Electron ionization (EI) mass spectra of some 3,4-disubstituted-1,2,4-oxadiazin-5-ones and -thiones and 3,5-disubstituted 1,2,4-oxadiazin-6-ones

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Abstract

The EI mass spectra of 3,4-disubstituted-1,2,4-oxadiazin-5-ones **1**–**6** and –thiones **7**,**8** and 3,5-disubstituted 1,2,4-oxadiazin-6-ones **9**,**10** were recorded and their fragmentation pathways solved and compared with each other. The fragmentation routes of 5-ones and 5-thiones do not differ very much from each other but compounds **9** and **10** behave differently as could be expected based on their lactone type structures. Only compounds **4**–**6** exhibit a loss of CO and compound **7** a loss of NO. The loss of a benzyl group dominates the behaviour of compounds **1** and **2** which showed only few additional fragmentations. Some earlier data on some 3,4-disubstituted-1,2,4-diazin-5-ones **11**–**13** and –thiones **14**,**15** have been reanalyzed and discussed in further detail.

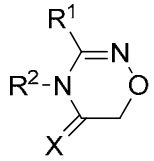
Keywords: Electron ionization mass spectrometry, heterocyclic compounds, fragmentation pathways, reaction mechanism

Introduction

The title compounds possess a diversity of pharmacological activities,[1-5] e.g. antibacterial against some micro-organisms and yeast cultures.[5] Only some low resolution EI data are available for a few 1,2,4-oxadiazin-5-ones[6,7] and two 1,2,4-oxadiazin-5-thiones.[6] No published mass spectrometric data was found for 1,2,4-oxadiazin-6-ones. Therefore we thought it interesting to discuss the mass spectrometric behaviour of the title compounds **1**–**10** (Figure 1) under electron ionization (EI) in detail. The syntheses of the studied compounds have been published earlier.[5,8]

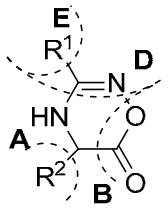
The low resolution EI mass spectra of some 3,4-disubstituted-1,2,4-oxadiazin-5-ones (cf. Figure 1: **11**–**13**) and -5-thiones (cf. Figure 1: **14** and **15**) have been reported.[6] In another report some EI mass spectrometric data have been given for seven 2-(2-thienyl)-4-substituted-1,2,4-oxadiazin-5-

ones but the results do not appear to agree with the present data or with those given in Ref. 6.[7] We have also reanalyzed the data for compounds **11**–**15**.



1-15

	R^1	R^2	X
1	2-Py	Bzl	O
2	4-Py	Bzl	O
3	3-Py	*p*-$CH_3C_6H_4$	O
4	4-Py	C_6H_5	O
5	C_6H_5	*p*-$CH_3C_6H_4$	O
6	4-Py	*p*-$CH_3OC_6H_4$	O
7	C_6H_5	*p*-$CH_3C_6H_4$	S
8	*p*-ClC_6H_5	*p*-$CH_3C_6H_4$	S
11	CH_3	H	O
12	C_6H_5	CH_3	O
13	C_6H_5	C_6H_5	O
14	C_6H_5	CH_3	S
15	C_6H_5	C_6H_5	S



9-10

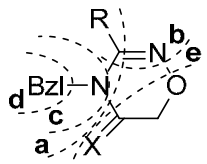
	R^1	R^2
9	2-Py	$(CH_3)_2CH$
10	2-Py	Bzl

Figure 1. Compounds **1**–**10** and **11–15** and typical fragmentations of **9** and **10**.

