

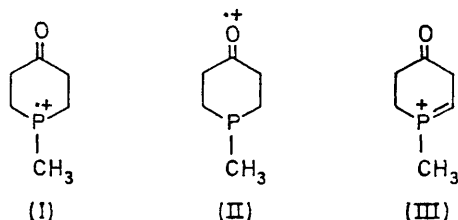
# Mass Spectra of 1-Methyl-4-Phosphorinanone and 1-Methyl-4-Piperidone

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The mass spectral fragmentation of 1-methyl-4-phosphorinanone was found to follow two major pathways, each involving initial cleavage of a C-P bond. In addition, fragments were detected which resulted from transfer of oxygen to phosphorus. The pattern was quite different from that of *N*-methyl-4-piperidone, the spectrum of which resembled that of *N*-methylpiperidine, with initial cleavage occurring at the 2,3-bond.

PHOSPHORINANS, six-membered cyclic phosphines, are of increasing importance in organophosphorus chemistry,<sup>1</sup> particularly from a stereochemical standpoint,<sup>2</sup> yet no study of the mass spectral characteristics of this ring system has been reported. Even among acyclic tertiary phosphines, only the simplest members, such as trimethyl and triethyl, have been studied in detail.<sup>3-5</sup> We report here the mass spectrum of a 4-phosphorinanone, and provide a comparison with the spectrum of the corresponding 4-piperidone. The fragmentation patterns proved to have little in common, the major difference arising from the readier cleavage of the C-P bond relative to the C-N bond.

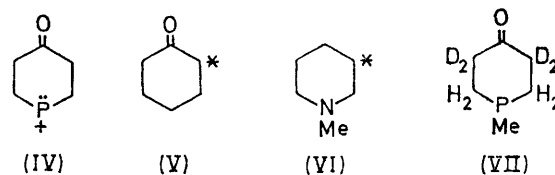
The base peak in the mass spectrum (Table) of 1-methyl-4-phosphorinanone is the molecular ion, which may be considered as (I) or (II). The lower ionization potential of phosphorus relative to oxygen (10.55 *vs.* 13.614 eV)<sup>6</sup> would suggest a preference for ion (I). This is supported by the high stability of the molecular ion; the stability of the molecular ion from cyclohexanone is much lower, amounting only to 30% of the base peak<sup>7</sup> (C<sub>6</sub>H<sub>8</sub>O, *m/e* 55). The *M*<sup>+</sup> - 1 peak is also quite large, and may be accounted for, as in the case of *N*-methylpiperidine,<sup>8</sup> by loss of a ring  $\alpha$ -hydrogen.



This ion is represented with a carbon-phosphorus double-bond (III) rather than as a diradical. While not common in ground-state phosphorus chemistry, the C-P double-bond ( $p_{\pi}-p_{\pi}$ ) has recently been shown to exist in the phosphorin (phosphabenzene) family.<sup>9</sup>

Fragmentation of (I) appears to follow two major paths, both of which involve initial cleavage of a C-P bond. (A) The methyl group on phosphorus is lost to form (IV), *m/e* 115. In both cyclohexanone<sup>7</sup> and

*N*-methylpiperidine,<sup>8</sup> it is the starred carbon in structures (V) and (VI), respectively, which has been found to be lost as CH<sub>3</sub> to give a *M*<sup>+</sup> - 15 peak. In the <sup>1</sup>H<sub>4</sub>-derivative (VII), the peak at *m/e* 115 was shifted to *m/e* 119, establishing that the corresponding ring



