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Mass Spectral Fragmentation of 5- and 6-Membered P-Heterocycles Resulting in Oxophosphines (Y–P = O)

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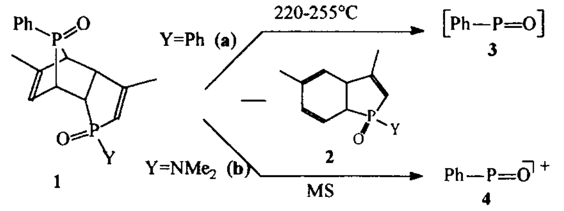
ABSTRACT

*Electron impact mass spectra of several 5- and 6-membered P-heterocycles having a tertiary phosphine oxide or phosphinic ester function (***5–11***) reveal the loss of the phosphorus-containing moiety formulated by* $P(O)Y+H^{\urcorner +}$, Y = Ph, Bu, EtO. In the case of the P-phenyl hexahydrophosphinine oxide (*9*), *the loss of the oxophosphine fragment is as intense as 100% on the relative scale. A 2,5-dihydro-1H-phosphole oxide having a sterically demanding aryl group on the phosphorus atom (12) undergoes thermal fragmentation at 250°C to result in the formation of oxophosphine* **14**. *© John Wiley & Sons, Inc.*

INTRODUCTION

Oxophosphines (R–P = O) and phosphenous acid derivatives (e.g., RO–P = O) and their sulfur-containing analogues form an important group of low-coordinate phosphorus species that may arise from the thermal fragmentation of phosphanorbornenes. In the presence of trapping agents, such as alcohols or butadiene derivatives, the intermediate oxophosphines could be utilized for phosphorylation and in the synthesis of phosphole derivatives [1–4].



SCHEME 1 [5,6]

Generally, thermal fragmentations show analogies to those observed in the mass spectrometer under electron impact (EI) conditions. This is also the case for P-phenyl phosphanorbornenes, as both the thermal examinations and the EI mass spectra re-

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Dedicated to Professor Louis D. Quin on the occasion of his retirement from the University of Massachusetts at Amherst.

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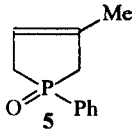
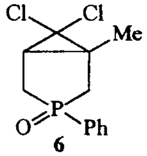
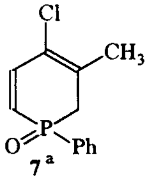
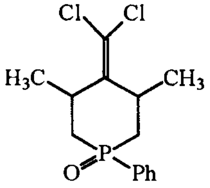
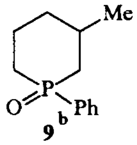
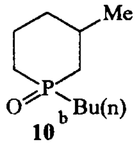
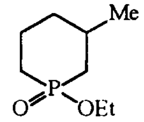
TABLE 1 Mass Spectral Fragmentation of P-Heterocycles **5–11**

Compound	*M*$^{+}$	*M-P(O)Y*$^{\urcorner +}$	*P-fragment* *m/z*	*(%)*	*Other*	
 **5**	192 (100)	68 (32)	P(O)Ph+H$^{\urcorner +}$ 125 (18)	M-Me$^{\urcorner +}$ 177 (20)	Ph^{+} 77 (16)	PO$^{\urcorner +}$ 47 (14)
 **6**	274 (8)	-	P(O)Ph+H$^{\urcorner +}$ 125 (22)	M-Cl$^{\urcorner +}$ 239 (100)	Ph^{+} 77 (25)	PO$^{\urcorner +}$ 47 (14)
 **7**[a]	238 (100)	114 (14)	P(O)Ph+H$^{\urcorner +}$ 125 (48)		Ph^{+} 77 (35)	PO$^{\urcorner +}$ 47 (24)
 **8**	298 (6)	174 (100)	P(O)Ph+H$^{\urcorner +}$ 125 (4)	174-Me$^{\urcorner +}$ 159 (28)	174-Cl$^{\urcorner +}$ 139 (18)	Ph 77 (15)
 **9**[b]	208 (98)	-	P(O)Ph+H$^{\urcorner +}$ 125 (100)	M-Me$^{\urcorner +}$ 193 (28)	$C_7H_7$$^{\urcorner +}$ 91 (35)	PO 47 (34)
 **10**[b]	188 (30)	-	P(O)Bu$^{\urcorner +}$ 104 (46)	M-Me$^{\urcorner +}$ 173 (20)	M-$C_3H_6$$^{\urcorner +}$ 146 (100)	PO 47 (17)
 **11**[b,c]	176 (49)	-	P(O)OEt+H$^{\urcorner +}$ 93 (100)	M-Me$^{\urcorner +}$ 161 (30)	M-$C_2H_5$$^{\urcorner +}$ 147 (32)	P(O)OH+H$^{\urcorner +}$ 65 (91)

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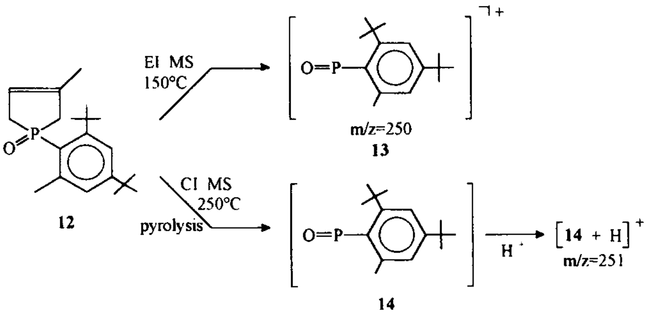
[a] The sample contained 25% of 4-chloro-5-methyl-1-phenyl-1,2-dihydrophosphinine 1-oxide.

[b] Diastereomeric mixtures of ca. 80–20%.

