

## Mass Spectral Fragmentation Pattern of 2,2'-Bipyridyls. Part V. 2,2'-Oxydipyridine

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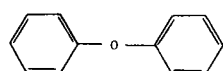
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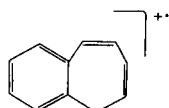
The mass spectrum of 2,2'-oxydipyridine obtained by electron impact is reported. The principal fragmentations involve loss of  $C_2HO$  and  $CO$  in addition to rupture of the central bonds. Molecular rearrangements accompany the fragmentations.

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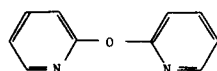
The mass spectrum of diphenyl ether (I) has been the subject of much interest (1-9). The spectrum is dominated by the peak due to the molecular ion at mass 170, which is the base peak. In addition to rupture of the central bonds, the initial major fragmentation involves loss of neutral  $CO$  from the molecular ion or the  $M-1$  ion to give species considered (1) to be the benzocycloheptatriene molecular ion (II) at mass 142 (about 20% of base peak) or its dehydrogenated form at mass 141 (about 40% of base peak). The spectrum of the closely related structure, 2-phenoxy pyridine has also been the subject of study (10) (11). We now report on the mass spectral fragmentation of 2,2'-oxydipyridine (III).



I



II



III

The base peak in the mass spectrum of 2,2'-oxydipyridine is due to the molecular ion  $C_{10}H_8N_2O$  at mass 172. Loss of  $H^+$  gives a high intensity peak at mass 171 (56% of molecular ion).

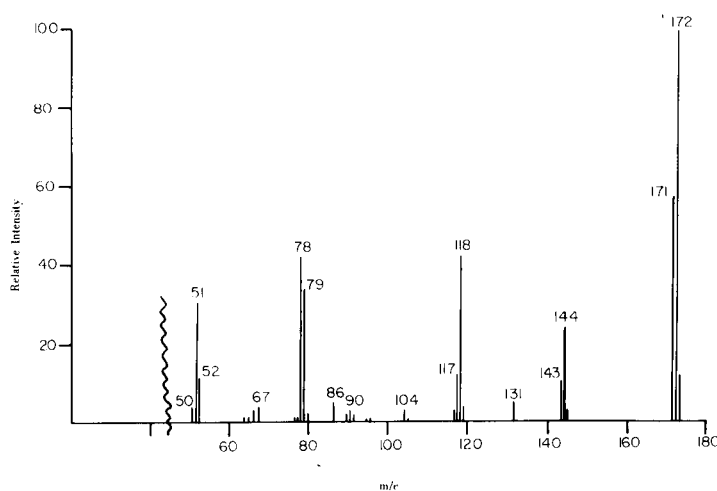
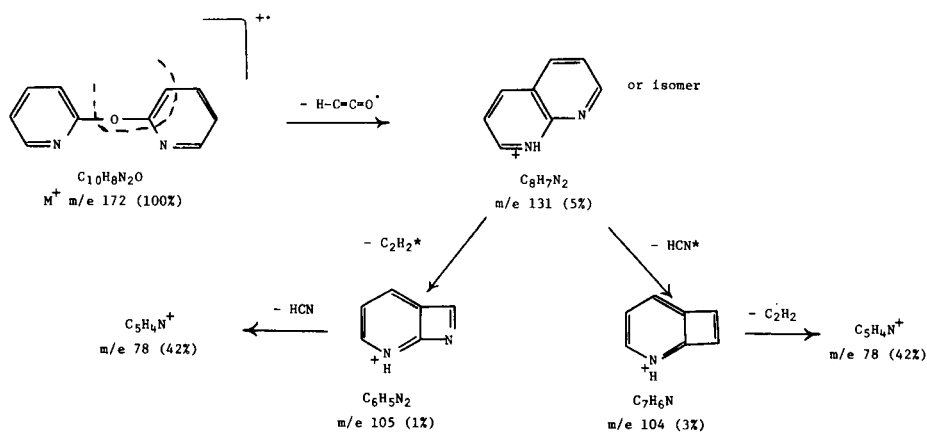


