Mass Spectral Fragmentation Pattern of 5*H*-Cyclopenta[2,1-*b*:3,4-*b'*]dipyridin-5-one

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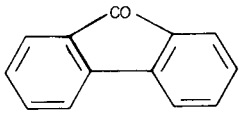
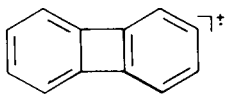
Received May 26, 1975

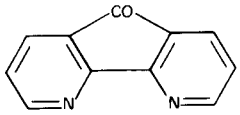
The mass spectrum of fluoren-9-one (I) has attracted much attention (1-6), the principal initial fragmentation being the loss of neutral CO from the molecular ion (I) (2) to afford the *o*-biphenylene molecular ion (II). This is followed by loss of mass 26 presumably due to fragmentation of one of the benzene rings (2) with loss of C_2H_2. There has been no report of the mass spectra of related diazafluorenones. The recently reported facile synthesis (7) of the hitherto difficultly accessible 5*H*-cyclopenta-[2,1-*b*:3,4-*b'*]dipyridin-5-one (4,5-diazafluoren-9-one) (III) enables its chemistry to be more readily studied. We now report on its mass spectral fragmentation pattern.



I

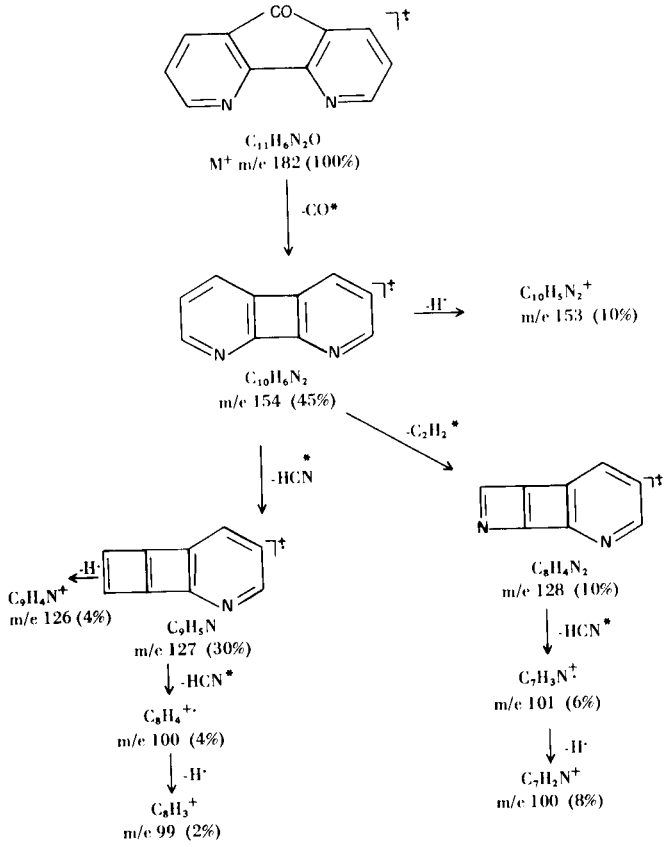


II



III

As expected the most intense peak in the mass spectrum of III is due to the molecular ion (Figure). The second most intense peak (45% of the molecular ion) results from loss of CO from the molecular ion to give a $C_{10}H_6N_2$ ion considered to be the corresponding diazabiphenylene ion formed by a process analogous to that observed with fluoren-9-one (I) (2). The fragmentation then proceeds along two pathways as depicted in the Scheme in addition to loss of H· to give the $C_{10}H_5N_2$ ion. Both pathways involve rupture of one of the pyridine rings with concomitant loss of neutral fragments. One pathway results in loss of HCN to give C_9H_5N ion of high intensity (30% of molecular ion) while the other involves loss of C_2H_2 to give a $C_8H_4N_2$ ion (10%). These two fragments are depicted as fused cyclobutadiene type structures. The C_9H_5N ion then loses a further HCN molecule to give the C_8H_4 ion of mass 100 which subsequently loses an H· to give the



SCHEME

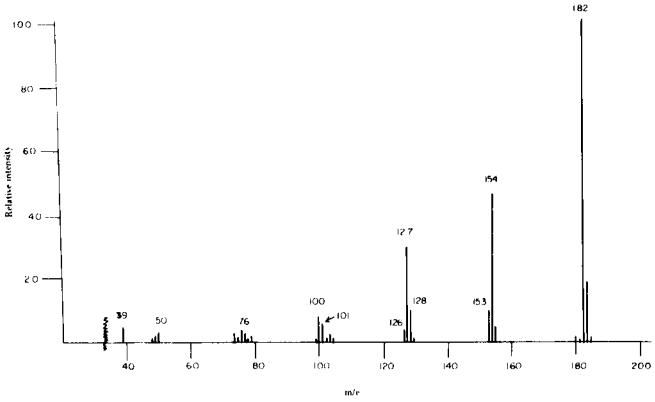
$C_8H_3^+$ species. Similarly the $C_8H_4N_2$ ion also loses an HCN molecule to afford the C_7H_3N ion. This too loses an H· to afford the C_7H_2N ion which also has a mass of 100. Further fragmentation of these ions results in the low intensity peaks below a mass of 80 in the spectrum.

The elemental composition of all the ions depicted in the Scheme was in accord with high resolution data (Table I). The loss of the five neutral components (depicted in the Scheme by an asterisk) was supported by the observation of the appropriate metastable transitions (Table II).

Table 1

High Resolution Data for
5*H*-Cyclopenta[2,1-*b*:3,4-*b*′]dipyridin-5-one

m/e	Elemental Composition	Observed Mass	Calculated Mass
154	$C_{10}H_6N_2$	154.0532	154.0531
153	$C_{10}H_5N_2$	153.0453	153.0452
128	$C_8H_4N_2$	128.0376	128.0374
127	C_9H_5N	127.0424	127.0422
126	C_9H_4N	126.0343	126.0344
101	C_7H_3N	101.0265	101.0265
100	C_7H_2N	100.0185	100.0187
100	C_8H_4	100.0311	100.0313
99	C_8H_3	99.0234	99.0235



Mass Spectrum of 5*H*-Cyclopenta[2,1-*b*:3,4-*b*′]dipyridin-5-one.

Table 2

Metastable Ions Present in the Mass Spectrum of
5*H*-Cyclopenta[2,1-*b*:3,4-*b*′]dipyridin-5-one

Initial Ion	Resultant Ion	Transition	Calculated m*	Found m*	Fragment Expelled
$C_{11}H_6N_2O$	$C_{10}H_6N_2$	182 → 154	130.3	130.5	CO
$C_{10}H_6N_2$	C_9H_5N	154 → 127	104.7	104.8	HCN
$C_{10}H_6N_2$	$C_8H_4N_2$	154 → 128	106.4	106.4	C_2H_2
C_9H_5N	C_8H_4	127 → 100	78.7	78.8	HCN
$C_8H_4N_2$	C_7H_3N	128 → 101	79.7	79.7	HCN

EXPERIMENTAL

The mass spectra were determined with an A.E.I. MS-30 mass spectrometer. The sample was analysed by a direct insertion probe at an ionising current of 70 eV. Elemental compositions were obtained by the peak matching method.

5*H*-Cyclopenta[2,1-*b*:3,4-*b*′]dipyridin-5-one.

This compound had m.p. 214-215° and was analytically pure (7).

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