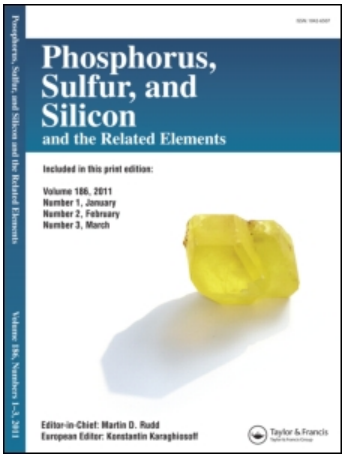

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CYCLIC ORGANOPHOSPHORUS COMPOUNDS. PART XVI[1]. MASS SPECTROMETRIC FRAGMENTATION OF SOME 5,5-DIMETHYL-1,3,2-DIOXAPHOSPHORINAN 2-OXIDES AND 2-SULPHIDES

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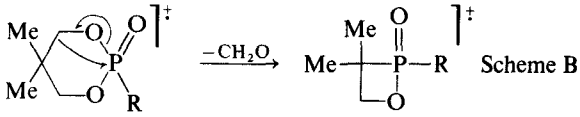
The mass spectra of seventeen 5,5-dimethyl-1,3,2-dioxaphosphorinan 2-oxides and nineteen 5,5-dimethyl-1,3,2-dioxaphosphorinan 2-sulphides, mostly with amino substituents on phosphorus, have been determined. In some cases, interpretation of the spectra was aided by accurate mass measurements and by the examination of deuterated compounds. For the 2-sulphides, sulphur is lost either as such or as the thiol radical, both processes often being of weak intensity, and the thiol hydrogen appears to be derivable from either a ring methylene group or a C-5 methyl group. Loss of S or HS· occurs more strongly for the phosphoramidothionates which, together with the phosphoramidates, also fragment to an important extent in the amido substituent with retention of the dioxaphosphorinan ring; P—N bond cleavage is also observed. For the 2-thiones, the ions at m/e 165 (**14**; R=H) and 133 (**15**; R=H) are characteristic.

INTRODUCTION

The spectroscopic examination of cyclic phosphate esters and related compounds has long been a popular and fruitful area of research. Not least in such researches have been the ^{1}H and ^{31}P nuclear magnetic resonance studies so extensively reported during the last ten to fifteen years, particularly in connection with the cyclic six-membered-ring esters—the 1,3,2-dioxaphosphorinans. More recently, a limited number of mass spectrometric studies on members of the same class of compound have also appeared.

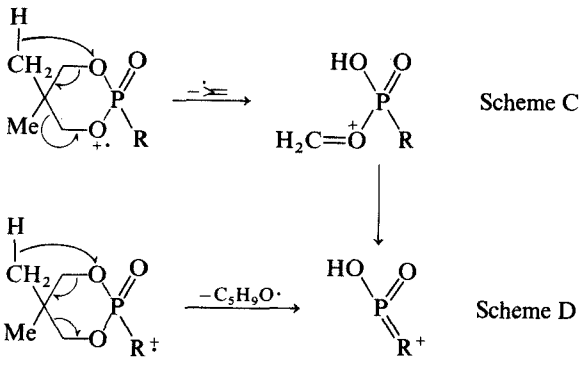
The main conclusions regarding the manner of electron-impact fragmentation of monocyclic, 5,5-dimethyl-1,3,2-dioxaphosph(V)orinans have thus far been based upon considerations of the compounds (**1** a–k) together with some of their deuterated derivatives,[2–4] and of the phosphorothionate (**2** c).[3] These conclusions are summarized below.

Two schemes have been advanced to account for the loss of a methyl group from the molecular ion without ring cleavage; one of these schemes (A) is illustrated. In the second, a hydrogen transfer takes place from a ring methylene group to phosphoryl oxygen. The rare loss of formaldehyde results in the formation of 1,2-oxaphosphetanium species and is indicated in scheme B.



