Mass Spectral Studies of Some 1,2,4-Oxa-(Thia)diazol-5(4*H*)-ones(thiones)

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Electron ionization mass spectra of some 3,4-disubstituted 1,2,4-oxadiazole-5(4*H*)-thiones, thiadiazol-5(4*H*)-ones and thiadiazole-5(4*H*)-thiones are reported and fragmentation pathways of their molecular ions are studied in view of metastable ion experiments and accurate mass measurements. The main fragmentation route of the compounds under investigation is retro 1,3-dipolar cycloaddition.

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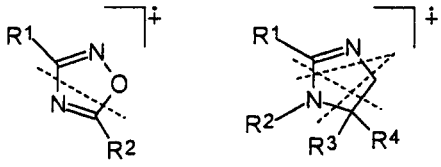
Introduction.

The electron ionization mass spectral studies of the five membered aromatic 1,2,4-oxadiazole derivatives have been reported in the literature [1-3]. In general, these heterocyclic compounds undergo a retro 1,3-dipolar cycloaddition to generate a nitrile (R^1-CN) and a nitrile oxide (R^2-CNO) under electron ionization conditions (Scheme 1, **A**). In some non-aromatic cases [4], *e.g.* 4,5-dihydro-1,2,4-oxadiazoles unsaturated ring may cleave in more than one way as depicted in Scheme 1, **B**.

Scheme 1

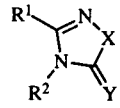


A **B**

In previous work [5] mass spectral behavior of some oxadiazole and oxadiazine derivatives was reported. Now we wish to report here, in the extension of available knowledge on the mass spectrometry of 1,2,4-oxadiazoles and related compounds, the electron impact mass spectra of some non-aromatic 1,2,4-oxa(thia)diazol-5(4*H*)-ones (thiones) bearing pyridyl groups. The structure of the compounds under investigation which showed a considerable biological activity [6] against fungus and bacteria species is given in Table 1.

Table 1

The Structure of the Compounds Studied



Compound	mp (°C)	X	Y	R^1	R^2
1	158-159	O	S	4-Pyridyl	Me
2	129-130	O	S	2-Pyridyl	Me
3	133-135	O	S	Me	Ph
4	71-72	O	S	4-Pyridyl	Et
5	95-96	O	S	2-Pyridyl	Et
6	163-165	O	S	Ph	*p*-MeC_6H_4
7	122-123	O	S	Ph	*o*-MeC_6H_4
8	106-107	S	O	4-Pyridyl	Me
9	94-95	S	O	2-Pyridyl	Me
10	67-68	S	O	2-Pyridyl	Et
11	119-120	S	O	Ph	*p*-MeC_6H_4
12	131-132	S	S	Ph	Me
13	149-150	S	S	Ph	*p*-MeC_6H_4

EXPERIMENTAL

The synthesis of the presently investigated compounds has already been published [7,8]. Low and high resolution mass spectra, metastable ion mass spectra of all molecular ions and some selected fragment ions, as well as parent ion mass spectra of some selected ions were recorded on a Finnigan MAT 90 (Finnigan MAT, Bremen, Germany), a magnetic sector insrument with a reversed geometry. Electron ionization was performed by 70 eV electrons using a trap current of 0.2 μA at a source temperature of 150°. A direct introduction probe was used for all compounds; sufficient evaporation occurs at probe temperatures ranging from 30°, for less bulky substituted, to 100° for more bulky substituted compounds.

Results and Discussion.

The significant peaks of the mass spectra of **1-13** are given in Table 2 (signals ≥5% of the base peak, isotopic signals of $M^{+\bullet}$ not given). Metastable ion mass spectra of the molecular ions are given in Table 3; intensity of the metastable ion signals is generally low, *i.e.* 0.005 to 0.05% of the main beam intensity. The mass spectra of each class of heterocycles; (3-(4-pyridyl)-4-ethyl-1,2,4-oxadiazole-5(4*H*)-thione **4**; 3-(4-pyridyl-4-methyl-1,2,4-thiadiazol-5(4*H*)-one **8**; 3-phenyl-4-methyl-1,2,4-thiadiazole-5(4*H*)-thione **12** are shown in Figures 1-3. The mass spec-

