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POLYNUCLEAR HETEROCYCLIC SYSTEMS—II

MASS SPECTRA OF CERTAIN BENZINDOLE AND DIHYDROBENZINDOLE ACIDS AND ESTERS

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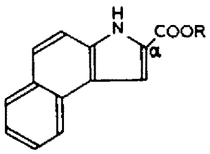
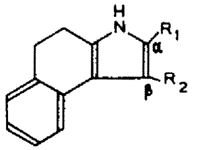
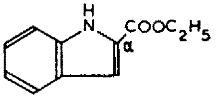
Abstract—The mass spectra of compounds I to VIII have been studied. Structural assignments have been made for the major fragments, and pathways leading to their formation have been postulated by recognition of the appropriate metastable ions. The diagnostic value of the mass spectra in assigning the position of the ester function is discussed.

THE potential application of electron-impact studies to the structure elucidation of certain dihydrobenzindole carboxylic esters has been indicated in an earlier communication.[1] In particular, it was observed that the fragmentation patterns of isomeric esters involving positional variation of the ester function exhibited significant differences which could be correlated with their structural assignments. We now wish to present in detail our results on the study of compounds I to VIII (Figs. 1 to 7) which incorporate a fully aromatic or hydroaromatic indole nucleus in their structure.







VIII

I R = H
II R = C_2H_5

III R_1 = COOH , R_2 = H
IV R_1 = $COOCH_3$, R_2 = H
V R_1 = H , R_2 = $COOCH_3$
VI R_1 = COOH , R_2 = $COOCH_3$
VII R_1 = $COOCH_3$, R_2 = $COOCH_3$

Compounds I, II and VIII were obtained according to procedures described in the literature[2,3] while the synthesis of the hydrobenzindole derivatives III to VII has been reported from this laboratory for the first time.[1]

The mass spectra of several alkylated indoles have been discussed in detail by Beynon *et al.*[4,5] A common feature of the fragmentation of these compounds consists

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[1] U. K. Pandit and H. O. Huisman, *Rec. Trav. Chim.* **83**, 50 (1964). The latter paper may be regarded as Paper I of this series.

[2] E. A. Goldsmith and H. G. Lindwall, *J. Org. Chem.* **18**, 507 (1953).

[3] R. V. Jardine and R. K. Brown, *Canad. J. Chem.* **41**, 2072 (1963).

[4] J. H. Beynon and A. E. Williams, *Applied Spectroscopy* **13**, 101 (1959).

[5] J. H. Beynon, *Mass Spectroscopy and its Application to Organic Chemistry* pp. 397–403. Elsevier, Amsterdam (1960).

of a process which involves the loss of 27 mass units. The latter has been ascribed to an expulsion of a neutral HCN molecule from the appropriate precursor ions. The consistent occurrence of this feature provides a useful correlation for the structural diagnosis of the indole nucleus.

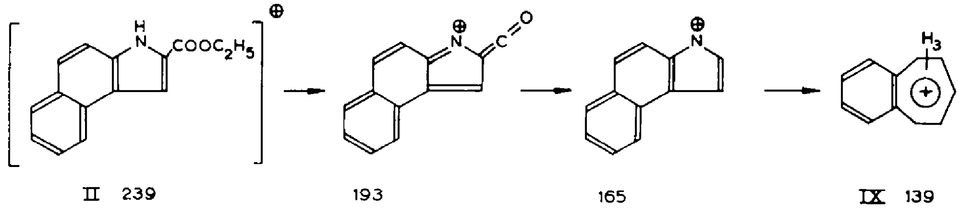
An examination of the spectra of compounds I to VIII reveals several noteworthy characteristics. In the first instance, it may be observed that compounds containing the carboxylic function, namely, I, III and VI fail to exhibit a mass peak corresponding to their molecular ions; instead, the peak with the highest mass in each case arises from a fragment representing the loss of 44 mass units from the parent molecule. In fact, the spectra of esters V and VI (Fig. 6) are superimposable when determined under identical conditions. That the ions M-44 are formed by thermal decarboxylation of the acids is strongly suggested from the observation that compounds I and V lose carbon dioxide readily when heated to temperatures similar to those employed in the heat-attended inlet system. The contribution to the peak *m/e* M-44 from an electronic process, involving a squeezing out of a carbon dioxide molecule, however, cannot be excluded.