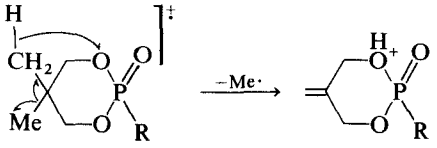
Scheme B

Several schemes have been proposed to account for the loss of hydrocarbon moieties from the molecular ion, including the isobutenyl (scheme C) and ethenyl (giving the ion **3**) radicals. Direct formation of a species of 85 a.m.u. (scheme D)

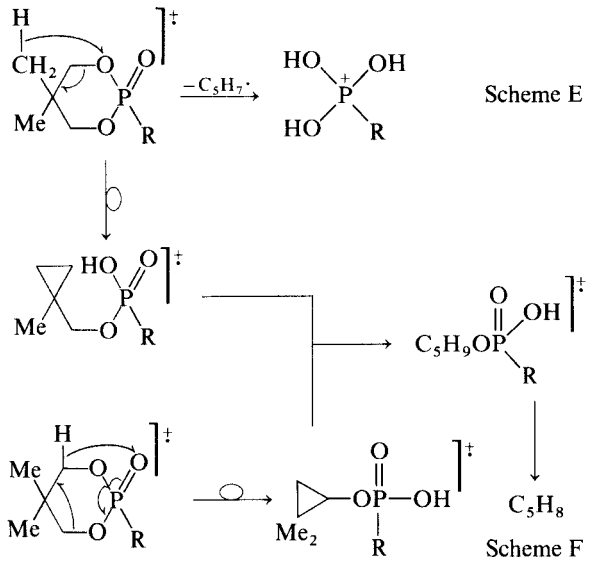


Scheme C

Scheme D



Scheme A

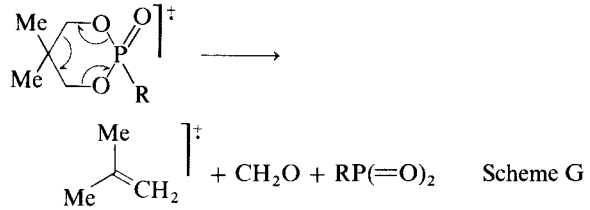


Scheme E

Scheme F

occurs to a small extent, and the result of this particular fragmentation can also be achieved by the loss of formaldehyde from the [M-55] ion.

Fragmentation pathways E and F lead to [M-67] and [M-68] ions. Finally, a cyclical elimination (scheme G) affords a hydrocarbon m/e 56 ion.



Scheme G

Fragmentation of the phosphorus-containing heterocyclic ring is thus accompanied by single, double or even triple, hydrogen transfers. Studies on compounds deuterated at positions 4 and 6 have indicated a lack of randomization of hydrogens among methyl and methylene groups, and aromatic rings attached to phosphorus, during the breakdown process.

The purpose of this paper is to indicate extensions to the generalizations outlined in schemes A–G, particularly with regard to replacement of the phosphoryl oxygen atom by sulphur, and also with regard to phosphorus amides (with exocyclic P—N bonds) in both the 2-oxo and 2-thiono series.

EXPERIMENTAL

The preparation of most of the compounds used in the present study has been described elsewhere.[5–8] Three new 5,5-dimethyl-1,3,2-dioxaphosphorinans were prepared by the same general methods; they are: (i) the 2-*t*-butylamino 2-oxide (**1** s) m.p. 166–166.5°C (from benzene).[9] Found: C, 49.1; H, 9.0; P, 13.75%. $C_9H_{20}NO_3P$ requires C, 48.85; H, 9.1; P, 14.0%. (ii) the 2-phenoxy 2-sulphide (**2** c), m.p. 96°C (from light petroleum, b.p. 60–80°C). Found: C, 51.2; H, 6.1; P, 11.55%. $C_{11}H_{15}O_3PS$ requires C, 51.1; H, 5.85; P, 11.9%. (iii) the 2-phenyl 2-sulphide (**2** s), m.p. 55.5–56°C (from cyclohexane). Found: C, 54.7; H, 6.1; P, 13.0%. $C_{11}H_{15}O_2PS$ requires C, 54.5; H, 6.2; P, 13.2%.

The [4,4,6,6 - $^2H_4$] - 5,5 - dimethyl - 1,3,2 - dioxaphos - phorinans were prepared from [1,1,3,3-$^2H_4$]-2,2-dimethylpropan-1,3-diol[10] by the standard procedures.

