

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

Kalevi Pihlaja,^{a*} Sanna Heinonen,^a Olli Martiskainen,^a Hikmet Ağırbaş,^b
and Nevin Arikan^c

^aDepartment of Chemistry, FI-20014 University of Turku, Finland.

^bDepartment of Chemistry, Kocaeli University, 41300 İzmit, Turkey ^cUludağ University, Science and Arts Faculty, Department of Chemistry, 16059, Bursa, Turkey

E-mail: kpihlaja@utu.fi

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**.

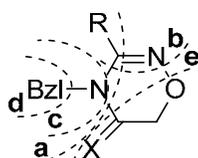
	R ¹	R ²	X		R ¹	R ²
	1 2-Py	Bzl	O			
	2 4-Py	Bzl	O		9 2-Py	(CH ₃) ₂ CH
	3 3-Py	<i>p</i> -CH ₃ C ₆ H ₄	O		10 2-Py	Bzl
	4 4-Py	C ₆ H ₅	O			
	5 C ₆ H ₅	<i>p</i> -CH ₃ C ₆ H ₄	O			
	6 4-Py	<i>p</i> -CH ₃ OC ₆ H ₄	O			
	7 C ₆ H ₅	<i>p</i> -CH ₃ C ₆ H ₄	S			
	8 <i>p</i> -ClC ₆ H ₅	<i>p</i> -CH ₃ C ₆ H ₄	S			
	11 CH ₃	H	O			
	12 C ₆ H ₅	CH ₃	O			
	13 C ₆ H ₅	C ₆ H ₅	O			
	14 C ₆ H ₅	CH ₃	S			
	15 C ₆ H ₅	C ₆ H ₅	S			

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 C₂H₂NO₂[•] 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**, C₇H₈N⁺, at *m/z* 106 the parent ion of which is **e+1** at *m/z* 210 (Table 1) which corresponds to loss of C₂HO₂[•] 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
R¹	2-Py	4-Py	3-Py	4-Py	C ₆ H ₅
R²	Bzl	Bzl	<i>p</i> -CH ₃ C ₆ H ₄	C ₆ H ₅	<i>p</i> -CH ₃ C ₆ H ₄
Fragment					
M⁺	267(19)	267(15)	267(100)	253(100)	266(100)
a	C ₁₃ H ₁₁ N ₂ ⁺ 195(18)	C ₁₃ H ₁₁ N ₂ ⁺ 195(10)	C ₁₃ H ₁₁ N ₂ ⁺ 195(8)	C ₁₂ H ₉ N ₂ ⁺ 181(13)	C ₁₄ H ₁₂ N ⁺ 194(9.5)
b+1	C ₆ H ₅ N ₂ ^{+,a} 105(2)	C ₆ H ₅ N ₂ ^{+,a} 105(6)	C ₆ H ₅ N ₂ ^{+,a} 105(16)	C ₆ H ₅ N ₂ ⁺ 105(24)	C ₇ H ₅ N [•] (b) 103(7)
c+1	-	C ₇ H ₈ N ⁺ 106(20.5)	C ₇ H ₈ N ⁺ 106(6)	C ₆ H ₆ N ⁺ 92(4)	-
c	C ₇ H ₇ N ^{+,a} 105(2)	C ₇ H ₇ N ^{+,a} 105(6)	C ₇ H ₇ N ^{+,a} 105(15)	C ₆ H ₅ N [•] 91(25)	C ₇ H ₇ N [•] 105(22)
c-1	C ₇ H ₆ N ^{+,a} 104(3)	C ₇ H ₆ N ^{+,a} 104(4.5)	C ₇ H ₆ N ^{+,a} 104(22)	-	C ₇ H ₆ N ⁺ (also b+1) 104(19)
d	C ₇ H ₇ ⁺ 91(100)	C ₇ H ₇ ⁺ 91(100)	C ₇ H ₇ ⁺ 91(95)	C ₆ H ₅ ⁺ 77(47)	C ₇ H ₇ ⁺ 91(61)
e+1	-	C ₁₃ H ₁₂ N ₃ ⁺ 210(5)	C ₁₃ H ₁₂ N ₃ ⁺ 210(6)	C ₁₂ H ₁₀ N ₃ ⁺ 196(10)	C ₁₄ H ₁₃ N ₂ ⁺ 209(2)
e	-	-	C ₁₃ H ₁₁ N ₃ [•] 209(93)	C ₁₂ H ₉ N ₃ [•] 195(90)	C ₁₄ H ₁₂ N ₂ [•] 208(95)
e-1	-	-	C ₁₃ H ₁₀ N ₃ ⁺ 208(32)	C ₁₂ H ₈ N ₃ ⁺ 194(5)	C ₁₄ H ₁₁ N ₂ ⁺ 207(27)
[M-CO]⁺	-	-	C ₁₄ H ₁₃ N ₃ O ^{•+}	C ₁₃ H ₁₁ N ₃ O ^{•+}	C ₁₅ H ₁₄ N ₂ O ^{•+}
f	-	-	239(12)	225(15)	238(4)
f-1	-	-	C ₁₄ H ₁₂ N ₃ O ⁺ 238(4)	C ₁₃ H ₁₀ N ₃ O ⁺ 224(8)	-
g	-	-	C ₈ H ₇ N ₂ ^{+,b} 131(18)	C ₇ H ₆ N ₂ ^{+,c} 118(28)	C ₈ H ₇ N ₂ ^{+,b} 131(18)
h	-	-	C ₈ H ₇ NO ^{•+} 133(5)	-	C ₈ H ₇ NO ^{•+} 133(3)
h-1	-	-	C ₈ H ₆ NO ⁺ 132(12.5)	-	C ₈ H ₆ NO ⁺ 132(8)
i	-	-	C ₈ H ₉ N ^{•+} 119(26)	-	C ₈ H ₉ N ^{•+} 119(17)
i-1	-	-	-	C ₇ H ₆ N ⁺ 104(5)	-

