Cyclic Organophosphorus Compounds

XVIII[†]—The Mass Spectroscopy of Some 2-Amino-1,3,2dioxaphosphorinans, Cyclic Phosphorodiamidates and Phosphorodiamidothionates

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Stepwise replacement of O in 1,3-dioxa-2-phospha(V)-cyclohexanes (or related ring systems) by NR (R=H or Me) leads to an increase in the stability of the hetero-ring ions produced under electron impact conditions. In the case of the 2-phenoxy derivatives, there is also an increased abundance of $[M-PhO]^+$ or $[M-PhOH]^+$ ions, and, for the 2-sulphides, a reduction in the abundance of $[M-S]^+$ and $[M-SH]^+$ ions, with a concurrent increase in that of $[M-PhS]^+$ ions. Such trends have been correlated with ultraviolet photoelectron spectral data on a qualitative basis.

INTRODUCTION

In general, OO-diphenyl phosphoramidates afford only relatively low intensities of $[M-PhO]^+$ and $[M-PhOH]^+$ ions under electron impact conditions.² A series of $\alpha\omega$ -bis(diphenoxyphosphinylamino)alkanes³ also yield these, or related ions, in only low abundance, although there is a tendency for their intensities to increase for longer central carbon chains; moreover, the P-N is retained in a profusion of ions.

The 2-amino-1,3,2-dioxaphosphorinans 1 ($\mathbb{R}^1 = \mathbf{H}$; $\mathbb{R}^2 = alkylamino$; X = 0) yield ions, e.g. those at m/z 110 and 138 (Table 1) in which the P—N bond is also evidently retained, and similar ions are formed in greater abundance from the dioxaphosphorinans 1 ($\mathbb{R}^1 = Me$; $\mathbb{R}^2 = alkylamino$; X = O or S).⁴

When a single ring oxygen atom is replaced by the nitrogen function NH or NMe, the resulting perhydro-1,3,2-oxazaphosphorines 2 ($R^1 = Me$; $R^2 = halogen$, phenoxy, alkyl, phenyl, alkylamino; $R^3 = H$ or Me; X = O or S) yield ions in which the hetero-ring system is evidently more stable. Neither the perhydro-1,3,2oxazaphosphorines 2 ($R^1 = Me$; $R^2 = OPh$; $R^3 = H$ or Me; X = O, nor the dioxaphosphorinans 1 ($R^1 = H$ or Me; $R^2 = OPh$; X = O) yield $[M - PhO]^+$ or $[M - PhO]^+$ PhOH]⁺⁻ ions. Furthermore, neither of these latter ions is produced in more than trace amounts from the 2-sulphide 1 ($R^1 = Me$; $R^2 = OPh$; X = S), nor does this compound provide $[M-PhS]^+$ or $[M-PhSH]^{+-}$ ions.^{4,5} However, $[M - PhO]^+$ and $[M - PhS]^+$ ions are formed in moderate abundance from the perhydro-1,3,2-oxazaphosphorine 2-sulphides. Here, also, ions based upon the retained perhydro-1,3,2-oxazaphosphorine ring assume a relatively greater degree of importance than do the ions based upon the corresponding 2-thiono-1,3,2-dioxaphosphorinans.

RESULTS AND DISCUSSION

The primary purpose of this communication is to report briefly on certain features of the electron impact (EI) induced fragmentation of the O-phenyl cyclic phosphorodiamidates and phosphorodiamido-thionates **3–7**.



Scheme 1 (* metastable observed)

[†] For Part XVII, see Ref. 1.

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Table 1. Mass spectral data for the 1,3,2-dioxosphorinans 1 (\mathbb{R}^1 =H)

	-		· · · · · · · · · · · · · · · · · · ·
	Compound R ²	x	m/z (% Rel. ab.)
а	OPh	0	214(71) [M] ⁺⁺ , 175(14), 174(8), 157(5), 156(33), 117(11), 116(76), 115(26), 95(8), 94(100), 77(21), 65(24), 51(8), 50(5), 41(47).
b	iso-NHBu	0	193(11) [M] ⁺⁺ , 178(5), 150(100), 138(5), ^a 122(8), 121(8), 120(8), ^b 110(26), 92(26), 47(8), 42(12), 41(49).
C	tert-NHBu	0	178(100) [M – 15] ⁺ , 150(4), 138(11), ^a 121(3), 120(47), ^b 101(4), 98(7), 87(3), 80(7), 58(9), 57(9), 56(9), 47(8), 42(24), 41(30).
d	NHC _c H ₁₁	0	219(15) [M] ⁺⁻ , 190(8), 176(100), 163(4), 138(27) ⁺ 118(9), 98(24), 41(26).
e	NMe ₂	S	181(77) [M] ⁺⁺ , 148(27), 137(8), 124(8), 105(98), 92(10), 90(15), 47(19), 44(100), 42(23), 41(33).
			$ \begin{array}{ccc} & O & & & & \\ & O & & & & \\ & & P & & & P & \\ & & & P & & P & \\ & & & & P & & P & \\ & & & & P & & P & \\ & & & & P & & P & \\ & & & & P & & P & \\ & & & & P & & P & \\ $