All compounds were chromatographically homogeneous and of analytical purity. The mass spectra were obtained using an AEI MS9 instrument operating at 70 eV, with the ion source temperature at 230–250°C. Accurate mass measurements were obtained using appropriate standards.

RESULTS

Data for the relative intensities of the major ion fragments for the 5,5-dimethyl-1,3,2-dioxaphosphorinan 2-oxides (**1** 1–bb), and for the 2-sulphides (**2** a–s) are listed in Table I and II respectively.

Most of the compounds examined displayed "metastables"; many compounds, particularly the phosphoramidates and phosphoramidothionates, showed several "metastables" in their spectra. The degradation pathways indicated below are consistent with the observed "metastables."

DISCUSSION

i) 5,5-Dimethyl-1,3,2-dioxaphosphorinan 2-oxides. In general, the [M-15] ions for these compounds are of low intensity, and may, indeed, be absent altogether, marked exceptions being afforded by the *N*-t-butylamide (1 s) and the *N*-isopropylamide (**1** p) for which the much more intense [M-15] ions probably contain a very large contribution from loss of Me· from the *N*-alkyl group and the formation of the ion (**5**; R^1 = Me, R^2 = H or Me). [M-28] ions are observed for very few compounds, consistent with the earlier reports on the compounds (**1** a–k), and [M-30] ions are not observed. Schemes C, D, E and G are consistent with the formation, from nearly all compounds, of the low intensity [M-55], [M-67], and [M-85] ions, and of the high intensity m/e 41 ($C_3H_5^+$), and 69 ($C_5H_9^+$) ions.

With particular regard to the phosphoramidates (**1** o–y), the general fragmentation pattern seems

TABLE I

Fragmentation data for 5,5-dimethyl-1,3,2-dioxaphosphorinan 2-oxides (1)

	Compound R	[M]	[M-15]	[M-28]	[M-55]	[M-67]	[M-85]	[m/e (%)] 41	56	67	68	69	110	148	149	150	166	167	178	179	Base
l	OH	166(4)	151(8)	138(12)	111(56)	99(100)	81(42)	(100)	(100)	(61)	(100)	(24)	—	—	—	—	(4)	(2)	—	—	99/68
m	OPr^i	208(1)	193(22)	—	153(*)	141(*)	123(*)	(98)	(98)	—	(68)	(97)	—	—	—	—	(24)	(68)	—	—	99
n	$OC_6H_4NO_2$-*p*	287(31)	272(20)	259(2)	232(10)	220(51)	202(3)	+	+	(16)	(100)	(44)	—	—	(5)	—	—	—	—	—	68
o	NHPr	207(12)	192(2)	179(14)	152(*)	140(3)	122(11)	(54)	(33)	(3)	(7)	(35)	(98)	(5)	—	(3)	—	—	(100)	(14)	178
p	$NHPr^i$	207(3)	192(28)	179(*)	152(*)	140(3)	122(6)	(50)	(30)	(3)	(5)	(29)	(3)	—	—	(3)	—	—	—	—	124
q	NHBu	221(14)	206(3)	193(*)	166(4)	—	—	(36)	(23)	(3)	(5)	(26)	(79)	—	(3)	—	—	(5)	(100)	—	178
r	$NHBu^i$	221(14)	206(2)	—	166(3)	—	136(4)	(43)	(24)	(3)	(6)	(32)	(97)	(5)	—	(3)	(3)	—	(100)	(14)	178
s	$NHBu^t$	221(*)	206(98)	—	166(2)	—	136(6)	+	(41)	(6)	(10)	(46)	+	(100)	(7)	(8)	(2)	—	(*)	(*)	138
t	NHPent.	235(21)	220(5)	—	180(4)	168(4)	150(5)	(72)	(35)	(4)	(9)	(49)	(97)	(5)	(4)	(5)	(12)	—	(100)	(27)	178
u	$NHPent^i$.	235(9)	220(4)	—	180(2)	168(4)	150(5)	(65)	(31)	(3)	(8)	(42)	(98)	—	—	—	(45)	(4)	(100)	(21)	178
v	NHHex.	249(14)	234(*)	—	—	—	—	(79)	(35)	(4)	(9)	(43)	(98)	(3)	—	—	(14)	—	(100)	(23)	178
w	NHHex.-cyclo	247(18)	232(2)	—	—	—	—	(54)	(20)	(6)	(9)	(20)	(11)	—	—	(5)	(21)	—	(20)	—	204
x	NPip	233(20)	218(5)	—	178(6)	166(3)	148(9)	(32)	(15)	(4)	(11)	(14)	(14)	(9)	(2)	(5)	(3)	—	(6)	—	84
y	NHPh	241(100)	226(5)	—	186(5)	174(23)	156(11)	(38)	(11)	(2)	(3)	(9)	—	—	—	—	—	—	—	—	256(M)
z	CH(OH)Ph	256(5)	—	—	—	—	—	+	+	(12)	(100)	(26)	—	—	—	—	—	—	—	—	68
aa	CH(NHPh)Ph	297(*)	—	—	—	—	—	+	+	(9)	(32)	(11)	—	(100)	(23)	(*)	—	—	—	—	148
bb	$OPO_3C_3H_{10}$	314(8)	299(13)	286(1)	259(3)	247(30)	229(37)	+	+	(10)	(27)	(100)	(7)	—	—	—	—	(5)	—	—	69