Table 2

The 70 eV Mass Spectra of Compounds **1-13**: m/z (Relative Abundance) (Relative Abundances >5% Included)

1 193 ($M^{+\bullet}$, 100), 177 (8), 132 (9), 123 (6), 121 (7), 120 (11), 119 (9), 111 (8), 106 (10), 105 (100), 104 (30), 85 (11), 83 (18), 82 (8), 81 (26), 79 (10), 78 (57), 77 (31), 76 (11), 75 (6), 73 (32), 72 (7), 71 (22), 70 (10), 69 (34), 67 (6), 60 (8), 57 (53), 56 (30), 55 (43), 53 (8), 52 (10), 50 (60), 49 (27), 42 (7), 40 (10), 39 (46), 38 (5), 36 (18)

2 193 ($M^{+\bullet}$,67), 133 (8), 119 (12), 79 (24), 78 (100), 61 (6), 51 (8), 50 (33), 49 (11), 36 (8)

3 192 ($M^{+\bullet}$,100), 151 (28), 135 (16),131 (12), 123 (33), 119 (34), 118 (21), 96 (17), 91 (36), 77 (41), 73 (20), 65 (10), 64 (22), 63 (12), 51 (22), 50 (7), 41 (10), 40 (5), 39 (11), 38 (5,6), 28 (8), 18 (10)

4 207 ($M^{+\bullet}$,59), 137 (11), 136 (18), 121 (8), 120 (38), 119 (11), 106 (12), 105 (100), 104 (34), 103 (7), 92 (7), 79 (8), 78 (38), 77 (22), 76 (9), 71 (11), 70 (83), 69 (7), 61 (11), 60 (7), 59 (9), 56 (15), 55 (8), 52 (8), 51 (44), 50 (23)

5 207 ($M^{+\bullet}$, 77), 164 (7), 121 (9), 120 (7), 106 (53), 105 (100), 104 (37), 79 (27), 78 (84), 77 (25), 76 (10), 71 (8), 70 (25), 56 (14), 52 (19), 50 (41), 49 (11)

6 268 ($M^{+\bullet}$,100), 209 (10), 208 (60), 207 (18), 165 (27), 149 (8), 145 (18), 137 (24), 136 (7), 135 (33), 133 (29), 132 (31), 131 (6), 123 (6), 119 (9), 110 (10), 105 (15), 104 (36), 103 (46), 92 (5), 91 (62), 90 (5), 89 (5), 83 (5), 81 (7), 79 (6), 78 (19), 77 (43), 76 (21), 73 (7), 71 (6), 69 (16), 65 (27), 64 (16), 63 (10), 60 (12), 57 (11), 52 (15), 51 (27), 50 (13), 45 (10)

7 268 ($M^{+\bullet}$,100), 252 (20), 235 (6), 231 (13), 209 (7), 208 (39), 207 (98), 206 (22), 205 (7), 194 (19), 189 (8), 180 (9), 149 (14), 136 (9), 135 (29), 133 (23), 132 (80), 131 (21), 119 (5), 117 (5), 105 (40), 104 (58), 103 (32), 91 (28), 90 (6), 89 (9), 79 (8), 78 (27), 77 (33), 76 (13), 65 (25), 63 (8), 52 (8), 51 (15), 50 (7), 39 (12)

8 193 ($M^{+\bullet}$, 65), 167 (9), 149 (28), 137 (7), 136 (100), 119 (21), 111 (7), 109 (9), 105 (9), 104 (25), 97 (14), 95 (10), 94 (13), 85 (13), 83 (20), 82 (6), 81 (16), 78 (38), 77 (15), 76 (7), 73 (6), 71 (34), 70 (16), 69 (38), 67 (10), 57 (80), 56 (16), 55 (53), 50 (43), 49 (14)

9 193 ($M^{+\bullet}$, 47), 166 (8), 165 (28), 164 (66), 137 (12), 136 (24), 134 (15), 119 (11), 109 (24), 106 (34), 105 (79), 94 (19), 92 (38), 83 (7), 81 (8), 79 (29), 78 (100), 71 (8), 69 (16), 55 (12), 52 (9), 51 (12), 42 (21), 40 (9), 36 (20)