Scheme 1 summarizes the proposed structures and relative abundance of the ions encountered in the degradation of the cyclic phosphorodiamidothionates 3-5 derived, from 1,2-diaminoethane,1,3-diaminopropane and 1,4-diaminobutane, respectively. The results, taken together with those for compounds 1 (a and b), 2 (a and b) and 6, demonstrate changes in ion intensities dependent on the nature of the 'phosphyl' group, P=O or P=S. The size of the phosphorus-containing ring is also a factor which contributes to trends in fragmentation pattern. Thus, within the group 3-5, an increase in the size of ring is associated with an increased importance of the molecular ion, but reduced importance of ion b. In further contrast to compounds already mentioned, compounds 3-5 produce $[M-PhO]^+$ and $[M-PhS]^+$ ions in high abundance. The [M-PhOH]⁺ ion (37% rel. ab.) is formed directly from a molecular ion only in the case of 2phenoxy-perhydro-1,3,2-diazaphosphorine 2-oxide 6, although the same ion is obtained from the corresponding 2-sulphide 4 after EI induced isomerization and subsequent liberation of thiophenol. Compounds 6 and 7 each yield $[M-PhO]^+$ ions in 100% relative abundance.

A further observed trend concerns the liberation of sulphur and thiol radical from the sulphides of the ring systems mentioned above. $[M-S]^+$ and $[M-SH]^+$ ions are quite prominent in the spectra of 1,3,2-dioxa-phosphorinan 2-sulphides 1 ($R^1 = H$) (Table 1) or ($R^1 = Me$; X = S)⁴ although less so for the 5,5-dimethyl-perhydro-1,3,2-oxazaphosphorine 2-sulphides, and both ions are completely absent from the spectra of the 2-sulphides 3–5 and 7.

An ion at m/z 74 formulated as d, is obtained from the 2-sulphide **4**, but not from the corresponding 2-oxide **6**; on the other hand, for compound **6** only, the ion f (n = 1) loses 28 u to give an ion at m/z 91 (16% rel. ab.) formulated as g or h. The perhydrodiazaphosphepine 2-sulphide **5** is unique in providing an ion at m/z 70; this has the composition of C₄H₈N (found: 70.0656, C₄H₈N requires 70.0657; C₃H₆N₂ requires 70.0531).



For 5,5-dimethyl-1,3,2-dioxaphosphorinan 2-oxides and 2-sulphides, fragmentations occurring via initial ionization on either a ring oxygen atom or the phosphoryl oxygen lead to low abundance ions; those processes which result in low to moderate abundance ions following ionization on exocyclic substituents on phosphorus, e.g. Ph or NMe₂, are exceptions.^{4,6} For compound **1a**, the first ionization energy at 8.43 eV is the lowest reported for compounds in the 1,3,2dioxaphosphorinan series and is thought to be associated with ionization of the aromatic ring.⁶ Available ionization energy data for organophosphorus compounds in general indicate that the presence of a



Figure 1. Photoelectron spectra of the compounds indicated. Ionization energies in eV.

nitrogen-containing functional group in molecules of the types O=PXYZ and S=PXYZ results in lower ionization energies, a feature consistent with the lower electronegativity of nitrogen.⁷ The observed ionization energy of 9.07 eV for compound 1 (X = O, R¹ = Me, R² = NMe₂) is not exceptional; lower values have been assigned to aromatic rings (if present).⁶ Apart from these data, assignments of initial ionization to particular sites are even more tenuous. Ionization energy values for 2-anilino-4-methyl-1,3,2-dioxaphosphorinan 2-oxides and 2-sulphides, determined mass spectrometrically, lie in the range 8.3–8.5 eV and correspond to the formation of $[M-C_4H_6]^{++}$ ions.⁸

The vertical ionization energies and shapes of the lower ultraviolet photoelectron spectral bands for the compounds discussed in this communication are indicated in Fig. 1. All the compounds show additional bands at c. 14 eV and 12.1-13 eV in the poorly resolved region extending up to c. 15 eV. Compounds 1b, 2a and 2b, 3 and 6 also show a band at 15.2 eV. Some trends are apparent. The oxides 1a and 2a show a single band at c. 9.4 eV with evidence of a shoulder at 8.8-9.0 eV; the 2-sulphides 1b and 2b exhibit a broadening of this band. When the phosphoruscontaining ring possesses two endocyclic nitrogen atoms, splitting of the band occurs giving sub-bands at c. 8.6 and 9.4 eV. Additionally, for this last group of compounds, a further low intensity band separates at c. 10.3 eV which is partly masked for compound 5, but which is more intense and at a higher energy for the

oxide 6. Clearly, both this feature and the band at 8.7 eV appear to be associated with the increased proportion of nitrogen in the hetero-ring. For the series 3-5, the band at c. 10.3 eV moves to lower values with increased size of the ring.

