MASS SPECTRA OF SUBSTITUTED 1,2,3,4-TETRAHYDRO-γ-CARBOLINES

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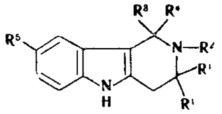
The mass-spectral behavior of substituted 1,2,3,4-tetrahydro-γ-carbolines has been investigated. For the 4-unsubstituted or 4-monosubstituted compounds a characteristic process is the primary retrodiene decomposition of the molecular ion. More characteristic for 4,4-disubstituted compounds is the primary loss of a substituent from position 4.

In the mass spectra of the polymethylindoles, the stability of the molecular ion decreases with an increase in the number of methyl groups in the indole nucleus but depends little on their positions [1-3]. In an investigation of indole derivatives containing an amino group in the side chain – tryptamines – it was established [4] that the main fragment in their mass spectra is an ion with m/e 130, i.e., the "benzyl" C–C bond is split, the charge remaining predominantly on the indole fragment. The main direction of the dissociation of cyclic analogs of tryptamine – 1,2,3,4-tetrahydro-γ-carbolines – under the action of electron impact [5] is the retrodiene decomposition of the molecular ion even when an alkyl group is present in position 1. It could be assumed that in the case of gem substitution adjacent to the nitrogen atom in the piperidine ring the nature of the decomposition would change, and therefore we have studied the behavior under the action of electron impact of the substituted 1,2,3,4-tetrahydro-γ-carbolines (I-IX):



I–IX

I $R^1=R^3=CH_3$, $R^2=R^4=R^5=H$. II $R^1=R^2=R^5=H$, $R^3=R^4=CH_3$, III $R^1=CH_3$, $R^2=R^3=R^4=R^5=H$; IV $R^1=R^3=R^4=CH_3$, $R^2=R^5=H$. V $R^1=R^2=R^3=R^4=CH_3$, $R^5=H$. VI $R^1=R^3=R^4=R^5=H$, $R^2=CH_3$, VII $R^1=R^3=R^4=H$, $R^2=R^5=CH_3$; VIII $R^1=R^3=R^4=H$, $R^2=CH_3$, $R^5=Br$, IX $R^1=R^3=R^4=H$, $R^2=CH_3$, $R^5=OCH_3$

The characteristics of the mass spectra and the stabilities of the molecular ions to electron impact calculated from them (W_M) (Table 1) show that on the whole an increase in the number of methyl groups in the piperidine ring leads to a decrease in the stability of the molecule. A particularly marked fall in stability is observed on passing from compound (IV) to compound (V).

It is known that the molecular ions of tertiary amines are more stable than the ions of secondary or primary amines. In actual fact, the stability of compound (VI) is considerably higher than that of compounds (I-IV) and, therefore, the sharp fall in the stability of the molecular ion of compound (V) must probably be explained by steric factors – by an increase of internal stresses in its structure and, as a consequence of this, an increase in the number of possible decomposition pathways. The introduction of donor substituents into the benzene ring also leads to a fall in the stability of the molecular ion (compounds VII-IX).

The molecular ions of compounds (I-IX) formed on electron impact dissociate in two different directions according to the degree of substitution and the positions of the substituents. The first direction is

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TABLE 1. Mass Spectra of 1,2,3,4-Tetrahydro-γ-carbolines

Comp.	m/e (relative intensity, %) *	
I	43 (7,0), 156 (12,8), 157 (100,0), 158 (15,7), 199 (23,4), 214 (10,5)	5,2
II	144 (5,8), 185 (100,0), 186 (7,4), 200 (5,5)	3,3
III	41 (10,2), 42 (5,9), 43 (17,2), 45 (14,8), 55 (8,4), 57 (26,6), 71 (6,2), 73 (7,4), 87 (8,7), 143 (100,0), 144 (11,0), 200 (7,2)	2,4
IV	41 (9,9), 42 (14,5), 43 (9,8), 55 (6,4), 156 (9,8), 170 (31,0), 186 (5,2), 213 (100,0), 214 (15,5), 228 (5,1)	1,8
V	41 (13,2), 42 (10,4), 43 (30,8), 55 (16,0), 56 (100,0), 57 (29,2), 69 (11,6), 70 (6,4), 71 (22,4), 72 (56,6), 73 (11,2), 77 (10,4), 78 (17,6), 81 (5,6), 83 (5,2), 85 (5,6), 127 (5,2), 128 (9,2), 129 (10,0), 130 (6,4), 154 (10,4), 156 (54,0), 170 (9,2), 171 (88,0), 172 (8,8), 227 (66,0), 228 (7,2)	0,06
VI	115 (5,2), 143 (100,0), 144 (15,4), 185 (10,6), 186 (24,6)	13,2
VII	156 (10,8), 157 (100,0), 158 (14,3), 199 (9,2), 200 (23,0)	7,5
VIII	85 (10,2), 142 (12,7), 143 (5,0), 221 (100,0), 222 (9,8), 223 (96,9), 224 (8,3), 263 (6,3), 264 (10,2), 265 (6,8), 266 (9,6)	5,9
IX	41 (6,7), 43 (20,0), 45 (40,2), 55 (8,2), 57 (12,8), 69 (6,7), 71 (5,6), 158 (37,0), 173 (100,0), 174 (9,7), 215 (8,0), 216 (17,3)	4,4

*Peaks with intensities greater than 5% are given.

