Studies in Organic Mass Spectrometry. Part 15 [1]. Electron Ionization Mass Spectra of Some 5-Nitro-3-thiophenecarboxanilides

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Received March 2, 1992

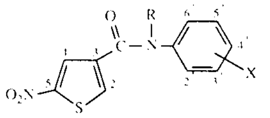
The study of the electron ionization mass spectra of 5-nitro-3-thiophenecarboxanilides **1-24** has shown peculiar effects induced by the 5-nitro group on the fragmentation of molecular ions M and the thenoyl cation *a* (Scheme 1). A comparison of the abundances of the important fragment ions for 5-nitro-3-thiophenecarboxanilides with those of the corresponding 3-thiophenecarboxanilides shows that the extent of C-N amide bond cleavage decreases in the former series as a consequence of the increased bond strength. The produced ion *a* does not eliminate carbon monoxide as 2- and 3-thenoyl cations usually do. Again this behaviour depends on the electronic effects of the nitro group which strongly destabilizes the 5-nitro-3-thienyl cation and consequently strengthens the carbon-3 carbonyl carbon bond. Recalling the behavior of the previously studied 2- and 3-thiophenecarboxanilides most of the 2'-substituted 5-nitro-3-thiophenecarboxanilides give loss of the '*ortho*' substituent of the phenyl ring furnishing the cyclic ion *g* (Scheme 2). In the instance of 2'-alkyl substituted derivatives the formation of abundant ions *h'* by loss of 5-nitrothenoyl radical from M (Scheme 3) was observed, thus confirming the occurrence of a cryptic '*ortho*' effect. The results are also discussed in relation to those obtained on some related benzoylanilides.

J. Heterocyclic Chem., **29**, 1657 (1992).

Introduction.

Substituted 2- and 3-thiophenecarboxanilides have been the object of several investigations concerning the kinetics of base [2] and acid [3] hydrolyses, protonation equilibria [4,5], ^{13}C nmr [6] and ir spectra [7]. More recently we have reported on their electron ionization mass spectra (ms) [8]. In such a study we observed that, beside the main fragmentation route which involves C-N amide bond cleavage followed by elimination of carbon monoxide [9-11], most of the 2'-substituted derivatives undergo a cyclisation reaction with loss of the substituent. In addition, a cryptic '*ortho*' effect was suggested as responsible for the charge retention in the aniline moiety after the C-N amide bond cleavage of 2'-methyl and 2'-ethyl derivatives. Hence, we thought it interesting to record the ms of the following 5-nitro-3-thiophenecarboxanilides **1-24** in order to investigate the effect of the 5-nitro group on the fragmentation reactions of such compounds. For instance we have found that compounds **1-24** exhibit mutagenic activity in *Salmonella typhimurium* TA 98 and TA 100 strains [12].

Formulas **1-24**



	X	R		X	R		X	R
1	4'-OMe	H	**9**	2'-Et	H	**17**	4'-Br	H
2	3'-OMe	H	**10**	H	H	**18**	3'-Br	H
3	2'-OMe	H	**11**	4'-F	H	**19**	2'-Br	H
4	4'-Me	H	**12**	3'-F	H	**20**	4'-NO_2	H
5	3'-Me	H	**13**	2'-F	H	**21**	3'-NO_2	H
6	2'-Me	H	**14**	4'-Cl	H	**22**	2'-NO_2	H
7	4'-Et	H	**15**	3'-Cl	H	**23**	2',6'-diMe	H
8	3'-Et	H	**16**	2'-Cl	H	**24**	H	Me

Results and Discussion.

The significant peaks of the ms of **1-24** are reported in Table 1.

The molecular ions of these compounds are always abundant [from 23.5 (**16**) up to 100% (**1, 3, 7, 13, 23**)] while the main fragmentation route involves the C-N amide bond cleavage as previously observed for the corresponding 5-H derivatives [8-11]. This fragmentation is responsible of the formation of the ion at m/z 156 (ion *a*, Scheme 1) that constitutes the most abundant fragment ion (except for **9, 16, 19** and **23**) and represents the base peak for the large majority of the compounds (exceptions are: **1, 3, 7, 9, 13, 16, 19** and **23**).