* trace only; —absent; + not estimated.

[a] [M-54] = 122(28); [M-53] = 123(18).

[b] This compound decomposes at ca. 230° to give the acid (**21**). The spectra of the two compounds were nevertheless sufficiently different to lend support to the values of ion intensities quoted here.

TABLE II

Fragmentation data for 5,5-dimethyl-1,3,2-dioxaphosphorinan 2-sulphides (2)

	Compound R	[M]	[M-15]	[M-32]	[M-33]	[M-67]	[M-85]	[m/e (%)] 41	56	67	68	69	133	165	Base
a	Cl	202(22)	185(*)	—	169(*)	135(5)	117(5)								
		200(64)	187(*)	—	167(*)	133(12)	115(8)	(100)	(34)	(20)	(88)	(68)	(12)	(12)	41
b	OMe	196(97)	181(10)	—	163(7)	129(80)	—	(100)	(35)	—	(87)	(50)	(7)	—	41
c	OPh	258(100)	243(2)	—	225(2)	191(34)	173(2)	(71)	(18)	(7)	(0)	(94)	(5)	(*)	M
d	$OC_6H_4NO_2$-p[a]	303(53)	—	(*)	—	236(14)	—	+	+	(11)	(35)	(100)	(5)	(8)	69
e	SH	198(62)	183(*)	166(22)	165(24)	131(5)	113(5)	(85)	(47)	(15)	(51)	(100)	—	(24)	69
f	SMe	212(80)	197(*)	—	—	145(6)	127(15)	(90)	(18)	(6)	(11)	(100)	(36)	(17)	69
g	SEt[b]	226(14)	—	—	—	—	141(2)	(46)	(9)	(3)	(14)	(100)	(52)	(12)	69
h	SPr^i[c]	240(16)	—	—	—	—	—	+	+	(4)	(23)	(100)	(43)	(18)	69
i	NMe_2	209(100)	194(*)	177(1)	176(27)	—	124(53)	(55)	—	(3)	(3)	(100)	(99)	(2)	M/100
j	NHPr	223(55)	—	—	190(28)	—	—	(38)	—	(4)	(5)	(62)	(69)	(1)	58
k	NHPr^i	223(28)	208(*)	191(*)	190(52)	—	138(7)	(72)	—	(10)	(40)	(100)	(72)	(10)	69
l	NHBu	237(40)	222(*)	205(41)	204(38)	—	152(5)	(48)	—	(4)	(10)	(74)	(83)	(8)	68
m	NHBu^i	237(47)	222(9)	205(3)	204(31)	—	152(6)	—	—	(4)	(18)	(100)	(52)	(21)	69
n	NHHex.	265(36)	250(*)	233(6)	232(44)	198(*)	180(*)	+	+	(3)	(5)	(56)	(100)	(11)	133
o	NHHex-cyclo	263(16)	—	231(13)	230(95)	—	178(3)	+	+	(8)	(22)	(91)	(100)	(4)	133
p	$OP(S)O_2C_5H_{10}$	346(60)	—	314(*)	313(*)	279(*)	261(2)	+	+	(7)	(16)	(100)	(29)	(13)	69
q	$SP(O)O_2C_5H_{10}$	346(50)	331(*)	314(*)	313(*)	279(−)	261(*)	+	+	(9)	(43)	(68)	(100)	(32)	133
r	$SP(S)O_2C_5H_{10}$	362(34)	347(*)	330(*)	329(4)	—	277(*)	+	+	(1)	(1)	(100)	(79)	(11)	69
s	Ph[c]	242(100)	227(7)	210(1)	209(4)	175(32)	157(84)	+	+	(6)	(23)	(44)	(8)	(*)	M