Figure: Mass Spectrum of 2,2'-Oxydipyridine

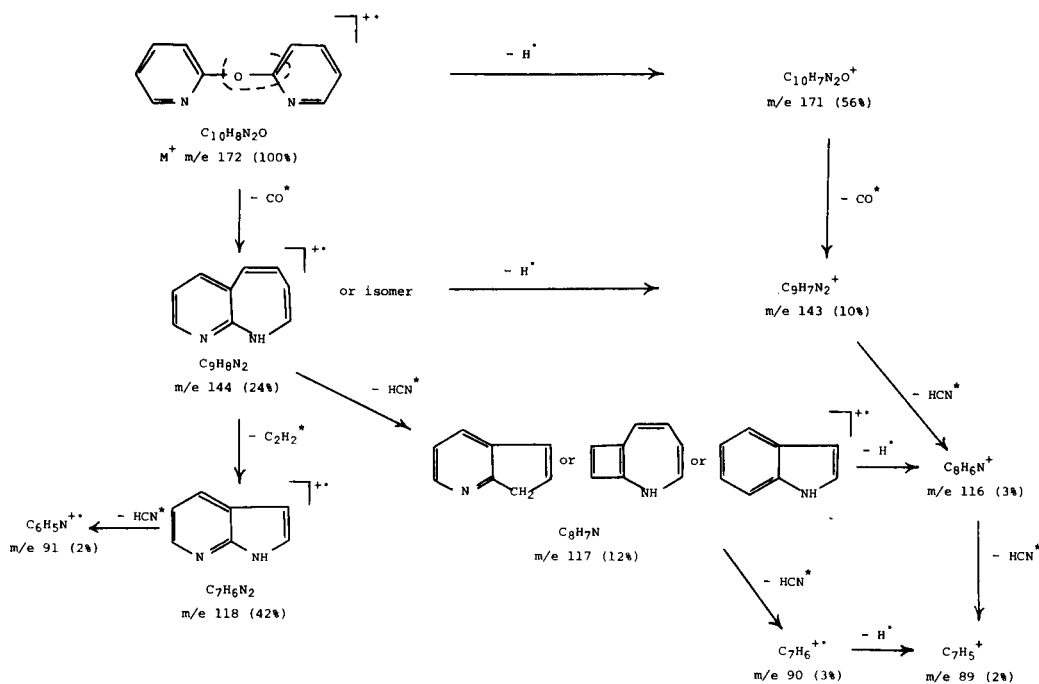
Apart from the loss of  $H^+$  the fragmentation of the molecular ion of 2,2'-oxydipyridine follows three different pathways. The minor route involves loss of the elements  $C_2HO$  (Scheme 1). The major routes either involve loss of  $CO$  with accompanying rearrangements of the molecule (Scheme 2) or rupture of the central bonds with the formation of ions from the remaining two fragments (Scheme 3). We will deal with these three routes in turn.

The loss of the elements of  $C_2HO$  from the molecular ion results in the formation of a  $C_8H_7N_2^+$  ion at mass 131 (5% of molecular ion) considered to be due to a naphthyridinium ion. Possible bond ruptures for this elimination (*cf.* 1) are indicated in Scheme 1. No clear metastable peak was observed, however, for this transition.