In contrast with the thenoyl cation arising from 5-H derivatives [8-10], which eliminates carbon monoxide, the 5-nitro-3-thenoyl cation *a* displays loss of nitrogen dioxide (ion *c*, m/z 110), nitrogen monoxide (ion *b'*, m/z 126) or oxygen atom (ion *b*, m/z 140). The formation of an odd

Table 1

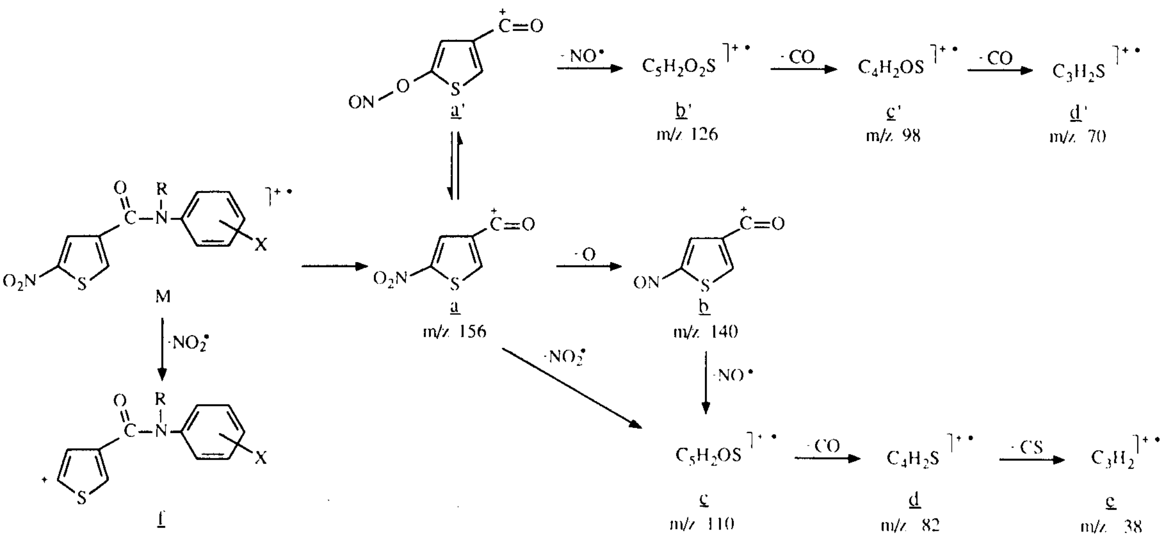
Significant Peaks of the Mass Spectra of 5-Nitro-3-Thiophenecarboxanilides (1-24)