10 207 ($M^{+\bullet}$, 37), 179 (6), 165 (7), 164 (70), 147 (45), 137 (11), 136 (35), 109 (12), 106 (51), 105 (100), 104 (19), 100 (8), 92 (9), 84 (5), 79 (27), 78 94), 77 (14), 76 (7), 71 (6), 70 (6), 56 (8), 52 (16), 51 (40), 50 (11),46 (9)

11 268 ($M^{+\bullet}$,38), 205 (9), 194 (24), 149 (14), 137 (9), 136 (16), 135 (100), 105 (5), 104 (9), 103 (10), 97 (9), 94 (40), 91 (30), 89 (6), 85 (10), 83 (12), 81 (10), 78 (7), 77 (20), 76 (7), 73 (6), 71 (24), 70 (11), 69 (26), 67 (6), 65 (29), 59 (6), 57 (55), 56 (12), 55 (36), 50 (15), 49 (6)

12 208 ($M^{+\bullet}$,78), 193 (11), 136 (5), 135 (65), 108 (8), 107 (5), 105 (61), 104 (25), 103 (77), 102 (5), 91 (12), 77 (69), 76 (60), 75 (16), 74 (10), 50 (29), 46 (10), 45 (19), 39 (17), 32 (13), 28 (38), 27 (5), 18 (13), 16 (6), 15 (9), 14 (9)

13 284 ($M^{+\bullet}$, 93), 283 (6), 268 (28), 208 (11), 207 (5), 194 (8), 183 (8), 182 (9), 181 (80), 180 (5), 165 (10), 154 (5), 149 (13), 142 (5), 137 (14), 136 (13), 135 (100), 133 (6), 132 (6), 125 (6), 123 (9), 118 (7), 117 (85), 116 (31), 111 (10), 109 (7), 104 (13), 103 (24), 97 (15), 95 (11), 94 (10), 91 (43), 90 (24), 89 (16), 85 (13), 84 (6), 83 (15), 82 (5), 81 (12), 78 (10), 77 (32), 76 (14), 71 (22), 70 (7), 69 (24), 65 (29), 64 (13), 63 (10), 60 (6), 57 (41), 56 (9), 55 (26), 50 (21), 49 (9)

Table 3

Metastable Ion Intensities [a] in the Fragmentation of the Molecular Ions of **1-13**

Compound	$[R^1CNX]^{+\bullet}$	$[M-XCY]^{+\bullet}$	$[R^1CN+H]^{+\bullet}$	$[M-R^1CN]^{+\bullet}$	$[M-HCN]^{+\bullet}$	$[M-YH]^{+}$	$[M-28]^{+}$	$[M-NXCY]^{+\bullet}$	$[R^1CNY]^{+\bullet}$
1	-	-	100	-	-	-	-	-	100
2	-	100	60	-	-	-	-	-	-
3	-	5	-	100	-	-	-	-	-
4	-	-	80	-	-	60	30	-	100
5	-	100	50	-	-	-	-	-	-
6	-	20	-	100	-	-	-	-	15
7 [b]	-	35	-	90	-	100	-	10	20
8	-	100	-	-	-	-	5	-	-
9	100	-	-	-	-	-	-	-	-
10	-	100	-	-	-	-	-	-	-
11	100	-	-	30	5	-	-	5	-
12	70	-	-	100	-	-	-	-	[c]
13	-	-	-	100	-	-	-	-	[c]

[a] Intensities as percentage, relative to the base peak; [b] A 10% signal is observed for $[M-R^1CN-SH]^{+\bullet}$; [c] Indistinct from $[R^1CNX]^{+\bullet}$.

tral data of the compounds show that most of the abundant fragmentation of these compounds involve retro 1,3-dipolar cycloadditions to produce odd electron ions (Scheme 2) which are in accord with the earlier reports for those of 4,5-dihydro-1,2,4-oxadiazoles [4]. Each of the retro-1,3-dipolar cycloadditions depicted in Scheme 2, **a**, **b** and **c**, formally results in two fragments of which either may retain charge, hence both complementary fragments may in principle be observed in the mass spectra. The loss of neutral COS or CS_2, pathway **a** in Scheme 2, may generate substituted isodiazirine type ions, $R^1C{=}N\text{-}N\text{-}R_2^{+\bullet}$;

