

Mass Spectral Fragmentation Pattern of 2,2'-Bipyridyls Part IV. Di-2-pyridyl Ketone

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The fragmentation of di-2-pyridyl ketone on electron impact involves elimination of neutral CO from the molecular ion and rearrangement to the 2,2'-bipyridyl molecular ion in addition to rupture of the central bonds to form $C_5H_4N^+$ and $C_6H_4NO^+$ ions.

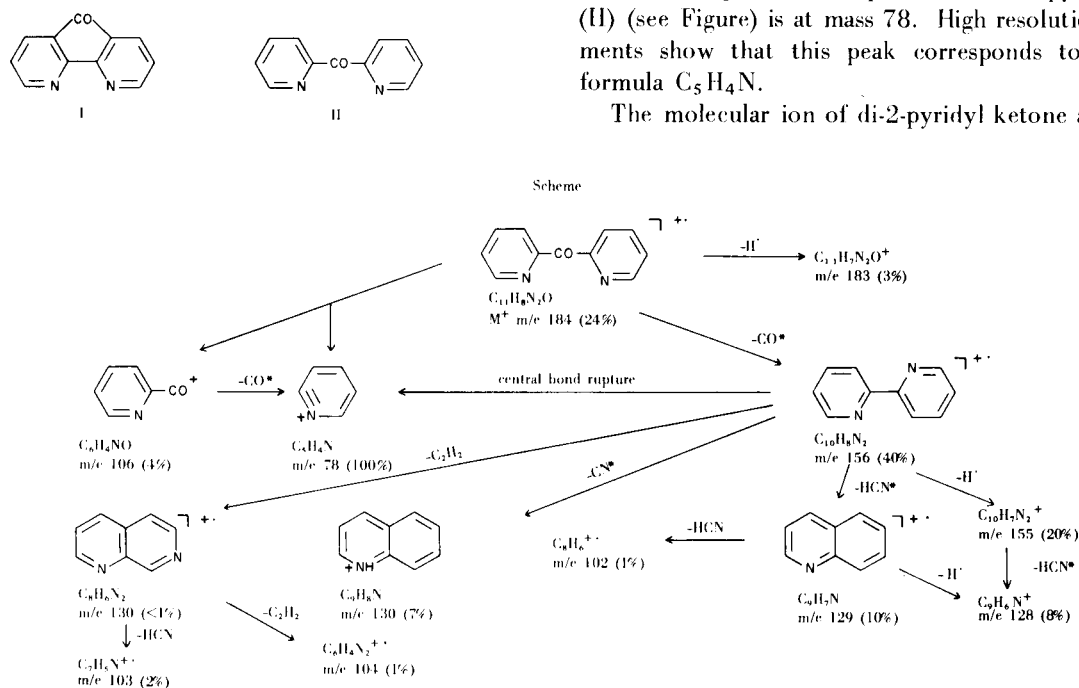
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The mass spectra of benzophenones obtained by electron impact have received much attention (2-17). The spectrum of benzophenone itself is relatively simple (2,3). The main fragmentation consists of rupture of one of the CO-Ph bonds to afford the $C_6H_5CO^+$ ion which is the base peak. The molecular ion and the $C_6H_5^+$ species are the only other prominent peaks above a mass of 70 in the spectrum. There is a cluster of very small peaks in the mass range 152-154 (1-2% of the base peak) corresponding to the $C_{12}H_{10}^{++}$ species and its dehydrogenated derivatives formed by elimination of neutral CO from the molecular ion. We recently reported (18) the fragmentation pattern of 5*H*-cyclopenta[2,1-*b*:3,4-*b'*]dipyridin-5-one (I). The principal initial fragmentation in this case

consisted of loss of neutral CO to form a diazabiphenylene molecular ion. As part of our study of the mass spectra of 2,2'-bipyridyl and its derivatives we have now carried out a careful study of the mass spectrum of di-2-pyridyl ketone (di-2-pyridinylmethanone) (II) to compare its behaviour with that of benzophenone and 5*H*-cyclopenta[2,1-*b*:3,4-*b'*]dipyridin-5-one. A very brief report of some of the peaks in the mass spectrum of di-2-pyridyl ketone was published several years ago (19) but no details of the spectrum were given. No high resolution mass measurements nor metastable transitions were reported. The spectra of closely related phenyl pyridyl ketones have been recorded (19,20).