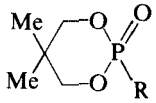
[a] [M-30] = 273(1).
[b] [M-28] = 198(52).
[c] [M-42] = 198(64).
[d] [M-30] = 212(2).
+ = not measured. * = trace.

to be one of retention of the dioxaphosphorinan ring with preferential cleavage of the amide function, at least in the initial stages. Structures in which the P—N bond is retained (see later) can be assigned to the fragments at m/e 178 and 179. Direct, but only weakly intense, fiission of the P—N bond, resulting in the formation of the m/e 149 ion (**4**), is observed for the compounds (**1** q, s, t and x). A fragment at m/e 150 although rather more common, is generally of weaker intensity (ca. 5%) and is probably associated with P—N bond cleavage coupled with hydrogen abstraction. The m/e 178 ion (**5**; $R^1 = R^2 = H$) in which the P—N bond is retained, and which is of such importance that it often forms the base peak, results from compounds having an alkylamide function unbranched at C-1.

For the phosphoramidates, generally, the m/e 166 (**6**) and m/e 150 (**7**) ions are of less importance, the former being more prominent only for compounds derived from the higher molecular weight amines. The formation of the latter ion could occur *via* a McLafferty elimination involving either a ring oxygen or the phosphoryl oxygen. The ion (**8**) formed by loss of formaledehyde from (**5**) is of importance only when the *N*-substituent is non-cyclic.

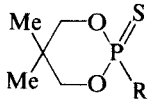
The m/e 204 ion, possibly (**9**), from the N-cyclohexylamide (**1** w) is formed directly ("metastable") from the molecular ion and is the base peak for this compound. In contrast, the isomeric ion (**10**) from the piperidide (**1** x), is rather weak (9%). Aruther difference between the spectra of these two compounds lies in the intensities of the m/e 136 ions, the ion (**11**; 47%) from the cyclohexylamide being much more important than the isomeric ion (**12**; 11%) from the piperidide. Further degradation of each of these ions leads to the common m/e 100 (10–15%) ion (**13**: $R^1 = R^2 = H$).

ii) 5,5-Dimethyl-1,3,2-dioxaphosphorinan 2-sulphides. The molecular ion peaks for the 5.5-dimethyl-1,3,2-dioxaphosphorinan 2-sulphides (Table II) are generally more intense, and the [M-15] ion peaks rather weaker, than those for the corresponding P-oxides. The loss of 28 a.m.u. can be attributed, in those few cases where it is seen to occur, to processes other than ring



(1)

R is (a)NH_2; (b) Me; (c) CH_2Ph
(d) CMe_3; (e) Ph; (f) Cl;
(g) OPh; (h) OMe; (i) SMe;
(j) NMe_2; (k) CCl_3



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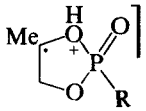
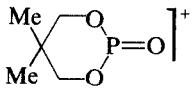


[M—28]

(3)



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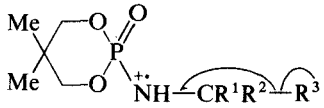

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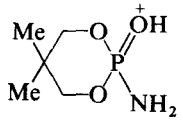

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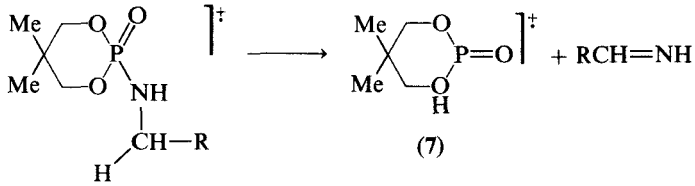

