

MASS SPECTRAL STUDIES OF AROMATIC AZA ANALOGUES OF JUVABIONE*

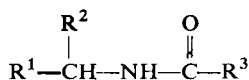
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Mass spectra of title compounds *I–VI* have been studied with a view to comparing the fragmentation pattern of secondary amides in different structural environments.

The aromatic aza analogues of juvabione *I–VI* whose mass spectra are reported in this communication were prepared by treatment of respective benzylamines with 3-methylbutanoyl chloride or 3-methyl-2-butenoyl chloride¹. These compounds are insect juvenile hormone analogues and their mass spectra have been studied with a view to comparing the fragmentation pattern of secondary amides in different structural environments. Gilpin² has discussed the mass spectra of a variety of aliphatic amides but only one secondary amide with a γ -hydrogen atoms in the alkyl chain, N-butyloctadecanamide, has been reported.

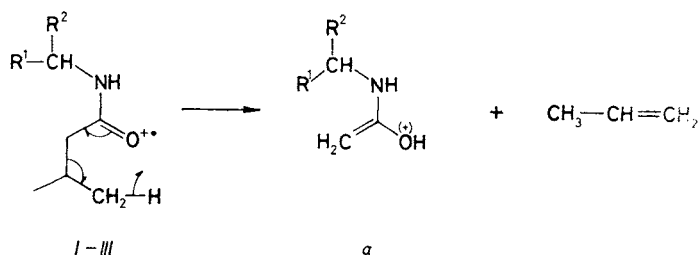


- I*, R¹ = C₆H₅; R² = CH₃; R³ = —CH₂CH(CH₃)₂
II, R¹ = 4-ClC₆H₄; R² = CH₃; R³ = —CH₂CH(CH₃)₂
III, R¹ = C₆H₅; R² = H; R³ = —CH₂CH(CH₃)₂
IV, R¹ = C₆H₅; R² = CH₃; R³ = —CH=C(CH₃)₂
V, R¹ = 4-ClC₆H₄; R² = CH₃; R³ = —CH=C(CH₃)₂
VI, R¹ = C₆H₅; R² = H; R³ = —CH=C(CH₃)₂

The most characteristic peaks of these compounds are given in Table I. An intense molecular ion peak (base peak; 100%) is observed in compound *IV* while all other compounds give molecular ions of moderate intensity (15–38%). The molecular ion is accompanied by [M + 1]⁺ peak of 5–15% intensity in all compounds. The compounds *II* and *V* also show [M + 2]⁺ peak of about 30% intensity of molecular ion peak due to the presence of ³⁷Cl.

* Part VI in the series: Juvenile Hormone-Like Substances; Part V: J. Agric. Food Chem., submitted.

Compounds *I–III* give an ion *a* at m/z $[M - 42]^+$ which can be rationalized in terms of McLafferty type rearrangement (Scheme 1). No such peak is observed in *IV–VI* because this rearrangement cannot take place due to the presence of double bond conjugated with carbonyl group. Compounds *IV–VI* show an intense $[M - 15]^+$ ion peak due to the loss of terminal methyl group while compounds *I–III* give $[M - 15]^+$ ion peak of very low intensity. It seems that a considerable amount of rearrangement takes place before the loss of terminal methyl group.