Results and Discussion

3,4-Disubstituted-1,2,4-oxadiazin-5-ones (1–6)

Compounds 3 and 2. The fragmentation of compounds **1** and **2** is dominated by formation of the tropylium ion **d** (Table 1) which forms the base peak in both cases (Scheme 1). This also explains why their molecular ions are only moderately abundant as compared with those of compounds **3**–**6** (Tables 1 and 2) for which they form the base peaks. The loss of $C_2H_2NO_2^{\bullet}$ leads to medium strong ions **a** at *m/z* 195 both for **1** and **2**. It is interesting that **2** gives a relatively abundant ion (RA 20.5%) **c**+**1**, $C_7H_8N^+$, at *m/z* 106 the parent ion of which is **e**+**1** at *m/z* 210 (Table 1) which corresponds to loss of $C_2HO_2^{\bullet}$ from the molecular ion. Both of the former ions are missing from **1** which obviously must be due to the influence of the 2-pyridyl substituent when compared to the 4-pyridyl substituent in **2.** Both compounds also show ions **b**+**1** (2- or 4-$PyNH^+$) and **c**–**1**, $[(Bzl–H)N]^+$. The few further low mass ions are listed in Table 3.



Scheme 1. Typical fragmentations of compounds **1** and **2**. The sites of fragmentations are also applicable for **3**–**8** and **11**–**15.**

Table 1. Main EI fragmentations [*m/z*(RA %)] of 3,4-disubstituted-1,2,4-oxadiazin-5-ones **1**–**5** at 70 eV

Compound	**1**	**2**	**3**	**4**	**5**
R^1	2-Py	4-Py	3-Py	4-Py	C_6H_5
R^2	Bzl	Bzl	*p*-$CH_3C_6H_4$	C_6H_5	*p*-$CH_3C_6H_4$
Fragment					
M$^{+\bullet}$	267(19)	267(15)	267(100)	253(100)	266(100)
a	$C_{13}H_{11}N_2^+$	$C_{13}H_{11}N_2^+$	$C_{13}H_{11}N_2^+$	$C_{12}H_9N_2^+$	$C_{14}H_{12}N^+$
	195(18)	195(10)	195(8)	181(13)	194(9.5)
b+1	$C_6H_5N_2^{+,a}$	$C_6H_5N_2^{+,a}$	$C_6H_5N_2^{+,a}$	$C_6H_5N_2^+$	$C_7H_5N^{+\bullet}$ (**b**)
	105(2)	105(6)	105(16)	105(24)	103(7)
c+1	-	$C_7H_8N^+$	$C_7H_8N^+$	$C_6H_6N^+$	-
	-	106(20.5)	106(6)	92(4)	-
c	$C_7H_7N^{+\bullet,a}$	$C_7H_7N^{+\bullet,a}$	$C_7H_7N^{+\bullet,a}$	$C_6H_5N^{+\bullet}$	$C_7H_7N^{+\bullet}$
	105(2)	105(6)	105(15)	91(25)	105(22)
c–1	$C_7H_6N^{+,a}$	$C_7H_6N^{+,a}$	$C_7H_6N^{+,a}$	-	$C_7H_6N^+$(also **b**+**1**)
	104(3)	104(4.5)	104(22)	-	104(19)
d	$C_7H_7^+$	$C_7H_7^+$	$C_7H_7^+$	$C_6H_5^+$	$C_7H_7^+$
	91(100)	91(100)	91(95)	77(47)	91(61)
e+1	-	$C_{13}H_{12}N_3^+$	$C_{13}H_{12}N_3^+$	$C_{12}H_{10}N_3^+$	$C_{14}H_{13}N_2^+$
	-	210(5)	210(6)	196(10)	209(2)
e	-	-	$C_{13}H_{11}N_3^{+\bullet}$	$C_{12}H_9N_3^{+\bullet}$	$C_{14}H_{12}N_2^{+\bullet}$
	-	-	209(93)	195(90)	208(95)
e–1	-	-	$C_{13}H_{10}N_3^+$	$C_{12}H_8N_3^+$	$C_{14}H_{11}N_2^+$
	-	-	208(32)	194(5)	207(27)
[M–CO]$^{+\bullet}$	-	-	$C_{14}H_{13}N_3O^{+\bullet}$	$C_{13}H_{11}N_3O^{+\bullet}$	$C_{15}H_{14}N_2O^{+\bullet}$
f	-	-	239(12)	225(15)	238(4)
f–1	-	-	$C_{14}H_{12}N_3O^+$	$C_{13}H_{10}N_3O^+$	-
	-	-	238(4)	224(8)	-
g	-	-	$C_8H_7N_2^{+,b}$	$C_7H_6N_2^{+\bullet,c}$	$C_8H_7N_2^{+,b}$
	-	-	131(18)	118(28)	131(18)
h	-	-	$C_8H_7NO^{+\bullet}$	-	$C_8H_7NO^{+\bullet}$
	-	-	133(5)	-	133(3)
h–1	-	-	$C_8H_6NO^+$	-	$C_8H_6NO^+$
	-	-	132(12.5)	-	132(8)
i	-	-	$C_8H_9N^{+\bullet}$	-	$C_8H_9N^{+\bullet}$
	-	-	119(26)	-	119(17)
i–1	-	-	-	$C_7H_6N^+$	-
	-	-	-	104(5)	-