	X	R	M		a	b	b'	c	d	e	c'	d'	f		g	h' or h	
			m/z	(I%)	m/z 156	m/z 140	m/z 126	m/z 110	m/z 82	m/z 38	m/z 98	m/z 70	m/z	(I%)	m/z 247	m/z	(I%)
1	4'-OMe	H	278	(100)	(50)	(2.8)		(25)	(9.2)	(2.1)	(1.4)	(1.7)	232	(2.8)	/	122	(42)
2	3'-OMe	H	278	(73)	(100)	(3.8)		(43)	(8.8)	(2.6)	(2.1)	(2.4)	232	(13)	/	122	(7.1)
3	2'-OMe	H	278	(100)	(65)	(3.3)		(25)	(8.0)	(1.1)	(1.5)	(1.5)	232	(3.3)	(11)	122	(4.7)
4	4'-Me	H	262	(75)	(100)	(3.7)	(1.2)	(32)	(7.5)	(2.3)	(2.0)	(2.4)	216	(2.0)	/	106	(5.2)
5	3'-Me	H	262	(53)	(100)	(5.5)	(1.2)	(22)	(4.6)	(1.1)	(1.0)	(1.0)	216	(3.5)	/	106	(1.8)
6	2'-Me	H	262	(46)	(100)	(3.6)	(2.3)	(62)	(3.5)	(0.8)	(5.0)	(0.8)	216	(11)	(0.7)	106	(69)
7	4'-Et	H	276	(100)	(87)	(3.2)		(37)	(4.5)	(0.6)	(1.6)	(1.0)	230	(2.9)	/	120	(2.4)
8	3'-Et	H	276	(90)	(100)	(4.3)	(0.7)	(40)	(7.6)	(4.3)	(1.9)	(2.4)	230	(5.5)	/	120	(1.9)
9	2'-Et	H	276	(51)	(69)	(3.7)		(35)	(7.1)	(1.0)	(1.6)	(1.2)	230	(10)	(1.6)	120	(100)
10	H	H	248	(61)	(100)	(3.5)		(32)	(6.8)	(1.7)	(1.4)	(1.6)	202	(2.1)	/	92	(1.2)
11	4'-F	H	266	(70)	(100)	(4.0)	(2.1)	(33)	(6.0)	(1.1)	(1.1)	(1.2)	220		/	110 [I]	
12	3'-F	H	266	(65)	(100)	(4.2)	(1.7)	(31)	(8.9)	(2.5)	(1.4)	(1.7)	220		/	110 [I]	
13	2'-F	H	266	(100)	(96)	(4.5)		(35)	(11)	(2.8)	(2.2)	(2.9)	220		/	110 [I]	
14	4'-Cl	H	282 284	(51) (20)	(100)	(4.4)	(1.3)	(29)	(5.7)	(1.3)	(1.4)	(1.4)	236 238		/	126 128	(1.3) (1.9)
15	3'-Cl	H	282 284	(41) (15)	(100)	(3.5)	(1.2)	(29)	(6.5)	(1.1)	(1.6)	(1.4)	236 238		/	126 128	(1.2) (1.1)
16	2'-Cl	H	282 284	(17) (6.5)	(97)	(4.9)	(1.6)	(36)	(7.1)	(2.2)	(1.4)	[illegible]	236 238		(100)	126 128	(1.6) (1.9)
17	4'-Br	H	326 328	(44) (47)	(100)	(5.8)	(2.0)	(41)	(9.6)	(2.1)	[illegible]	[illegible]	280 282		/	170 172	(1.3) (2.5)
18	3'-Br	H	326 328	(33) (34)	(100)	(5.0)		(36)	(10)	(4.9)	(2.0)	(2.5)	280 282		/	170 172	(1.0) (1.0)
19	2'-Br	H	326 328	(12) (13)	(75)	(4.7)	(1.1)	(34)	(7.7)	(1.9)	(1.3)	(1.7)	280 282		(100)	170 172	(0.8) (0.8)
20	4'-NO_2	H	293	(53)	(100)	(3.6)		(39)	(12)	(2.9)	(2.2)	(2.2)	247		/	138	(13)
21	3'-NO_2	H	293	(40)	(100)	(3.1)	(2.9)	(30)	(7.1)	(1.3)	(1.4)	(1.3)	247		/	138	(1.5)
22	2'-NO_2	H	293	(34)	(100)	(4.0)	(0.5)	(58)	(18)	(2.3)	(3.8)	(3.5)	247 [II]		(77)	138	
23	2',6'-diMe	H	276	(100)	(68)	(4.8)	(1.0)	(42)	(7.4)	(1.6)	(1.0)	(1.9)	230	(68)	(10) [III]	120	(97)
24	H	Me	262	(48)	(100)	(4.5)		(36)	(6.7)	(1.5)	(1.5)	(2.1)	216	(6.7)	/	106	(7.3)

[I] The peak overlaps c. [II] Undistinguishable from g. [III] In this case m/z 261.

Scheme 1

Common Fragmentations of 5-Nitro-3-Thiophenecarboxanilides



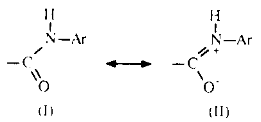
R = H, Me

electron ion from an even electron one is not a frequent process in mass spectrometry [13-15]. However, the thermodynamic stability of either charged or neutral fragmentation products and the lability of the bond being cleaved are also determinant in discriminating between competitive fragmentation pathways of even electron ions [16]. Indeed the loss of stable nitrogen dioxide or monoxide radicals from even electron ions constitutes a relatively common process in mass spectrometry of nitro compounds [17]. In addition it should be considered that loss of carbon monoxide from ion *a* (m/z 156) would give a thienyl cation strongly destabilized by the presence of the nitro group.

Elimination of carbon monoxide occurs from both ions *c* and *c'*, where the nitro group is no longer present, affording to ions *d* (m/z 82) and *c'* (m/z 98), respectively (Scheme 1).

The ion *f* formed by direct loss of nitrogen dioxide from the molecular ion was observed only for the *N*-methyl derivative **24**, the unsubstituted derivative **10** and the derivatives bearing electron-donating substituents (**1-9** and **23**), being particularly abundant for the 2',6'-dimethyl derivative **23**. Then the formation of this ion *f* is possible only when the molecular ion contains a C–N amide bond with significant double bond character (see Formulas). The character of this bond depends on the nature of the substituent on the amide nitrogen.

