzylidene thiazolidinediones

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ABSTRACT

In the present investigation, a study of the electron impact mass spectrometry data is reported for seven compounds of a series of some 3-(4-chlorobenzyl)-5-benzylidene-imidazolidine-2,4-diones and 3-(4-fluoro or chlorobenzyl)-5-benzylidene-thiazolidine-2,4-diones previously synthesized.

INTRODUCTION

As a part of a research project on anti-microbial agents, a series of 5-benzylidene pyrrolone, furanone and thiophenone derivatives is prepared and the pharmacological data analysed in terms of structure-activity relationships ¹⁻⁴. The most important fragmentation reactions of this class of compounds under electron-impact were established ^{5,6}.

In this paper a compilation of electron-impact mass spectra of novel 3-chlorobenzyl-5-benzylidene-imidazolidine-2,4-diones **1-4** and 3-fluoro- or 3-chlorobenzyl-5-benzylidene-thiazolidine-2,4-diones **5-7** is reported and possible fragmentation routes are outlined.

The compounds studied are included in the investigational anti-microbial agents. A generalized structural formula of the imidazolidinediones and thiazolidinediones studied and previously synthesized is shown in table 1.

EXPERIMENTAL

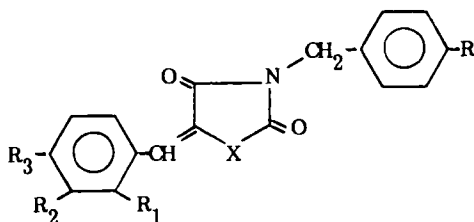
Electron-impact mass spectra were recorded with the aid of an Kratos - AEI MS 30 double-beam of C.E.R.M.A.V de Grenoble - France, operating at 70 eV using direct inlet. The data processing is carried out by a SS 100 MS (Varian) computer, coupled to the MS 30.

RESULTS AND DISCUSSION

The results obtained are summarized in tables 2 and 3. The proposed fragments and fragmentation routes are shown in figures 1 and 2.

TABLE 1.

The structural formula of the benzylidene imidazolidinediones and thiazolidinediones



Compounds	Formula	X	R	R ₁	R ₂	R ₃
1	C ₁₇ H ₁₃ ClN ₂ O ₂	NH	Cl	H	H	H
2	C ₁₇ H ₁₂ ClN ₃ O ₄	NH	Cl	H	H	NO ₂
3	C ₁₇ H ₁₂ Cl ₂ N ₂ O ₂	NH	Cl	H	H	Cl
4	C ₁₇ H ₁₂ ClFN ₂ O ₂	NH	Cl	F	H	H
5	C ₁₇ H ₁₀ Cl ₂ FNSO ₂	S	F	H	Cl	Cl
6	C ₁₈ H ₁₄ FNSO ₃	S	F	H	H	OCH ₃
7	C ₁₇ H ₁₁ ClN ₂ SO ₄	S	Cl	H	H	NO ₂

In all cases, one of the major peaks in the electron-impact mass spectra was that of the β -cleavage in relation to the ring of the side chain. For 5-benzylidene-imidazolidine-2,4-dione **2,3,4** and 5-benzylidene-thiazolidine-2,4-dione **5,7** compounds these resonance-stabilized benzyl ions (**a**) and (**g**) or the tropylium ion are the base peaks.

The more specific fragmentation of heterocyclic imidazolidinedione **7** and thiazolidinedione rings is the doubly-breakage of δ carbon-carbon single bond and of either one of the α nitrogen-carbon bond in imidazolidinediones or α sulfur-carbon one in thiazolidinediones, leading to the formation of the

TABLE 2.
The Electron-Impact Mass Spectra of benzylidene imidazolidinediones

I = Intensity of the peak. given in % of the intensity of the highest peak.