[a] $C_6H_5N_2^+$ dominates. [b] Also $C_9H_9N^{+\bullet}$. [c] **g+1**.

Table 2. Main EI fragmentations [*m/z*(RA %)] of 3,4-disubstituted-1,2,4-oxadiazin-5-one **6** and 3,4-disubstituted-1,2,4-oxadiazin-5-thiones **7**–**8** at 70 eV

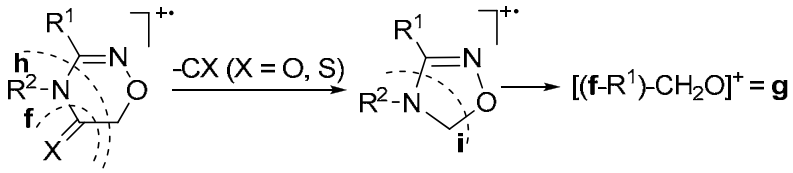
Compound	**6**	**7**	**8**
R^{1}	4-Py	C_6H_5	*p*-ClC_6H_4
R^{2}	*p*-$CH_3OC_6H_4$	*p*-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$
Fragment			
M$^{+\bullet}$	283(100)	282(63)	316(40)/318(16)
a	$C_{13}H_{11}N_2O^+$	$C_{14}H_{12}N^+$	$C_{14}H_{11}NCl^+$
	211(5.5)	194(11)	228(6)
b+1	$C_6H_5N_2^+$	$C_7H_5N^{+\bullet}$ (**b**)	$C_7H_4NCl^{+\bullet}$ (**b**)
	105(5)	103(9)	137(13)
c	$C_7H_7NO^{+\bullet}$	$C_7H_7N^{+\bullet}$	$C_7H_7N^{+\bullet}$
	121(13)	105(19)	105(13)
c–1	-	$C_7H_6N^+$(also **b+1**)	-
	-	104(4.5)	-
d	-	$C_7H_7^+$	$C_7H_7^+$
	-	91(61)	91(41)
e	$C_{13}H_{11}N_3O^{+\bullet}$	$C_{14}H_{12}N_2^{+\bullet}$	$C_{14}H_{11}N_2Cl^{+\bullet}$
	225(34)	208(8)	242(5)
e–1	-	$C_{14}H_{11}N_2^+$	-
	-	207(9)	-
[M–CO]$^{+\bullet}$	$C_{14}H_{13}N_3O_2^{+\bullet}$	[M–NO]$^{+\bullet}$ (**F**)	-
f	255(5)	252(5)	-
g	-	$C_8H_7N_2^{+,a}$	$C_8H_7N_2^{+,a}$
	-	131(9)	131(5)
h+1	-	$C_8H_8NS^+$	$C_8H_8NS^+$
	-	150(5)	150(4)
h	-	$C_8H_7NS^{+\bullet}$	$C_8H_7NS^{+\bullet}$
	-	149(100)	149(100)
h–1	-	$C_8H_6NS^+$	$C_8H_6NS^+$
	-	148(10)	148(7)
i	$C_8H_9NO^{+\bullet}$	$C_8H_9N^{+\bullet}$	-
	135(19)	119(5)	-
i–1	$C_8H_8NO^+$	$C_8H_8N^{+,b}$	$C_8H_8N^+$
	134(6)	118(24)	118(18)

[a]Also $C_9H_9N^{+\bullet}$. [b]Contains 1/9 of $C_7H_6N_2^{+\bullet}$.