Scheme 1



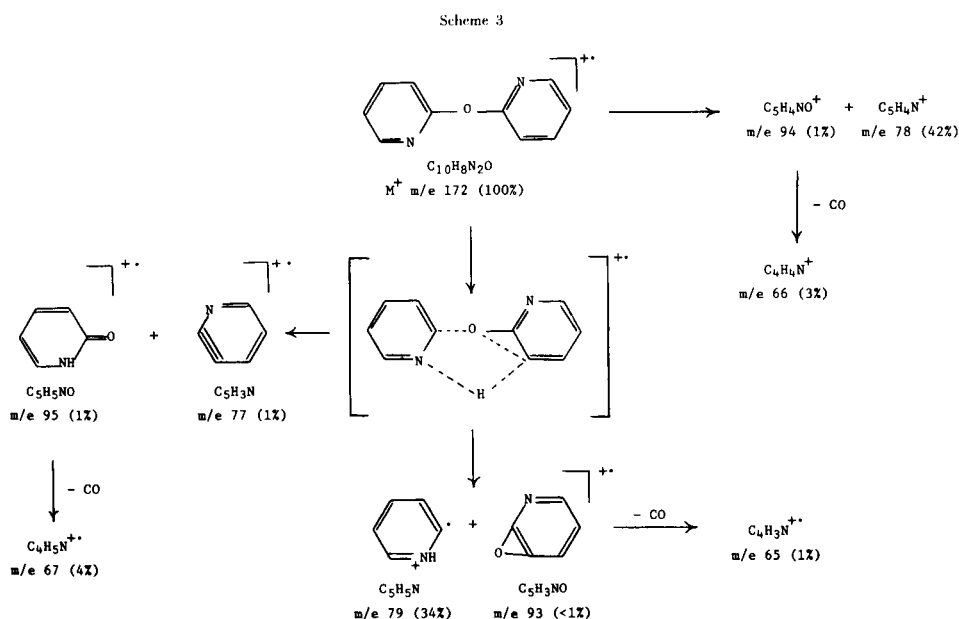
Scheme 2



Some support for the formulation of the  $C_8H_7N_2^+$  ion as a naphthyridine derivative comes from its subsequent fragmentation which results in the formation of a  $C_6H_5N_2^+$  ion at mass 105 (1%) and a  $C_7H_6N^+$  ion at mass 104 (3%) by loss of the neutral fragments  $C_2H_2$  and  $HCN$ , respectively. Metastable transitions corresponding to both these fragmentations were observed. Naphthyridines are known to disintegrate on electron impact in these two ways (12). The  $C_6H_5N_2^+$  ion and the  $C_7H_6N^+$  ion can then lose  $HCN$  and  $C_2H_2$  respectively, to give rise in each case to a  $C_5H_4N^+$  species of mass 78 which is a prominent peak in the spectrum of 2,2'-oxydipyridine (see also Scheme 3).

One of the major fragmentation routes from the 2,2'-oxydipyridine molecular ion ( $C_{10}H_8N_2O$ ) involves loss of neutral  $CO$  (Scheme 2) presumably in a manner analogous to that observed with diphenyl ether (1). This gives rise to a peak at mass 144 (24%) due to a species of empirical formula  $C_9H_8N_2$  depicted as a pyridoazepine molecular ion. The 2,2'-oxydipyridine molecular ion may lose  $H\cdot$  to form the M-1 ion before loss of neutral  $CO$  to form a  $C_9H_7N_2^+$  ion of mass 143 (10%). This species at mass 143 can also be formed from the pyridoazepine molecular ion (mass 144) by loss of  $H\cdot$ .

The subsequent fragmentation of the pyridoazepine



molecular ion at mass 144 involves either loss of  $C_2H_2$  to give a strong peak at mass 118 (42%) of empirical formula  $C_7H_6N_2$  depicted as a pyrrolopyridine molecular ion or loss of HCN to give a peak at mass 117 (12%) of formula  $C_8H_7N$  considered to be due to the pyridine or indole molecular ion or related species (see Scheme 2). Metastable peaks for these two transitions were observed. The species at mass 117 ( $C_8H_7N$ ) may lose  $H^+$  to form the ion  $C_8H_6N^+$  at mass 116 (3%). The  $C_8H_6N^+$  ion is also formed from the pyridoazepine molecular ion less one hydrogen ( $C_9H_7N_2^+$ ) at mass 143 by loss of HCN.

The pyrrolopyridine molecular ion (mass 118) and the pyridine or indole molecular ion (mass 117) and its M-1 species (mass 116) disintegrate further by loss of neutral HCN to give small peaks (2-3%) at mass 91 ( $C_6H_5N^{++}$ ), 90 ( $C_7H_6^{++}$ ) and 89 ( $C_7H_5^+$ ), respectively.

The second major fragmentation route (Scheme 3) from the molecular ion of 2,2'-oxydipyridine involves rupture of the central bonds. It gives rise to some interesting ions the formation of which must involve hydrogen migrations. For instance, the peak at mass 95 (1%) is due to a species of empirical formula  $C_5H_5NO$  considered to be due to the 2-pyridone molecular ion perhaps formed by the hydrogen migration route depicted in the Scheme. The accompanying fragment of mass 77 and empirical formula  $C_5H_3N$ , due to the pyridine molecular ion less two hydrogens, is present in small amounts (1%). Another central bond rupture with concomitant hydrogen migration gives rise to the strong peak (34%) at mass 79 due to the  $C_5H_5N^{++}$  species presumably the pyridine molecular ion. The accompanying fragment  $C_5H_3NO^{++}$  at mass 93 is present in only very small amounts.

