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THE MASS SPECTRA OF 4-(BENZALAMINO) ANTIPYRINES

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THE mass spectral fragmentation of several pyrazoles[1] and pyrazolones[2-4] have been studied. It has been found that the heterocyclic ring system undergoes extensive rearrangement and ring opening during the mass spectral fragmentation of pyrazolone derivatives. Also, the position and general type of substitution have been observed to have a pronounced effect on the fragmentation of pyrazolones[1].

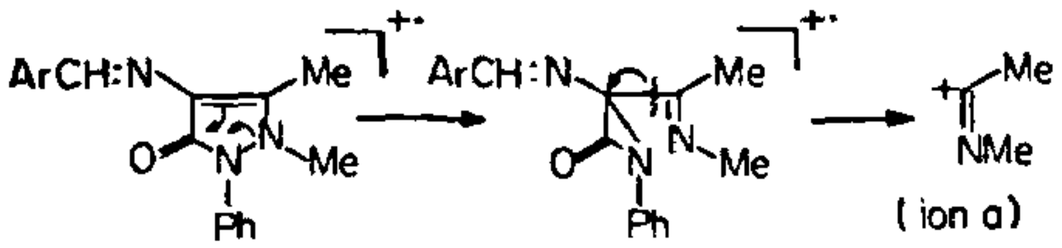
The present investigation was undertaken with a view to studying the effects of a 4-benzalamino substituent on the pyrazolone ring fragmentation. The compounds studied are 4-benzalamino and 4-(2-fluro, 2-chloro, 2-bromo, 2-hydroxy, 4-hydroxy and 4-methoxybenzal amino) antipyrines (1a-g) which are useful chelating agents for various transition metal ions[5]. The general trends observed are discussed and tentative assignment of the structure to the ions made.

The main fragments can be classified into two groups. Those which retain the aryl group of the arylidine part and those which arise from the pyrazolone part. Generally the M^+ peaks are strong, reflecting the stability of the system. The base peaks of all the compounds occur at m/e 56. This fragment should be the result of the cleavage of the pyrazolone ring system. It is noteworthy that aminoantipyrine also shows this fragment along with one at m/e 57. This fragment is thought to arise directly from the molecular ion (Scheme I).

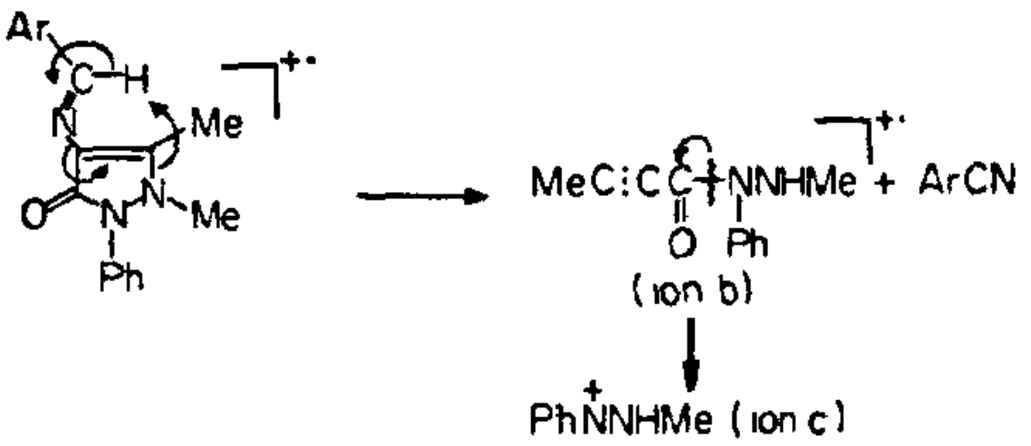
Two other important fragments which are common to all compounds studied and which have comparatively large abundance are the ions at m/e 188 and m/e 121. The former is assigned the structure (M-ArCN). The loss of ArCN (Scheme II) could lead to the ion of parent antipyrine. However, the ion (M-ArCN) is not assigned such a structure, since the ion is thought to decompose further into the ion at m/e 121. The mass spectra of antipyrine[2] does not show the presence of the ion at the m/e value 121. The pathway suggested for the fragmentation of the above two ions is shown in Scheme II.

The ion next in importance belongs to the set of ions having the aryl ring of the arylidine part and is thought to be formed by the loss of the 92 mass units corresponding to (PhNH) from the M^+ ion. It is to be noted that those pyrazolones without a 2-Me substituent do not give this fragmentation[2,4]. Therefore, it is assumed that the hydrogen lost in the neutral radical arises from the N-Me group as shown in Scheme III.

