

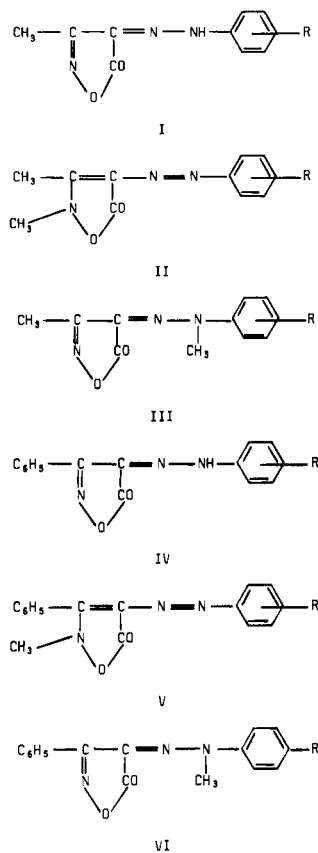
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Received December 11, 1985

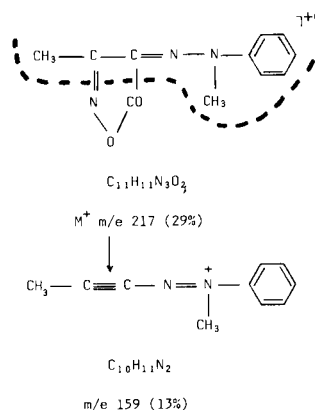
3-Methyl-4-(*N*-methylarylhydrazono)isoxazol-5-ones and 3-phenyl-4-(*N*-methylarylhydrazono)isoxazol-5-ones undergo considerable fragmentation on electron impact involving rupture of the isoxazolone ring and bonds in the *N*-methylarylhydrazono side chain.

J. Heterocyclic Chem., **23**, 1119 (1986).

It was recently reported [1] that methylation of 3-methyl-4-arylhydrazonoisoxazol-5-ones (I) with methyl iodide gave a mixture of 2,3-dimethyl-4-arylazoisoxazol-5-ones (II) and 3-methyl-4-(*N*-methylarylhydrazono)isoxazol-5-ones (III). 3-Phenyl-4-arylhydrazonoisoxazol-5-ones (IV) likewise afforded 2-methyl-3-phenyl-4-arylazoisoxazol-5-ones (V) and 3-phenyl-4-(*N*-methylarylhydrazono)isoxazol-5-ones (VI). We have already discussed the mass spectral fragmentation pattern [2] of 2,3-dimethyl- and 2-methyl-3-phenyl-4-arylazoisoxazol-5-ones and have summarized other work on the mass spectra of isoxazol-5-ones. This paper is concerned with the mass spectral fragmentation patterns of some 3-methyl-4-(*N*-methylarylhydrazono)isoxazol-5-ones



Scheme 1



and 3-phenyl-4-(*N*-methylarylhydrazono)isoxazol-5-ones.

The electron impact mass spectra of seven 3-methyl-4-(*N*-methylarylhydrazono)isoxazol-5-ones, namely 3-methyl-4-(*N*-methylphenylhydrazono)isoxazol-5-one (III, R = H), 3-methyl-4-(*N*-methyl-*o*-methylphenylhydrazono)isoxazol-5-one (III, R = 2-CH₃), 3-methyl-4-(*N*-methyl-*m*-methylphenylhydrazono)isoxazol-5-one (III, R = 3-CH₃), 3-methyl-4-(*N*-methyl-*p*-methylphenylhydrazono)isoxazol-5-one (III, R = 4-CH₃), 3-methyl-4-(*N*-methyl-*o*-chlorophenylhydrazono)isoxazol-5-one (III, R = 2-Cl), 3-methyl-4-(*N*-methyl-*m*-chlorophenylhydrazono)isoxazol-5-one (III, R = 3-Cl) and 3-methyl-4-(*N*-methyl-*p*-chlorophenylhydrazono)isoxazol-5-one (III, R = 4-Cl) and three 3-phenyl-4-(*N*-methylarylhydrazono)isoxazol-5-ones, namely 3-phenyl-4-(*N*-methylphenylhydrazono)isoxazol-5-one (VI, R = H), 3-phenyl-4-(*N*-methyl-*p*-methylphenylhydrazono)isoxazol-5-one (VI, R = CH₃) and 3-phenyl-4-(*N*-methyl-*p*-chlorophenylhydrazono)isoxazol-5-one (VI, R = Cl) were examined. Details of the principal peaks in the spectra are given in Tables 1 and 2 and the spectra of the parent compounds of the two series, 3-methyl-4-(*N*-methylphenylhydrazono)isoxazol-5-one (III, R = H) and 3-phenyl-4-(*N*-methylphenylhydrazono)isoxazol-5-one (VI, R = H) are given in Figures 1 and 2 respectively by way of illustration. The synthesis of the ten compounds has been reported [1].

