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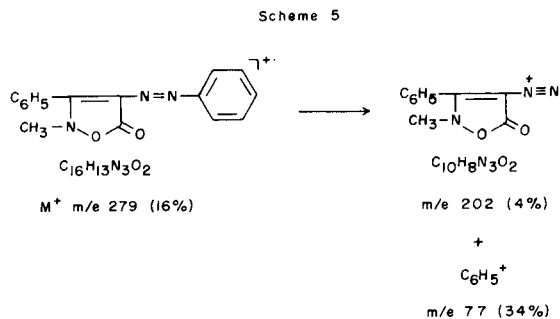
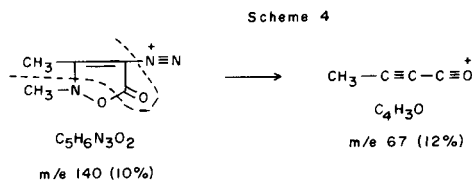
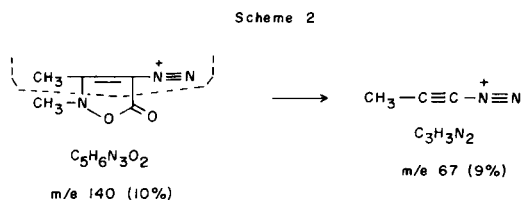
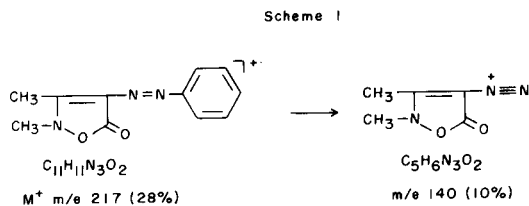
2,3-Dimethyl-4-arylazoisoxazol-5-ones and 2-methyl-3-phenyl-4-arylazoisoxazol-5-ones undergo considerable fragmentation on electron impact. The base peaks in the mass spectra are at mass 56 and 118 respectively attributed to the *N*-methylacetonitrile cation and the *N*-methylbenzonitrile cation.

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There has been some interest in the electron impact mass spectra of isoxazol-5-ones. In 3-phenylisoxazol-5-one (I) the base peak is due to a species of mass 103 ( $C_8H_7$ ) due to loss of N-O-CO from the molecular ion [1-3] and the spectrum includes peaks arising from deep-seated molecular rearrangements. Likewise the base peak in the spectrum of 3-methylisoxazol-5-one (II) is due to a species of mass 41 ( $C_3H_5$ ) [1,3] and related systems behave similarly. With 2,3-dimethylisoxazol-5-one (III) and 2-methyl-3-phenylisoxazol-5-one (IV) the base peaks are due to the molecular ions at mass 113 and 175 respectively but both compounds undergo considerable fragmentation and related systems behave in a similar way [3]. Recent work with substituted 2-aryl-3-phenylisoxazol-5-ones has also been reported [4]. With 3-methyl-4-benzylideneisoxazol-5-one (V) the base peak is at mass 128 ( $C_{10}H_8$ ) due to the loss of N-O-CO plus H from the molecular ion [1]. In the mass spectra of 3-methyl-4-arylhydrazonoisoxazol-5-ones (e.g. VI) fragmentation is initiated both by cleavage of the heterocyclic ring and by the exocyclic arylhydrazono moiety [5]. In 3-methyl-4-arylaminomethyleneisoxazol-5-ones (e.g. VII) the base peaks are due to the molecular ions. The main fragmentation routes involve loss of H, OH,  $H_2O$ ,  $CO_2$  and

COOH from the molecular ions as well as rupture of the exocyclic CH-NH bond [6]. We now report the mass spectral fragmentation patterns of some 2,3-dimethyl- and 2-methyl-3-phenyl-4-arylazoisoxazol-5-ones.

The electron impact mass spectra of seven 2,3-dimethyl-4-arylazoisoxazol-5-ones, namely 2,3-dimethyl-4-phenylazoisoxazol-5-one (VIII, R = H), 2,3-dimethyl-4-(*o*-methylphenylazo)isoxazol-5-one (VIII, R = 2- $CH_3$ ), 2,3-dimethyl-4-(*m*-methylphenylazo)isoxazol-5-one (VIII, R = 3- $CH_3$ ), 2,3-dimethyl-4-(*p*-methylphenylazo)isoxazol-5-one (VIII, R = 4- $CH_3$ ), 2,3-dimethyl-4-(*o*-chlorophenylazo)isoxazol-5-one (VIII, R = 2-Cl), 2,3-dimethyl-4-(*m*-chlorophenylazo)isoxazol-5-one (VIII, R = 3-Cl) and 2,3-dimethyl-4-(*p*-chlorophenylazo)isoxazol-5-one (VIII, R = 4-Cl), and three 2-methyl-3-phenyl-4-arylazoisoxazol-5-ones, namely 2-methyl-3-phenyl-4-phenylazoisoxazol-5-one (IX, R = H), 2-methyl-3-phenyl-4-(*p*-methylphenylazo)isoxazol-5-one



