

## COMPARATIVE STUDIES OF MASS SPECTRA OF SOME DISUBSTITUTED PYRROLES AND PIPERAZINE DERIVATIVES. PART VI

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The comparative studies of mass spectra of  $\alpha, \alpha'$ -di-(3-keto-5-phenylpent- $\Delta^4$ -enyl)pyrrole (I),  $\alpha, \alpha'$ -di-(3-keto-5-phenylpentyl) pyrrole (II),  $\alpha, \alpha'$ -di-(2-benzoylethyl) pyrrole (III), *N,N*-diskatyl piperazine (IV) and *N,N*-di( $\beta$ -benzoylethyl) piperazine (V) have been described. The mass spectral fragmentation pattern of the above compounds showed regular and similar losses.

The earlier comparative studies of PMR and mass spectra<sup>1-6</sup> of different groups of synthetic compounds have not only established the structure of these compounds, but also revealed the very interesting rearrangements and migration of some protons when subjected to electron bombardment in the ionizing chamber. In previous papers the synthesis of disubstituted pyrroles<sup>7</sup> and piperazines<sup>8,9</sup> have been described in aqueous medium at different pH. In the present communication their mass spectral studies are described in detail.

The mass spectrum of  $\alpha, \alpha'$ -di-(3-keto-5-phenylpent- $\Delta^4$ -enyl) pyrrole (I) showed an intense molecular ion peak at  $m/e$  383<sup>+</sup>, which readily underwent fragmentation with the loss of 18 and 28 mass units corresponding to the loss of a molecule of water and carbon monoxide, forming very stable charged species 1 and 2 respectively. The loss of water can only occur with the migration and elimination of the two  $\alpha$ -protons from the adjacent carbons of the keto groups and thus forming a cumulene type of ionic species as shown in (1). The loss of carbon monoxide occurred due to the fission of two carbon-carbon single bonds and then making new bond between methylene and methine groups of the side-chain. Ionic species 1 underwent further fragmentation to lose 127 mass units ( $C_{10}H_7$ ) forming a much stable charged species (3), which readily loses 14 mass units ( $CH_2$ ) giving rise to the ionic species (4). The charged species (4) shows stepwise losses of 132 ( $C_9H_8O$ ), 26 ( $C_2H_2$ ), 25 ( $C_2H$ ) and 27 (CHN), in the side chain, giving rise to peaks at  $m/e$  92<sup>+</sup>, 66<sup>+</sup>, 41<sup>+</sup> and 39<sup>+</sup> respectively.

The molecular ion also loses one benzene ring at the end of the side chain, giving rise to a very intense peak at  $m/e$  306<sup>+</sup> (5). This ionic species underwent systematic losses of 14 ( $CH_2$ ), 14 ( $CH_2$ ), 26 ( $C_2H_2$ ) and 93 ( $C_6H_5O$ ), giving rise to peaks at  $m/e$  292<sup>+</sup>, 278<sup>+</sup>, 252<sup>+</sup> and 159<sup>+</sup>. The ionic species (6) simultaneously loses 18 mass units due to the loss of a molecule of water and the resulting ionic species then loses 90 mass units ( $C_7H_6$ ) forming charged species 7 and 8 respectively.

In yet another mode of fragmentation the molecular ion loses 28 mass units ( $-CO$ ) forming

charged species (2) which loses 15 mass units (NH) due to the rupture of C-N bond giving rise to peaks at  $m/e$  340<sup>+</sup> (9). The ionic species (9) underwent stepwise fragmentation to lose 103 ( $C_8H_7$ ), 103 ( $C_8H_7$ ), 14 ( $CH_2$ ), 55 ( $C_3H_3O$ ), and 14 ( $CH_2$ ), mass units giving rise to peaks at  $m/e$  237<sup>+</sup>, 134<sup>+</sup>, 120<sup>+</sup>, 65<sup>+</sup> and 51<sup>+</sup>, corresponding to ionic species (10), (11), (12), (13), and (14) respectively. All these ionic species are outlined in Chart 1.

The mass spectrum of  $\alpha, \alpha'$ -di-(3-keto-5-phenylpentyl) pyrrole (II) showed a very intense molecular ion peak at  $m/e$  387<sup>+</sup>, which loses a molecule of water with the simultaneous migration of two hydrogen atoms from the two methylene groups  $\alpha$  to the carbonyl group. It is interesting to observe that in the saturated compounds the loss of CO does not occur, but the charged ionic species  $m/e$  369<sup>+</sup> again loses a molecule of water, giving rise to a charged species  $m/e$  351<sup>+</sup> (15). This ion underwent stepwise losses of 129 ( $C_{10}H_9$ ), 13 (CH), 129 ( $C_{10}H_9$ ), 14 ( $CH_2$ ) and 27 (CHN) mass units, corresponding to the charged species (16), (17), (18), (19) and (20), at  $m/e$  222<sup>+</sup>, 209<sup>+</sup>, 80<sup>+</sup>, 66<sup>+</sup>, and 39<sup>+</sup>. The ionic species (19) also gave rise to an ionic species  $m/e$  41<sup>+</sup> (21) with the loss of 25 ( $C_2H$ ) mass units.

