Mass Spectral Fragmentation Pattern of 5-Methyl-4-[(phenylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-one and its 2-Methyl and 2-Phenyl Derivatives

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The mass spectral fragmentation patterns of 5-methyl-4-[(phenylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-one and its 2-methyl and 2-phenyl derivatives have been elucidated. The principal initial fragmentation route involves rupture of the exocyclic CH-NH bond. Minor routes involve loss of H, OH and C_6H_5 from the molecular ion and rupture of the pyrazolone ring.

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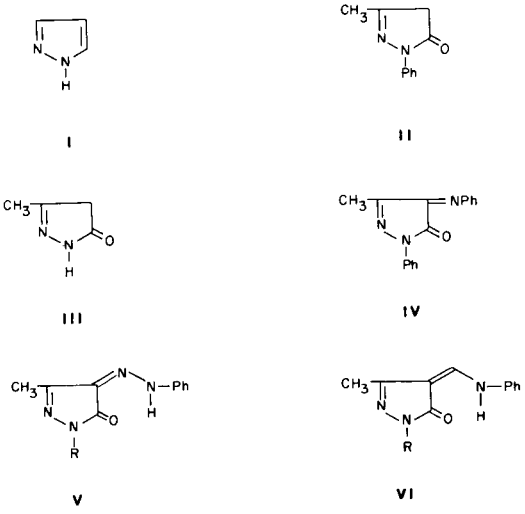
There has been considerable interest in the electron impact mass spectra of pyrazoles and pyrazolones over the past fifteen years. After some preliminary studies (1-4) the full spectrum of the parent compound, pyrazole (I) was described in 1967 (5). The base peak was due to the molecular ion. The most prominent fragmentation route showed loss of HCN involving, *inter alia*, splitting of the N-N bond. Likewise in 3-methylpyrazole loss of the elements of acetonitrile was found to be an important fragmentation route (5). Considerable further work on the mass spectra of a variety of pyrazoles has been reported (6-40). With pyrazolones the splitting pattern is different. For example, with 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (II) initial loss of acetonitrile was not observed (5). Instead carbon monoxide and keten were eliminated from the molecular ion. The base peak was at mass 77 presumably due to the $C_6H_5^+$ ion although another report gives the base peak as the molecular ion (41). Likewise with 5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (III) loss of CO, $CH_2{\bullet}CO$ and N_2H were prominent fragmentation routes. Loss of the elements of acetonitrile was not observed. The base peak was due to the molecular ion (42). With 5-methyl-2-phenyl-4-phenylimino-2,4-dihydro-3*H*-pyrazol- 3-one (IV) splitting of the pyrazolone ring, but not the N-N bond, was involved in the initial prominent fragmentation routes (43). With the phenylhydrazono analogues (V; R = H or Ph) the initial fragmentation involved cleavage at either side of or at the exocyclic N-N bond (44-46). Much work on the mass spectra of a variety of other pyrazolones, including antipyrine and its metabolites (47,48), has also been reported (19, 41-43, 49-55). This paper is concerned with the electron impact mass spectra of 5-methyl-4-[(phenylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-ones (VI, R = H) and its 2-methyl (VI, R = CH_3) and 2-phenyl (VI, R = Ph) derivatives. These compounds have been shown to exist as structure VI with hydrogen bonding between the CO and NH groups and not as other possible tautomeric forms both in solution and in the solid state (56).



In the spectrum of 5-methyl-4-[(phenylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-one (VI, R = H) (Figure 1) the peak due to the molecular ion at mass 201 amounts to 73% of the intensity of the base peak. The principal fragmentation route involves splitting of the exocyclic CH-NH bond. This gives rise to a $C_5H_5N_2O^+$ ion at mass 109 which is responsible for the base peak and the aniline molecular ion less one hydrogen ($C_6H_6N^+$) at mass 92 (2%). As was noted in the spectrum of the related 3-methyl-4-phenylaminomethyleneisoxazol-5-one (57) rupture of the exocyclic CH-NH bond may be accompanied by a hydrogen migration as evidence by the presence of the aniline molecular ion ($C_6H_7N^{+\cdot}$) at mass 93 (32%). The accompanying fragment, the $C_5H_4N_2O^{+\cdot}$ ion at mass 108, survives in only very small amounts (< 1%).