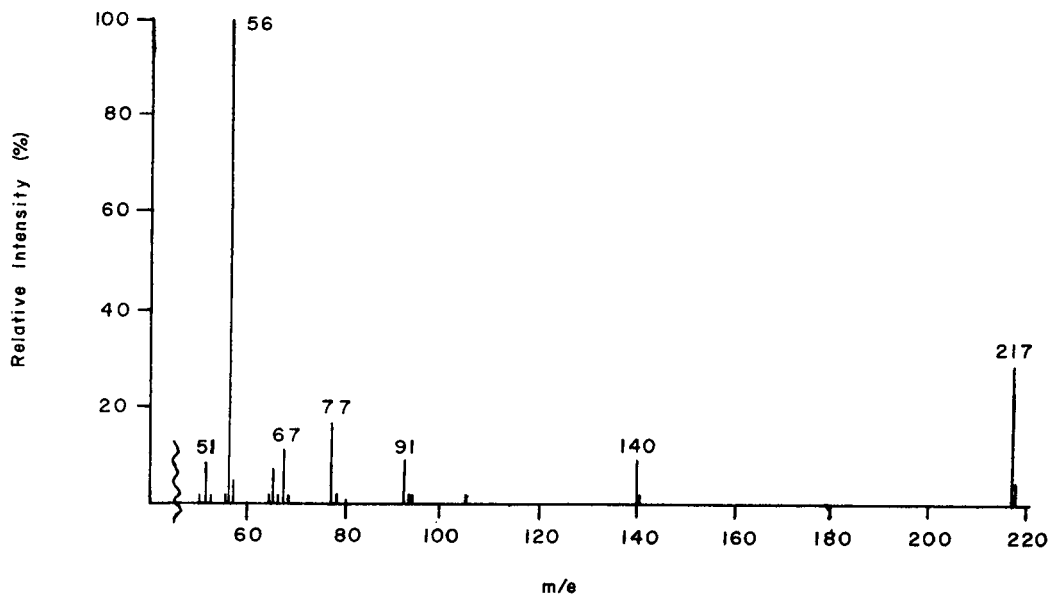


Figure 1. Mass spectrum of 2,3-dimethyl-4-phenylazoisoxazol-5-one (VIII, R = H).