^aC₆H₅N₂⁺ dominates. ^bAlso C₉H₉N^{•+}. ^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

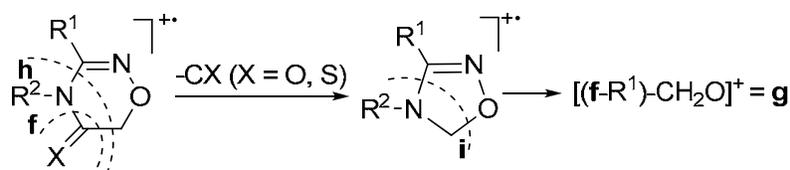
Compound	6	7	8
R¹	4-Py	C ₆ H ₅	<i>p</i> -ClC ₆ H ₄
R²	<i>p</i> -CH ₃ OC ₆ H ₄	<i>p</i> -CH ₃ C ₆ H ₄	<i>p</i> -CH ₃ C ₆ H ₄
Fragment			
M^{+•}	283(100)	282(63)	316(40)/318(16)
a	C ₁₃ H ₁₁ N ₂ O ⁺ 211(5.5)	C ₁₄ H ₁₂ N ⁺ 194(11)	C ₁₄ H ₁₁ NCl ⁺ 228(6)
b+1	C ₆ H ₅ N ₂ ⁺ 105(5)	C ₇ H ₅ N ^{+•} (b) 103(9)	C ₇ H ₄ NCl ^{+•} (b) 137(13)
c	C ₇ H ₇ NO ^{+•} 121(13)	C ₇ H ₇ N ^{+•} 105(19)	C ₇ H ₇ N ^{+•} 105(13)
c–1	-	C ₇ H ₆ N ⁺ (also b+1) 104(4.5)	-
d	-	C ₇ H ₇ ⁺ 91(61)	C ₇ H ₇ ⁺ 91(41)
e	C ₁₃ H ₁₁ N ₃ O ^{+•} 225(34)	C ₁₄ H ₁₂ N ₂ ^{+•} 208(8)	C ₁₄ H ₁₁ N ₂ Cl ^{+•} 242(5)
e–1	-	C ₁₄ H ₁₁ N ₂ ⁺ 207(9)	-
[M–CO]^{+•}	C ₁₄ H ₁₃ N ₃ O ₂ ^{+•} 255(5)	[M–NO]^{+•} (F) 252(5)	-
f	-	C ₈ H ₇ N ₂ ^{+,a} 131(9)	C ₈ H ₇ N ₂ ^{+,a} 131(5)
g	-	C ₈ H ₈ NS ⁺ 150(5)	C ₈ H ₈ NS ⁺ 150(4)
h+1	-	C ₈ H ₇ NS ^{+•} 149(100)	C ₈ H ₇ NS ^{+•} 149(100)
h	-	C ₈ H ₆ NS ⁺ 148(10)	C ₈ H ₆ NS ⁺ 148(7)
h–1	-	C ₈ H ₉ NO ^{+•} 135(19)	-
i	C ₈ H ₈ NO ⁺ 134(6)	C ₈ H ₈ N ^{+,b} 118(24)	C ₈ H ₈ N ⁺ 118(18)

^aAlso C₉H₉N^{+•}. ^bContains 1/9 of C₇H₆N₂^{+•}.