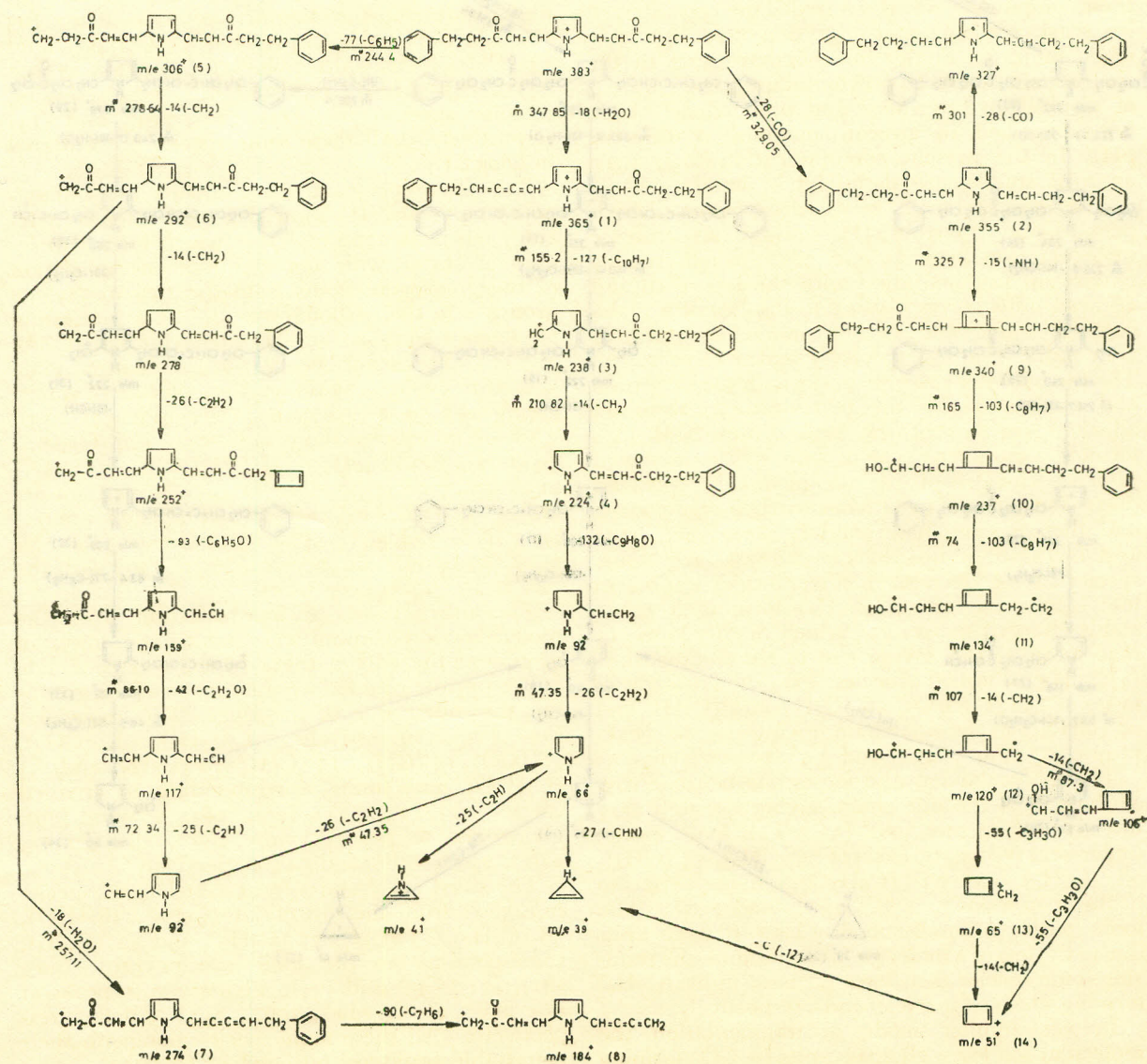
The other route of fragmentation from the molecular ion showed very systematic losses of groups at the end of the side-chain on one side of the pyrrole ring followed by losses of the groups on the other side of the ring. The molecular ion loses successively 91 ( $C_7H_7$ ), 14 ( $CH_2$ ), 28 (CO), 14 ( $CH_2$ ), 13 (CH), 79 ( $C_6H_7$ ) and 54 ( $C_3H_2O$ ) mass units, corresponding to charged species (22), (23), (24), (25), (26), (27) and (28), giving rise to peaks at  $m/e$  296<sup>+</sup>, 282<sup>+</sup>, 254<sup>+</sup>, 240<sup>+</sup>, 227<sup>+</sup>, 148<sup>+</sup> and 94<sup>+</sup> respectively.

The third route starts from the charged species  $m/e$  369<sup>+</sup> from the loss of 91 ( $C_7H_7$ ), 18 ( $H_2O$ ), 38 ( $C_3H_2$ ), 13 (CH), 77 ( $C_6H_5$ ), and 52 ( $C_4H_4$ ), corresponding to the ionic species (29), (30), (31), (32), (33) and (34), giving rise to peaks at  $m/e$  278<sup>+</sup>, 260<sup>+</sup>, 222<sup>+</sup>, 209<sup>+</sup>, 132<sup>+</sup> and 80<sup>+</sup> respectively. All these ionic species along with their metastable peaks are outlined in Chart 2.