Several other minor fragmentation routes from the molecular ion of (VI, R = H) take place. Loss of $H^{\cdot}$ to form the M-1 ion occurs. This gives rise to a peak due to the $C_{11}H_{10}N_3O^+$ ion at mass 200 (12%). Loss of $OH^{\cdot}$ occurs to a small extent to give a $C_{11}H_{10}N_3^+$ ion of mass 184 depicted as an azetopyrazole derivative (3%). A strong metastable for the transition 201 → 184 was observed in

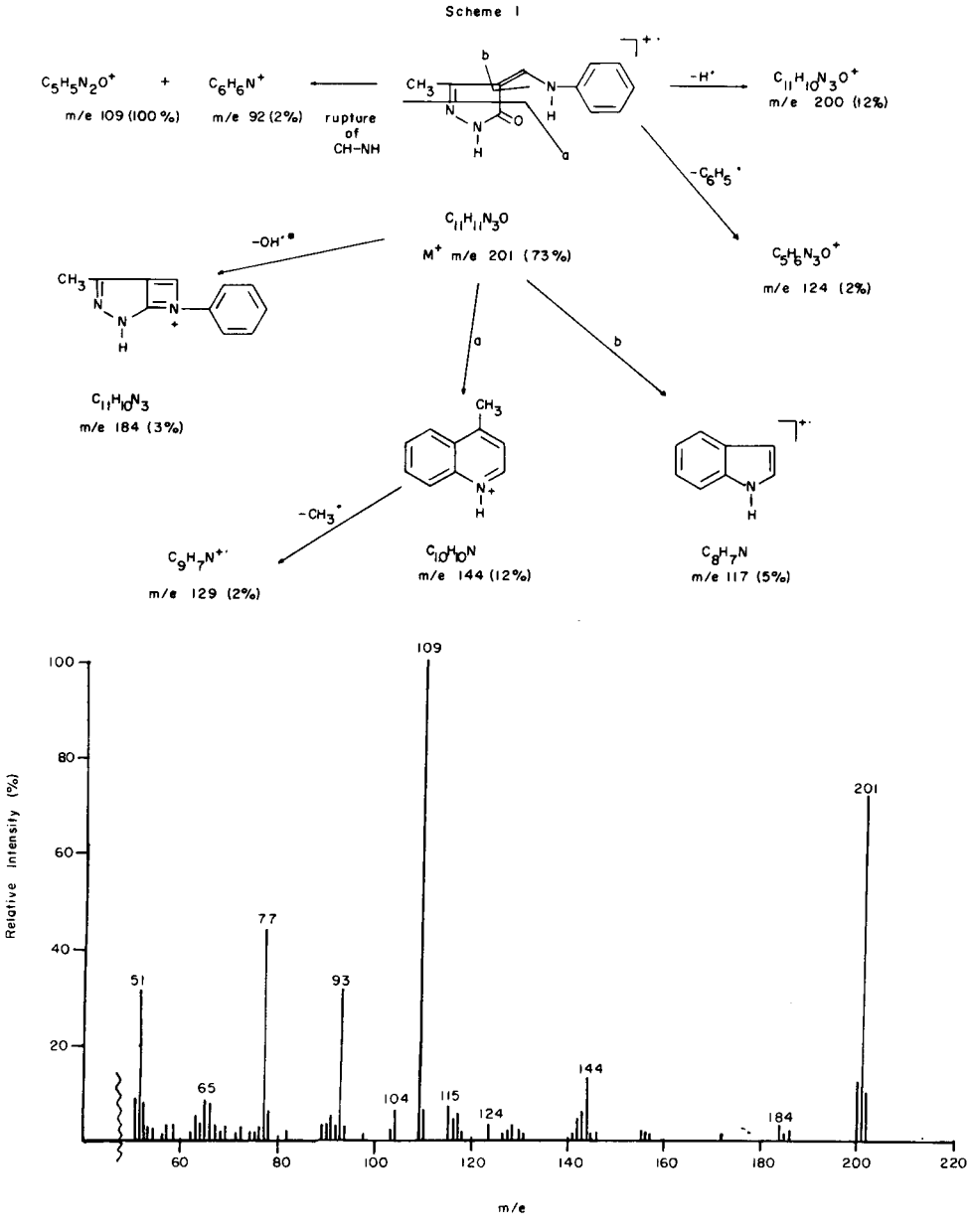


Figure 1. Mass spectrum of 5-methyl-4-[(phenylamino) methylene]-2,4-dihydro-3*H*-pyrazol-3-one.

the spectrum. Loss of C_6H_5 accounts for the $C_5H_6N_3O^+$ ion at mass 124 (2%).

At least two routes involve fragmentation of the pyrazolone ring without splitting the N-N bond. Thus disintegration as in route (a) in the Scheme gives a peak at mass 144 (12%) due to a $C_{10}H_{10}N^+$ ion depicted as the 4-methylquinolinium ion. The peak at mass 143 (6%, $C_{10}H_9N$) and 142 (4%; $C_{10}H_8N$) may arise by further loss of hydrogen or by similar pyrazolone ring rupture from the M-1 ion followed by loss of H·. Loss of CH_3 from the 4-methylquinolinium ion accounts for the peak at mass 129 (2%; C_9H_7N). Rupture of the pyrazolone ring as in route (b) gives a $C_8H_7N^+$· ion (5%) at mass 117 depicted as the indole molecular ion.

A very similar picture emerges from the spectrum of 2,5-dimethyl-4-[(phenylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-one (VI, R = CH_3) (Figure 2). The peak due to the molecular ion at mass 215 amounts to 83% of the intensity of the base peak. Fracture of the exocyclic CH-NH bond is the principal fragmentation route. This gives rise to the base peak at mass 123 ($C_6H_7N_2O^+$). In this case the $C_6H_6N^+$ ion at mass 92 is present only to about 1%. The hydrogen migration accompanying the CH-NH bond rupture is not so pronounced with (VI, R = CH_3), the aniline