carbon was not lost from the phosphorinanone. Loss of the elements of water from the ion, *m/e* 115 gives rise to a peak *m/e* 97 (*m*<sup>\*</sup> 81.8; 97<sup>2</sup>/115 = 81.82). *M*<sup>+</sup> - CH<sub>3</sub> from deuteriated ketone (VII) loses HOD, in accord with loss of one proton each from positions C-2 and C-3 relative to carbonyl, as has been observed for cyclohexanone.<sup>7</sup> (B) A more important cleavage of (I) is loss of ethylene to form *m/e* 102.0230 (C<sub>4</sub>H<sub>7</sub>OP requires 102.0233; *m*<sup>\*</sup> *m/e* 80.0, 102<sup>2</sup>/130 = 80.03). The corresponding peak from the deuteriated ketone was at *m/e* 104. The ion of *m/e* 102, which can be written as (VIII), loses either an ethylene molecule [CH<sub>2</sub>CD<sub>2</sub> from (VII)] to form *m/e* 74.0285 [(IX), C<sub>2</sub>H<sub>3</sub>OP<sup>+</sup> requires 74.0285] or a molecule of carbon monoxide to form *m/e* 73.9920 [(X), C<sub>3</sub>H<sub>7</sub>P<sup>+</sup> requires 73.9922; *m/e* 76 from (VII)]. The two ions at nominal *m/e* 74 are of approximately equal abundance. Metastable peaks indicate that *m/e* 102 also fragments to give *m/e* 76 (*m*<sup>\*</sup> 56.7; 76<sup>2</sup>/102 = 56.63) and *m/e* 55.0182 (*m*<sup>\*</sup> 29.70; 55<sup>2</sup>/102 = 29.66. C<sub>3</sub>H<sub>3</sub>O requires 55.0184). The C<sub>3</sub>H<sub>3</sub>O ion may be written [CH<sub>2</sub>=CH-CO<sup>+</sup>] as proposed for the base peak of cyclohexanone.<sup>7</sup> In the spectrum of (VII), this peak is shifted to *m/e* 56, suggesting an origin from *m/e* 102 as in Scheme 1. Scheme 2 summarizes the major fragmentation patterns of (I).

A peak of moderate intensity (11%) at *m/e* 78 appears to have resulted from transfer of oxygen to phosphorus. Its formula is C<sub>2</sub>H<sub>7</sub>OP (*m/e* 78.0231; calc. 78.0235), and it is difficult to write a reasonable structure for it

<sup>1</sup> K. D. Berlin and D. M. Hellwege, in 'Topics in Phosphorus Chemistry,' eds. M. Grayson and E. J. Griffith, Interscience, New York, 1969, vol. 6, ch. 1.

<sup>2</sup> M. J. Gallagher and I. D. Jenkins, in 'Topics in Stereochemistry,' eds. E. L. Eliel and N. L. Allinger, Interscience, New York, 1968, vol. 3, ch. 1.

<sup>3</sup> R. G. Gillis and G. J. Long, *Org. Mass Spec.*, 1969, **2**, 1315.

<sup>4</sup> M. Halmann, *J. Chem. Soc.*, 1962, 3270.

<sup>5</sup> Y. Wada and R. W. Kiser, *J. Phys. Chem.*, 1964, **68**, 2290.

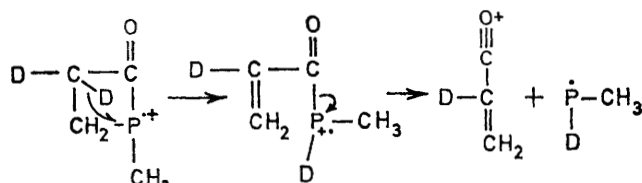
<sup>6</sup> J. Kleinberg, W. J. Argersinger, jun., and E. Griswold, 'Inorganic Chemistry,' D. C. Heath, Boston, Mass., 1960, p. 96.

<sup>7</sup> D. H. Williams, H. Budzikiewicz, Z. Pelah, and C. Djerassi, *Monatsh.*, 1964, **95**, 166.