The mass spectrum of  $\alpha,\alpha'$ -di-(2-benzoyl-ethyl) pyrrole (III) showed molecular ion peak at  $m/e$  331<sup>+</sup>. The fragmentation pattern of this compound is quite analogous to that of the previous two compounds. However, it is interesting to note that fragmentation process does not commence with the loss of a molecule of water as in the case of  $\alpha,\alpha'$ -di-(3-keto-5-phenylpent- $\Delta^4$ -enyl)pyrrole (I) or  $\alpha,\alpha'$ -di(3-keto-5-phenylpentyl)pyrrole (II) as described earlier. This can be due to absence of unsaturation and absence of two methylene groups—one each on either side of the two keto groups in the molecule. The molecular ion underwent fragmentation to lose 105 (C<sub>7</sub>H<sub>5</sub>O),

14 (CH<sub>2</sub>), 13 (CH), 105 (C<sub>7</sub>H<sub>5</sub>O), 14 (CH<sub>2</sub>), and 14 (CH<sub>2</sub>) mass units, corresponding to the charged species (35), (36), (37), (38), (39) and (40), giving rise to intense peaks at  $m/e$  226<sup>+</sup>, 212<sup>+</sup>, 199<sup>+</sup>, 94<sup>+</sup>, 80<sup>+</sup> and 66<sup>+</sup>. The charged species  $m/e$  226<sup>+</sup> (35) underwent successive losses of 106 (C<sub>7</sub>H<sub>6</sub>O), 27 (C<sub>2</sub>H<sub>3</sub>), 28 (C<sub>2</sub>H<sub>4</sub>) and 16 (NH<sub>2</sub>) corresponding to the ionic species (41), (42), (43) and (44); giving rise to peaks at  $m/e$  120<sup>+</sup>, 93<sup>+</sup>, 65<sup>+</sup> and 49<sup>+</sup> respectively. All these charged species and the other most intense peaks at  $m/e$  106<sup>+</sup>, 93<sup>+</sup>, 79<sup>+</sup>, 67<sup>+</sup>, 66<sup>+</sup>, 65<sup>+</sup>, 41<sup>+</sup> and 28<sup>+</sup> are shown in Chart 3. The mass spectrum of *N,N*-diskatylpiperazine (IV) showed a molecular ion peak at  $m/e$  344<sup>+</sup>.

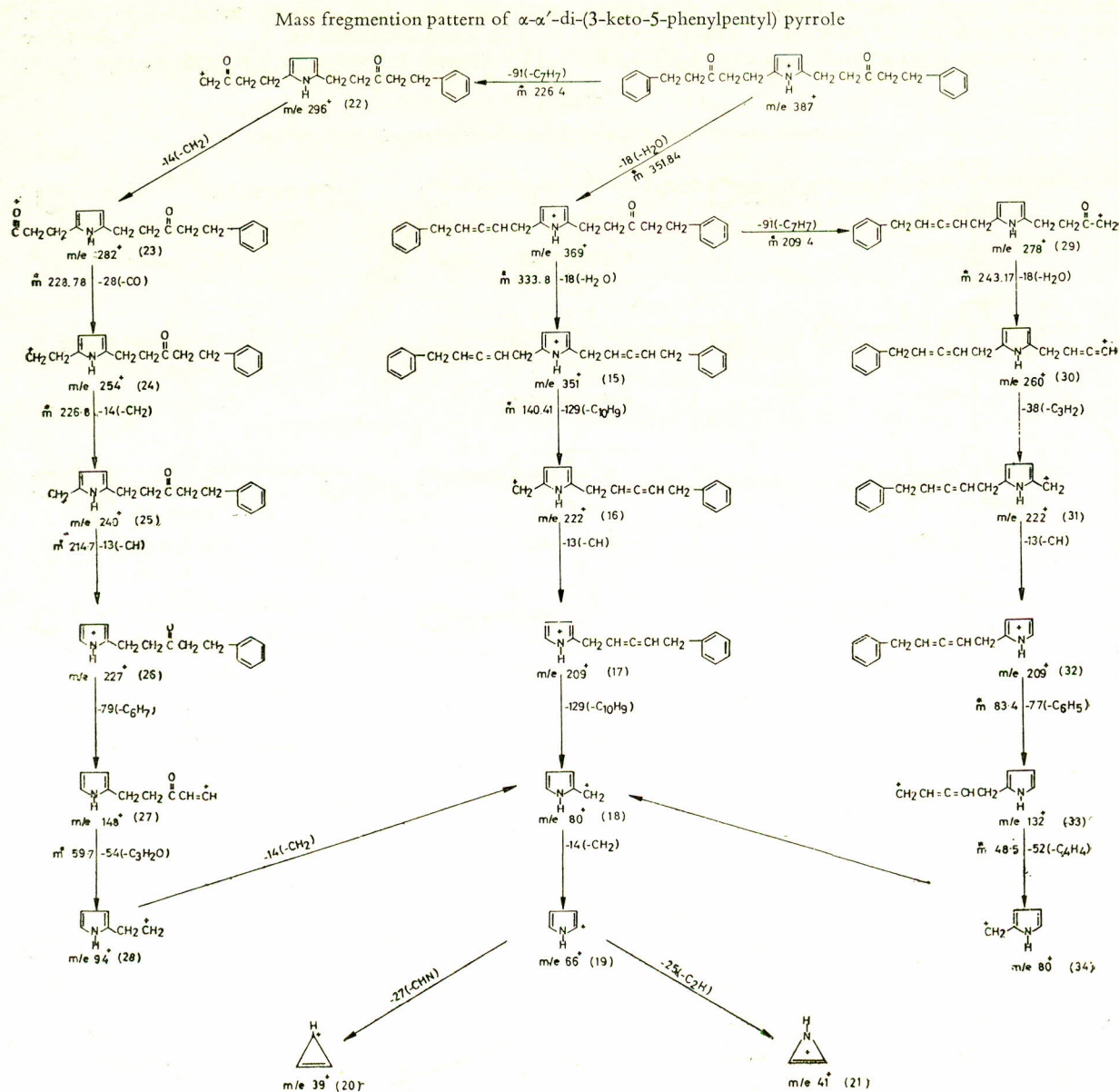
Chart 1  
 Mass fragmentation pattern of  $\alpha,\alpha'$ -di(3-keto-5-phenylpent- $\Delta^4$ -enyl) pyrrole