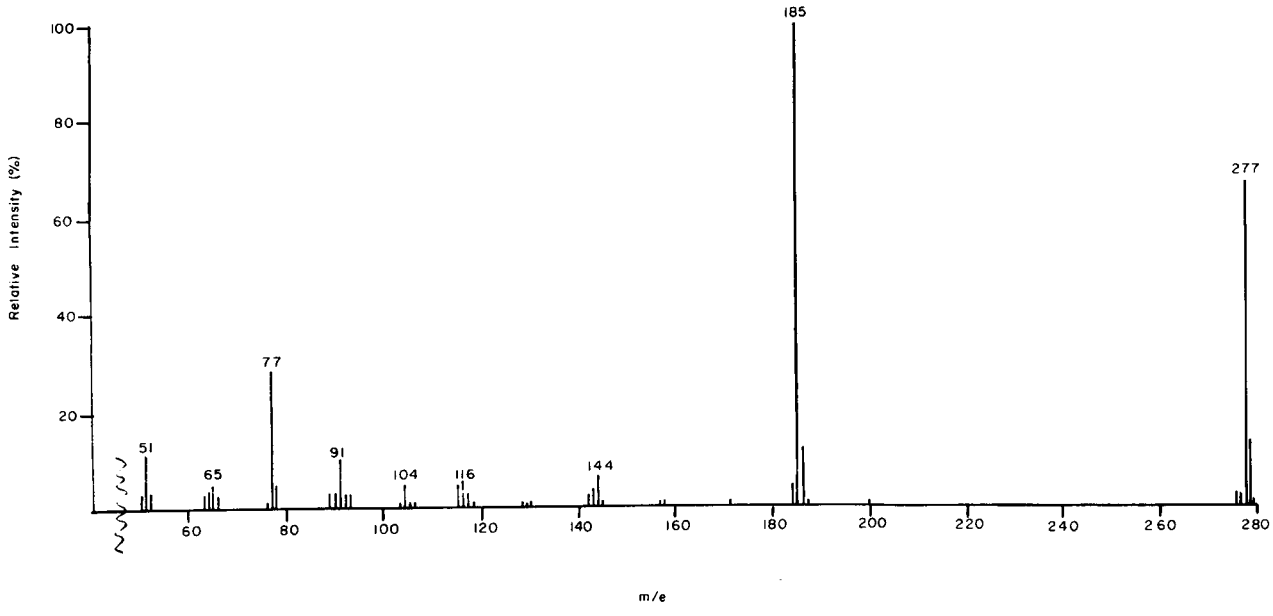


Figure 2. Mass spectrum of 2,5-dimethyl-4-[(phenylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-one.

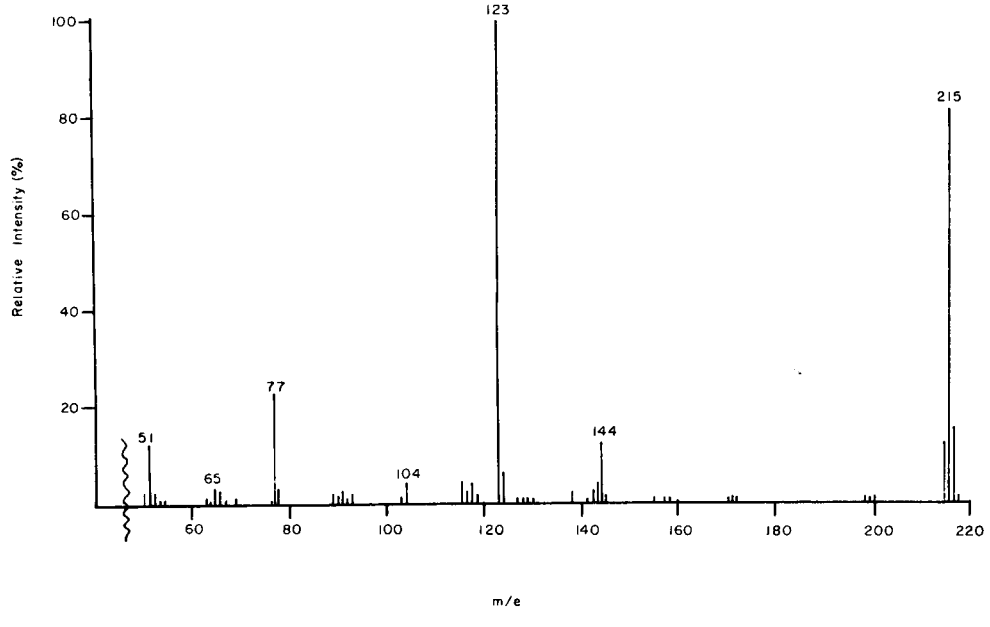


Figure 3. Mass spectrum of 5-methyl-2-phenyl-4-[(phenylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-one.

molecular ion at mass 93 ($C_6H_7N^{+\cdot}$) giving a peak of only 3% of the intensity of the base peak. The other minor fragmentation routes are very similar to those already discussed for (VI, R = H). Loss of H· from the molecular ion gives the M-1 ion $C_{12}H_{12}N_3O^+$ (13%), while loss of OH· forms the $C_{12}H_{12}N_3^+$ ion at mass 198 (2%), and loss of C_6H_5· gives the $C_6H_8N_3O^+$ ion at mass 138 (3%). The same fragmentations of the pyrazolone ring also take place. Thus, the $C_{10}H_{10}N^+$ ion (13%) at mass 144 is formed by route (a) and the $C_8H_7N^{+\cdot}$ ion (5%) at mass 117 by route (b).