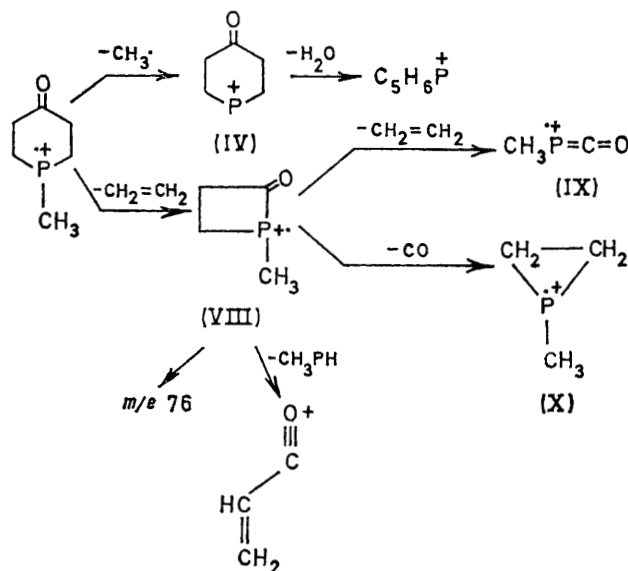
<sup>8</sup> A. M. Duffield, H. Budzikiewicz, D. H. Williams, and C. Djerassi, *J. Amer. Chem. Soc.*, 1965, **87**, 810.

<sup>9</sup> G. Märkl, *Angew. Chem. Internat. Edn.*, 1966, **5**, 846.

other than (XI). The ion does not originate from a *P*-oxide impurity in the starting ketone, for it is absent in the spectrum of its oxide.<sup>10</sup> (The sample of the ketone was loaded on to the probe and inserted into the

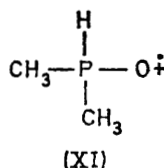


SCHEME 1



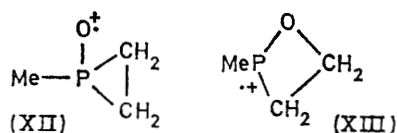
SCHEME 2

instrument in a dry bag filled with dry nitrogen: oxidation could therefore only have been effected by residual oxygen in the spectrometer itself.) In the deuterated



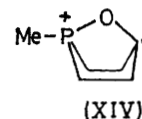
ketone, peaks of equal intensity are observed at *m/e* 78 and 80 suggesting that two different modes of cleavage can give this fragment.

A smaller peak [ $C_3H_7OP$ , *m/e* 90.0233; calc. 90.0235; *m/e* 92 from (VII)] also appeared to contain a *P*-*O* bond. Possible representations are (XII) and (XIII). A



reasonable hypothesis for the transfer of oxygen to phosphorus is that a bridged structure such as (XIV)

contributes to the molecular ion, and indeed may in part be responsible for the high stability of this ion. Ions such as *m/e* 78 and 90, which must arise from complex rearrangement processes, are more likely to occur in the mass spectra of compounds with large molecular ion peaks, *i.e.* whose molecular ions have barely enough excess energy to fragment at all.



Accurate mass measurements have established the identity of several small fragments. Some are of the same formula as observed in the mass spectrum of trimethylphosphine.<sup>3-5</sup> These are  $C_3H_5^+$  (*m/e* 41.0390; calc. 41.0391),  $CH_2P^+$  (*m/e* 44.9894; calc. 44.9894),  $CH_3P^+$  (*m/e* 45.9972; calc. 45.9972),  $C_2H_2P^+$  (*m/e* 56.9894; calc. 56.9894),  $C_2H_4P^+$  (*m/e* 59.0050; calc. 59.0051),  $C_2H_5P^+$  (*m/e* 60.0129; calc. 60.0129). Also,  $C_2H_3P^+$  (*m/e* 63.0362; calc. 63.0364) has been observed from triethylphosphine.<sup>5</sup>

The fragmentation of *N*-methyl-4-piperidone was found to follow a quite different path than that seen above for its phosphorus counterpart. Cleavage of the *C*-*N* bond occurred much less readily than did the *C*-*P* bond, as might be expected from the relative bond energies (80 and 65 kcal./mole, respectively).<sup>11</sup> The major fragmentation patterns for *N*-methylpiperidone are summarized in Scheme 3; other details are provided

Mass spectra of 1-methyl-4-phosphorinanone (XV) and 1-methyl-4-piperidone (XVI) \*