This ion underwent successive losses of 115 ( $C_8H_5N$ ), 14 ( $CH_2$ ), 85 ( $C_4H_9N_2$ ), 13 ( $CH$ ), 27 ( $CHN$ ) and 14 ( $CH_2$ ) mass units, corresponding to ionic species (45), (46), (47), (48), (49) and (50), giving rise to intense peaks at  $m/e$  229<sup>+</sup>, 215<sup>+</sup>, 130<sup>+</sup>, 117<sup>+</sup>, 90<sup>+</sup> and 76<sup>+</sup>. The ionic species (45) underwent stepwise losses of 116 ( $C_8H_6N$ ), 14 ( $CH_2$ ), 14 ( $N$ ), 29 ( $-CH_3N$ ), 5 ( $H_3$ )

and 12 ( $C$ ) mass units, corresponding to ionic species (51), (52), (53), (54), (55), and (56), giving rise to peaks at  $m/e$  113<sup>+</sup>, 99<sup>+</sup>, 85<sup>+</sup>, 56<sup>+</sup>, 51<sup>+</sup>, and 39<sup>+</sup>. Whereas the formation of all these peaks are simple straightforward losses of each group, the charged species  $m/e$  246<sup>+</sup> was formed due to the intermolecular rearrangement in the ionizing chamber. It was formed with the loss of 98