[c] The mass spectrum was recorded on an MS 25-RFA instrument at 70 eV.

TABLE 2 HRMS Peak Match for the Ejected P-Fragments

Compound	*Fragment*	*Formula*	m/z_{measured}	$m/z_{\text{calculated}}$
5	$\text{P(O)Ph+H}^{\urcorner +}$	C_6H_6OP	125.0159	125.0156
6	$\text{P(O)Ph+H}^{\urcorner +}$	C_6H_6OP	125.0158	125.0156
7	$\text{P(O)Ph+H}^{\urcorner +}$	C_6H_6OP	125.0160	125.0156
9	$\text{P(O)Ph+H}^{\urcorner +}$	C_6H_6OP	125.0156	125.0156
10	$\text{P(O)Bu}^{\urcorner +}$	C_4H_9OP	104.0394	104.0391
11	$\text{P(O)OEt+H}^{\urcorner +}$	$C_2H_6O_2P$	93.0097	93.0106



SCHEME 2

vealed loss of the bridging phosphorus moiety in a two-coordinate form. Thus, dimer **1a** loses Ph–P = O in the range of 220–255 °C (Scheme 1) [5], while the mass spectrum of phosphanorbornene **1b** shows a strong signal (20% relatively to the base peak) for the species $\text{Ph–P} = \text{O}^{\urcorner +}$, as confirmed by high-resolution mass spectrometry (HRMS) (Scheme 1) [6].

During our work with 5- and 6-membered P-heterocycles, it was often experienced that the mass spectral fragmentation involved loss of the phosphorus moiety. Because of this, we decided to examine systematically the fragmentation of some of their representatives having a tertiary-phosphine oxide or phosphinic ester function and resulting in oxophosphines.

RESULTS AND DISCUSSION

The P-heterocycles studied were dihydro-1H-phosphole **5** [7], phosphabicyclo[3.1.0]hexane oxide **6** [8], 1,2-dihydrophosphinine oxide **7** [9], 1,4-dihydrophosphinine oxide **8** [10], and hexahydrophosphinine oxides **9–11** [11,12].

The EI mass spectra of the P-phenyl-substituted heterocycles (**5–9**) showed that the ejection of the P(O)Ph moiety was indeed remarkable (Table 1). The P-fragment $\text{P(O)Ph+H}^{\urcorner +}$, $m/z = 125$ could be observed in all cases, but with variable intensities. In the mass spectrum of hexahydrophosphinine **9**, it was as intense as 100%, while in that of 1,4-dihydrophosphinine **8**, it was only of 4%, being the $\text{M–P(O)Ph}^{\urcorner +}$ fragment, the base peak, in the latter case. In the case of dihydrophosphole **5** and dihydrophosphinine **7**, relative intensities of the $\text{P(O)Ph+H}^{\urcorner +}$ and the $\text{M–P(O)Ph}^{\urcorner +}$ fragments were comparable. The mass spectrum of phosphabicyclohexane **6** revealed a $\text{P(O)Ph+H}^{\urcorner +}$ peak of 22%. Elemental composition of the P-fragments was confirmed by HRMS peak matches in all cases (Table 2). The structures of the ejected P-fragments were also confirmed by mass analyzed ion kinetic energy spectra (MIKES) and by spectra obtained by the collision induced decomposition (CID) technique, as they clearly showed that the fragments are stabilized by the loss of C_6H_5 to give the PO species (Table 1).

The increased ability of the phenylhexahydrophosphinine (**9**) to lose the P-moiety under EI mass spectral conditions prompted us to examine two other derivatives also. The P-*n*-butyl and the P-ethoxy derivatives (**10** and **11**, respectively) fragmented to result in the corresponding P-moieties (46% and 100% relative intensities, respectively) (Table 1). Elemental compositions of these fragments were confirmed by HRMS (Table 2).

Mass spectral behavior of 1-(2,4-di-*t*-butyl-6-methylphenyl)-3-methyl-2,5-dihydro-1H-phosphole 1-oxide (**12**) [13] was also studied. The EI mass spectrum obtained at 150 °C revealed the $\text{P(O)Ar}^{\urcorner +}$ fragment (**13**) ($m/z = 250$) with a relative intensity of 64% (with M^+ ($m/z = 318$) being the base peak [13]). Interestingly, the CI mass spectrum of **12**, obtained at 250°C in a special range of pressure, revealed not only M + H ($m/z = 319$), but also P(O)Ar + H ($m/z = 251$). Appearance of the latter species can be explained by assuming that the ejection of P(O)Ar (**14**) precedes the protonation (Scheme 2). This also means that dihydrophosphole **12**, having a sterically demanding aryl group on the phosphorus atom, can be pyrolyzed at 250°C to release the oxophosphine (**14**) moiety. The details and extension of this process are examined further and the results will form the subject of another paper. The other P-heterocycles (**5–11**) could not be involved in similar pyrolyses at 250°C under CI conditions, indicating the special role of the sterically demanding P-substituent.

Mass spectral fragmentation of the P-heterocycles studied (**5–12**) encourages us to try to utilize these compounds in preparative scale phosphorylations. It is of interest that not only phosphanorbornene derivatives, but also simple 5- and 6-membered P-heterocycles are capable of losing the P-fragment in a low-coordinate form.

EXPERIMENTAL

The P-heterocycles were prepared as described earlier [7–13]. EI mass spectra were obtained on an MS-902 instrument, while the MIKE and the CID spectra were recorded on a ZAB-2SEQ spectrometer. All spectra were obtained at 70 eV. In the case of CID measurements, argon was the collision gas, the transmission being 80%. The CI mass spectrum was recorded on an MS 25-RFA instrument (with isobutylene).

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