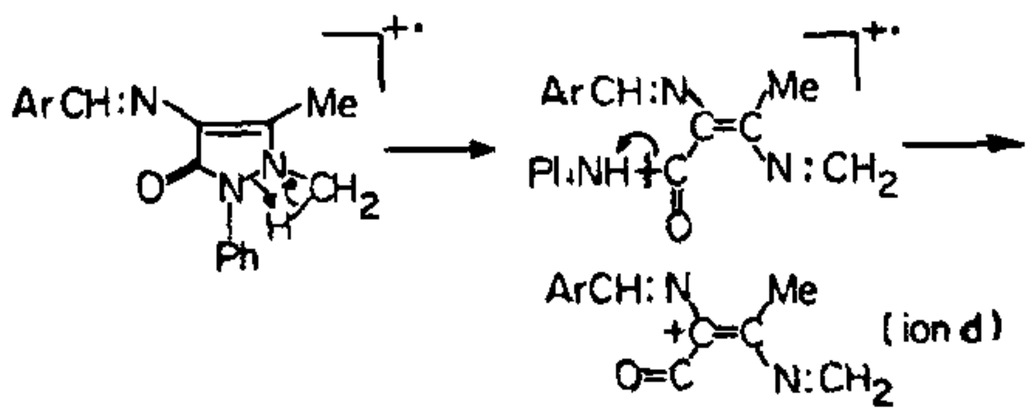
Another ion also incorporating the aryl moiety of the aryl aldehyde is (M-109) ion and which may have the composition (ArCHNHPh) ion. It is very difficult



Scheme - I



Scheme - II



Scheme - III

TABLE 1
Fragmentation data of 4-(Benzalamino) antipyrines.

Compound	Ar	Ions m/e (%) a	b	c	d	e	M^+
1a	C_6H_5	56 (100)	188 (23)	121 (25)	199 (18)	182 (11)	291 (55)
1b	2-FC_6H_4	56 (100)	188 (29)	121 (29)	217 (16)	200 (9)	209 (51)
1c	2-ClC_6H_4	56 (100)	188 (31)	121 (40)	233 (14)	216 (6)	325 (35)
1d	2-BrC_6H_4	56 (100)	188 (33)	121 (31)	277 (13)	260 (5)	369 (26)
1e	4-HO-C_6H_4	56 (100)	188 (13)	121 (20)	215 (14)	198 (11)	307 (54)
1f	2-HO-C_6H_4	56 (100)	188 (32)	121 (32)	215 (25)	198 (3)	307 (70)
1g	2-CH_3O-C_6H_4	56 (100)	188 (5)	127 (7)	229 (5)	212 (5)	321 (18)

to assign a straight forward mechanistic pathway for the formation of this ion. It is clear that extensive skeletal rearrangement has taken place leading to the formation of the above ion. The ion has only a low abundance (ion e).

The chloro and bromo derivatives give M–X ions also of moderate intensity.

Thus in comparison with the mass spectra of antipyrine[2] the present compounds show interesting fragmentation modes obviously brought about by the introduction of the arylidine amino moiety at the 4th position of the antipyrine ring. Ring fragmentation involving the loss of CO or loss of Ph NCO is not observed.

The mass spectra were taken Varian MAT-CH7 at the inlet temperature 195° C. Direct inlet system was used to introduce the compounds. The m/e values and the percentage abundance of selected ions are given in table 1. The compounds were obtained by a procedure reported earlier[5]. Satisfactory elemental analysis data were obtained for all the compounds. The purity was ascertained by thin layer chromatography using silica gel (benzene).

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SYNTHESIS OF 2,6-DIARYL-4H-1,3,4-OXADIAZINES AS ANTI-BACTERIAL AGENTS

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THE synthesis of many substituted and fused 1,3,4-oxadiazines as monamine oxidase inhibitors have been reported earlier[1-5]. 5,6-dihydro-4H-1,3,4-oxadiazines were synthesized from certain 2-(β-hydroxyalkyl) acid hydrazides[6]. Reactions of certain acid hydrazides with quinones gave fused oxadiazine systems[7]. It is of interest to extend this reaction with phenacyl chloride to synthesise oxadiazines and to screen them for antibacterial activity.

Phenacyl chloride (I) was made to react with acid hydrazides (IIa-f) to get 1-N-phenacyl acid hydrazides (IIIa-f). For the subsequent cyclisation acetic acid, acetic acid-sulphuric acid and acetic acid-phosphoric acid were used.

1-N-Phenacyl anisic acid hydrazide (IIIc):

It was prepared in two ways.

(1) A mixture of phenacyl chloride (0.0064 mol), anisic acid hydrazide (0.0064 mol) and 2 or 3 drops of piperidine in alcohol (30 ml) was refluxed for 6 hr and poured into crushed ice with constant stirring. It was kept aside for a few minutes and the product separated was filtered, washed with cold water, dried and recrystallized.

(2) To a solution of phenacyl chloride (0.1 mol) in acetic acid (20 ml) *p*-anisic acid hydrazide (0.1 mol) in acetic acid (20 ml), was added. The mixture was heated under reflux for 3-4 hr. The reaction mixture was cooled and poured into ice with constant stirring. The resultant solid was filtered, washed with water, dried and purified by crystallization. Similarly other