The fully aromatic systems II and VIII, whose structures are well established from their synthesis, follow a recognizable decomposition pattern. The spectra of the α-esters II and VIII both show their *base* peaks at *m/e* values of M-46, indicating the loss of elements of ethanol from the parent molecule in a primary process. The presence of conspicuous metastable peaks at 156·0 and 108·4 in the spectra of II and VIII confirms the fragmentation of their molecular ions according to processes (a) and (d) respectively. Further fragmentation of the M-46 ions from both esters proceeds in an identical fashion with consecutive losses of a molecule of carbon monoxide and a neutral cyanide radical. The operation of these processes (b, c, e and f) has also been confirmed by the recognition of the appropriate metastable peaks.

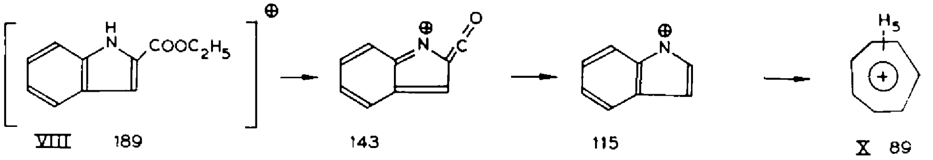
Considerable interest centres around the peak at *m/e* 139 since it is significantly present in the spectra of all benzindole derivatives I to VII. This fact suggests both a similarity in the decomposition patterns of the aromatic and partially hydrogenated benzindole systems and an extraordinary stability for the ion *m/e* 139 itself. A formulation of the latter ion which is consistent with the fragmentation scheme A developed for II and which is also characterized by pronounced stability is presumably the

	Reaction	Metastable Peak	
		Calculated	Found
(a)	(II) $239^+ \rightarrow 193^+ + 46$ (C_2H_5OH)	155·9	156·0
(b)	$193^+ \rightarrow 165^+ + 28$ (CO)	141·1	141·2
(c)	$165^+ \rightarrow 139^+ + 26$ (CN)	117·1	117·0
(d)	(VIII) $189^+ \rightarrow 143^+ + 46$ (C_2H_5OH)	108·2	108·4
(e)	$143^+ \rightarrow 115^+ + 28$ (CO)	92·5	92·7
(f)	$115^+ \rightarrow 89^+ + 26$ (CN)	68·9	68·4
(g)	(VII) $285^+ \rightarrow 253^+ + 32$ (CH_3OH)	224·6	224·8

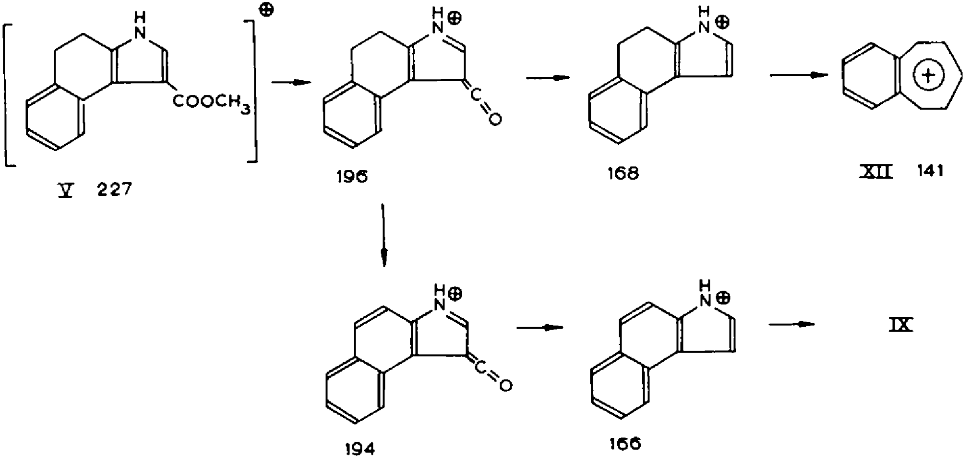
Scheme A



Scheme B



Scheme C



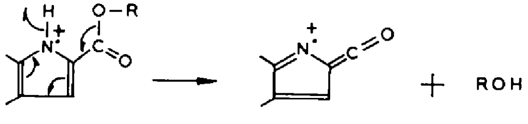
dehydro-benztropylium system IX. An identical scheme B for the indole ester VIII leads to the analogous tropylium ion X which is represented in its spectrum (Fig. 3) by a prominent peak at *m/e* 89.