The mass spectra of the seven 3-methyl-4-(*N*-methylarylhydrazono)isoxazol-5-ones are interesting (Table 1). With the parent compound 3-methyl-4-(*N*-methylphenylhydrazono)isoxazol-5-one (III, R = H) the base peak is due to the $C_6H_5^+$ ion at mass 77. The molecular ion $C_{11}H_{11}N_3O_2^+$ at mass 217 gives a peak amounting to 29% of the intensity of the base peak. Fragmentation of the molecular ion proceeds along a number of routes involving either rupture of the isoxazolone ring or rupture of bonds in the *N*-methylphenylhydrazono side chain. Rupture of the isox-

azolone ring with loss of CO_2 and N affords a $C_{10}H_{11}N_2^+$ ion of mass 159 (13%) as depicted in Scheme 1, while loss of CH_3CN and CO_2 affords a $C_8H_8N_2^+$ species of mass 132 (11%) depicted as a benzopyrazole derivative (Scheme 2). This latter ion can lose H^+ to afford a $C_8H_7N_2^+$ ion of mass 131 (8%) and lose CH_3^+ to afford a $C_7H_5N_2^+$ ion at mass 117 (9%) (Scheme 2). Rupture of the N-N bond of the *N*-methylphenylhydrazono side chain affords a $C_7H_8N^+$ ion of mass 106 (56%) depicted as a benzaziridine derivative (Scheme 3). This ion may lose H^+ to afford a $C_7H_7N^+$

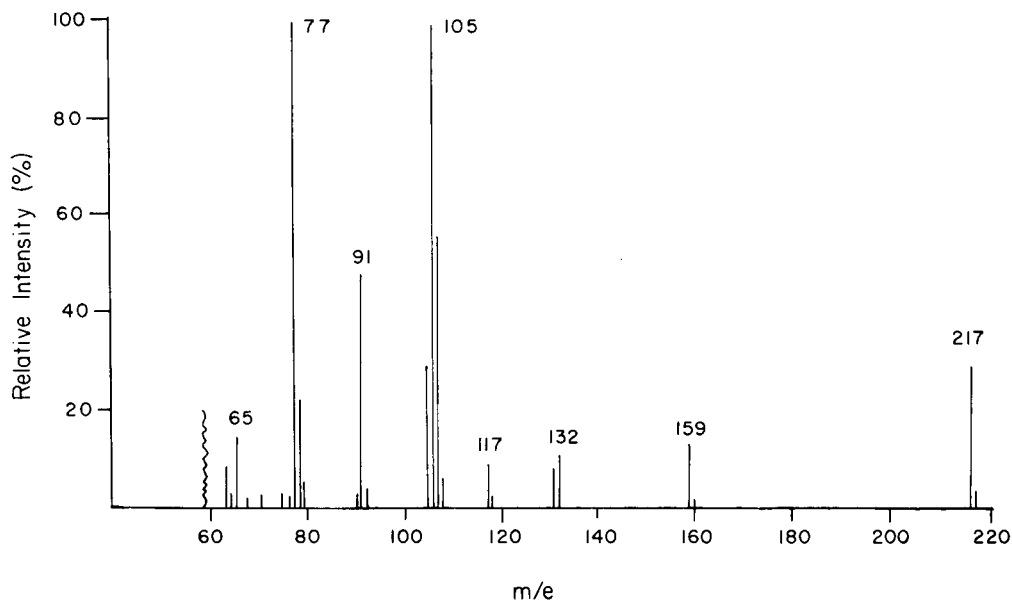


Figure 1. Mass spectrum of 3-methyl-4-(*N*-methylphenylhydrazono)isoxazol-5-one (III, R = H).