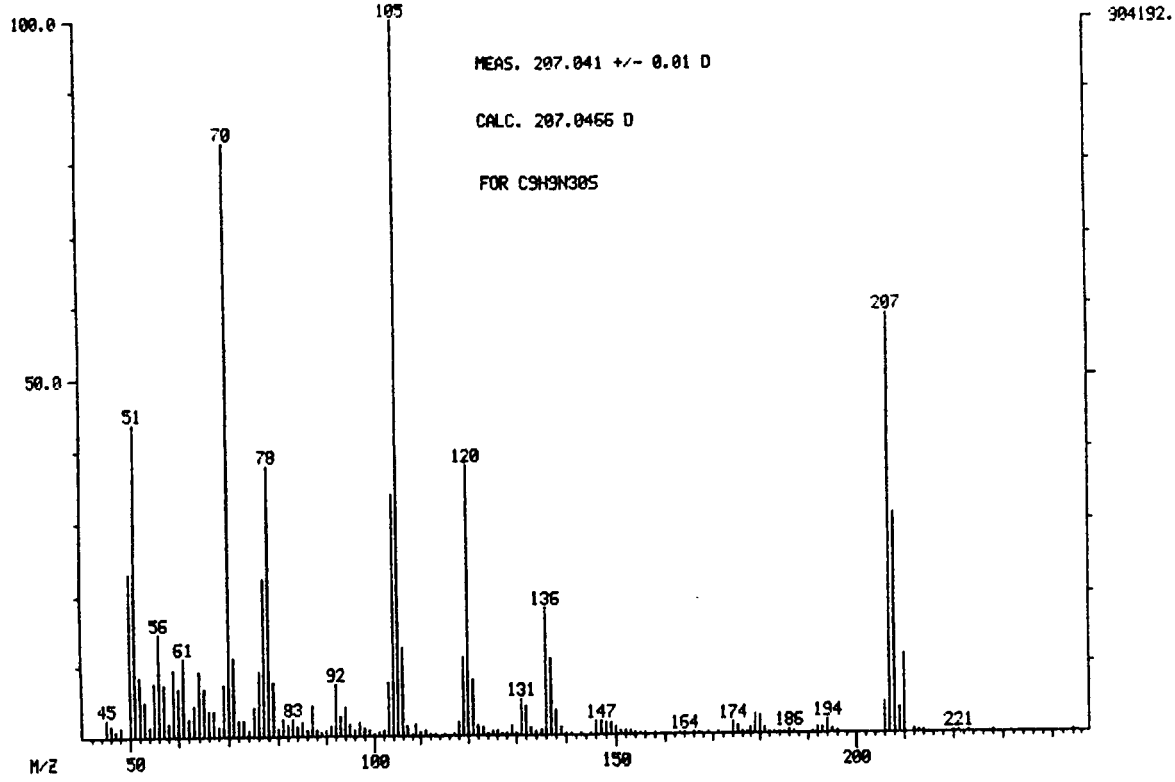


Figure 1. Mass spectrum of 3-(4-pyridyl)-4-ethyl-1,2,4-oxadiazole-5(4*H*)-thione **4**.