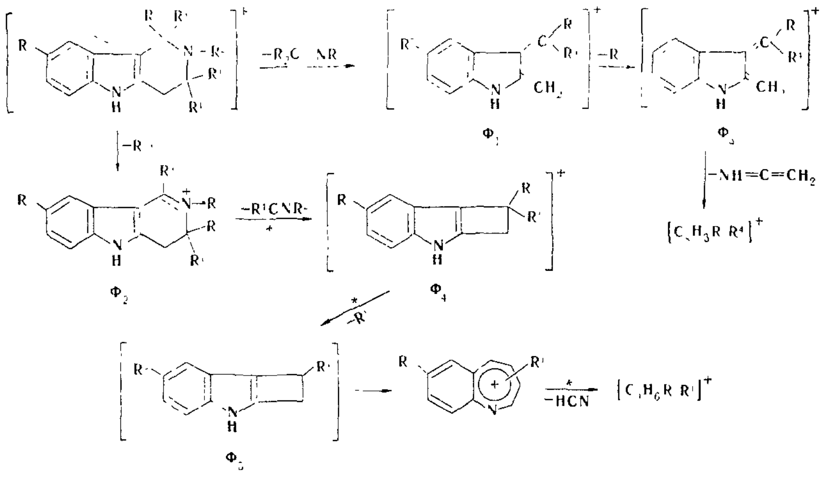
TABLE 2. Intensities of Some Ions in the Mass Spectra of the 1,2,3,4-Tetrahydro-γ-carbolines

Intensity, % of total ion current	Compound								
	I	II	III	IV	V	VI	VII	VIII	IX
Φ_1	48,5	0,7	31,9	9,9	12,3	52,3	30,1	27,0	25,6
Φ_2	11,7	57,8	0,9	32,0	9,2	—	—	—	—
Φ_3	—	—	—	—	—	—	0,3	4,0	0,4

retrodiene decomposition with ejection of the piperidine nitrogen atom together with the second carbon atom. This type of fragmentation is characteristic for all 4-unsubstituted and 4-monosubstituted 1,2,3,4-tetrahydro-γ-carbolines (compounds I, III, and VI-IX). As a rule, the ion Φ_1 so formed has the maximum intensity (25.6-52.3% of the total ion current; see Table 2) and gives practically no products of secondary decomposition.

Only when there is a substituent in the benzene ring (compounds VII-IX) does the further decomposition of the ion Φ_1 characterizing this substituent take place to a very slight extent: loss of CH_3 in the case of compound (VII), loss of bromine in the case of (VIII), loss of OCH_3 in the case of (IX). In the case of compound (IX), the loss of a methyl group by the Φ_1 ion gives a strong peak with m/e 158 (9.9% of the total ion current).

The second pathway of dissociative ionization for the 4,4-disubstituted 1,2,3,4-tetrahydro-γ-carbolines is characterized by the primary loss of a methyl group (most probably from position 4) with the formation of the ion Φ_2, which is generally the maximum ion in the mass spectrum. The proportions of this ion in the total ion currents in the mass spectra of compounds (II) and (IV) are, respectively, 57.8 and 32%.



The assumption of the predominant loss of a methyl group from position 4 is based on the fact that on passing from compound (III) to compounds (I, IV, and II) the proportion of the Φ_2 ion in the total ion current rises continuously from 0.9 to 57.8%. The further decomposition of the Φ_2 ion takes place predominantly with the formation of the ions Φ_4 and Φ_5 (see scheme above).

It must be mentioned that in the spectrum of compound (V) both processes (i.e., the formation of both the Φ_1 and the Φ_2 ions) are reflected, but the proportion of the ion Φ_1 in the total ion current is somewhat higher than that of the ion Φ_2.

EXPERIMENTAL

The mass spectra were taken on an MKh-1303 instrument with a modified system of introduction directly into the ion source and with the recording of the spectra by means of an M-105 loop oscillograph on photographic paper at an energy of the ionizing electrons of 50 eV with an accelerating voltage of 2 kV in the temperature range from 100 to 120°C.

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