Formulas I-II



Electron-donating groups in the aryl moiety (by π-polarization) or alkyl groups directly linked (by inductive effect) help dispersion of the positive charge on the ammonium nitrogen. Such substituents increase the weight of the resonance structure II with the nitrogen-carbon double bond.

On the other hand the presence of an ion at m/z 247 for the 2'-nitro derivative **22** (but not for the 4'-nitro and 3'-nitro derivatives **20** and **21**) is due to an *ortho* elimination reaction as discussed later rather than the formation of an $[M-NO_2]^+$ ion deriving from the elimination of the nitro group bound to the thiophene ring. A comparison of relative abundances of corresponding ions together with the fact that molecular ions are always more abundant for compounds of the present 5-NO_2 series (Table 1) than those of the 5-H series [8], shows that the presence of a nitro group makes the C–N amide bond cleavage a relatively less important process in the former than in the latter series. This should be attributed to the electron-withdrawing effect of the 5-nitro group that destabilizes the 5-nitro-3-thenoyl cation and increases the strength of the amide bond.

Even if it is known that free energy relationships in mass spectrometry are complicated by various factors (*e.g.* internal energy distribution, reaction rates, further fragmentations, degrees of freedom and so forth) [18] an attempt to evaluate quantitatively the effect of the substituent in the aryl moiety of **1-24** was made. Poor free energy relationships were found by correlating log $[M]/[M_o]$ (where M_o represents the total number of ions formed by the electron impact process) and log Z/Z_o (where $Z = [a]/[M]$ and $Z_o = [a]_H/[M]_H$) with Hammett's σ or σ^+ substituent constants for 3'- and 4'-substituted compounds. The following results were obtained:

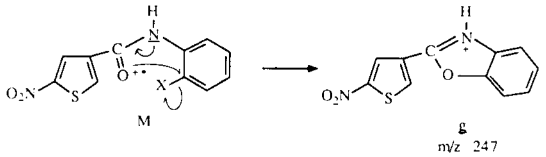
$$\begin{array}{ll} \log [M]/[M_o] & (\rho\ -0.21,\ r\ 0.84,\ n\ 15) \\ & (\rho^+\ -0.15,\ r\ 0.80,\ n\ 15) \\ \log Z/Z_o & (\rho\ 0.37,\ r\ 0.70,\ n\ 15) \\ & (\rho^+\ 0.33,\ r\ 0.82,\ n\ 15) \end{array}$$

In agreement with independent kinetic [2,3], thermodynamic [5,19] and spectroscopic evidence [6] the above results show that the strength of the amide bond and its consequent cleavage is only weakly affected by the substituents in the phenyl ring.

As previously observed for the corresponding 2'-substituted 2- and 3-thiophenecarboxanilides [8] and acetanilides [20], the loss of the *ortho* substituent in the phenyl ring (except for X = H and F) gives rise to the formation of the cyclic ion *g* (m/z 247) from compounds **3, 6, 9, 16, 19, 22** and **23** (see Scheme 2).

Scheme 2

Loss of 'Ortho' Substituents by Ring Closure Reactions



X = OMe, Me, Et, Cl, Br, NO_2

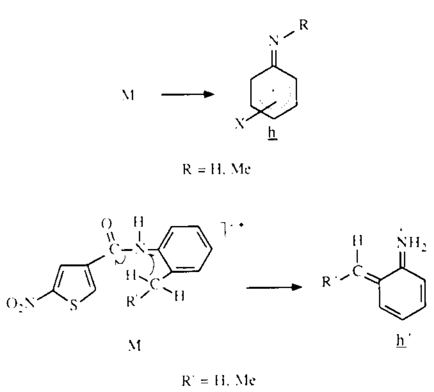
This process is considerably more relevant for compounds of the present 5-NO_2 series than for corresponding compounds of the previously investigated 5-H [8] series as can be seen by comparing, for example, the abundances of ion *g* of Scheme 2 for X = OMe, NO_2, Br and Cl (11, 77, 100 and 100%, respectively) with the abundances of the corresponding ion for the same substituents in the 5-H series [8] (2.2, 12, 51 and 33%).