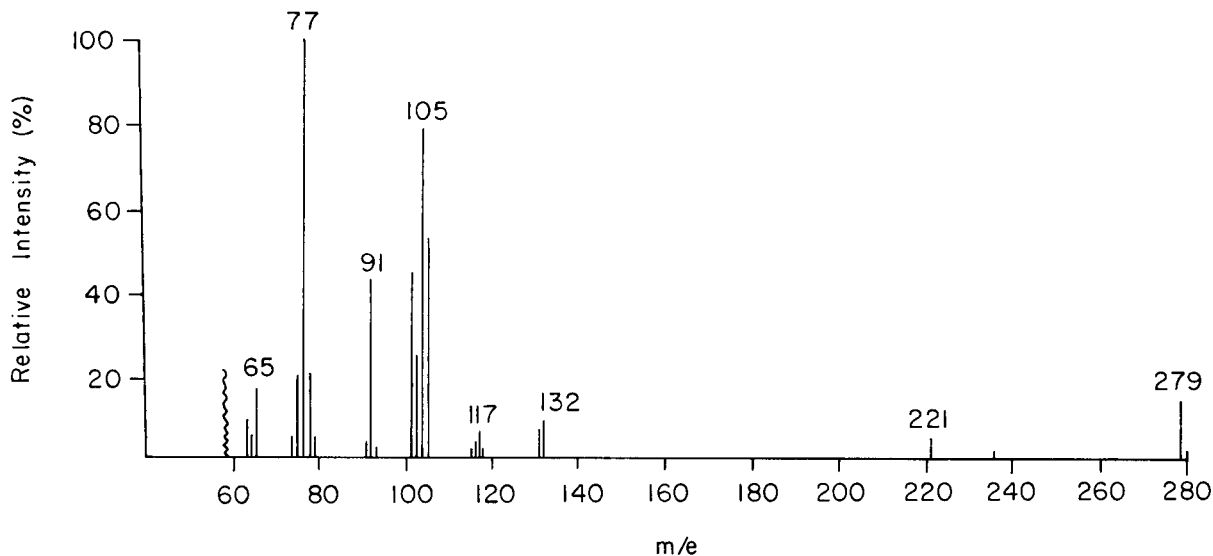
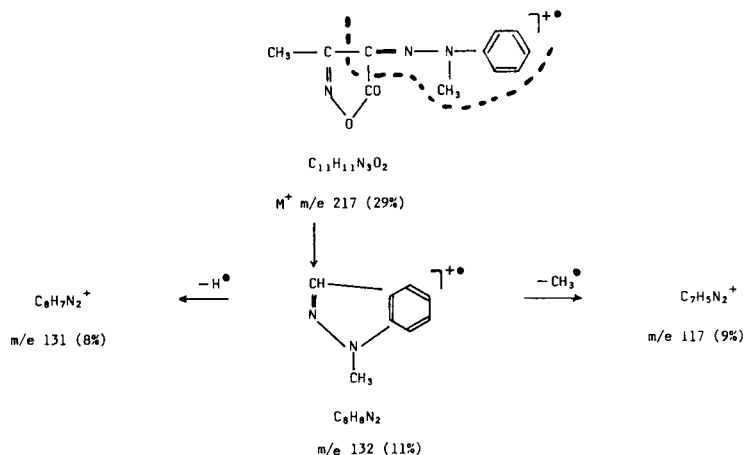
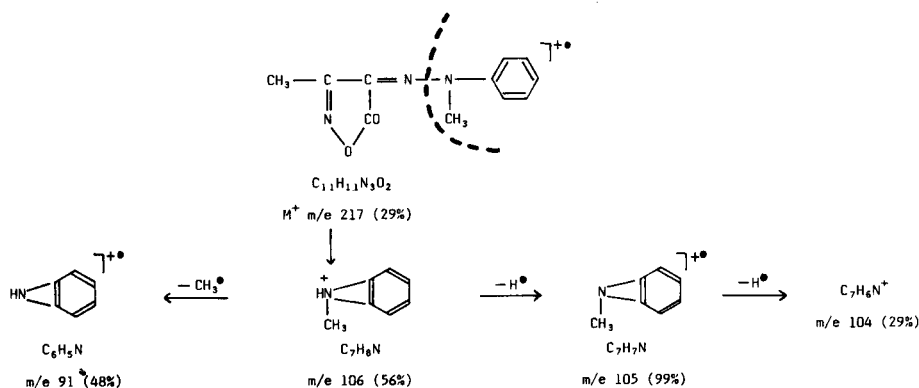