Directing our attention to the hydroaromatic esters IV, V and VI it may be observed that the ester IV (Fig. 5) exhibits its most abundant mass peak at *m/e* = 195 (M − 32). Since the latter compound possesses an ester function in the α-position to the pyrrole nitrogen, the loss of a fragment of 32 mass units can be readily understood in terms of the elimination of a methanol molecule from the molecular ion; a process which is completely analogous to that observed in the case of the α-esters II and VIII. In contrast to this behaviour the spectrum of β-ester V (Fig. 6) reveals that the molecular ion (*m/e* = 227) clearly represents the most abundant species. Decomposition of this ion follows a conventional pattern for fragmentation of esters[6] as evidenced by strong peaks at *m/e* values of 196 and 168, indicating successive losses of OCH_3 and CO units. A prominent peak at 194 suggests the significance of aromatization of the

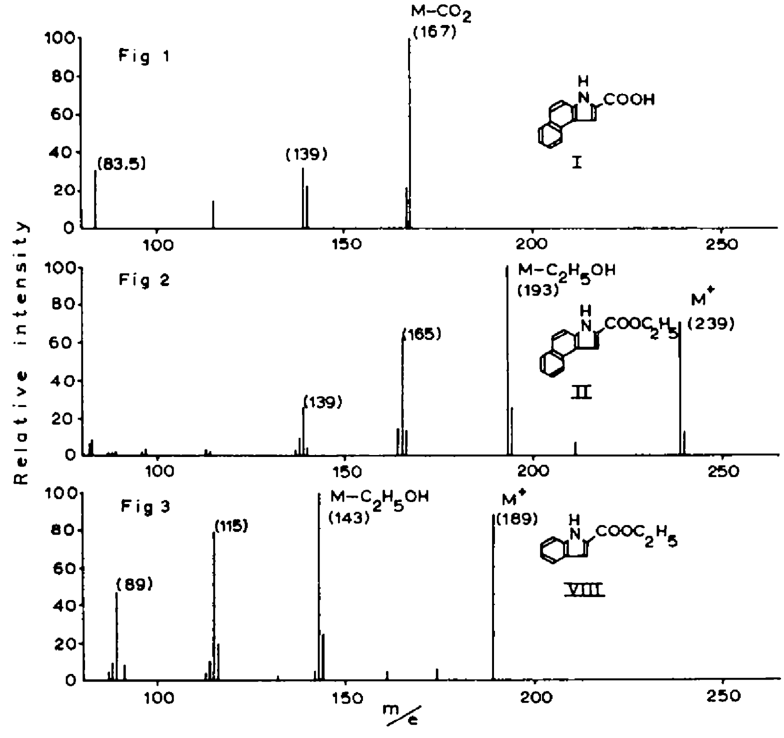
[6] [a] A. G. Sharkey, J. L. Schultz and R. A. Friedel, *Analyt. Chem.* **31**, 87 (1959);
[b] R. Ryhage and E. Stenhagen, *Arkiv. Kemi.* **13**, 523 (1959);
[c] J. H. Beynon, R. A. Saunders and A. E. Williams, *Analyt. Chem.* **33**, 221 (1961).

ion *m/e* 196 to the corresponding benzindole nucleus. This fragmentation pathway is represented in scheme C.

The diester VII provides an interesting case for examining the fate of the ester functions located both at the α- and β-positions of the pyrrole nucleus in one and the same molecule. An examination of the spectrum of VII (Fig. 7) indicates that the breakdown patterns observed for the individual monoesters are clearly retained in the diester. Thus it may be seen that a peak at *m/e* 253 (M − 32) appears as the *base* peak of the spectrum. The implied loss of methanol from the parent molecule is in complete agreement with the behaviour of the α-esters examined in this series of compounds. A metastable peak at 224·8 confirms the operation of the latter process (g). A significant peak at *m/e* 222 suggests that further decomposition of the ion *m/e* 253 involves the loss of an OCH_3 unit from the ester function located at the β-position. The elimination of the alcohol moiety from the α-esters is reminiscent