Table 3. Some further ions from compounds **1**–**8**

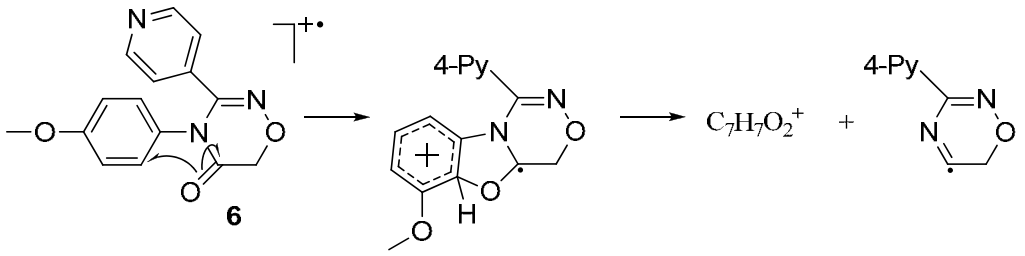
Compound	Ions, *m/z*(RA %)
1	$C_5H_4N^+$, $C_6H_6^{+\bullet}$: 78(4.5); $C_5H_5^+$: 65(10); 51(5)
2	$C_5H_4N^+$, $C_6H_6^{+\bullet}$: 78(6); $C_5H_3N^{+\bullet}$, $C_6H_5^+$: 77(5); $C_5H_5^+$: 65(10); 51(8)
3	$[M–CH_3O]^+$= $C_{14}H_{10}N_3O^+$: 236(6); $C_7H_6N_2^{+\bullet}$ = [**e**–$C_6H_5N_2$]$^{+\bullet}$: 118(5); $C_6H_4N^+$: 90(6); $C_7H_5^+$: 89(7); $C_5H_5N^{+\bullet}$: 79(8.5); $C_5H_4N^+$: 78(29); $C_5H_3N^{+\bullet}$: 77(18); $C_6H_4^{+\bullet}$: 76(5); $C_5H_5^+$: 65(36); 64(4.5); 63(8); 52(9.5); 51(25); 50(8); 41(5.5); 39(7)
4	$C_{11}H_8N_2^{+\bullet}$=[**e**–HCN]$^{+\bullet}$: 168(4); 119(6), 117(6); **i–2** = $C_7H_5N^{+\bullet}$: 103(12); $C_5H_4N^+$: 78(23); 76(4.5); 65(5); 64(12); 63(5); 51(47); 50(8), 39(7)
5	$C_7H_5^+$: 89(5); $C_6H_6^{+\bullet}$: 78(9); $C_6H_5^+$: 77(24); 76(5); 65(23), 63(5), 52(5); 51(13); 39(10)
6	$C_{12}H_8N_3O^+$ = [**e**–CH_3]$^+$: 210(76); $C_{11}H_8N_3^+$ = [**e**–CH_3–CO]$^+$: 182(5); $C_9H_9NO^{+\bullet}$: 147(7) = [(M–C_5H_4N)–CNO]$^+$; $C_7H_5N_2O^+$: 133(5); $C_7H_7O_2^+$: 123(7); $C_6H_4NO^+$: 106(10); $C_6H_6N^+$: 92(9); 80(5); 78(37); 77(11); 64(12); 63(7); 52(6); 51(21); 50(5)
7	$[M–C_7H_5NO]^{+\bullet}$ = $C_9H_9NS^{+\bullet}$: 163(12); $C_9H_8NS^+$: 162(5); $C_8H_9S^+$: 137(9); $[M–CH_2O–C_8H_7N]^{+\bullet}$ = $C_7H_5NS^{+\bullet}$: 135(5); $C_8H_6S^{+\bullet}$: 134(7); $C_8H_7NO^{+\bullet}$ = [M–**h**]$^{+\bullet}$: 133(5); **i**–**2**: $C_8H_7N^{+\bullet}$: 117(11); $C_8H_6N^+$: 116(8); 90(7); 89(9); 77(16); 76(5), 65(37), 63(7), 51(10); 45(5); 41(7); 39(13)
8	$[M–C_7H_4NOCl]^{+\bullet}$ = $C_9H_9NS^{+\bullet}$: 163(13); $C_9H_8NS^+$: 162(4); $C_8H_6S^{+\bullet}$: 134(6); **i**–**2**: $C_8H_7N^{+\bullet}$ 117(9); $C_8H_6N^+$: 116(5.5); 90(6); 89(6); 65(26); 63(5); 51(5); 39(9)