In sharp contrast with compounds of the 5-H series [8], the ion *h* $[M-156]^+$ formed by loss of the 5-nitrothenoyl radical from M is generally present [2'-nitro derivative **22** is one exception]. This fact could be due to the polar effect of the 5-nitro group which increasing the ionisation energy of the thenoyl radical, makes competitive the charge retention in the aniline moiety [8]. However, the presence of this peak cannot be unambiguously appreciated for the three fluoro substituted derivatives **11**, **12** and **13** as its m/z ratio has the same value as that of the largely predominant ion *c* (*i.e.* m/z 110).

Moreover the particularly abundant ion $[M - 156]^+$ observed for 2'-methyl- **6**, 2'-ethyl- **9** and 2',6'-dimethyl- **23** derivatives confirms that a hydrogen migration from the *ortho*-alkyl group to the amide nitrogen through a five-membered transition state is responsible for the process of Scheme 3, that we call a cryptic '*ortho*' effect [8]. The resulting ion *h'* is strongly stabilised by its *ortho*-quinoid structure and is again much more abundant than that deriving from the previously studied 2'-alkyl substituted 3-thiophenecarboxanilides [8]. In fact the abundance of this ion increases from 5.5 to 69% for X = Me, from 37 to 100% for X = Et and from 20 to 97% for 2',6'-diMe on passing from compounds of the 5-H to compounds of the 5-NO_2 series. The enhancement of both rearrangement processes (loss of 2'-substituent and formation of *h'* through hydrogen migration from 2'-alkyl groups) in 2'-substituted 5-nitro derivatives indicates again an higher activation energy for amide bond cleavage as a consequence of the higher strength of the amide bond.

Scheme 3

C-N Amide Bond Cleavage



Finally we have examined the ms of benzoylanilide (**25**), 3-nitrobenzoylanilide (**26**) and 3-nitrobenzoyl-2',6'-dimethylanilide (**27**). The relevant results are collected in Table 2.

The significant fragmentation process of the molecular ions of compounds **25** and **26** involves rupture of the amide bond subject to a '*meta*'-nitro group effect similar to that discussed above for the thiophene series.

Also the behavior of 2',6'-dimethyl derivative **27** generally parallels that of the corresponding thiophene derivative **23**. In fact **27** displays both '*ortho*-induced' reactions: loss of methyl radical affording to the equivalent of ion *g* and loss of 3-nitrobenzoyl radical affording to ion *h'* (the base peak).

However direct loss of nitrogen dioxide, with formation of the equivalent of ion *f*, was not detected for **26** and **27**. This might be due to the absence of those factors which strengthen the amide bond in 5-nitro-3-thiophenecarboxanilides (electron-withdrawing effect of the sulphur atom and the high polarizability of the aromatic π-system of thiophene, which cooperate with the electron-donating effect of the substituents in the benzene moiety or the electron-repelling effect of the methyl group directly linked to the amide nitrogen atom). Another interesting feature of the benzene series is that the equivalent of ion *a* arising from compounds **26** and **27** displays elimination of carbon monoxide, a process which is absent in compounds of the thiophene series (**1-24**).

Conclusions.

The presence of a nitro group in position 5 of the thiophene ring affects the fragmentation patterns of 3-thiophenecarboxanilides in the following ways: (i) the extent of C-N amide bond cleavage is reduced because of the increased strength of this bond and the relative instability of the 5-nitro-3-thenoyl cation; (ii) the 5-nitro-3-thenoyl cation does not eliminate carbon monoxide as 2- and 3-thenoyl cations (and the 3-nitrobenzoyl cation) usually do. Instead loss of nitrogen dioxide, nitrogen monoxide or oxygen atom is observed; (iii) the 5-nitro group promotes loss of

Table 2

Significant Peaks [I] of the Mass Spectra of Benzoylanilide (**25**), 3-Nitrobenzoylanilide (**26**) and 3-Nitrobenzoyl-2',6'-Dimethylanilide (**27**)

	M		a		a - CO		c		d		g		h or h'		d - C_2H_2	
	m/z	(I%)	m/z	(I%)	m/z	(I%)	m/z	(I%)	m/z	(I%)	m/z	(I%)	m/z	(I%)	m/z	(I%)
25 [II]	197	(37)	105	(100)	77	(58)						/	92	(1.5)	51	(1.9)
26	242	(57)	150	(100)	122	(2.2)	104	(36)	76	(28)		/	92	(5.0)	50	(6.4)
27	270	(56)	150	(77)	122	(7.6)	104	(35)	76	(26)	255	(3.4)	120	(100)	50	(6.0)

[I] Identical letters for the different ions refer to the equivalent ions resulting from the analogous fragmentations reported in Table 1. [II] The peak intensities well compare with those reported by V. A. Puchkov, Yu. S. Nekrasov and N. S. Wulfson, Izv. Akad. Nauk. SSSR, Ser. Khim., **7**, 1635 (1968).