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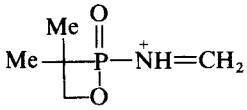

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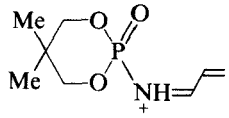

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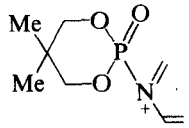

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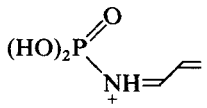

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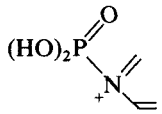
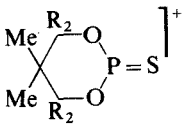


(12)

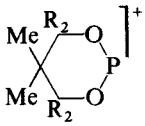
$(HO)_3\overset{+}{P}—N=CR^1R^2$

(13)

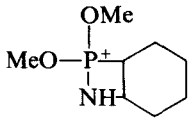
(i) $R^1=R^2=H$
(ii) $R^1=H$; $R^2=Me$
(iii) $R^1=R^2=Me$



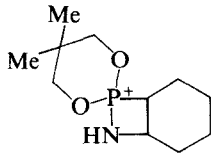
(14)



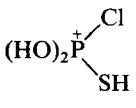
(15)



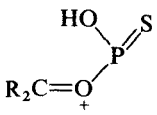
(16)



(17)



(18)



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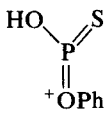


(20)

$\overset{+}{S}P(OH)_2$

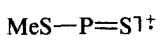
(21)

$(HS)_2\overset{+}{P}O$

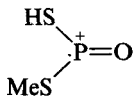
(22)

$(HS)_2\overset{+}{P}H(OH)$

(23)



(24)



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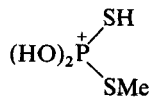

(26)

contraction.[12,13] [M-30] and [M-55] ions are absent, or at most, present only as traces, and [M-85] ion intensities are similar to those for the corresponding P-oxides. With the exception of the 2-methoxy compound (**2** b) and the 2-phenyl compound (**2** s), the [M-67] ion is of little significance. The m/e 68 ion, and more particularly, the m/e 69 ion, take on a much greater significance than for the series of P-oxides.

Electron-impact desulphurization from the molecular ions of the P-sulphides is observed in intensities ranging from trace only to around 40%; (**2** e, l, and o) exceptionally give high intensity [M—S] ions. On the other hand, loss of sulphur from the m/e 165 ion (**14**; R=H) to give the m/e 133 ion (**15**; R=H) is of considerable importance for many of the compounds in this group.

More pronounced for the whole series (**2**), but particularly for the phosphoramidothionates, is the loss of sulphur as HS· resulting in the medium-to-high intensity [M-33] ions; loss of sulphur in this way might occur through abstraction of hydrogen from (i) a methylene group of the dioxaphosphorinan ring; (ii) a substituent on a ring carbon atom, e.g. a methyl group at C-5; or (iii) the substituent attached to phosphorus.

For the dithioate esters (**2** g, h), loss of HS· follows ("metastables") upon loss of alkenyl radical to give the moderately intense m/e 165 ion, and the loss of HS· from (**2** f) follows transfer of hydrogen to thiophosphoryl sulphur and elision of $\cdot SCH_2$. Reaction (iii) obviously cannot occur for the phosphorochloridothionate (**2** a), and evidence based on deuteration studies, and on examination of acyclic phosphoramidothionates derived from secondary amines suggests that, in the case of the cyclic phosphoramidothionates, also, the last reaction does not occur,[14,15] Further, though *OO*-dimethyl *N*-cyclohexyl-phosphoramidothionate loses sulphur as HS· *via* the cyclic ion (**16**),[15] the cyclic *N*-cyclohexylphosphoramidothionate (**2** o) does not display the corresponding ion, i.e. (**17**), m/e 224.