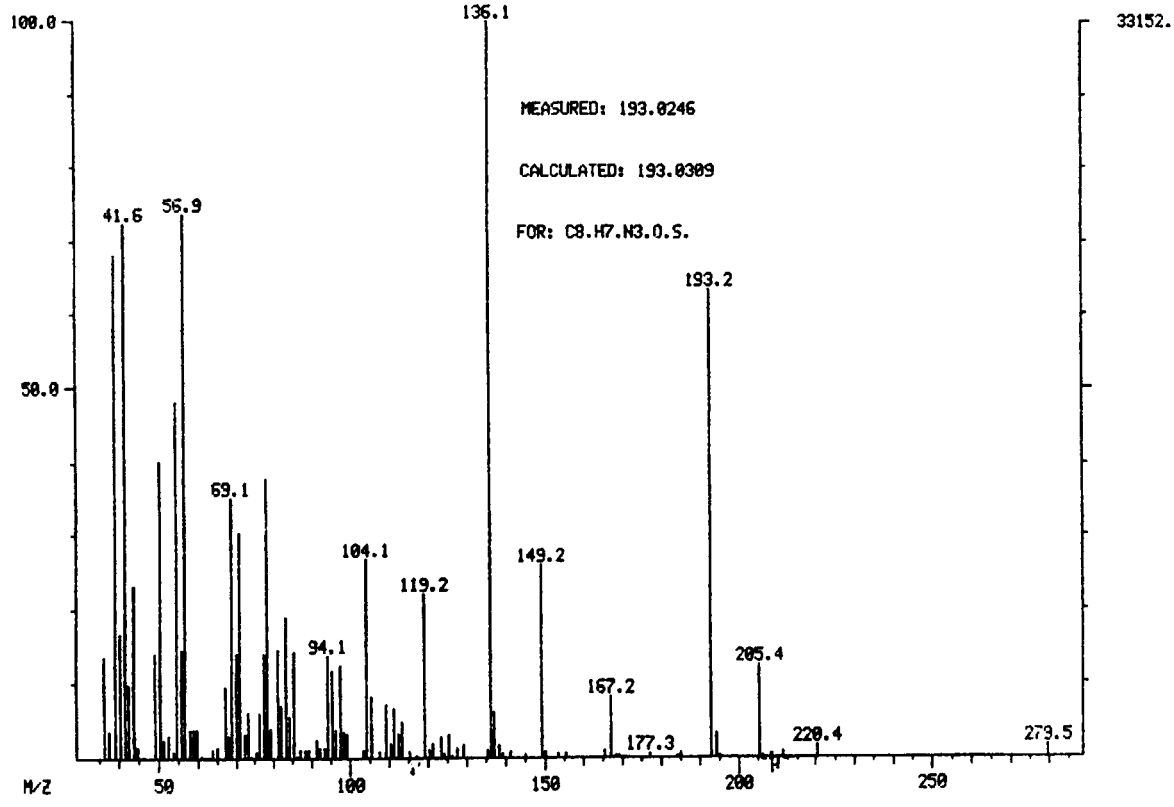


Figure 2. Mass spectrum of 3-(4-pyridyl)-4-methyl-1,2,4-thiadiazol-5(4*H*)-one **8**.

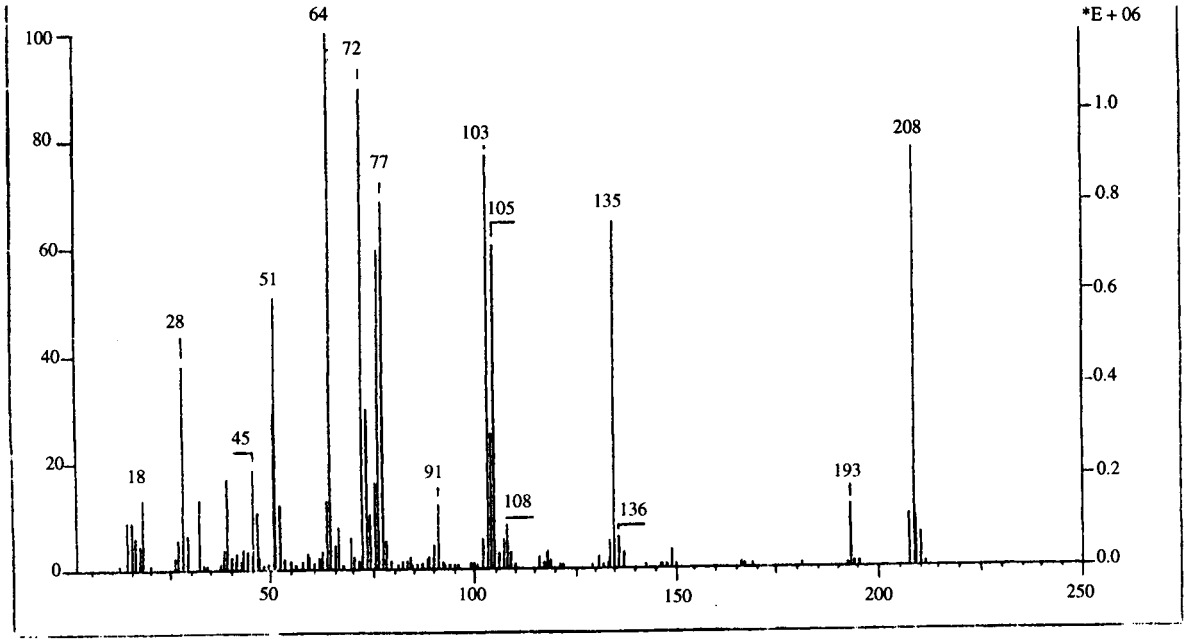
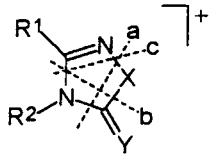