Chart 2



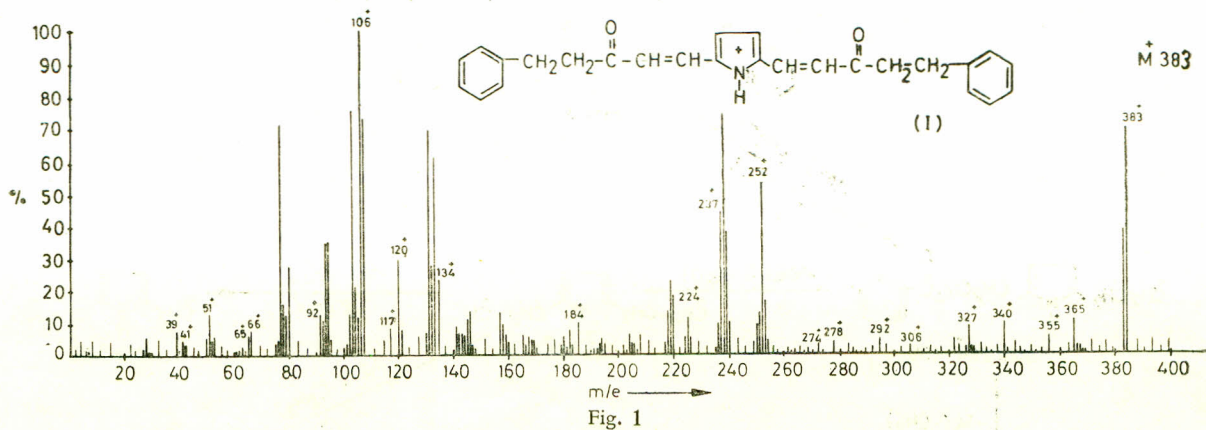
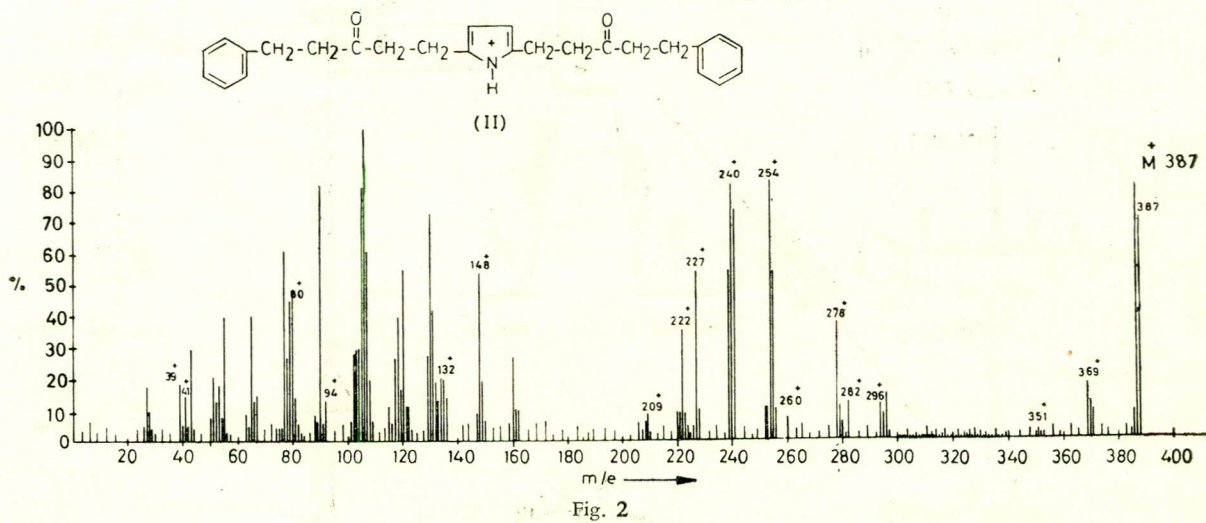
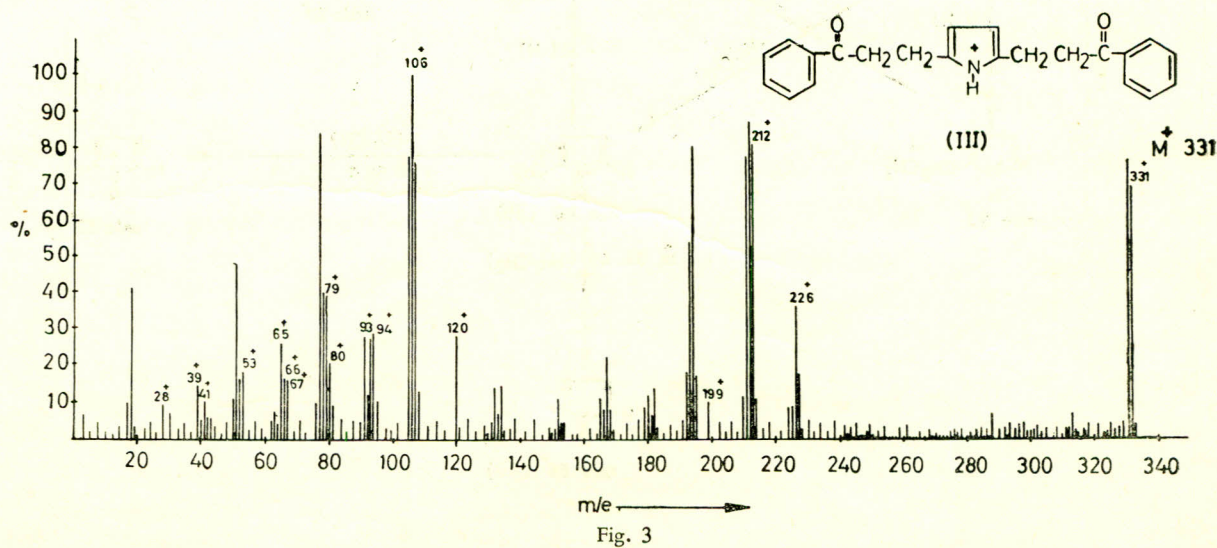
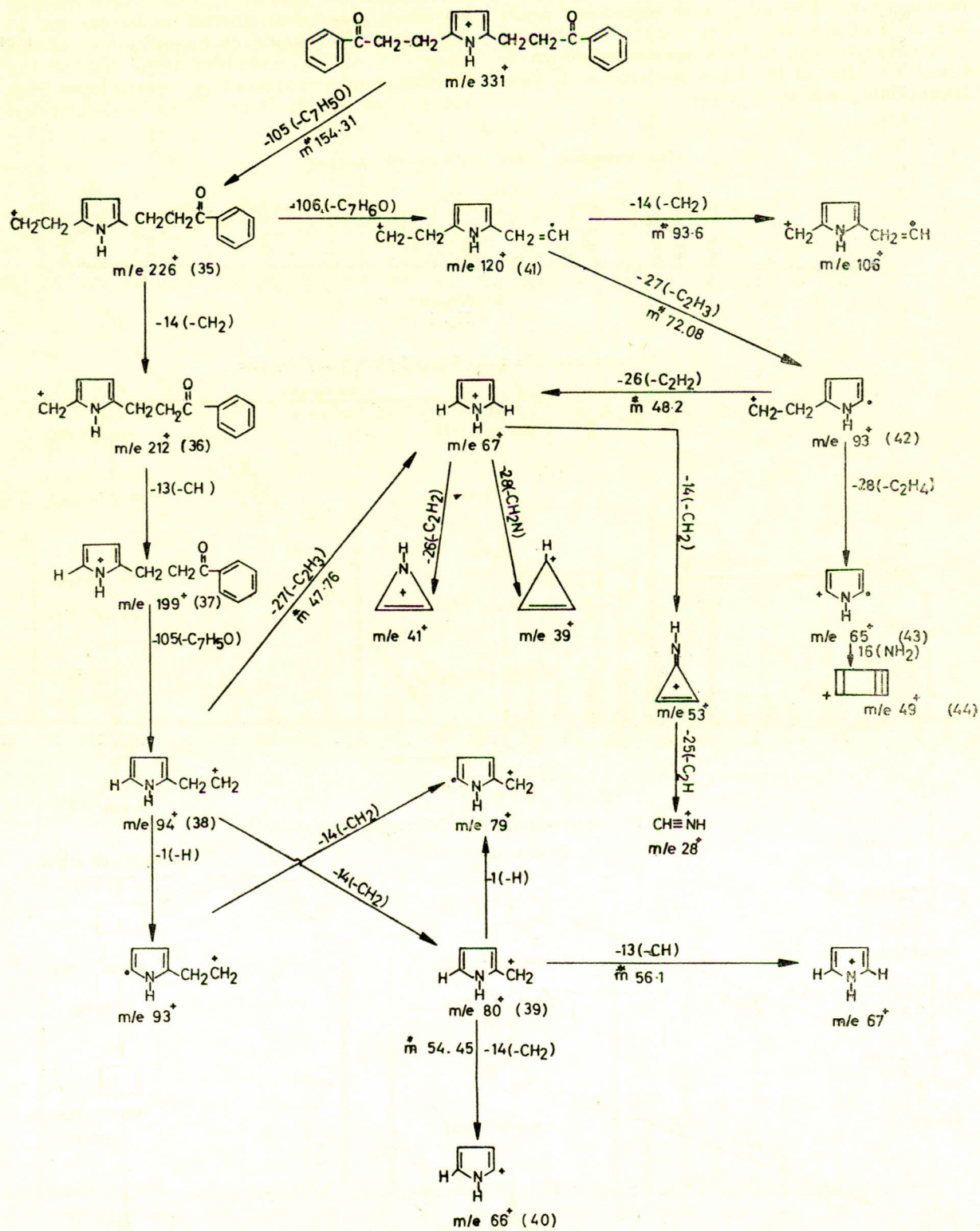
Mass spectrum of  $\alpha,\alpha'$ -di-(3-keto-5-phenyl-pent- $\Delta^4$ -enyl)-pyrrole