(XV)				(XVI)			
<i>m/e</i>	R.A.	<i>m/e</i>	R.A.	<i>m/e</i>	R.A.	<i>m/e</i>	R.A.
130 ( <i>M</i> <sup>+</sup> )	100	72	4	113 ( <i>M</i> <sup>+</sup> )	100	67	4
129	50	71	2	112	34	59	7
115	5	68	2	85	2	58	4
102	11	63	5	83	5	57	8
97	2	60	5	82	3	56	7
90	2	59	5	81	4	55	9
87	2	58	6	71	28	54	4
78	11	57	10	70	53	44	8
77	2	55	10	69	4	43	96
76	4	48	5	68	2	42	55
75	6	46	6			41	16
74	40	45	11				
73	5	41	10				

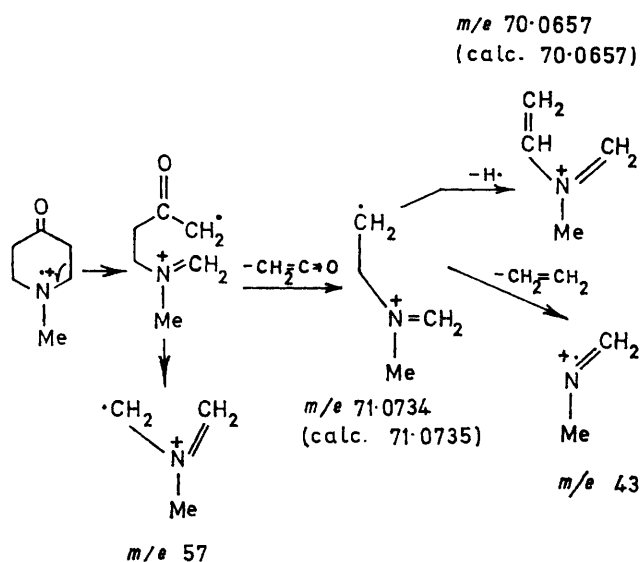
\* Peaks of relative abundance less than 1% are excluded.

in the Table. In general, the pattern is very similar to that described for *N*-methylpiperidine,<sup>8</sup> and involves initial cleavage of the 2,3-bond. Fragmentation through cleavage of *N*-*CH*<sub>3</sub> was not detectable, and loss of ethylene *via* 1,2-cleavage was not an important process.

Although differing greatly in their fragmentation patterns, the two ketones do have in common high stability of their molecular ions, as well as comparable stability for the *M*<sup>+</sup> - 1 ion. Substantial differences

<sup>10</sup> L. D. Quin and J. J. Breen, unpublished work.

<sup>11</sup> R. F. Hudson, 'Structure and Mechanism in Organo-Phosphorus Chemistry,' Academic Press, London, 1965, p. 11.



SCHEME 3

in these regards have been noted<sup>12</sup> in a comparison of the spectra of trimethylphosphine with that of tri-

<sup>12</sup> R. G. Kostyanovskii and V. V. Yakshin, *Izvest. Akad. Nauk S.S.S.R., Sec. khim.*, 1967, 2363.

methylamine: the  $M^+ - 1$  peak for the phosphine was only 25% of  $M^+$ , while for the amine it was 238%.

#### EXPERIMENTAL

Mass spectra were determined by direct insertion with an AEI MS902 instrument (ionization potential 70 eV). High-resolution measurements were made relative to heptacosafuorotributylamine.

1-Methyl-4-phosphorinanone was obtained as described previously.<sup>13</sup> A sample deuteriated at positions 3 and 5 (62%  $^2\text{H}_4$ -, 23%  $^2\text{H}_3$ -, 15%  $^2\text{H}_2$ -, 0·4%  $^2\text{H}_1$ -) was available from a  $\text{D}_2\text{O}$  exchange study.<sup>10</sup> *N*-Methyl-4-piperidone was obtained commercially (Aldrich Chemical Co., Milwaukee, Wisconsin) and purified by distillation.

We thank Mr Peter Cook for determining the mass spectra, which for the air-sensitive phosphines required skilful manipulation. We also thank Mr D. E. Loeber for the use of a computer programme for determining parent and daughter peaks of metastable ions, and Dr James Kane for purification of compound (VII) on a vacuum line.

[0/1544 Received, September 9th, 1970]

<sup>13</sup> H. E. Shook, jun., and L. D. Quin, *J. Amer. Chem. Soc.*, 1967, **89**, 1841.