2-Chloro-5,5-dimethyl-1,3,2-dioxaphosphorinan 2-sulphide (**2** a) loses both S and HS·, although each to a very weak extent only. The [M-32]/[M], [M-33]/[M], and [M-34]/[M] ratios for this compound were found to be 0.015, 0.061 and 0.11 respectively, the last figure probably representing a general "background" level. The corresponding values for the [4,4,6,6–$^2H_4$] compound were 0.016, 0.016 and 0.040. Thus it would appear that the thiol hydrogen is derived primarily from a ring methylene group. 5,5-Dimethyl-2-phenyl-1,3,2-dioxaphosphorinan 2-sulphide (**2** s) behaves similarly; the corresponding ion ratios were found to be 0.015, 0.040 and 0.002, and for the tetradeutero compound, 0.035, 0.060 and 0.023 respectively. The relative increase in the [M-34]/[M] value suggests that here, too, thiol hydrogen is derivable from a ring methylene group, but the results are not so conclusive, and it could well be that the 5-methyl group also participates to a small extent in providing hydrogen.

By contrast, 5,5-dimethyl-2-*N*-cyclohexylamino-[4,4,6,6-$^2H_4$]-1,3,2-dioxaphosphorinan 2-sulphide loses S and HS· strongly from the molecular ion ("metastable"). The [M-32]/[M] and [M-33]/[M] ratios were found to be 1.0 and 7.8, compared with 0.8 and 5.9 for the non-deuterated compound; [M-34] ions were not observed in either case. Here, then, the lack of participation of the ring methylene groups in loss of HS· is clearly demonstrated.

Loss of HS· from *OO*-diphenyl phosphorochloridothionate occurs through a cyclic ion, and loss of S follows directly upon that of Cl·. For *OO*-dimethyl phosphorochloridothionate, the transfer of H to S and subsequent loss of HS· is accompanied by elision of formaldehyde.[15] (**2** a) also loses S mainly, although very weakly, as HS· and this is followed by loss of Cl· to give the m/e 132 ion. However, the direct loss of Cl· from the molecular ion is more important and affords the m/e 165 ion (11%); this ion, by loss of S would give the m/e 133 ion and the m/e 132 ion by loss of HS·. Accurate mass measurements confirm that the m/e 165 ion corresponds to (**14**; R = H) (Found: 165.01467. Calc.: 165.01392) obtained by P—Cl bond cleavage. The weak ion at m/e 167. (Found: 167.00375) forms parts of the doublet for the composition ($C_5H_9ClO_2P$); the other line is so weak as to be not apparent. The fragments having m/e 133 (11%) and 135 (4%) (Found: 132.92911 and 134.92491) correspond to the ion (**18**) (Calc.: 132.92799 and 134.92503). The intensities of the m/e 169 (**14**; R = D) and 137 (**15**; R = D) ions are 15% and 3%; the values for the corresponding ions with R = H are 10% and 11%. The absence of [M-55] ion (**19**; R = H) or the corresponding [M-57] ion (**19**; R = D) from the tetradeutero compound, suggests that scheme C is not operative.

Below about 130 a.m.u., the spectra of the 2-methoxy compound (**2** b) and the isomeric 5,5-dimethyl-2-methylthio-1,3,2-dioxaphosphorinan

2-oxide16 differ mainly in respect of the intensities of their m/e 41, 67, 68 and 69 fragments, all of which are greater for the 2-sulphide, and also with regard to the m/e 79 (OPS) ion which, although present for the sulphide, is not observed for the isomeric oxide. However, the spectrum of (**2** b) exhibits neither [M—OMe] nor [M—SMe] fragments; nor does the spectrum of the isomeric oxide (**1** j) exhibit the former of these two ions, but the m/e 150 (10%) ion here corresponds to [M-SMe]. The formation of the [M-SH] ion (7%) for (**2** b) is followed ("metastable") by loss of formaldehyde. Thione-thiol isomerization is also seen to occur for the *O*-aryl thionophosphates (**2** c) and (**2** d) for which the relative intensities of the [M-SAr] ions are 18% and 23% respectively. Neither of these compounds shows direct loss of S or HS· from the molecular ion.