Figure 3. Mass spectrum of 3-phenyl-4-methyl-1,2,4-thiadiazole-5(4*H*)-thione **12**.

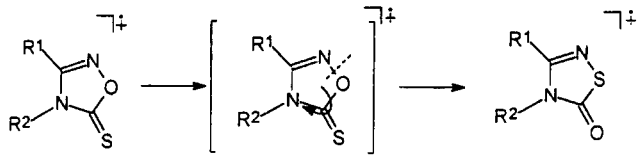
Scheme 2



substituted diazirine ions have also been proposed to be major product ions in the fragmentation of ionized, substituted tri- and tetrazoles [1-4,9,10]. The loss of COS from metastable molecular ions, observed in compounds **2**, **3** and **5-10**, produces a broad signal (T 0.5 ranging from 375 meV, in **6**$^{+\bullet}$, to 520 meV, in **5**$^{+\bullet}$, and with a dish shaped signal, T_{horns} = 147 meV, in **9**$^{+\bullet}$). The complementary formation of COS or CS_2 ions, *via* pathway **a**, is not observed. The product ions of both fragmentations described by reaction pathway **b**, $R^2NCY^{+\bullet}$ (+R^1CNX) on the one hand, and $R^1CNX^{+\bullet}$ (+R^2NCY) on the other hand, are observed. This fragmentation pathway is analogous to the formation of ionized nitrile oxides and nitriles from the above mentioned 1,2,4-oxadiazoles [1-3]. Pathway **c**, the formation of $R^1CN^{+\bullet}$, is also a similar behavior of the 1,2,4-oxadiazoles [1-3], although the complementary fragmentation, *i.e.* loss of R^1CN neutrals is only observed in the mass spectra of some of the compounds, **3**, **4**, **6**, **7** and **10-13** (with intensities ranging from 3-67%). From the metastable ion spectra it is clear that loss of R^1CN does indeed occur directly from the molecular ions. It should also be noted that the tendency to lose R^1CN from the molecular ion is low (or absent) in compounds with R^1 being pyridyl; owing to a relatively high heat of formation of cyanopyridines [10] (ΔHf 2-pyrCN = 281 and ΔHf[4-PyrCN] = 284 kJ/mole) as compared to cyanobenzene, ΔHf = 219 kJ/mole and acetonitrile ΔHf = 81 kJ/mole the other fragmentation pathways may be occurred in the pyridine substituted compounds.The metastable ion spectra of the product ions, $[R^1CN]^{+\bullet}$ in similarly substituted oxadiazolethiones and thiadiazolones are identical; they show the loss of CO as the base peak (100%, typically 0.08% of the mainbeam intensity) and losses of COS (typically ≈10% of base peak) and SH$^{\bullet}$ (≤20%) as minor signals. From the metastable ion mass spectra of $[M\text{-}R^1CN]^{+\bullet}$ from **12**$^{+\bullet}$ and **13**$^{+\bullet}$; the base peak is found for $S_2^{+\bullet}$ and, further, loss of HCN (≈50%), SH$^{\bullet}$ (≈40%), CS_2 (≈20%), is observed. It may be proposed that the product ions, $[M\text{-}R^1CN]^{+\bullet}$, from **3**, **4**, **6**, **7**, **10** and **11** are *N*-substituted azathiiraneones, $[R^2\text{-}NCS{=}O]^{+\bullet}$ and that the product ions from **12** and **13** are azathiiranethiones, $[R^2\text{-}NSC{=}S]^{+\bullet}$. These ion structures are based on the consideration that the three-membered ring in these product ions may result from ring closure after the elimination of R^1CN, as given in pathway **c** (Scheme 2). This proposal is supported by the observation of CO-loss in $[M\text{-}R^1CN]^{+\bullet}$, from **3**, **4**, **6**, **7**, **10** and **11**; moreover the unobserved analogous elimination of CS from **12** and **13** is expected to be relatively unfavorable (ΔHf[CO] = -111 and ΔHf[CS] = 267 kJ/mole).