The ease of ionization of a lone pair electron from nitrogen should be dependent upon the delocalization of the lone pair into the 'phosphyl' bond; the extent of such $p_{\pi}-d_{\pi}$ overlap will, in turn, be indicated by the length of the P-N bond. Where the question of overlap does not arise, and the bond is thus assumed to be single in character, lengths lie within the range 1.73 to 1.79 Å.9 Diffraction techniques have shown that exocyclic P--N bonds in 2-amino-1,3,2-dioxaphosphorinan 2-oxides and 2-sulphides and in some 2amino-perhydro-1,3,2-oxazaphosphorine 2-oxides. and endocyclic P-N bonds in the latter group of compounds, are all considerably shorter. Average values for *exo*- and *endo*-cyclic P-to-N bonds are 1.625 Å and 1.65 Å, respectively.¹⁰⁻¹² A value (1.617 Å) found for the P-sulphide of a representative of the 1,3,2-oxazaphospholidine system,¹³ suggests greater orbital overlap in the more flexible 5membered ring. However, such marginal differences must be treated with caution in attempts to extend these arguments in view of the lack of available bond length data for 5- and 7-membered phosphoruscontaining rings.

Whereas a lone pair electron would normally be more readily ionized from nitrogen than from the more electronegative oxygen, geometrical constraints within the perhydro-oxazaphosphorine and similar nitrogen-containing rings allow the increased possibility of orbital overlap with the 'phosphyl' bond, with reduced possibility of ionization on nitrogen. Thus, initial ionization takes place preferentially elsewhere and the presence of nitrogen stabilizes the phosphorus-containing ring.

Ions produced from 2-phenoxy-2,3-dihydro-1H-1,3,2-benzodiazaphosphole 2-sulphide 7 and recognizable, at least in terms of their m/z values, include the benzologues (or valence tautomers thereof) of ions aand b (n = 0; of 99% and 84% rel. ab.), ion c (n = 0; 37% rel. ab.) and thence the ion at m/z 136 (25% rel. ab.) formulated as i, and of ion e (n = 0; 30% rel. ab.) also occurring with that at m/z 105 (14% rel. ab.) formulated as j. Thus, the degradation of compound 7 is totally different from that of 2-p-nitrophenoxy-2,3dihydro-1H-1,3,2-benzodiazaphosphole 2-oxide reported recently.¹⁴

EXPERIMENTAL

The preparation of compounds **3–7** has been described elsewhere.¹⁵ The 2-amino-1,3,2-dioxaphosphorinans **1** ($\mathbf{R}^1 = \mathbf{H}$) were prepared (**b**, **c** and **d**) by reaction between 2-chloro-1,3,2-dioxaphosphorinan 2-oxide¹⁶ and the amine (1 equiv.) in the presence of triethylamine (1 equiv.) in benzene or ether) and (**e**) by the addition of sulphur to the corresponding com-

pound of tervalent phosphorus. The 2-phenoxy compound 1 ($\mathbf{R}^1 = \mathbf{H}$) (a) had m.p. 72–73 °C (from CCl₄) (Lit. 17, m.p. 76-77 °C). 2-Isobutylamino-1,3,2-dioxaphosphorinan 2-oxide $\mathbf{1}$ ($\mathbf{R}^1 = \mathbf{H}$) **b**, (plates from benzene-light petroleum b.p. 60-80 °C) had m.p. 82-83 °C (found: C, 43.5; H, 8.2; P, 15.95. C₇H₁₆NO₃P requires C, 43.5; H, 8.35, P, 16.0%). The 2-tertbutylamino compound 1 ($R^1 = H$) c, had m.p. 130.5-132 °C (from benzene-light petroleum) (found: C, 43.65; H, 8.4; 15.3%); in common with other N-tertbutyl phosphoramidates, this compound showed no molecular ion in its mass spectrum. The 2-cyclohexylamino compound $\mathbf{1}$ (R¹ = H) **d**, had m.p. 150.5–152 °C (from benzene-light petroleum) (found: C, 49.55; H, 8.25; P, 14.15. C₉H₁₈NO₃P requires C, 48.9; H, 8.2; P, 14.0%). 2-NN-dimethylamino-1,3,2-dioxaphosphorinan 2-sulphide 1 ($\mathbf{R}^1 = \mathbf{H}$) **e** had b.p. 80 °C at $0.05 \text{ mm}, n_{D}^{20}$ 1,5123 (found: C, 33.1; H, 6.55; P, 16.9. C₅H₁₂NO₂PS requires C, 33.15; H, 6.6; P, 17.1%).

Mass spectra were determined using an AEI MS 9 instrument operating at 70 eV and with the ion source temperature 230–250 °C. Compounds were chromatographically homogeneous and of analytical purity. Low resolution spectra were obtained by Mr R. Nettleton, University of Bradford, and the accurate mass measurements by Dr B. Watson, University of Leeds, both of whom are thanked.

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