Table 3

Physical Properties of 5-Nitro-3-Thiophenecarboxanilides

	X	R	Crystallization solvent	m.p. °C	Colour	$\frac{\lambda_{max}}{nm}$ [I] (log ε) 95% ethanol
1	4'-OMe	H	dioxane	189-190	orange	210 [II] (4.34), 285 (4.28)
2	3'-OMe	H	methanol	171-172	pale yellow	220 (4.49), 277 (4.32), 292 [II] (4.31)
3	2'-OMe	H	methanol/dioxane	133	yellow	217 (4.36), 292 (4.14)
4	4'-Me	H	methanol/dioxane	180	yellow	213 [II] (4.22), 278 (4.15)
5	3'-Me	H	methanol	131	yellow	214 (4.42), 275 (4.30)
6	2'-Me	H	methanol	142	colourless	212 (4.67), 271 (4.34), 308 [II] (4.15)
7	4'-Et	H	methanol	142	yellow	212 [II] (4.35), 277 (4.28)
8	3'-Et	H	methanol	144	yellow	214 (4.38), 275 (4.25)
9	2'-Et	H	methanol	143	colourless	212 (4.43), 270 (4.06), 307 [II] (3.89)
10	H	H	methanol/dioxane	182	pale yellow	273 (4.26)
11	4'-F	H	methanol	184	yellow	272 (4.22)
12	3'-F	H	methanol/dioxane	166-168	pale brown	213 [II] (4.26), 276 (4.23), 282 (4.23)
13	2'-F	H	dioxane	205	colourless	215 [II] (4.25), 273 (4.11), 316 [II] (3.77)
14	4'-Cl	H	methanol/dioxane	194-195	orange	275 (4.32)
15	3'-Cl	H	methanol	137	yellow	216 (4.48), 270 (4.33)
16	2'-Cl	H	methanol/dioxane	179	colourless	214 (4.43), 265 (4.10), 309 [II] (3.84)
17	4'-Br	H	methanol/dioxane	215	yellow	276 (4.42)
18	3'-Br	H	methanol/dioxane	160	pale yellow	216 (4.47), 271 (4.30)
19	2'-Br	H	methanol/dioxane	162	pale yellow	213 (4.46), 268 (4.09), 309 [II] (3.85)
20	4'-NO_2	H	dioxane	225-226	yellow	224 (4.27), 316 (4.41)
21	3'-NO_2	H	dioxane	241-242	pale brown	215 (4.42), 263 (4.56), 313 [II] (4.05)
22	2'-NO_2	H	dioxane	177-178	yellow	243 (4.37), 313 [II] (3.96)
23	2',6'-diMe	H	methanol	212	pale pink	214 (4.54), 272 (4.06), 305 [II] (3.95)
24	H	Me	methanol	119	pale yellow	217 [II] (4.24), 273 (3.98), 306 [II] (3.81)

[I] λ Range: 210 nm ≤ λ ≤ 330 nm. [II] Shoulder.

the '*ortho*' substituents from 2'-substituted thiophene-3-carboxanilides as well as the cryptic '*ortho*' effect observed in 2'-alkyl substituted derivatives.

EXPERIMENTAL

The compounds under investigation were prepared by reacting 5-nitro-3-thiophenecarboxyl chloride [21] with the appropriate aniline as previously described [12]. The physical properties of all compounds are reported in Table 3.

The mass spectra were recorded on a "VG 70 70E" mass spectrometer. Ions were generated in the built-in electron impact ionization source operating at an ionization potential of 70 eV and a total emission current of 18 mA. The accelerating voltage was 6 kV. The ionization chamber temperature was about 180°. All compounds were heated at 100-180° under reduced pressure (10^{-8} torr).

Acknowledgements.

We wish to thank CNR and MURST (Italy) for financial support.

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