The straightforward central bond rupture with no hydrogen migration also occurs and is largely responsible (see also Scheme 1) for the very strong peak at mass 78 (42%) due to a species of formula  $C_5H_4N$  presumably the pyridine molecular ion less one hydrogen. The accompanying pyridyloxy ion  $C_5H_4NO^+$  at mass 94 is present

Table I  
High Resolution Data

m/e	Elemental Composition	Observed Mass	Calculated Mass
144	$C_9H_8N_2$	144.0687	144.0687
143	$C_9H_7N_2$	143.0607	143.0609
131	$C_8H_7N_2$	131.0609	131.0609
118	$C_7H_6N_2$	118.0531	118.0531
117	$C_8H_7N$	117.0577	117.0578
116	$C_8H_6N$	116.0500	116.0500
105	$C_6H_5N_2$	105.0451	105.0453
104	$C_7H_6N$	104.0499	104.0500
95	$C_5H_5NO$	95.0371	95.0371
94	$C_5H_4NO$	94.0292	94.0293
93	$C_5H_3NO$	93.0213	93.0215
91	$C_6H_5N$	91.0421	91.0422
90	$C_7H_6$	90.0468	90.0469
89	$C_7H_5$	89.0390	89.0391
79	$C_5H_5N$	79.0422	79.0422
78	$C_5H_4N$	78.0344	78.0344
77	$C_5H_3N$	77.0263	77.0265
76	$C_5H_2N$	76.0186	76.0187
67	$C_4H_5N$	67.0422	67.0422
66	$C_4H_4N$	66.0344	66.0344
65	$C_4H_3N$	65.0265	65.0265
64	$C_4H_2N$	64.0187	64.0187

Table II  
Metastable Ions

Initial Ion	Resultant Ion	Transition	Found m*	Calculated m*	Fragment Expelled
C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> O	C <sub>9</sub> H <sub>8</sub> N <sub>2</sub>	172 → 144	120.6	120.6	CO
C <sub>10</sub> H <sub>7</sub> N <sub>2</sub> O	C <sub>9</sub> H <sub>7</sub> N <sub>2</sub>	171 → 143	119.7	119.5	CO
C <sub>9</sub> H <sub>8</sub> N <sub>2</sub>	C <sub>7</sub> H <sub>6</sub> N <sub>2</sub>	144 → 118	96.7	96.7	C <sub>2</sub> H <sub>2</sub>
C <sub>9</sub> H <sub>8</sub> N <sub>2</sub>	C <sub>8</sub> H <sub>7</sub> N	144 → 117	95.2	95.1	HCN
C <sub>9</sub> H <sub>7</sub> N <sub>2</sub>	C <sub>8</sub> H <sub>6</sub> N	143 → 116	94.2	94.1	HCN
C <sub>8</sub> H <sub>7</sub> N <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> N <sub>2</sub>	131 → 105	84.5	84.2	C <sub>2</sub> H <sub>2</sub>
C <sub>8</sub> H <sub>7</sub> N <sub>2</sub>	C <sub>7</sub> H <sub>6</sub> N	131 → 104	82.5	82.5	HCN
C <sub>7</sub> H <sub>6</sub> N <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> N	118 → 91	70.3	70.2	HCN
C <sub>8</sub> H <sub>7</sub> N	C <sub>7</sub> H <sub>6</sub>	117 → 90	69.2	69.2	HCN
C <sub>8</sub> H <sub>6</sub> N	C <sub>7</sub> H <sub>5</sub>	116 → 89	68.3	68.3	HCN

in small amounts (1%). The three oxygen containing moieties at mass 95 (C<sub>5</sub>H<sub>5</sub>NO<sup>+</sup>), 94 (C<sub>5</sub>H<sub>4</sub>NO<sup>+</sup>) and 93 (C<sub>5</sub>H<sub>3</sub>NO<sup>+</sup>) all lose neutral CO. This loss results in the small peaks (1-4%) at mass 67 (C<sub>4</sub>H<sub>5</sub>N<sup>+</sup>), 66 (C<sub>4</sub>H<sub>4</sub>N<sup>+</sup>) and 65 (C<sub>4</sub>H<sub>3</sub>N<sup>+</sup>). The peak at mass 64 (1%) (C<sub>4</sub>H<sub>2</sub>N<sup>+</sup>) presumably arises by further loss of hydrogen.

The peak at mass 86 (5%) is due to the M<sup>++</sup> ion.

The peaks below a mass of 60 in the spectrum are typical of those to be expected from pyridine derivatives. The elemental composition of the ions are recorded in Table I and the metastable transitions in Table II.

#### EXPERIMENTAL

The mass spectra were determined with an A.E.I. MS-30 mass spectrometer. The sample was analysed by a direct insertion gas probe at 150° at an ionising current of 70 eV. Elemental compositions were obtained by the peak matching method.

2,2'-Oxydipyridine (13) was analytically pure.

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