A remarkable reaction which does not fit one of the retro cycloadditions of Scheme 2 is the formation of both $R^2NCX^{+\bullet}$ and $R^1CNY^{+\bullet}$ ions, which particularly occurs in the fragmentation of ionized oxadiazolethiones, **1**$^{+\bullet}$-**7**$^{+\bullet}$ (X = O, Y = S). It should be noted that signals due to possibly analogous product ions in the fragmentation of thiadiazolethiones, **12**$^{+\bullet}$ and **13**$^{+\bullet}$, can in principle not be distinguished from the retro-cycloaddition products. The presence of both $R^2NCO^{+\bullet}$ and $R^1CNS^{+\bullet}$ ions in the mass spectra of oxadiazolethiones, and of R^1CNS in the metastable ion spectra of **4**$^{+\bullet}$, **6**$^{+\bullet}$ and **7**$^{+\bullet}$, implies that it is possible that the 1,2-NO bond of the ring is cleft, as in the retro-cycloaddition **c** (Scheme 2), and that a subsequent rearrangement reaction occurs as it is illustrated in Scheme 3; this rearrangement may then be followed by a retro-cycloaddition, as outlined before (route **b** in Scheme 2 giving $R^2NCO^{+\bullet}$ and $R^1CNS^{+\bullet}$ as the complementary fragments). The proposed reaction scheme is supported

Scheme 3

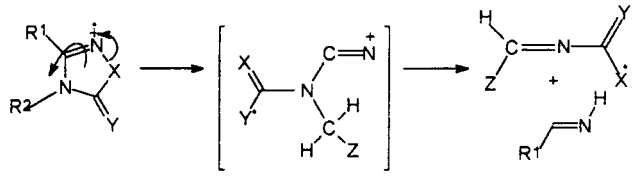


by the following considerations. Reported *ab initio calculations* (at the CI/6-31G* //3-21G level of theory) on the breaking of 1,2-NO bond in ionized 1,2-oxazole showed an exothermicity of 275 kJ/mole for the process [11]. Earlier, the bond strength of the 1,2-NO bond in 4,5-dihydro-1,2,4-oxadiazoles was estimated to be 222, which is weak as compared to the other ring bonds [4]. Furthermore the 1,2-NO bond is also broken in two more common and more abundant retro-cycloadditions, given as pathways **a** (loss of YCX) and **c** (formation of $R^1CN^{+\bullet}$) in Scheme 2. The rejoining of a 1,2-NS bond, is expected to be accessible on the basis of the fact that NS bonds will be less strong than NO bonds; hence only a fraction of the internal energy which goes into the breaking of the NO bond would suffice to form the NS bond. This is corroborated by the observation that the (reverse) rearrangement reaction, as outlined in Scheme 3, does not take place in the fragmentation of thiadiazolethiones, **8-11**. Thus, it is found that an earlier reported thermal rearrangement of oxadiazolethiones [7,8] has an analogous counterpart in ionized oxadiazolethiones.