Differences in ring fragmentation pattern when alkoxy (methoxy) is replaced by aryloxy, are to be noticed. The 2-methoxy compound fragments to a moderate extent *via* scheme E, as judged from the intense [M-67] ion; on the other hand, the 2-phenoxy derivative fragments *via* scheme D to give ion (**20**) which, by loss of hydrogen, gives the [M-86] ion (m/e 172; 9%) and finally the m/e 63 ion (PO_2; 9%) by loss of PhS· and also *via* scheme G, with, ultimately, the same result.

The number of more easily recognisable smaller mass fragments from the dithio compounds includes the weakly intense ions at m/e 97 (**21**), 113 (**22**) and 115, probably (**23**), from the dithioic acid (**2** e). The m/e 113 ion (**22**) is not exhibited by the 2-methylthio compound (**2** f) and only weakly by the corresponding ethylthio and isopropylthio derivatives. In contrast to these latter compounds, the compound (**2** f) shows a more pronounced molecular ion peak, and also shows ions at m/e 110 (**24**; 3%), 127 (**25** or isomer; 15%), and 145 (**26**; 6%) which would result from fragmentation through schemes D and E. Traces of [M-15] ion are presumably the result of removal of the 5-methyl group since there is no relative intensification of the [M-18] peak in the spectrum of the 2-[$^2H_3$]-methylthio compound. The presence of the appropriate "metastable" is consistent with the loss of 47 a.m.u. (MeS·) from the molecular ion so affording the ion (**14**; R = H), which, in turn, loses 38 a.m.u. to give the [M-85] ion (CH_4OPS_2). The m/e 166 ion (4%) corresponds to loss of SCH_2 following transfer of hydrogen to the thiophosphoryl sulphur, and is followed, as evidenced by the metastable at 106.7, by loss of HS· to give the [M-79] ion. The trideuteromethylthio compound loses 48 a.m.u. to form the m/e 167 ion and subsequent loss of DS· from this gives ion (15; R = H). The two ions at m/e 130 (17%) and 132 (11%) correspond to those at m/e 127 (15%) and 129 (16%) (for the proto compound), the composition of the last of these (CH_6OPS_2) is confirmed by accurate mass measurement (Found: 128.95808, calc.: 128.95977).

Direct loss of S or HS· from the molecular ions of the anhydrides (2 p, q, r) is unimportant, although there is slight evidence that the trithiopyrophosphate is able to lose two sulphur atoms, and alternatively HS·. For all three compounds, the [M-15], [M-67] and [M-85] ions are of lower intensity than those for the pyrophosphate (**1** bb). Of the three sulphur-containing anhydrides, only (**2** p) shows a (single) "metastable"; this corresponds to the formation of the ion composition ($C_5H_{11}O_2PS$) [M-164] by loss of ($C_5H_9O_2PS$). Further loss of HO· from the former ion affords the familiar m/e 165 ion. The unsymmetrical dithiopyrophosphate (**2** q) provides only traces of the m/e 198 ion ($C_5H_{11}O_2PS_2$) as a result of hydrogen transfer from the 2-oxo-1,3,2-dioxaphosphorinan system. The fragment at m/e 182 is now much more intense (34%) suggesting preferential fission at the dithiolate anhydride bond rather than at the thiolate portion.

Although there is evidence, already referred to, that the amide hydrogen atom plays no direct part in the loss of HS· from phosphoramidothionates, it is to be seen that all of these compounds, with the marked exception of the *N*-n-butyl compound (**2** l), show pronounced [M-22] ions together with weak [M-32] ions. In addition the m/e 133 ion is formed much more intensely for this group of compounds than for the remainder of the 2-sulphides listed. In addition to the general points of contrast between the 2-sulphides and the 2-oxides, already mentioned, it is to be seen that [M-67] and m/e 56 ions are absent from the spectra of the phosphoramidothionates; moreover the m/e 68 and 69 ions are much more intense than those provided by the corresponding phosphoramidates.

Of the analogues of ions (**5**–**12**) containing one sulphur atom, only that of (**5**), m/e 194 sometimes assumes any importance, intensities for (**2**; j, k, l, m, n and o) being 7, 0, 10, 36, 12 and 3% respectively. Intensities of the analogues of (**13**; $R^1 = R^2 = H$) are 9% for (**2** n) and only 5% for each of (**2** m) and (**2** l).

ACKNOWLEDGEMENT

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