Mass Spectral Fragmentation Pattern of 2,2'-Bipyridyls. Part 1. 2,2'-Bipyridyl

N. C. Keats and L. A. Summers

Department of Chemistry, University of Newcastle, 2308, New South Wales, Australia

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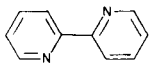
The mass spectrum of 2,2'-bipyridyl (I) has been reported and a fragmentation pattern suggested (1) although few metastable transitions and no high resolution mass measurements were obtained to support the proposed decomposition scheme. We have re-investigated its mass spectrum as a preliminary to the study of a series of substituted 2,2'-bipyridyls. Our results show that some of the suggested fragmentations are incorrect and that the decomposition of 2,2'-bipyridyl in the mass spectrometer is more complex than previously supposed.



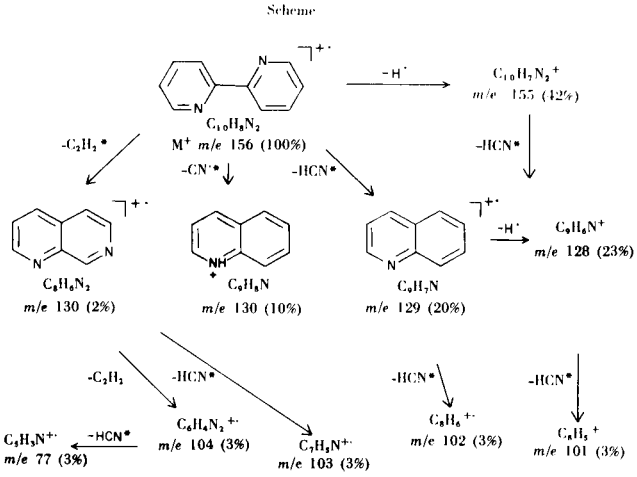
I

The most intense peak in the mass spectrum of 2,2'-bipyridyl is due to the molecular ion (Figure). The second most intense peak (42% of the molecular ion) at mass 155 results from loss of H· to give the $C_{10}H_7N_2$ ion. This result recalls the similar predominance of the molecular ion and the M-1 species in the mass spectrum of biphenyl (2).

The peak at mass 130 was considered by the Russian group (1) to result from the loss of C_2H_2 from the molecular ion to give a $C_8H_6N_2$ species depicted as a naphthyridine molecular ion. Accurate mass measurements of this peak, however, show that it is made up of two components. The principal component (10% of the molecular ion) has empirical formula of C_9H_8N due to loss of CN· from the molecular ion. It is depicted as being due to the quinolinium ion. A small peak (2% of the molecular ion) corresponds to the formula $C_8H_6N_2$ resulting from loss of C_2H_2 from the molecular ion.

The peak at mass 129 (20% of the molecular ion) corresponds to loss of neutral HCN from the molecular ion to give the $C_9H_7N^{+\cdot}$ species in agreement with the Russian group (1). It is considered to be due to the quinoline molecular ion. The peak at mass 128, C_9H_6N, (23% of the molecular ion) can result from loss of H· from the quinoline molecular ion. A strong metastable transition is present, however, which is due to the loss of HCN from the $C_{10}H_7N_2$ ion giving the C_9H_6N species.

Scheme



This indicates that the ion $C_9H_6N^+$ arises from more than one source.

There is a cluster of small intensity peaks (2-3% of the molecular ion) of mass 101-104 in the spectrum of 2,2'-bipyridyl. These are due to the loss of C_2H_2 or HCN from higher mass species as indicated in the Scheme. In most cases appropriate metastable transitions were observed.

The strong peak at mass 78 (22% of the molecular ion) is made up of contributions from the M^{++} species and the $C_5H_4N^+$ ion presumably formed by rupture of the central bond of 2,2'-bipyridyl.