An exceptional fragmentation is observed in the mass spectra of **9** and **10**, where intense signals at m/z 164, imply a loss of 29 and 43 mass units, respectively from the molecular ion. In both cases, the exact mass of m/z 164 only fits the elemental composition $C_7H_6N_3S$, corresponding to the overall loss of HCO and C_2H_3O, respectively. A second field free region parent ion scan of m/z 164 ions from **10** reveals that these ions are generated from ions m/z 179, necessarily by the loss of $CH_3^{\bullet}$. Furthermore, the signal at m/z 179 in the mass spectrum of **10** appears to be a mass doublet of $C_7H_5N_3OS$ ($[M-C_2H_4]^{+\bullet}$, from the ethyl substituent at N4) and $C_8H_9N_3S$ ($[M-CO]^{+\bullet}$ in the ratio $[M-C_2H_4]^{+\bullet}$: $[M-CO]^{+\bullet}$ = 4:5. Although the loss of CO from the $\mathbf{10}^{+\bullet}$ is not observed in the metastable ion mass spectra, $\mathbf{9}^{+\bullet}$ shows a metastable ion loss of CO. The loss of 28 mass units in the metastable ion spectrum of ionized **4** is probably due to a β-hydrogen rearrangement to eliminate C_2H_4. Moreover, the isotopic contribution from $^{13}CC_6H_6N_3S^+$ and $C_7H_6{}^{15}NN_2S^+$ for the signal at m/z 165 in the mass spectrum of **9** leaves 2/3 of the signal intensity for $[M-CO]^{+\bullet}$. It can therefore be concluded that the loss of CO from the ring is followed by a radical elimination ($H^{\bullet}$ in $[\mathbf{9}-CO]^{+\bullet}$ and $CH_3^{\bullet}$ in ($[\mathbf{10}-CO]^{+\bullet}$). In addition, the absence of the analogous loss of CS from the corresponding oxadiazolethiones, **1** and **5** respectively, is probably due to the relatively high heat of formation of CS (267 kJ/mole [8] as compared to that of CO (-110 kJ/mole [8]). Since the related thiadiazoleones **8** and **11** show no CO loss (and associated radical loss) in its fragmentation, the role of the pyridine nitrogen atom must be the driving force of this fragmentation reaction. Since both **9** and **10** have an alkyl substituent as R^2 (Table 1) which is likely to be retained in the $[M-CO]^{+\bullet}$, the latter product ions may well undergo an α cleavage to lose $H^{\bullet}$ ($[\mathbf{9}-CO]^{+\bullet}$) or $CH_3^{\bullet}$ ($[\mathbf{10}-CO]^{+\bullet}$).

An exclusive feature of the mass spectra of alkyl/pyridyl-(R^2/R^1 respectively) substituted oxadiazolethiones is the formation of ions $[R^1CNH]^+$ directly from the molecular ions. Although signals that are in accord with $[R^1CNH]^+$ are present in the mass spectra of all compounds, only the oxadiazolethiones, **1**, **2**, **4**, and **5**, show these ions in their metastable ion mass spectra (Table 3). From this observation it can be proposed that $[R^1CNH]^+$ ions are formed from ionized **1**, **2**, **4** and **5**, *via* the pathway depicted in Scheme 4. This suggestion is supported

Scheme 4



by the trend in the proton affinities [8] of pyridine cyanides, aryl cyanides and alkyl cyanides (for 4-cyanopyridine 820 kJ/mole; 2-cyanopyridine 871 kJ/mole; cyanobenzene 820 kJ/mole; cyanomethane 787 kJ/mole) which reveals that the reaction is driven by a proton transfer to the R^1CN moiety. Moreover, since metastable, ionized thiadiazoleones, $\mathbf{8}^{+\bullet}$-$\mathbf{10}^{+\bullet}$, do not behave like similarly substituted oxadiazolethiones, $\mathbf{1}^{+\bullet}$, $\mathbf{2}^{+\bullet}$, $\mathbf{4}^{+\bullet}$ and $\mathbf{5}^{+\bullet}$, the fragmentation reaction to produce $[R^1CNH]^+$ may undergo a NO bond cleavage that is consistent with the above mentioned rearrangement reaction (Scheme 3). In Scheme 4, a proposed mechanism is given for the formation of $[R^1CNH]^+$ in oxadiazolethiones having an appropriate hydrogen atom to be abstracted by nitrogen. For other compounds, the fragmentation would occur through an ion/molecule complex *via* a high-energy barrier and therefore no metastable ion signals could be observed.

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