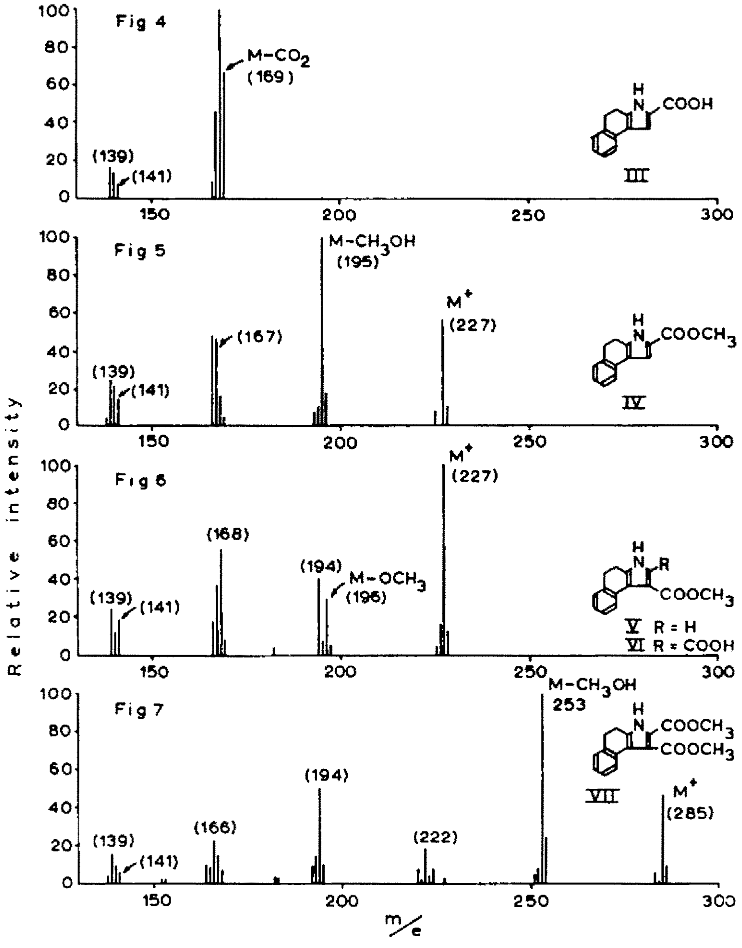
XI



Figs. 1-3

of the *ortho effect*[7] observed for several aromatic systems and presumably proceeds via a cyclic mechanism XI involving an E_2 type elimination.[8,9]

A comparison of the spectra of acids I and III (Figs. 1 and 4) emphasizes the close similarity between the breakdown of the aromatic and hydroaromatic systems. The $M - CO_2$ ion from I ($m/e = 167$, Fig. 1) loses a molecule of hydrogen cyanide in a manner analogous to the known behaviour of indole derivatives, and, the resulting species presumably attains added stability by further loss of a hydrogen atom to form a non-nitrogenous fragment of odd mass ($m/e = 139$). The dihydro acid III also exhibits conspicuous peaks at m/e values of 167 and 139 in its spectrum (Fig. 4)



FIGS. 4–7

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[7] F. W. McLafferty, *Mass Spectrometry of Organic Ions* p. 337. Academic Press, New York (1963).

[8] K. Biemann, *Mass Spectrometry* p. 77. McGraw-Hill, New York (1962).

[9] The fishhook representation used in describing the mechanism implies that the departing atom carries with it only one of the bonding electrons. See H. Budzikiewicz, C. Djerassi and D. H. Williams, *Interpretation of Mass Spectra of Organic Compounds* p. XII. Holden-Day, San Francisco (1964).

strongly suggesting that the decomposition of the dihydrobenzindole nucleus proceeds, at least in part, via an initial aromatization process. The presence of a peak at *m/e* 141 in Fig. 4 as well as in the spectra of hydrobenzindole derivatives III to VII indicates that in those cases where a sufficient number of hydrogen atoms are present in the system a loss of the appropriate fragment(s) can result in the formation of the benztropylium ion XII.

The characteristic and essentially uncomplicated nature of the spectra of benzindole and hydrobenzindole derivatives enables their utilization as an independent means of recognizing the latter heterocyclic compounds. Further, the consistently encountered difference between the major fragmentation pathways of the α- and β-esters points to the diagnostic value of the mass spectra in assigning the position of the ester function in these systems.

EXPERIMENTAL

The mass spectra measurements were carried out on a A.E.I. M.S. 2H spectrometer with the technical assistance of Messrs. W. J. Rooselaar, J. A. M. Spitteler and J. D. van Wageningen. The ionizing potential employed in all measurements was 70 ev.