 Mass spectrum of  $\alpha,\alpha'$ -di-(3-keto-5-phenylpentyl) pyrrole

 Mass spectrum of  $\alpha,\alpha'$ -di-(2-benzoyl ethyl) pyrrole


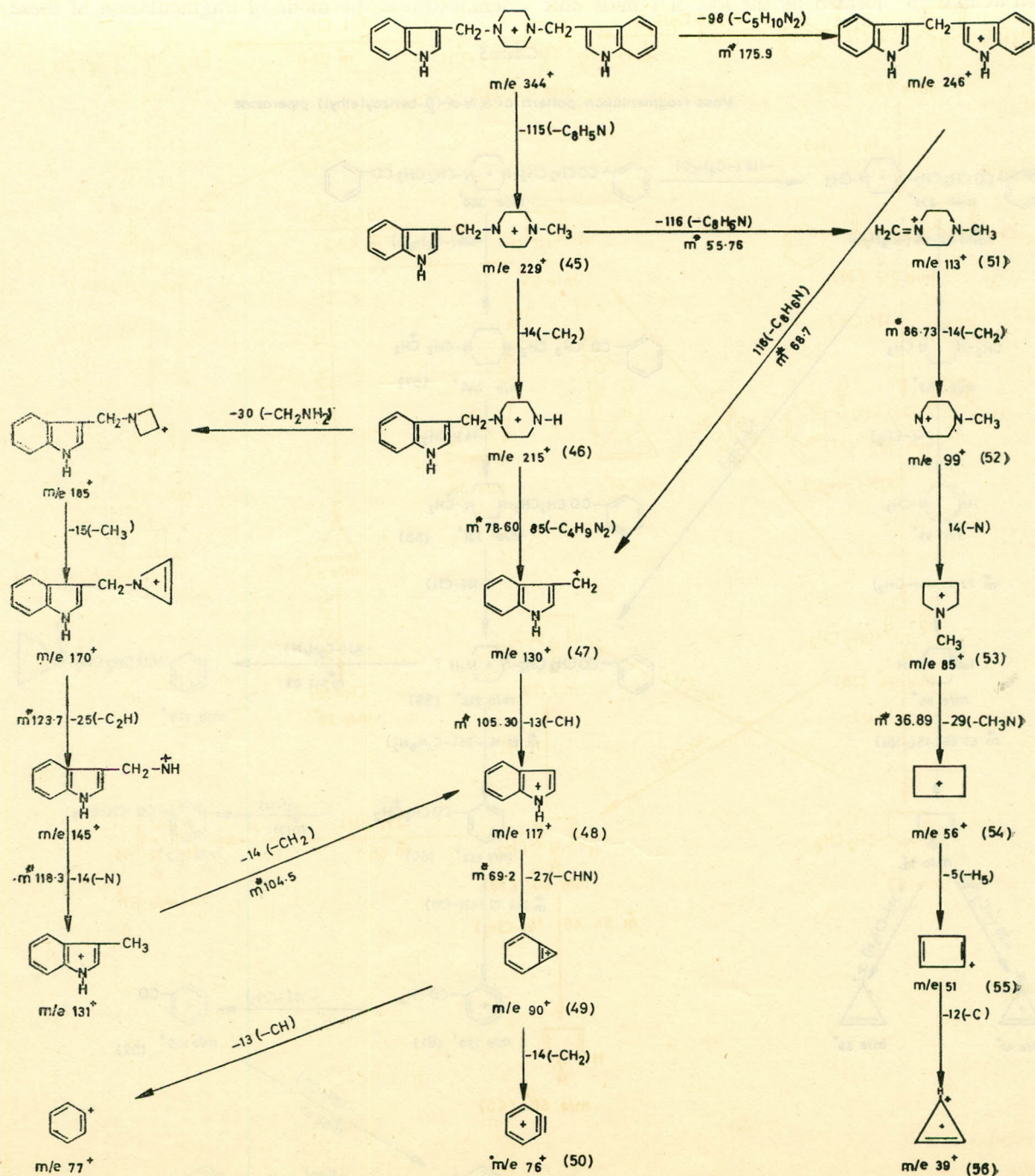
Chart 3

Mass fragmentation pattern of  $\alpha,\alpha'$ -di-(2 benzoyl ethyl) pyrrole

$(C_5H_{10}N_2)$  mass units, giving rise to this very intense peak. The other most significant peaks appeared at  $m/e$  185<sup>+</sup>, 170<sup>+</sup>, 145<sup>+</sup>, 131<sup>+</sup>, and 77<sup>+</sup>, corresponding to ionic species as shown in Chart 4. Most of the losses occurred with their appropriate metastable peaks.