The base peak in the spectrum of di-2-pyridyl ketone (II) (see Figure) is at mass 78. High resolution measurements show that this peak corresponds to species of formula C_5H_4N .

The molecular ion of di-2-pyridyl ketone at mass 184



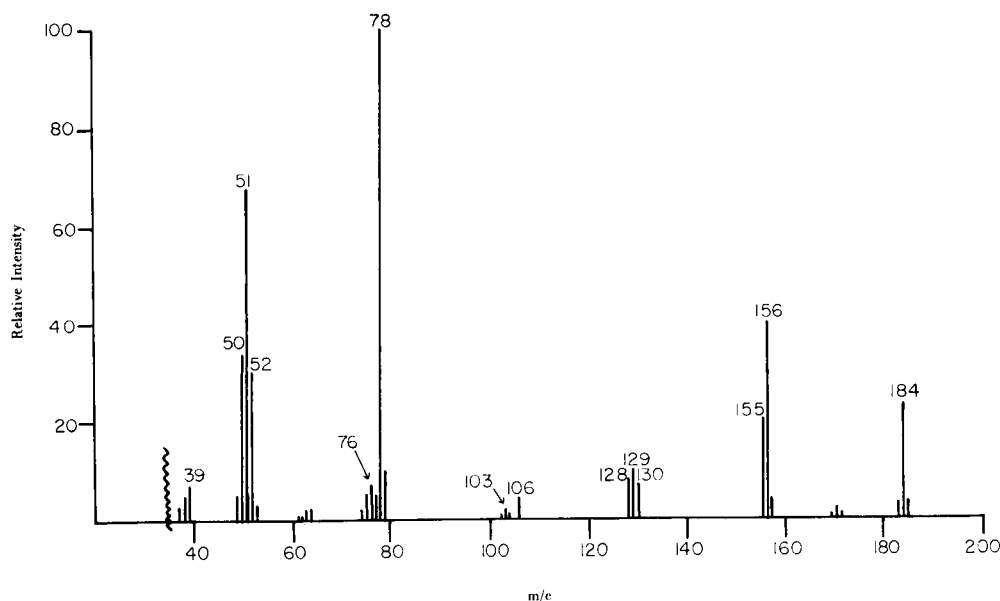


Figure: Mass Spectrum of Di-2-pyridyl Ketone.

gives a peak of about 24% of the intensity of the base peak. A small peak (3% of base peak) is present at mass 183 corresponding to the loss of H^+ from the molecular ion.

A strong peak (40%) at mass 156 of empirical formula $C_{10}H_8N_2$ corresponds to the loss of neutral CO from the molecular ion. There is a strong metastable peak analogous to this transition. This fragmentation route is much more pronounced than the corresponding loss of CO from the benzophenone molecular ion but is similar to that observed with the 5*H*-cyclopenta[2,1-*b*:3,4-*b'*]-dipyridin-5-one molecular ion. The peak at mass 156 ($C_{10}H_8N_2$) is considered to be due to the 2,2'-bipyridyl molecular ion (see Scheme).