Compounds 3–6. For all of them the molecular ion forms the base peak. The fragmentations of these compounds resemble very much each other although **6** gives fewer fragments than the other three compounds. In contrast to **1** and **2** they all exhibit ion **f**, $[M–CO]^{+\bullet}$, and **3** and **4** also the ion **f**–**1** (Table 1). Like **1** and **2** they all show ions **a**, **b**+**1** (**5** contains also ion **b** and in this case ion **b**+**1** is identical with **c**–**1**) and **c** but in addition ions **d** (except **6**), **e**+**1** (except **6**), **e**–**1** (except **4**), **h** and **h**–**1** (except **4** and **6**). Compounds **3** and **4** exhibit also ions **c**+**1**, **g** (also **5**) and **3** and **5** the ion **i** (Table 1, Schemes 1 and 2). Some further fragments for **3**–**6** are shown in Tables 1 and 2. Some of them deserve a special mention. Only compound **3** gives the ion $[M–CH_3O]^+$ at *m/z* 236 (RA 6%) which is difficult to explain, but the total ion current and the B/E scan prove that it is formed from the molecular ion of **3**. Compounds **3** and **4** gave also another special ion, namely, $C_7H_6N_2^{+\bullet}$ at *m/z* 118 which corresponds to [**e**–C_6H_5N]$^{+\bullet}$ (RA 5%) for **3** and [**e**–C_5H_3N]$^{+\bullet}$ (RA 28%) for **4**, the latter being also equal to **g**+**1**.



Scheme 2. Typical fragmentations of compounds **3**–**8**. The sites of fragmentations (**h** and **i**) are also applicable for **11**–**15.**

Another special ion for **4** is $[\mathbf{e}–HCN]^{+\bullet} = C_{11}H_8N_2^{+\bullet}$ at *m/z* 168 (RA 4%). Furthermore it gives the ions $C_7H_yN_2^{+(\bullet)}$ where y is equal to 5–7 from the ions **e**+**1** and **e** (Tables 1 and 2). Compound **6** exhibits a few unique ions, namely formally $[\mathbf{e}–CH_3–CO]^+ = C_{11}H_8N_3^+$ at *m/z* 182 (RA 5%), $C_8H_8NO^+$ at *m/z* 134 (RA 6%), $C_7H_5N_2O^+$ at *m/z* 133 (RA 5%) and $C_7H_7O_2^+$ at *m/z* 123 (RA 7%) (Tables 1 and 3). The latter ion is formed directly from the molecular ion, i.e. through a cyclization between the *ortho* position and the C=O oxygen assisted by the *p*-methoxy substituent (Scheme 3) and the consequent fragmentation gives the ion $C_7H_7O_2^+$ at *m/z* 123.



Scheme 3. The fragmentation of **6** through cyclization

3,4-Disubstituted-1,2,4-oxadiazin-5-thiones (7,8)

The fragmentations of these two compounds resemble very much those of compounds **1**–**6** although the effect of sulfur, i.e. the thione instead of the oxo function is clearly reflected in their fragmentation (Table 2). Compound **7** is the only one giving the ion **F**, $[M–NO]^{+\bullet}$, (RA 5%). As compared to the ions from **1**–**6**, compounds **7** and **8** give **a**, **b**, **c**, **d**, **e**, **g, h** and **h–1** and in addition **h**+**1** the latter ions including sulfur instead of oxygen. Compound **7** gave also the ion **c–1** which in this case is equal to **b+1**. The fragmentation routes are shown in Schemes 1 and 2. The ions $C_8H_xN^{+(\bullet)}$ (**i**, **i**–**1** and **i**–**2**, Tables 2 and 3) were obtained via ions **a**, **e** as well as the ions *m/z* 149 and 163 both for **7** and **8**. Compound **7** exhibits also the counter ions $C_9H_9NS^{+\bullet}$ (*m/z* 163) and $C_7H_5NO^{+\bullet}$ (*m/z* 119) and the ions $C_9H_8NS^+$ (*m/z* 162), $C_8H_9S^+$ (*m/z* 137), and $[M–\mathbf{h}]^{+\bullet} = C_8H_7NO^{+\bullet}$ (*m/z* 133) (Table 3).