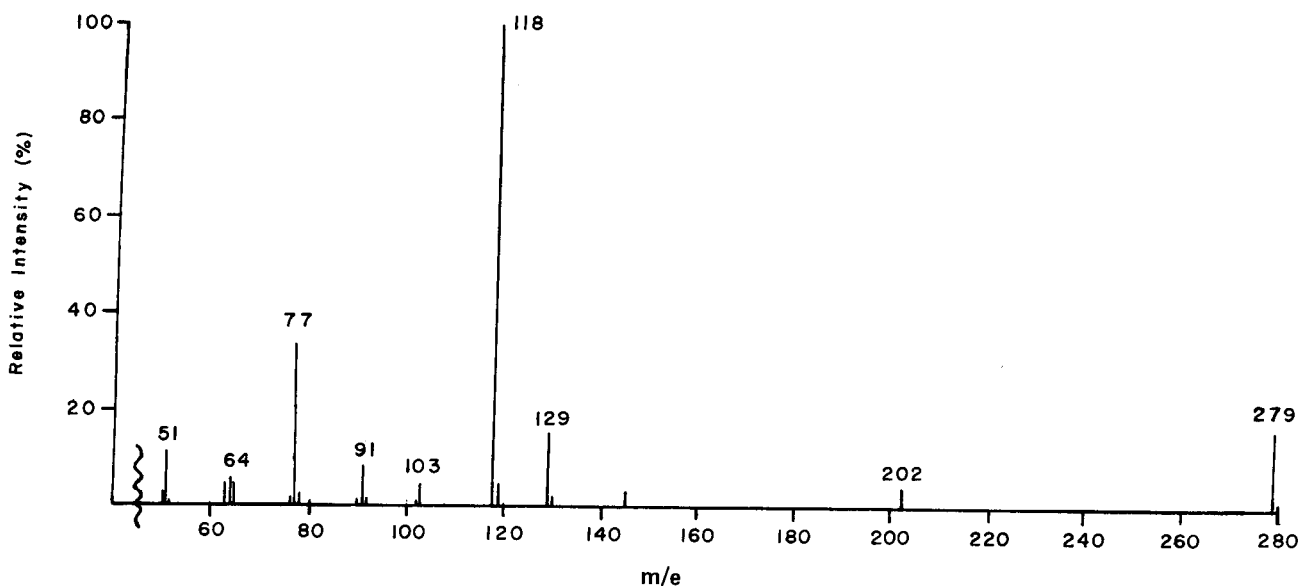


Figure 2. Mass spectrum of 2-methyl-3-phenyl-4-phenylazoisoxazol-5-one (IX, R = H).

(IX, R = CH<sub>3</sub>) and 2-methyl-3-phenyl-4-(*p*-chlorophenylazo)isoxazol-5-one (IX, 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, 2,3-dimethyl-4-phenylazoisoxazol-5-one (VIII, R = H) and 2-methyl-3-phenyl-4-phenylazoisoxazol-5-one (IX, R = H), are given in Figures 1 and 2 respectively by way of illustration. The synthesis of the ten compounds has recently been reported [7].

The mass spectra of the seven 2,3-dimethyl-4-arylazoisoxazol-5-ones are very interesting (Table 1). In all cases

the base peak is at mass 56 due to a C<sub>3</sub>H<sub>6</sub>N<sup>+</sup> ion depicted as the *N*-methylacetonitrile cation (see Scheme 3). It is interesting to recall that in the spectra of 2,3-dimethylisoxazol-5-one (III) and 2-methyl-3-phenylisoxazol-5-one (IV)

Scheme 6

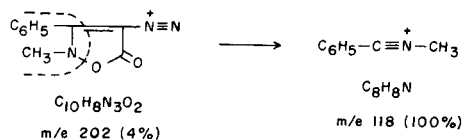


Table 1

Empirical Formula of Fragment Ions [a] in the Mass Spectra of 2,3-Dimethyl-4-arylazoisoxazol-5-ones VIII

m/e	Formula	Intensity (%)						
		R = H	R = 2-CH <sub>3</sub>	R = 3-CH <sub>3</sub>	R = 4-CH <sub>3</sub>	R = 2-Cl	R = 3-Cl	R = 4-Cl
253	C <sub>11</sub> H <sub>10</sub> <sup>37</sup> ClN <sub>3</sub> O <sub>2</sub>	—	—	—	—	5	4	4
251	C <sub>11</sub> H <sub>10</sub> <sup>35</sup> ClN <sub>3</sub> O <sub>2</sub>	—	—	—	—	16	13	11
231	C <sub>12</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub>	—	15	16	6	—	—	—
217	C <sub>11</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub>	28	—	—	—	—	—	—
140	C <sub>5</sub> H <sub>6</sub> N <sub>3</sub> O <sub>2</sub>	10	5	6	—	10	8	4
111	C <sub>6</sub> H <sub>4</sub> <sup>35</sup> Cl	—	—	—	—	8	8	7
104	C <sub>7</sub> H <sub>6</sub> N	—	6	—	—	—	—	—
91	C <sub>6</sub> H <sub>5</sub> N	10	—	—	—	—	—	—
	C <sub>7</sub> H <sub>7</sub>	—	12	11	7	—	—	—
90	C <sub>6</sub> H <sub>4</sub> N	—	—	—	—	—	—	5
78	C <sub>6</sub> H <sub>6</sub>	—	4	—	4	—	—	—
77	C <sub>6</sub> H <sub>5</sub>	17	—	—	4	—	—	—
76	C <sub>6</sub> H <sub>4</sub>	—	—	—	—	—	—	5
75	C <sub>6</sub> H <sub>3</sub>	—	—	—	—	—	4	6
67	C <sub>3</sub> H <sub>3</sub> N <sub>2</sub>	9	—	—	—	—	5	—
	C <sub>4</sub> H <sub>3</sub> O	12	9	9	8	13	15	9
65	C <sub>5</sub> H <sub>5</sub>	8	6	5	5	—	—	—
64	C <sub>5</sub> H <sub>4</sub>	—	—	—	—	—	—	4
63	C <sub>5</sub> H <sub>3</sub>	—	—	—	—	—	4	11
56	C <sub>3</sub> H <sub>6</sub> N	100	100	100	100	100	100	100
51	C <sub>4</sub> H <sub>3</sub>	9	—	—	—	—	—	7

[a] Only those ions of mass >50 and of intensity ≥4% of the base peak are recorded. Peaks due to <sup>13</sup>C species are omitted from the table.

corresponding peaks due to the *N*-methylacetonitrile cation (mass 56, 19%) and the *N*-methylbenzonitrile cation (mass 118, 22%) respectively were observed [3] although in these cases they are not the base peaks in the spectra.