Fragment	1	Compounds 2	m/e / I	3	4
M+	312 / 100	357 / 20.3	346 /	89.0	330 / 27.3
M+1	313 / 25.5	358 / 5.3	347 /	23.9	331 / 6.1
M+2	314 / 34.2	359 / 7.3	348 /	57.9	332 / 9.4
M+4			350 /	10.5	
M-H	311 / 4.7	356 / 0.5	345 /	3.7	329 / 0.4
M-Cl	277 / 6.1	322 / 1.8	311 /	4.8	295 / 1.6
M-NO		327 / 1.7			
a	125 / 80.5	125 / 100	125 /	100	125 / 100
b	99 / 5.3		99 /	6.3	99 / 5.2
c	117 / 19.0	162 / 0.3	151 /	10.1	135 / 28.6
d	166 / 2.8	166 / 0.2	166 /	5.5	166 / 5.1
e	144 / 2.2		178 /	2.0	162 / 1.7
f	283 / 2.1		317 /	1.1	301 / 0.6
M-a	187 / 0.5		221 /	0.2	205 / 0.5
a-Cl	90 / 26.0		90 /	8.4	90 / 7.9
a-HCl	89 / 38.3		89 /	36.5	89 / 24.8
b-HCl	63 / 10.3		63 /	7.0	63 / 24.9

TABLE 3.

**The Electron-Impact Mass Spectra of benzylidene
thiazolidinediones**

I = Intensity of the peak, given in % of the intensity of the highest peak.

Fragment	Compounds		
	5	6	7
M ⁺	381 / 16.8	343 / 58.6	374 / 14.4
M+1	382 / 4.1	344 / 14.9	375 / 3.5
M+2	383 / 12.4	345 / 4.9	376 / 5.1
M+4	385 / 2.7		
M-Cl	346 / 0.3		
M-CO	353 / 0.3		
g	109 / 100	109 / 59.4	125 / 100
h	83 / 14.2	83 / 7.4	99 / 3.3
i			63 / 19.4
j	202 / 20.5	164 / 100	179 / 16.3
k	179 / 10.7	179 / 0.1	179 / 16.3
l	70 / 20.9	70 / 12.0	70 / 7.2
j -NO			149 / 10.3
j -Cl	167 / 4.7		
j -Cl ₂	132 / 4.2		
j -CH ₃		149 / 43.1	
j -CH ₃ -CO		121 / 14.1	

ions (**c**) and (**j**). This route is obviously very important for 3-(4-fluorobenzyl)-5-(4-methoxybenzyli-
dene)-thiazolidine-2,4-dione **6**, the fragment (**j**) (m/e 164) is the base peak accompanied by a reasonably intense molecular ion peak. In the 5-benzylidene-thiazolidine-2,4-diones **5,7** this α,δ doubly-breakage gives the fragment (**k**) (m/e 179) accompanied by the formation of the ions (**l**) (m/e 70), possibly by loss of the fluoro- or chlorobenzylic side chain from (**k**).

Another important fragmentation route of the molecular ions in 5-benzylidene-imidazolidine-2,4-dione