The subsequent fragmentation of the $C_{10}H_8N_2$ species is in keeping with this structural assignment. There is a fairly intense peak (20%) at mass 155 of formula $C_{10}H_7N_2$ due to the 2,2'-bipyridyl molecular ion less one hydrogen and a group of peaks at mass 130 ($C_9H_8N^+$), 129 ($C_9H_7N^+$) and 128 ($C_9H_6N^+$) of 7-10% of the intensity of the base peak considered to be due to the quinolinium ion, the quinoline molecular ion, and the quinoline molecular ion less one hydrogen respectively obtained by rearrangement of the 2,2'-bipyridyl molecular ion. The peak at mass 130 is in fact made up of two components, the lesser contribution (< 1%) being due to a species of formula $C_8H_6N_2$ considered to be a naphthyridine molecular ion. These peaks are all of the same composition and similar relative intensity to those already reported in the mass spectrum of 2,2'-bipyridyl (21). Moreover, as in the spectrum of 2,2'-bipyridyl there

is a cluster of small intensity peaks (1-2% of base peak) at mass 104 ($C_6H_4N_2^+$), 103 ($C_7H_5N^+$) and 102 ($C_8H_6^+$).

The peak at mass 106 (4%) corresponds to the formula C_6H_4NO and is clearly due to the $C_5H_4N-CO^+$ ion formed by rupture of one of the CO-pyridyl bonds of di-2-pyridyl ketone.

The base peak at mass 78 of formula C_5H_4N is mainly due to the pyridine molecular ion less one hydrogen. It can be formed by rupture of a CO-pyridyl bond in di-2-pyridyl ketone or by loss of CO from the $C_6H_4NO^+$ ion of mass 106. Contributions to the $C_5H_4N^+$ ion can also come from rupture of the central bond of 2,2'-bipyridyl.

Table 1

High Resolution Data for Di-2-pyridyl Ketone

m/e	Elemental Composition	Observed Mass	Calculated Mass
156	$C_{10}H_8N_2$	156.0687	156.0687
155	$C_{10}H_7N_2$	155.0609	155.0609
130	$C_8H_6N_2$ (< 1%)	130.0532	130.0531
130	C_9H_8N (7%)	130.0655	130.0657
129	C_9H_7N	129.0577	129.0578
128	C_9H_6N	128.0500	128.0500
106	C_6H_4NO	106.0293	106.0293
104	$C_6H_4N_2$	104.0376	104.0374
103	C_7H_5N	103.0418	103.0422
102	C_8H_6	102.0470	102.0469
78	C_5H_4N	78.0346	78.0344
77	C_6H_5 (1%)	77.0390	77.0391
77	C_5H_3N (5%)	77.0265	77.0265
76	C_6H_4 (1%)	76.0312	76.0313
76	C_5H_2N (7%)	76.0185	76.0187
75	C_6H_3 (1%)	75.0235	75.0235
75	C_5HN (5%)	75.0108	75.0109

Table 2

Metastable Ions Present in the Mass Spectrum of Di-2-pyridyl Ketone

Initial Ion	Resultant Ion	Transition	Calculated m*	Found m*	Fragment Expelled
C ₁₁ H ₈ N ₂ O	C ₁₀ H ₈ N ₂	184 → 156	132.3	132.3	CO
C ₁₀ H ₈ N ₂	C ₉ H ₈ N	156 → 130	108.3	108.4	CN
C ₁₀ H ₈ N ₂	C ₉ H ₇ N	156 → 129	106.7	106.6	HCN
C ₁₀ H ₇ N ₂	C ₉ H ₆ N	155 → 128	105.7	105.8	HCN
C ₆ H ₄ NO	C ₅ H ₄ N	106 → 78	57.4	57.4	CO

The M⁺⁺ ion of 2,2'-bipyridyl will also contribute to the base peak.

The peaks below a mass of 78 in the spectrum are typical of those to be expected from pyridine and quinoline derivatives (22) and require little comment. For instance the peaks at mass 77 (5%), 76 (7%) and 75 (5%) are each made up of two components (see Table 1). The nitrogen containing components are clearly derived from pyridine moieties by successive loss of hydrogen. The hydrocarbon components, all of which contain six carbons, are considered to be similarly derived from the benzene ring of quinoline which is formed by rearrangement of the 2,2'-bipyridyl 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.

Di-2-pyridyl ketone was analytically pure.

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