SCHEME 1

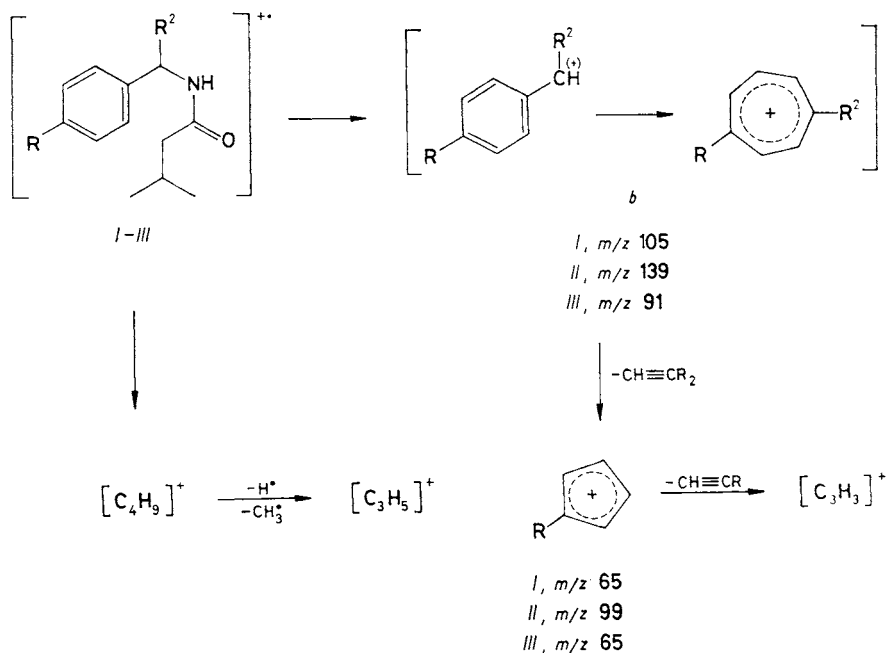
TABLE I

Location of peaks (in m/z) and relative abundance in the mass spectra of compounds *I–VI*

Ion	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>	<i>VI</i>
$[M]^+$	205/31	239/35	191/15	203/100	237/38	189/38
$[M + 1]^+$	206/7	240/4	192/11	204/15	238/7	190/10
$[M + 2]^+$	—	241/10	—	—	239/13	—
$[M - 15]^+$	190/4	224/4	176/4	188/29	222/89	174/98
$[M - 42]^+$	163/13	197/12	149/19	—	—	—
$ \begin{array}{c} \text{R}^2 \\ \\ \text{R}^1-\text{C}=\text{NH}_2 \end{array} $	120/40	154/30	106/67	120/21	154/21	106/32
	105/100	139/100	91/100	105/44	139/87	91/100
$(+)$ $\text{O}=\text{C}-\text{R}^3$	85/6	85/16	85/9	83/68	83/100	83/100
$[\text{C}_6\text{H}_5]^+$	77/67	77/66	77/78	77/36	77/30	77/41
$[\text{C}_5\text{H}_5]^+$	65/7	—	65/29	65/4	—	65/42
$[\text{C}_5\text{H}_4\text{Cl}]^+$	—	99/4	—	—	99/21	—
$(+)$ R^3	57/45	57/89	55/8	55/46	55/36	55/44

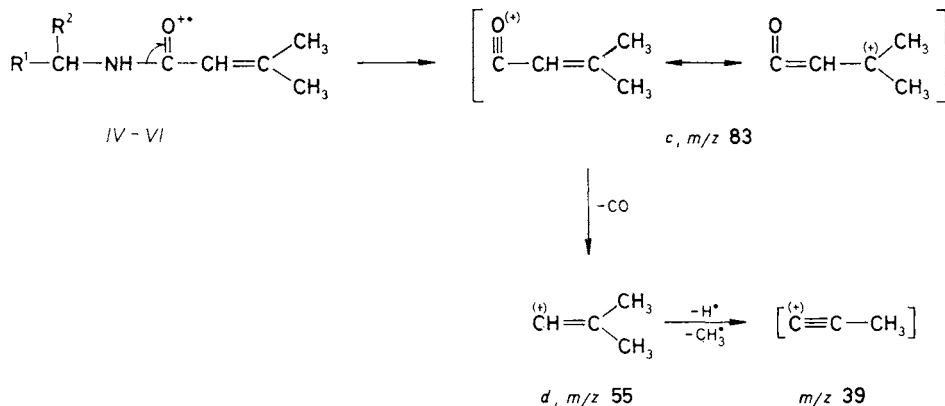
^a R = H or Cl.