5-Isopropyl- (9) and 5-benzyl-1,2,4-oxadiazin-6-one (10)

The fragmentations of these two compounds (Figure 1, Table 4), possessing a lactone function, is very simple and differs completely from those of 5-ones **1**–**6** and 5-thiones **7** and **8** which in turn resemble fairly much each other. In both cases (Table 4) the base peak (ion **A**) corresponds to loss of the 5-substituent (i-Pr or Bzl). A weak ion $[M–CO_2]^{+\bullet}$ (**B)** is also present both for **9** and **10**. The ion **C** at *m/z* 148 in turn corresponds to $[\mathbf{A}–CO]^+$. Both compounds exhibit also the ion **D**, 2-$PyCNH^+$, at *m/z* 105 and the ion **E**, 2-Py^+, at *m/z* 78. Compound **10** shows also a relatively weak $BzlCHN^{+\bullet}$ ion at *m/z* 119 (Table 4).

Table 4. Significant fragments from 3-(2-pyridyl),5-isopropyl- **9** and -5-benzyl-1,2,4-oxadiazin-6-ones **10** at 70 eV

Compound	R	$M^{+\bullet}$	Relevant ions, *m/z*(RA %)
9	$(CH_3)_2CH$	219(7.5)	**A**: $[M–C_3H_7]^+ = C_8H_6N_3O_2^+$: 176(100), **B**: $[M–CO_2]^{+\bullet} = C_{10}H_{13}N_3^{+\bullet}$: 175(1), **C**: $[M–C_3H_7–CO]^+ = C_7H_6N_3O^+$: 148(12), **D**: 2-PyCNH$^+$ = $C_6H_5N_2^+$: 105(21), **E**: 2-Py$^+$ = $C_5H_4N^+$: 78(23), 51(5.5)
10	Bzl	267(1)	**A**: $[M–Bzl]^+ = C_8H_6N_3O_2^+$: 176(100), **B**: $[M–CO_2]^{+\bullet} = C_{14}H_{13}N_3^{+\bullet}$: 223(3), **C**: $[M–Bzl–CO]^+ = C_7H_6N_3O^+$: 148(4), BzlCHN$^{+\bullet}$ = $C_8H_9N^{+\bullet}$: 119(4), **D**: 2-PyCNH$^+$ = $C_6H_5N_2^+$: 105(18); 104(5); $C_7H_7^+$: 91(16), **E**: 2-Py$^+$ = $C_5H_4N^+$: 78(19); 65(5), 51(6)

3,4-Disubstituted-1,2,4-diazin-5-ones (11–13) and -5-thiones (14,15)

Compounds 11–15.[6] We have reanalyzed the data for these compounds (Schemes 1 and 2 and Table 5) based on the present results and they appear to be in general agreement with our observations for **1–8**. The brief comments given in the original paper are mainly correct although there are also some shortcomings. First of all, the reported $[M+1]^+$ and $[M+2]^+$ peaks for **11**–**15** are due to the carbon and sulfur isotopes. The authors[6] state that compounds **11**–**15** also exhibit peaks due to the nitrile oxide ions, R^1CNO^+. This appears to be true only for **11** (*m/z* 57 (4%), **13** (*m/z* 119(5%) and **15** (*m/z* 119(8%) since for **12** and **14** the peak at *m/z* 119 is due to the ^{13}C equivalent of the ion **a**. However, the compounds studied in our work did not give nitrile oxide ions at all. The ions $R^1CN^{+\bullet}$ (**b**) and/or R^1CNH^+ (**b**+**1**) instead are relatively abundant for all compounds **11**–**15**. Only compound **15** appears to give the ion **c**. As to the ion *m/z* 42 one should emphasize that in the case of **11** it can be either **a** or **b+1** (Table 5). Also ions **e**–**1**, **e, e+1**, **i** and **i**–**1** appear in most of **11**–**15**, like in **1–8**. The diaziridine ion, $[R^1CNR^2]^{+\bullet}$, is most abundant for **13**, not for the thio analogs **14** and **15** as stated in Ref. 6. Based on its mass spectrum,[6] compound **15** still appears to contain a substantial amount of **13** from which it was prepared[9] as may be deduced from the appearance of the ion *m/z* 252 (RA 21%) which can be explained only by being due to the molecular ion of **13**. Based on this observation we have corrected the relative abundances of those ions for **15** which also appear in the mass spectrum of 1**3**.