With the 2,3-dimethyl-4-arylazoisoxazol-5-ones it is evident that there is much fragmentation of the molecule since the peaks due to the molecular ions amount to only about 10-30% of the intensity of the base peaks. Fragmentation of the molecular ion of the parent member of the se-

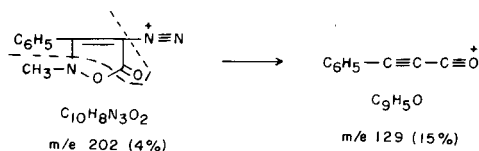
Table 2

Empirical Formula of Fragment Ions [a] in the Mass Spectra of 2-Methyl-3-phenyl-4-arylazoisoxazol-5-ones IX

m/e	Formula	Intensity (%)		
		R = H	R = CH <sub>3</sub>	R = Cl
313	C <sub>16</sub> H <sub>12</sub> <sup>35</sup> ClN <sub>3</sub> O <sub>2</sub>	—	—	8
293	C <sub>17</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub>	—	6	—
279	C <sub>16</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub>	16	—	—
202	C <sub>10</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub>	4	—	—
129	C <sub>9</sub> H <sub>5</sub> O	15	14	8
118	C <sub>8</sub> H <sub>6</sub> N	100	100	100
111	C <sub>6</sub> H <sub>4</sub> <sup>35</sup> Cl	—	—	6
103	C <sub>7</sub> H <sub>5</sub> N	4	—	7
91	C <sub>6</sub> H <sub>5</sub> N	8	—	—
77	C <sub>6</sub> H <sub>5</sub>	34	15	19
65	C <sub>5</sub> H <sub>5</sub>	4	4	—
64	C <sub>5</sub> H <sub>4</sub>	5	—	—
63	C <sub>5</sub> H <sub>3</sub>	4	—	—
51	C <sub>4</sub> H <sub>3</sub>	11	6	10

[a] Only those ions of mass >50 and of intensity ≥4% of the base peak are recorded. Peaks due to <sup>13</sup>C species are omitted from the table.

Scheme 7



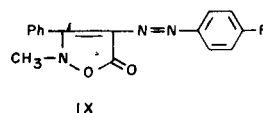
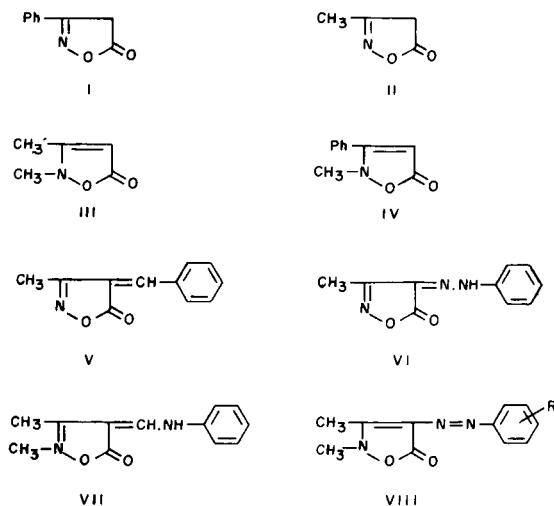
ries 2,3-dimethyl-4-phenylazoisoxazol-5-one (VIII, R = H) (Scheme 1) includes rupture of the bond between the azo linkage and the phenyl group to afford the C<sub>5</sub>H<sub>6</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> ion at mass 140 (10%) and the C<sub>6</sub>H<sub>5</sub><sup>+</sup> ion at mass 77 (17%). Subsequent rupture of the isoxazolone ring of the C<sub>5</sub>H<sub>6</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> ion accounts for the peak at mass 67 due to a C<sub>3</sub>H<sub>3</sub>N<sub>2</sub><sup>+</sup> ion (9%) (Scheme 2). Fragmentation of the C<sub>5</sub>H<sub>6</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> ion at mass 140 may also involve loss of N<sub>2</sub> as well as rupture of the isoxazolone ring. Rupture with loss of N<sub>2</sub> and C<sub>2</sub>O<sub>2</sub> affords the base peak at mass 56 (C<sub>3</sub>H<sub>6</sub>N<sup>+</sup>, 100%) (Scheme 3) while loss of N<sub>2</sub> and CH<sub>3</sub>NO affords the species C<sub>4</sub>H<sub>3</sub>O<sup>+</sup> at mass 67 (12%) (Scheme 4). Analogous fragmentation routes occur with the three 2,3-dimethyl-4-methylphenylazoisoxazol-5-ones and the three 2,3-dimethyl-4-chlorophenylazoisoxazol-5-ones (Table 1). In some of the spectra there was a metastable peak at 32.1 corresponding to the 140 → 67 transition.