The most abundant ion (base peak) in *I–III* is formed by the rupture of alkyl–nitrogen bond to give a relatively stable benzylum ion, or perhaps the tropylium ion^{3,4} *b*, which is accompanied by the expected $[\text{C}_5\text{H}_5]^+$ ion at m/z 65 by the loss of C_2HR_2 , and $[\text{C}_3\text{H}_3]^+$ ion at m/z 39 by a further loss of C_2H_2 . Compounds *IV–VI* also show the formation of ion *b* but its intensity is relatively lower in *IV* and *V* while it is a base peak in *VI*. The other plausible fragment ion from the alkyl–nitrogen bond rupture bearing the charge on nitrogen atom is not formed at all, Scheme 2.



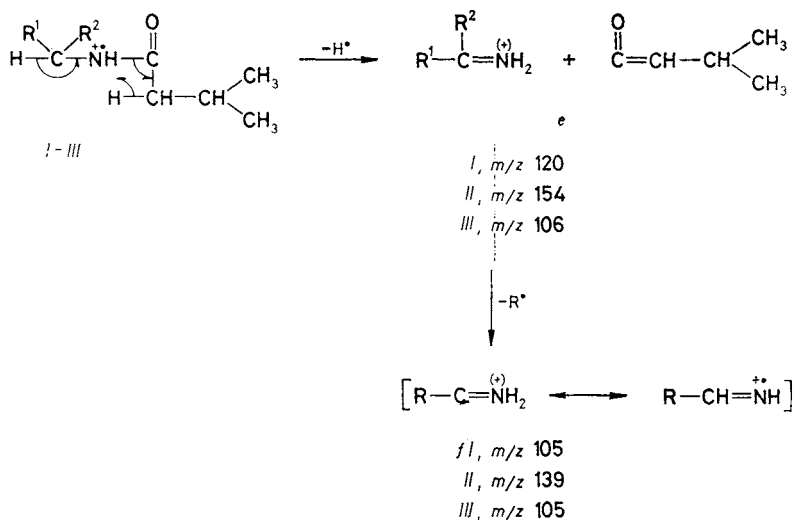
SCHEME 2

Another important fragmentation path which can be envisaged in the above compounds is through the rupture of acyl–nitrogen bond. This can take place in two different ways to form different ions: (i) Cleavage of C–N bond to form ion *c* in which the positive charge is retained by oxygen atom. This is the most abundant ion (base peak) observed in compounds *IV–VI* because in these cases the ion can be resonance stabilized. Loss of CO from *c* results in the formation of ion *d* (Scheme 3). The relative intensity of the ion *c* in *I–III* is relatively smaller because here it cannot be resonance stabilized. (ii) A double α - and C–N cleavage with hydrogen rearrangement to form ion *e* in which the positive charge is retained by nitrogen



SCHEME 3

atom. This type of fragmentation is observed more in *I-III* than in *IV-VI* because of preferential formation of the ion *c* in *IV-VI* (Scheme 4). Yet another significant fragmentation observed in all the compounds *I-VI* is the loss of side chain from the aromatic ring to form the ion $[\text{C}_6\text{H}_5]^+$, m/z 77, and other ions corresponding in empirical composition to $[\text{C}_3\text{H}_3]^+$, $[\text{C}_4\text{H}_2]^+$, $[\text{C}_4\text{H}_3]^+$, and $[\text{C}_4\text{H}_5]^+$ known to be associated with the decomposition of the phenyl ring⁵. A direct rupture of the carbonyl-alkyl bond also seems to take place to form ions of m/z 57 in *I-III* and of m/z 55 in *IV-VI*.



SCHEME 4

The spectra of compounds *II* and *V* show significant ions at m/z 138, 104, and 103. The ion at m/z 138 can be attributed to the loss of hydrogen from the ion *b*. The ions at m/z 104 and 103 suggest that the halogen cleavage takes place predominantly after the initial rupture of the alkyl–nitrogen bond (loss of 35 from m/z 139 and 138).

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Note added in proof: In Scheme 2 for $-\text{CH}\equiv\text{CR}_2$ should read $-\text{CH}\equiv\text{CR}^2$.