Figure 2. Mass spectrum of 3-phenyl-4-(*N*-methylphenylhydrazono)isoxazol-5-one (VI, R = H).

Scheme 2



Scheme 3

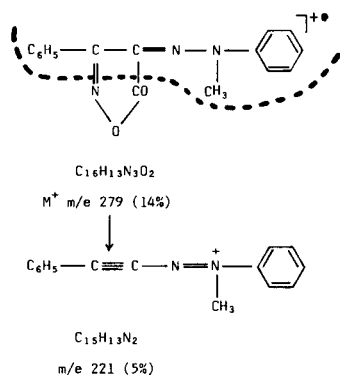


species which gives an intense peak at mass 105 (99%). Further loss of H^+ accounts for the peak at mass 104 (29%), and loss of CH_3 gives the peak at mass 91 (48%) due to a $\text{C}_6\text{H}_5\text{N}^+$ species (Scheme 3). The only other peak

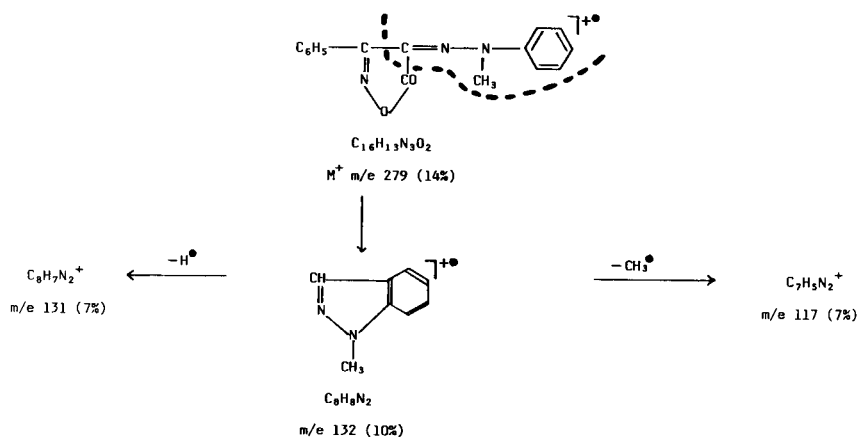
in the spectrum which deserves comment is the one due to the C_6H_6^+ species at mass 78 (22%). This must arise by a hydrogen migration to the C_6H_5^+ ion at mass 77 which is the base peak in the spectrum.