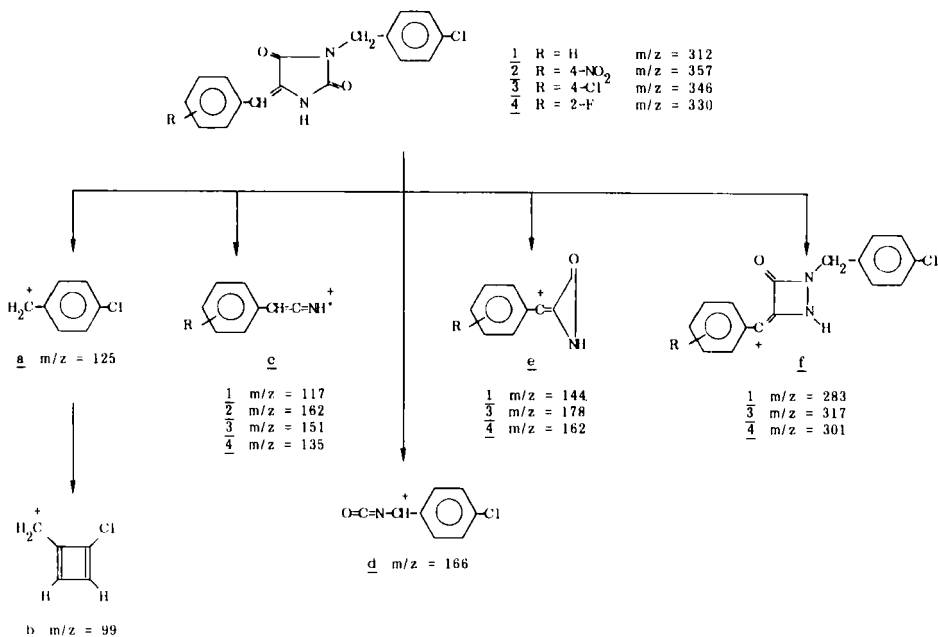


FIG. 1

substituted compounds is the α,γ nitrogen-carbon doubly-breakage with the formation of the ions (d) and (e).

In some cases, an intramolecular cyclisation reaction giving ions (f), with four-membered ring structure, may also occur by elimination of hydrogen and carbon monoxide from the molecular ion of the imidazolidinediones.

CONCLUSION

It results that electron-impact mass spectra of some 3-chlorobenzyl-5-benzylidene-imidazolidine-2,4-

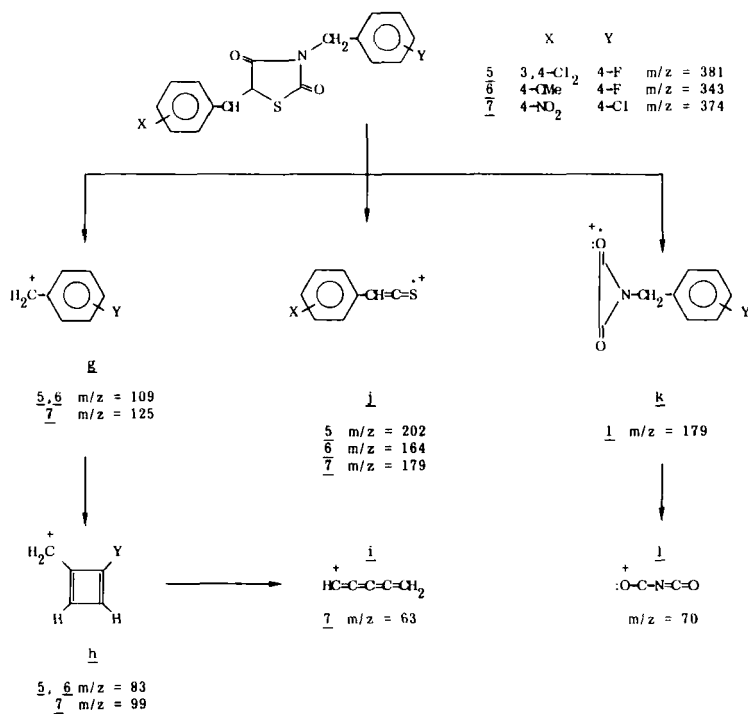


FIG. 2

dione and 3-fluorobenzyl- or 3-chlorobenzyl-5-benzylidene-thiazolidine-2,4-dione substituted compounds show important β -cleavage of the side chain in the 3-position.

The fragmentation of the various congeners imidazolidinedione and thiazolidinedione rings appears to occur similarly, the main paths involving doubly-breakage of the α, δ single bond.

The extensive possibilities for resonance stabilization of the degradation products explain the formation of the fragments observed.

Elimination of a neutral acetylene molecule from the tropylium ion has been observed in every compound.

The electron-impact mass spectra of the unsubstituted 3-(4-chlorobenzyl)-5-benzylidene-imidazolidine-2,4-dione 1 compound differs from the substituted compounds by a more intense molecular ion peak (m/e 312).

The relative abundance of the peaks (molecular ion, $M+2$ and $M+4$) from the 3 and 5 compounds is the confirmation that these compounds contain two chlorine atoms.

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Date Received: 04/30/91

Date Accepted: 05/23/91