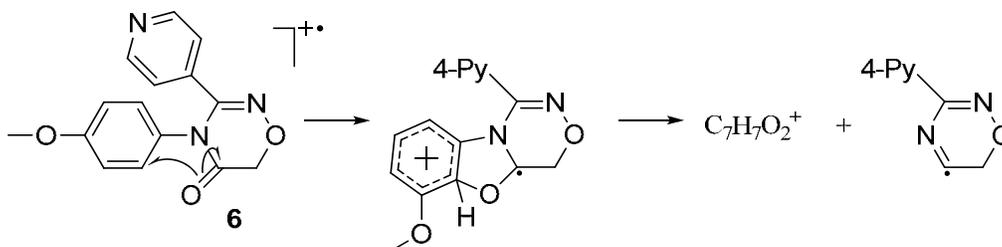
Table 3. Some further ions from compounds **1–8**

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 $[\text{e-HCN}]^{+\bullet} = \text{C}_{11}\text{H}_8\text{N}_2^{+\bullet}$ at m/z 168 (RA 4%). Furthermore it gives the ions $\text{C}_7\text{H}_y\text{N}_2^{+(\bullet)}$ 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 $[\text{e-CH}_3\text{-CO}]^+ = \text{C}_{11}\text{H}_8\text{N}_3^+$ at m/z 182 (RA 5%), $\text{C}_8\text{H}_8\text{NO}^+$ at m/z 134 (RA 6%), $\text{C}_7\text{H}_5\text{N}_2\text{O}^+$ at m/z 133 (RA 5%) and $\text{C}_7\text{H}_7\text{O}_2^+$ 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 $\text{C}_7\text{H}_7\text{O}_2^+$ 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**, $[\text{M-NO}]^{+\bullet}$, (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 $\text{C}_8\text{H}_x\text{N}^{+(\bullet)}$ (**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 $\text{C}_9\text{H}_9\text{NS}^{+\bullet}$ (m/z 163) and $\text{C}_7\text{H}_5\text{NO}^{+\bullet}$ (m/z 119) and the ions $\text{C}_9\text{H}_8\text{NS}^+$ (m/z 162), $\text{C}_8\text{H}_9\text{S}^+$ (m/z 137), and $[\text{M-h}]^{+\bullet} = \text{C}_8\text{H}_7\text{NO}^{+\bullet}$ (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 $[\text{M-CO}_2]^{+\bullet}$ (**B**) is also present both for **9** and **10**. The ion **C** at m/z 148 in turn corresponds to $[\text{A-CO}]^+$. 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 $\text{BzlCHN}^{+\bullet}$ 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 ^{+•}	Relevant ions, <i>m/z</i> (RA %)
9	(CH ₃) ₂ CH	219(7.5)	A: [M-C ₃ H ₇] ⁺ = C ₈ H ₆ N ₃ O ₂ ⁺ : 176(100), B: [M-CO ₂] ^{+•} = C ₁₀ H ₁₃ N ₃ ^{+•} : 175(1), C: [M-C ₃ H ₇ -CO] ⁺ = C ₇ H ₆ N ₃ O ⁺ : 148(12), D: 2-PyCNH ⁺ = C ₆ H ₅ N ₂ ⁺ : 105(21), E: 2-Py ⁺ = C ₅ H ₄ N ⁺ : 78(23), 51(5.5)
10	Bzl	267(1)	A: [M-Bzl] ⁺ = C ₈ H ₆ N ₃ O ₂ ⁺ : 176(100), B: [M-CO ₂] ^{+•} = C ₁₄ H ₁₃ N ₃ ^{+•} : 223(3), C: [M-Bzl-CO] ⁺ = C ₇ H ₆ N ₃ O ⁺ : 148(4), BzlCHN ^{+•} = C ₈ H ₉ N ^{+•} : 119(4), D: 2-PyCNH ⁺ = C ₆ H ₅ N ₂ ⁺ : 105(18); 104(5); C ₇ H ₇ ⁺ : 91(16), E: 2-Py ⁺ = C ₅ H ₄ N ⁺ : 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 authors⁶ state that compounds **11–15** also exhibit peaks due to the nitrile oxide ions, R¹CNO⁺. 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 ¹³C equivalent of the ion **a**. However, the compounds studied in our work did not give nitrile oxide ions at all. The ions R¹CN^{+•} (**b**) and/or R¹CNH⁺ (**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, [R¹CNR²]^{+•}, 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 prepared⁹ 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 **13**.

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, CH₃, Ph) and -5-thiones (**14,15**: R = CH₃; 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 P₂S₅.^{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
R¹	CH ₃	Ph	Ph	Ph	Ph
R²	H	CH ₃	Ph	CH ₃	Ph
Fragment					
M⁺	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.

^bThis is most probably a combination of R¹ and R² since also **12** and **14** exhibit the ion C₆H₅⁺ (RA 27 and 39%, respectively).

^cElemental 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 B²/E-linked scans were used to clarify these pathways. The low resolution, B/E and B²/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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