The spectra of the three 3-methyl-4-(*N*-methylmethylphenylhydrazono)isoxazol-5-ones (III, $\text{R} = 2\text{-CH}_3$), (III, $\text{R} = 3\text{-CH}_3$) and (III, $\text{R} = 4\text{-CH}_3$) can be explained in a similar way by fragmentation routes analogous to those in Schemes 1-3. The base peaks in the case of compound (III, $\text{R} = 2\text{-CH}_3$) and compound (III, $\text{R} = 3\text{-CH}_3$) are at mass 91 due to the respective tolyl (C_7H_7^+) ions. With compound (III, $\text{R} = 4\text{-CH}_3$) the tolyl ion amounts to 96% of the base peak which is due to the $\text{C}_8\text{H}_{10}\text{N}^+$ ion at mass 120 (*cf.* Scheme 3). Peaks due to $\text{C}_8\text{H}_{10}\text{N}^+$ ions are also prominent in the spectra of compound (III, $\text{R} = 2\text{-CH}_3$) (77%) and compound (III, $\text{R} = 3\text{-CH}_3$) (85%). As in the spectrum of the parent member of the series, compound (III, $\text{R} = \text{H}$), hydrogen migrations are invoked to explain some of the

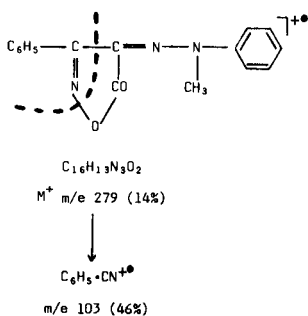
Scheme 4



Scheme 5



Scheme 6



peaks, notably those due to $C_8H_{11}N^{+}$ species at mass 121 and $C_7H_8N^+$ ions at mass 106.

The spectra of the three 3-methyl-4-(*N*-methylchloro-

phenylhydrazono)isoxazol-5-ones (III, R = 2-Cl), (III, R = 3-Cl) and (III, R = 4-Cl) are also readily explained along similar lines. The base peak in all three cases is due to a $C_7H_6ClN^+$ species at mass 139 (*cf.* Scheme 3). It is interesting to note that rupture of the isoxazolone ring and the *N*-methylaryldiazo side chain frequently occurs before loss of chlorine.

The spectra of the three 3-phenyl-4-(*N*-methylaryldiazo)isoxazol-5-ones (VI, R = H), (VI, R = CH₃) and (VI, R = Cl) are explained by fragmentation patterns similar to those in the 3-methyl-4-(*N*-methylaryldiazo)isoxazol-5-one series (Table 2) although there are some interesting differences. With the parent member of the series compound (VI, R = H) the molecular ion $C_{16}H_{13}N_3O_2^{+}$ gives a peak at mass 279 of 14% of the in-

Scheme 7

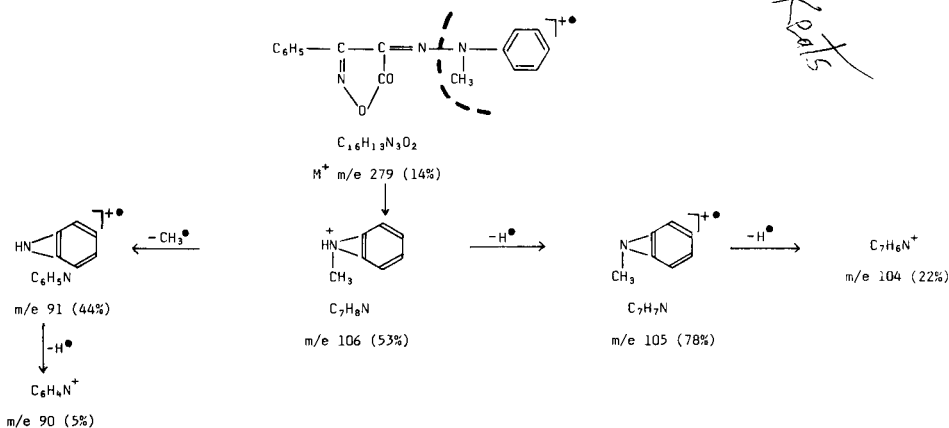


Table 1

Empirical Formula of Fragment Ions [a] in the Mass Spectra of 3-Methyl-4-(*N*-methylarylhydrazono)isoxazol-5-ones III