The mass spectrum of *N,N*-di-( $\beta$ -benzoylethyl) piperazine showed an intense molecular ion at  $m/e$  350<sup>+</sup>. The mode of fragmentation of this compound closely resembles with that of the previous compounds recording stepwise losses from one side of the molecule. The molecular ion

Chart 4

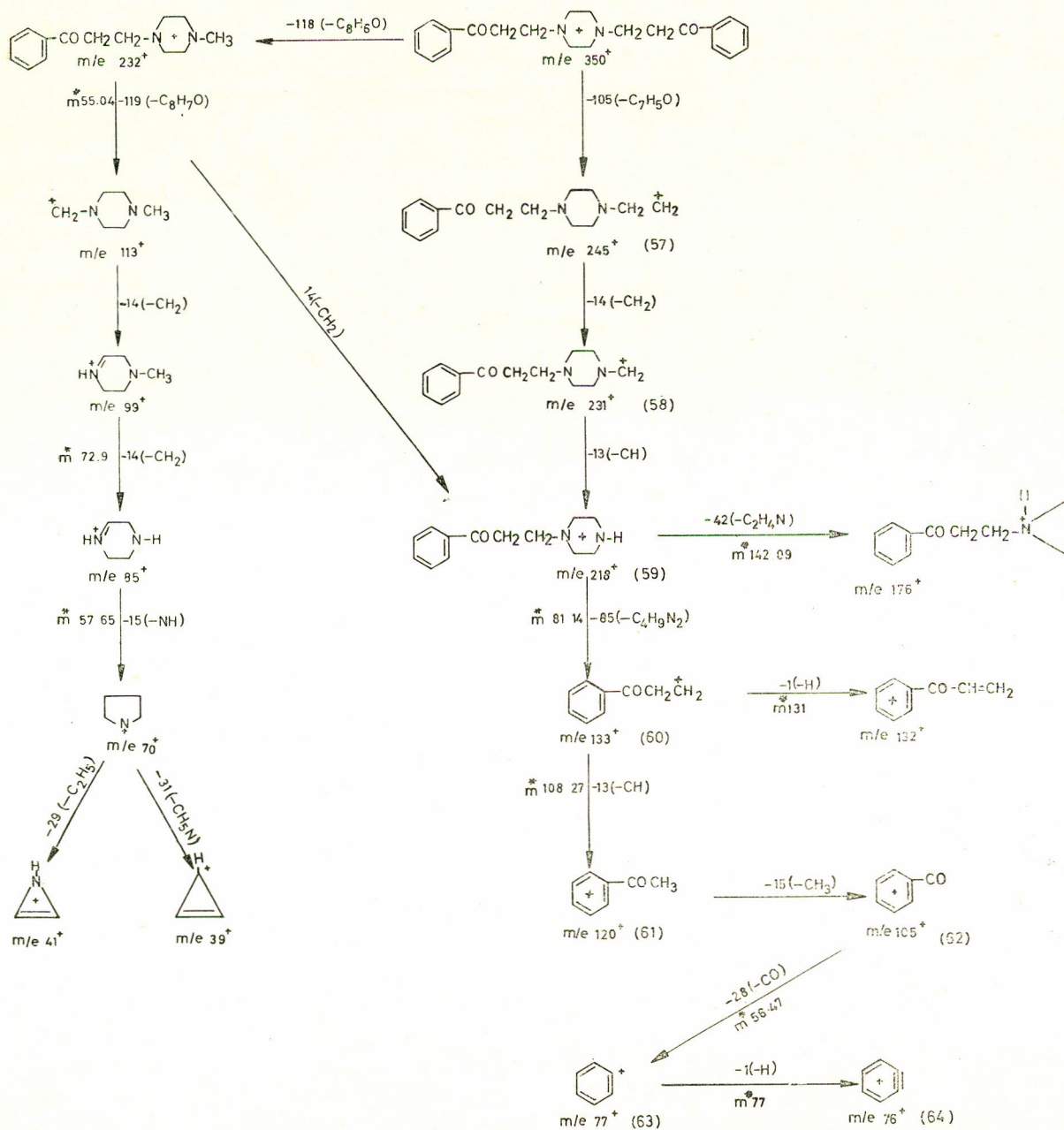
 Mass fragmentation pattern of *N,N*-diskatyl piperazine


underwent fragmentation successively to lose 105 ( $C_7H_5O$ ), 14 ( $CH_2$ ), 13 ( $CH$ ), 85 ( $C_4H_9N_2$ ), 13 ( $CH$ ), 15 ( $CH_3$ ), and 28 ( $CO$ ) mass units, corresponding to charged species (57), (58), (59), (60), (61), (62) and (63), giving rise to peaks at  $m/e$  245<sup>+</sup>, 231<sup>+</sup>, 218<sup>+</sup>, 133<sup>+</sup>, 120<sup>+</sup>, 105<sup>+</sup>, and 77<sup>+</sup> respectively. The losses of all these fragments are due to fission of carbon-carbon single bonds. The last species (64) was the very stable phenonium ion at  $m/e$  76<sup>+</sup> formed by the loss of 1 mass unit

(H) from charged species (63). The second mode of fragmentation from the molecular ion occurred due to the transfer of one proton from the adjacent group to form much more stable charged ions at  $m/e$  232<sup>+</sup>, 113<sup>+</sup>, 99<sup>+</sup>, 85<sup>+</sup>, 70<sup>+</sup>, 41<sup>+</sup> and 39<sup>+</sup>. All these ionic species followed by their appropriate metastable peaks are outlined in Chart 5.