Table 1

High Resolution Data for 2,2'-Bipyridyl

m/e	Elemental Composition	Observed Mass	Calculated Mass
130	$C_8H_6N_2$	130.0532	130.0531
130	C_9H_8N	130.0654	130.0657
129	C_9H_7N	129.0579	129.0578
128	C_9H_6N	128.0499	128.0500
104	$C_6H_4N_2$	104.0371	104.0374
103	C_7H_5N	103.0423	103.0422
102	C_8H_6	102.0470	102.0469
101	C_8H_5	101.0390	101.0391
78	C_5H_4N	78.0345	78.0344
77	C_5H_3N	77.0263	77.0265
77	C_6H_5	77.0394	77.0391

Table 2

Metastable Ions Present in the Mass Spectrum of 2,2'-Bipyridyl

Initial Ion	Resultant Ion	Transition	Calculated m*	Found m*	Fragment Expelled
$C_{10}H_8N_2$	C_9H_8N	156 → 130	108.3	108.2	CN
$C_{10}H_8N_2$	$C_8H_6N_2$	156 → 130	108.3	108.2	C_2H_2
$C_{10}H_8N_2$	C_9H_7N	156 → 129	106.7	106.6	HCN
$C_{10}H_7N_2$	C_9H_6N	155 → 128	105.7	105.8	HCN
$C_8H_6N_2$	C_7H_5N	130 → 103	81.6	81.6	HCN
C_9H_7N	C_8H_6	129 → 102	80.7	80.7	HCN
C_9H_6N	C_8H_5	128 → 101	79.7	79.8	HCN
$C_6H_4N_2$	C_5H_3N	104 → 77	57.0	57.0	HCN

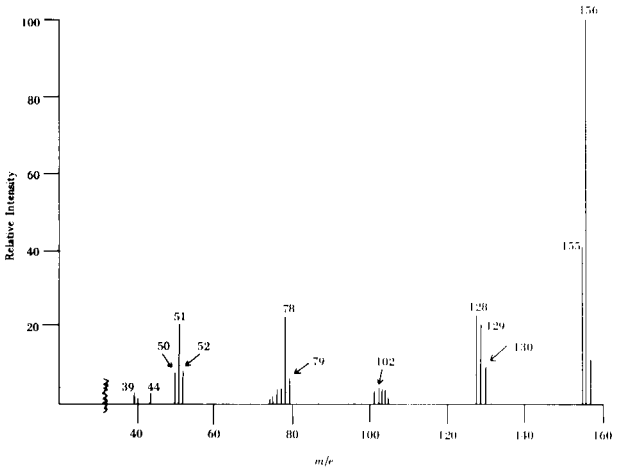


Figure. Mass Spectrum of 2,2' Bipyridyl

The peaks of mass lower than 78 in the spectrum are typical of those obtained from pyridine and quinoline (3) and do not require comment apart from the peak at mass 77 (3% of the molecular ion). This peak was considered by the Russians (1) to be due to the $C_6H_5^+$ ion. Accurate mass measurements reveal that the principal component of the peak at mass 77 is due to the $C_5H_3N^{+\cdot}$ species which is formed from the $C_6H_4N_2^{+\cdot}$ species (mass 104) by loss of HCN. The $C_6H_5^+$ ion is present in only very small amounts (less than 1% of the molecular ion).

The elemental composition of all the ions depicted in the Scheme was in accord with high resolution data (Table 1). The loss of the components, depicted in the Scheme by an asterisk, was supported by the observation of the appropriate metastable transitions.

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 70eV. The ion source temperature was 60°. Elemental compositions were obtained by the peak matching method.

2,2'-Bipyridyl was analytically pure.

REFERENCES AND NOTES

(1) R. A. Khmel'nitskii, N. A. Klyuev and P. B. Terent'ev, *Zh. Org. Khim.*, **7**, 395 (1971).

(2) P. Natalis and J. L. Franklin, *J. Phys. Chem.*, **69**, 2935 (1965); J. H. D. Eland and C. J. Danby, *J. Chem. Soc.*, 5935 (1965); J. L. Laseter, U. Mende and G. W. Griffin, *Org. Mass Spectrom.*, **4**, 599 (1970).

(3) Q. N. Porter and J. Baldas, "Mass Spectrometry of Heterocyclic Compounds", Wiley-Interscience, New York, 1971, p. 376 and p. 399.