m/e	Formula	Intensity (%)						
		R = H	R = 2-CH ₃	R = 3-CH ₃	R = 4-CH ₃	R = 2-Cl	R = 3-Cl	R = 4-Cl
253	C ₁₁ H ₁₀ ³⁷ ClN ₃ O ₂	-	-	-	-	-	6	12
251	C ₁₁ H ₁₀ ³⁵ ClN ₃ O ₂	-	-	-	-	11	19	36
231	C ₁₂ H ₁₃ N ₃ O ₂	-	26	28	45	-	-	-
217	C ₁₁ H ₁₁ N ₃ O ₂	29	-	-	-	-	-	-
195	C ₁₀ H ₁₀ ³⁷ ClN ₂	-	-	-	-	6	-	-
193	C ₁₀ H ₁₀ ³⁵ ClN ₂	-	-	-	-	21	12	13
173	C ₁₁ H ₁₃ N ₂	-	8	5	9	-	-	-
166	C ₈ H ₇ ³⁵ ClN ₂	-	-	-	-	-	-	16
165	C ₈ H ₆ ³⁵ ClN ₂	-	-	-	-	-	-	6
159	C ₁₀ H ₁₁ N ₂	11	-	-	-	-	-	-
153	C ₇ H ₄ ³⁷ ClN ₂	-	-	-	-	-	-	12
152	C ₇ H ₅ ³⁵ ClN ₂	-	-	-	-	-	-	7
151	C ₇ H ₄ ³⁵ ClN ₂	-	-	-	-	-	-	43
146	C ₉ H ₁₀ N ₂	-	5	14	12	-	-	-
145	C ₉ H ₉ N ₂	-	6	7	20	-	-	-
142	C ₇ H ₇ ³⁷ ClN	-	-	-	-	17	12	27
141	C ₇ H ₆ ³⁷ ClN	-	-	-	-	37	37	46
140	C ₇ H ₇ ³⁵ ClN	-	-	-	-	60	43	85
139	C ₇ H ₆ ³⁵ ClN	-	-	-	-	100	100	100
138	C ₇ H ₅ ³⁵ ClN	-	-	-	-	21	17	26
132	C ₈ H ₈ N ₂	11	-	-	-	-	-	-
131	C ₈ H ₇ N ₂	8	9	5	13	23	23	6
127	C ₆ H ₄ ³⁷ ClN	-	-	-	-	-	7	10
125	C ₆ H ₄ ³⁵ ClN	-	-	-	-	-	26	27
121	C ₈ H ₁₁ N	-	13	41	29	-	-	-
120	C ₈ H ₁₀ N	-	77	85	100	-	-	-
119	C ₈ H ₉ N	-	67	67	82	-	-	-
118	C ₈ H ₈ N	-	96	27	23	-	-	-
117	C ₈ H ₇ N	-	8	-	-	-	-	-
	C ₇ H ₅ N ₂	9	-	-	-	-	-	-
114	C ₆ H ₅ ³⁷ Cl	-	-	-	-	-	5	-
113	C ₆ H ₄ ³⁷ Cl	-	-	-	-	8	16	20
112	C ₆ H ₅ ³⁵ Cl	-	-	-	-	-	17	-
111	C ₆ H ₄ ³⁵ Cl	-	-	-	-	21	47	53
106	C ₇ H ₈ N	56	11	12	8	-	-	-
105	C ₇ H ₇ N	99	16	41	30	8	15	21
104	C ₇ H ₆ N	29	15	14	14	6	15	12
101	C ₅ H ₄ ³⁷ Cl	-	-	-	-	5	-	6
99	C ₆ H ₄ ³⁵ Cl	-	-	-	-	17	11	18
92	C ₇ H ₈	-	15	19	19	-	-	-
91	C ₇ H ₇	-	100	100	96	-	-	-
	C ₆ H ₅ N	48	-	-	-	-	-	-
90	C ₆ H ₄ N	-	-	-	-	11	23	13
89	C ₇ H ₅	-	6	7	-	-	-	-
78	C ₆ H ₆	22	24	19	15	-	-	-
77	C ₆ H ₅	100	30	27	26	96	40	43
76	C ₆ H ₄	-	-	-	-	-	7	7
75	C ₆ H ₃	-	-	-	-	22	32	36
73	C ₃ H ₂ ³⁵ Cl	-	-	-	-	9	7	10
67	C ₃ H ₃ N ₂	-	-	-	-	9	8	7
65	C ₅ H ₅	15	47	36	32	-	-	-
63	C ₅ H ₃	9	11	11	8	15	22	17