The above comparative studies of mass spectra of pyrrole and piperazine derivatives have clearly demonstrated the mode of fragmentation of these

Chart 5

Mass fragmentation pattern of *N,N*-di-( $\beta$ -benzoyl)ethyl piperazine

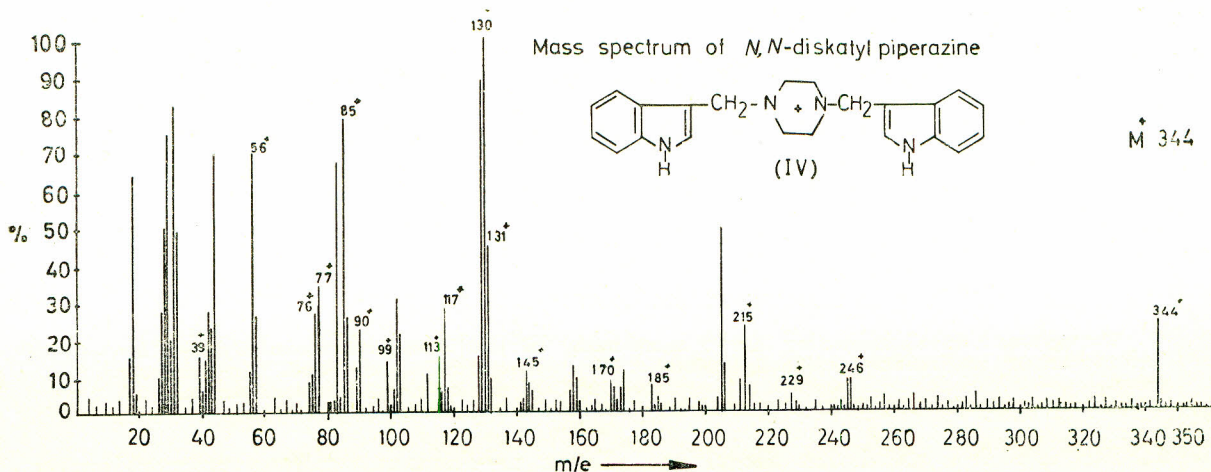


Fig. 4

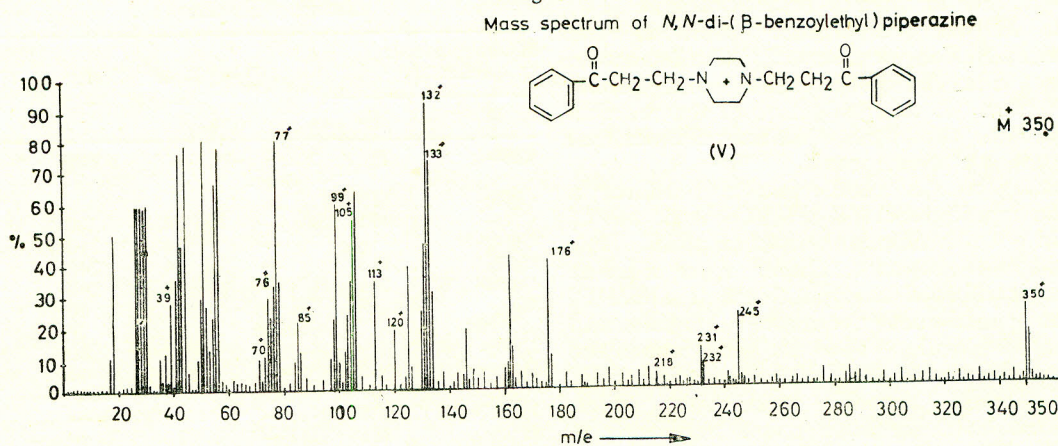


Fig. 5

symmetrical disubstituted compounds, losing successively groups from the side chain in a very rational manner. Moreover, most of the ionic species formed due to rearrangement or transfer of protons, mainly depending on the degree of unsaturation in the side chain. The loss of a molecule of water in pyrrole series could only be explained with the migration of a proton to the carbonyl oxygen from the methylene or the methine groups, on one side followed by elimination of a molecule of water formed with the proton contributed by the  $\alpha$ -methylene on the other side of the same keto group. It is further interesting to observe the loss of carbon monoxide from the middle of the side-chain ( $m/e$  327<sup>+</sup> from  $m/e$  355 (2) in  $\alpha,\alpha'$ -di-(3-keto-5-phenylpent- $\Delta^4$ -enyl)pyrrole (I) which has a double bond in the side-chain. This elimination is reminiscent of similar losses in the case of cyclic ketone. This elimination of CO is not however, observed in the case of  $\alpha,\alpha'$ -di-(3-keto-5-phenylpentyl) pyrrole (II),  $\alpha,\alpha'$ -di-(2-benzoyl ethyl) pyrrole (III), and *N,N*-di-( $\beta$ -benzoyl ethyl)piperazine (V).

#### Experimental

The mass spectra were measured on AEI MS9 at 70 eV.

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