The same general fragmentation pattern is maintained in the spectrum of 5-methyl-2-phenyl-4-[(phenylamino)-methylene]-2,4-dihydro-3*H*-pyrazol-3-one (VI, R = Ph)

Table 1

Empirical Formula of Fragment Ions (a) in the Mass Spectra of 5-Methyl-4-[(phenylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-ones (VI)

m/e	Formula	Intensity (%)		
		R = H	R = CH_3	R = Ph
277	$C_{17}H_{15}N_3O$			68
276	$C_{17}H_{14}N_3O$			3
215	$C_{12}H_{13}N_3O$		83	
214	$C_{12}H_{12}N_3O$		13	
201	$C_{11}H_{11}N_3O$	73		
200	$C_{11}H_{10}N_3O$	12		
198	$C_{12}H_{12}N_3$		2	
185	$C_{11}H_9N_2O$			100
184	$C_{11}H_{10}N_3$	3		
	$C_{11}H_8N_2O$			5
144	$C_{10}H_{10}N$	12	13	6
143	$C_{10}H_9N$	6	5	6
142	$C_{10}H_8N$	4	4	3
138	$C_6H_8N_3O$		3	
129	C_9H_7N	2		
124	$C_5H_6N_3O$	2		
123	$C_6H_7N_2O$		100	
117	C_8H_7N	5	5	3
116	C_9H_8	2		
	C_8H_6N	3	3	5
115	C_9H_7	7	6	4
109	$C_5H_5N_2O$	100		
104	C_7H_6N	5	5	5
93	C_6H_7N	32	3	3
92	C_6H_6N	2		2
91	C_7H_7	4	3	
	C_6H_5N	3	3	10
90	C_7H_6	3	2	
	C_6H_4N			2
89	C_7H_5	3	2	3
78	C_6H_6	7	4	4
	C_5H_4N			4
77	C_6H_5	44	25	30

(a) Only those ions of mass > 76 and of intensity ≥ 2% of the base peak are recorded. Peaks due to ^{13}C species are omitted from the table.

(Figure 3). Here the peak due to the molecular ion at mass 277 ($C_{17}H_{15}N_3O^{+\cdot}$) amounts to 68% of the intensity of the base peak. Rupture of the exocyclic CH-NH bond is again the principal fragmentation route giving rise to the base peak in the spectrum at mass 185 ($C_{11}H_9N_2O^+$) and the $C_6H_6N^+$ ion (2%) at mass 92. The aniline molecular ion at mass 93 ($C_6H_7N^{+\cdot}$) formed by hydrogen migration is also present (3%). A strong metastable peak for the transition 277→185 is observed. Loss of H· from the molucular ion of (VI; R = Ph) gives the $C_{17}H_{14}N_3O^+$ ion (3%) but loss of OH· and C_6H_5· is much less pronounced than with (VI, R = H) or (VI, R = CH_3) giving peaks less than 1% of the intensity of the base peak. The pyrazolone ring rupture by route (a) gives the $C_{10}H_{10}N^+$ ion (6%) at mass 144 and by route (b) the $C_8H_7N^+$ ion (3%) at mass 117.

The empirical formulae of the fragment ions are given in Table 1.

EXPERIMENTAL

The spectra was determined with an A.E.I. 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 100° C. Elemental compositions were obtained by the peak matching method.

5-Methyl-4-[(phenylamino)methylene]-2,4-dihydro-3*H*-pyrazol-3-one (VI, R = H) and its 2-methyl (VI, R = CH_3) and 2-phenyl (VI, R = Ph) derivatives were analytically pure (56).

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