[a] Only those ions of mass >60 and of intensity ≥5% of the base peak are recorded. Peaks due to ¹³C species are omitted from the table.

tensity of the base peak which is due to the C₆H₅⁺ ion at mass 77. Fragmentation of the molecular ion proceeds as in the 3-methyl series either by rupture of the isoxazolone ring or by rupture of bonds in the *N*-methylphenylhydra-

zono side chain. Rupture of the isoxazolone ring with loss of CO₂ and N affords a C₁₅H₁₃N₂⁺ ion of mass 221 (5%) as shown in Scheme 4, while loss of C₆H₅CN and CO₂ affords a C₈H₈N₂⁺ species of mass 132 (10%) depicted as before

Table 2

Empirical Formula of Fragment Ions [a] in the Mass Spectra of
3-Phenyl-4-(*N*-methylarylhydrazono)isoxazol-5-ones VI

m/e	Formula	Intensity (%)		
		R = H	R = CH ₃	R = Cl
315	C ₁₆ H ₁₂ ³⁷ ClN ₃ O ₂	-	-	7
313	C ₁₆ H ₁₂ ³⁵ ClN ₃ O ₂	-	-	22
293	C ₁₇ H ₁₅ N ₃ O ₂	-	46	-
279	C ₁₆ H ₁₃ N ₃ O ₂	14	-	-
235	C ₁₆ H ₁₅ N ₂	-	6	-
221	C ₁₅ H ₁₃ N ₂	5	-	-
166	C ₈ H ₇ ³⁵ ClN ₂	-	-	16
153	C ₇ H ₄ ³⁷ ClN ₂	-	-	8
151	C ₇ H ₄ ³⁵ ClN ₂	-	-	22
146	C ₉ H ₁₀ N ₂	-	15	-
145	C ₉ H ₉ N ₂	-	21	-
143	C ₉ H ₇ N ₂	-	5	-
	C ₇ H ₈ ³⁷ ClN	-	-	10
142	C ₇ H ₇ ³⁷ ClN	-	-	25
141	C ₇ H ₈ ³⁵ ClN	-	-	45
140	C ₇ H ₇ ³⁵ ClN	-	-	72
139	C ₇ H ₆ ³⁵ ClN	-	-	54
138	C ₇ H ₅ ³⁵ ClN	-	-	15
132	C ₈ H ₈ N ₂	10	-	-
131	C ₈ H ₇ N ₂	7	14	-
129	C ₈ H ₅ N ₂	-	6	-
127	C ₆ H ₄ ³⁷ ClN	-	-	5
125	C ₆ H ₄ ³⁵ ClN	-	-	19
121	C ₈ H ₁₁ N	-	14	-
120	C ₈ H ₁₀ N	-	100	-
118	C ₈ H ₈ N	-	20	-
117	C ₈ H ₇ N	-	5	-
	C ₇ H ₅ N ₂	7	-	-
116	C ₈ H ₆ N	-	5	-
113	C ₆ H ₄ ³⁷ Cl	-	-	11
111	C ₆ H ₄ ³⁵ Cl	-	-	32
106	C ₇ H ₈ N	53	7	-
105	C ₇ H ₇ N	78	44	12
104	C ₇ H ₆ N	22	17	16
103	C ₇ H ₅ N	46	42	100
101	C ₅ H ₄ ³⁷ Cl	-	-	6
99	C ₅ H ₄ ³⁵ Cl	-	-	15
92	C ₇ H ₈	-	22	-
91	C ₆ H ₈ N	44	-	-
	C ₇ H ₇	-	88	-
90	C ₆ H ₄ N	5	-	6
	C ₇ H ₆	-	5	-
89	C ₇ H ₅	-	6	-
78	C ₆ H ₆	21	16	-
77	C ₆ H ₅	100	37	49
76	C ₆ H ₄	20	13	33
75	C ₆ H ₃	6	7	29
74	C ₆ H ₂	-	-	7
73	C ₃ H ₂ ³⁵ Cl	-	-	6
65	C ₅ H ₅	18	41	-
64	C ₅ H ₄	6	-	-
63	C ₅ H ₃	10	12	13