With 2,3-dimethyl-4-phenylazoisoxazol-5-one (VIII, R = H) and 2,3-dimethyl-4-(*o*-methylphenylazo)isoxazol-5-one (VIII, R = 2-CH<sub>3</sub>) there is evidence of rupture of the molecular ion at the azo linkage. This fragmentation route gives rise to the peak at mass 91 (C<sub>6</sub>H<sub>5</sub>N, 10%) with (VIII,

R = H) and the peak at mass 104 ( $C_7H_6N$ , 6%) with (VIII, R = 2- $CH_3$ ), the latter case also involving the loss of H. With 2,3-dimethyl-4-(*p*-chlorophenylazo)isoxazol-5-one (VIII, R = 4-Cl) the peak at mass 90 ( $C_6H_4N$ , 5%) likewise involves rupture at the azo linkage and in addition loss of Cl.

The other peaks listed in Table 1 are all due to hydrocarbon entities of mass 78 or less. They require no comment as they can be readily accounted for by further fragmentation of species already discussed.

The mass spectra of the three 2-methyl-3-phenyl-4-arylazoisoxazol-5-ones are recorded in Table 2. Interestingly in all cases the base peak is at mass 118 due to a  $C_8H_8N^+$  ion depicted as the *N*-methylbenzotrile cation (see Scheme 6) analogous to the  $C_3H_6N^+$  ion depicted as the *N*-methylacetitrile cation which is the species responsible for the base peaks in the spectra of the 2,3-dimethyl-4-arylazoisoxazol-5-ones. In other respects too the fragmentation routes of the 2-methyl-3-phenyl-4-arylazoisoxazol-5-ones bear some resemblance to those of the 2,3-dimethyl-4-arylazoisoxazol-5-ones. There is much fragmentation of the molecules since the peaks due to the molecular ions amount to only about 5-15% of the intensity of the base peaks. Fragmentation of the molecular ion of the parent member of the series, 2-methyl-3-phenyl-4-phenylazoisoxazol-5-one (IX, R = H) (Scheme 5) includes rupture of the bond between the azo linkage and the phenyl group to afford the  $C_{10}H_8N_3O_2^+$  ion at mass 202 (4%) and the  $C_6H_5^+$  ion at mass 77 (34%). The latter ion may also presumably arise by loss of the 3-phenyl group.



Fragmentation of the  $C_{10}H_8N_3O_2^+$  ion at mass 202 may involve loss of  $N_2$  as well as rupture of the isoxazolone ring. Rupture with loss of  $N_2$  and  $C_2O_2$  affords the base peak at mass 118 ( $C_8H_8N^+$ , 100%) (Scheme 6) while loss of  $N_2$  and  $CH_3NO$  affords the species  $C_6H_5O^+$  at mass 129 (15%) (Scheme 7). Analogous fragmentation routes occur with 2-methyl-3-phenyl-4-(*p*-methylphenylazo)isoxazol-5-one (IX, R =  $CH_3$ ), and 2-methyl-3-phenyl-4-(*p*-chlorophenylazo)isoxazol-5-one (IX, R = Cl) although in these cases the abundance of the  $C_{10}H_8N_3O_2^+$  ion at mass 202 is less than 4% of that of the base peaks.

With 2-methyl-3-phenyl-4-phenylazoisoxazol-5-one (IX, R = H) there is evidence of rupture of the molecular ion at the azo linkage. This fragmentation route gives rise to the peak at mass 91 ( $C_6H_5N$ , 8%). With 2-methyl-3-phenyl-4-(*p*-chlorophenylazo)isoxazol-5-one (IX, R = Cl) there is a peak due to a  $C_7H_5N^+$  ion at mass 103 of intensity of 4-7% of that of the base peak. This peak is presumably due to the benzotrile molecular ion formed by loss of  $CH_3$  from the species  $C_8H_8N^+$  responsible for the base peaks in the spectra. The other peaks listed in Table 2 require no comment.

## EXPERIMENTAL

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

The 2,3-dimethyl- and 2-methyl-3-phenyl-4-arylazoisoxazol-5-ones were analytically pure [7].

## REFERENCES AND NOTES

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