Conclusions

The fragmentation routes of 3,4-disubstituted-1,2,4-diazine-5-ones and 5-thiones were proved to closely resemble each other. Those of 3,5-disubstituted-1,2,4-diazine-6-ones instead were substantially different and fairly simple which was anticipated based on their lactone type structures. Reanalysis of the low resolution reference data for some 3-phenyl-4-R-substituted 1,2,4-

diazine-5-ones (**11**–**13**: R = H, CH_3, Ph) and -5-thiones (**14**,**15**: R = CH_3; Ph, respectively)[6] indicated that they obeyed the rules confirmed in this paper but also needed some revision.

Experimental Section

General. All the studied compounds have been prepared earlier.[5,8] 1,2,4-Oxadiazin-5-ones (**1**–**6**) were obtained from the reaction of the correspondingly *N*-substituted pyridine carboxamide oximes with chloroacetyl chloride in the presence of triethylamine.[5,8] 1,2,4-oxadiazin-5-thiones (**7**,**8**) were obtained from the corresponding 5-ones by treating them with P_2S_5.[5,8] The reaction of 2-pyridine hydroxamic acid chloride hydrochloride with L-amino acid ester hydrochloride led in turn to the formation 1,2,4-oxadiazin-6-ones.[5]

Table 5. Some reanalyzed literature data [*m/z*(RA %)] for 3,4-disubstituted -1,2,4-oxadiazin-5-ones (**11–13**) and -5-thiones (**14**–**15**)[6]

Compound	**11**	**12**	**13**	**14**	**15**
R^1	CH_3	Ph	Ph	Ph	Ph
R^2	H	CH_3	Ph	CH_3	Ph
Fragment					
$M^{+\bullet}$	114(84)	190(100)	252(94)	206(100)	268(100)
a	42(100)[a]	118(50)	180(10)	118(32)	180(14)
b	41(9)	103(25)	103(6)	103(20)	103(13)
b+1	42(100)[a]	104(24)	104(4)	104(18)	104(30)
c	-	-	-	-	91(12)
d	-	-	77(44)[b]	-	77(55)[b]
e+1	57(4)	-	-	133(7)	-
e	56(3)	132(8)	194(100)	132(36)	194(22)
e–1	55(17)	131(3)	-	-	-
h	-	-	-	73(11)	135(52)
i	29(15)	-	105(16)	-	105(4)
i-1	-	-	104(4)[c]	-	104(30)[c]

[a]**a** and **b+1** have the same elemental composition.
[b]This is most probably a combination of R^1 and R^2 since also **12** and **14** exhibit the ion $C_6H_5^+$ (RA 27 and 39%, respectively).
[c]Elemental composition the same as that of **b+1**.

The EI mass spectra were recorded on a VG ZABSpec mass spectrometer (VG Analytical, Division of Fisons, Manchester, UK), that was equipped with Opus V3.3X program package (Fisons Instruments, Manchester, UK). The ionization energy was 70 eV, accelerating voltage 8 kV and source temperature 160 °C. Direct insertion probe was used. Perfluorokerosene (PFK) was used for

calibration of the mass scale. The fragmentation pathways were confirmed by B/E-linked scans (1st FFR) for metastable ions. Also B^2/E-linked scans were used to clarify these pathways. The low resolution, B/E and B^2/E spectra were measured using resolution of 3000. To solve the ion structures the accurate masses (Tables 1 - 3) were determined practically for all ions by voltage scanning (10% valley definition) using 6,000-10,000 resolution.

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