[a] Only those ions of mass >60 and of intensity ≥5% of the base peak are recorded. Peaks due to ¹³C species are omitted from the table.

as a benzopyrazole derivative (Scheme 5). This species can lose H⁺ to afford a C₈H₇N₂⁺ ion of mass 131 (7%) and lose CH₃⁺ to afford a C₇H₅N₂⁺ ion at mass 117 (7%). The benzonitrile molecular ion C₇H₅N⁺ at mass 103 (46%) gives rise to a prominent peak in the spectrum (Scheme 6). The corresponding fragmentation to afford the acetonitrile molecular ion C₂H₃N⁺ at mass 41 was not noticed in the spectrum of 3-methyl-4-(*N*-methylphenylhydrazono)isoxazol-5-one (III, R = H) possibly due to the low mass of the acetonitrile molecular ion. Rupture of the N-N bond of the *N*-methylphenylhydrazono side chain of 3-phenyl-4-(*N*-methylphenylhydrazono)isoxazol-5-one (VI, R = H) affords a C₇H₈N⁺ ion at mass 106 (53%) depicted as a benzaziridine derivative (Scheme 7). This ion may lose H⁺ to afford a C₇H₇N⁺ species at mass 105 (78%). Further loss of H⁺ accounts for the peak at mass 104 (22%) and loss of CH₃⁺ gives the peak at mass 91 (44%) due to a C₆H₅N⁺ species (Scheme 7). The C₆H₅N⁺ species may lose H⁺ to give a C₆H₄N⁺ ion at mass 90 (5%). The only other peak in the spectrum which deserves comment is the one due to the C₆H₆⁺ species at mass 78 (21%). This species must arise, as in the 3-methyl series, by a hydrogen migration.

The spectrum of 3-phenyl-4-(*N*-methyl-*p*-methylphenylhydrazono)isoxazol-5-one (VI, R = CH₃) can be explained by fragmentation routes analogous to those shown in Schemes 4-7. The base peak is at mass 120 due to a C₈H₁₀N⁺ ion analogous to the C₇H₈N⁺ ion shown in Scheme 7. The benzonitrile molecular ion C₇H₅N⁺ at mass 103 in this case results in a peak of 42% of the intensity of the base peak. The *p*-tolyl ion, C₇H₇⁺ at mass 91 gives rise to a prominent peak in the spectrum (88%).

The spectrum of 3-phenyl-4-(*N*-methyl-*p*-chlorophenylhydrazono)isoxazol-5-one (VI, R = Cl) can be explained in a similar way. In this case the base peak is at mass 103 due to the benzonitrile molecular ion C₇H₅N⁺ (*cf.* Scheme 6). As before it is interesting to note that rupture of the isoxazolone ring and the *N*-methylarylhydrazono side chain frequently occurs before loss of chlorine and hydrogen migrations have sometimes to be invoked to explain a few of the peaks.

EXPERIMENTAL

The spectra were determined with an A. E. I. MS-30 mass spectrometer. The samples were analysed by a direct insertion probe at an ionizing current of 70 eV. The ion source temperature was 200°.

The 3-methyl- and 3-phenyl-4-(*N*-methylarylhydrazono)isoxazol-5-ones were analytically pure [1].

REFERENCES AND NOTES

- [1] S. K. Singh and L. A. Summers, *J. Heterocyclic Chem.*, **22**, 457 (1985).
- [2] N. G. Keats, S. K. Singh and L. A. Summers, *J. Heterocyclic Chem.*, **22**, 1531 (1985).