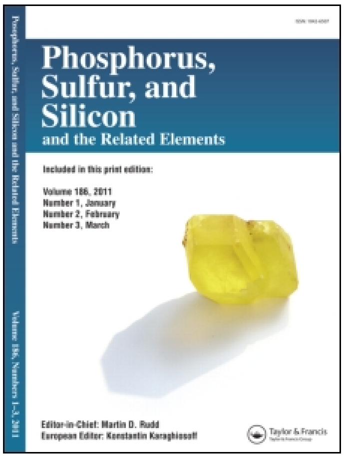

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SYNTHESIS AND MASS SPECTRA OF FIVE- AND SIX-MEMBERED HETEROCYCLIC MOLECULES CONTAINING PHOSPHORUS, OXYGEN, AND NITROGEN

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SYNTHESIS AND MASS SPECTRA OF FIVE- AND SIX-MEMBERED HETEROCYCLIC MOLECULES CONTAINING PHOSPHORUS, OXYGEN, AND NITROGEN

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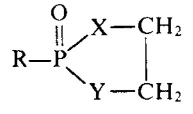
2-Trichloromethyl-1,3,2-dioxaphospholane-2-oxide, dioxaphosphorinane-2-oxide and oxazaphospholane-2-oxide derivatives were synthesized by the stepwise esterification of trichloromethylphosphonyl dichloride with 1,2-, 1,3-, 2,3-diols, aminoethanols (*N*-methyl, ethyl, phenyl, benzyl etc.), 2-amino-2-methyl-1-propanol and 1-amino-2-propanol.

Structures of synthesized heterocyclic molecules were characterized by IR, ^{1}H NMR and mass spectrometry. The electron-impact (EI) mass spectra of a series of dioxaphospholanes, dioxaphosphorinanes, and oxazaphospholanes have been examined, and the principal fragmentation pathways are described. Attempts also were made to compare the EI decompositions of the dioxaphospholanes, which produce four-membered cyclic ions by ring contraction under electron impact, and the dioxaphosphorinane derivatives with those of the other heterocyclic compounds containing P—N and P—S bonds, which gave mostly base peaks from cleavage of the P—C bond.

Synthesis of new organophosphorus compounds and introduction of phosphorus containing functionalities into other molecules in order to modify their physicochemical properties has been frequent. Over the past several years, there has been an increasing amount of synthesis and stereochemical study of trivalent cyclic phosphorus compounds.[1-3] However, heterocyclic molecules containing tetravalent phosphorus derived from alkylphosphonyl dichlorides have been less studied.[4]

In a previous paper,[5] we described the synthesis and mass spectra of 2-trichloromethyl-1,3,2-dioxaphospholane-2-oxide,-diazaphospholane, -oxathiaphospholane, and -oxazaphospholane (I–IV).

$$\mathrm{RP(O)Cl_2 + HX{-}CH_2CH_2{-}YH + 2Et_3N \xrightarrow[\text{solvent}]{-20\text{–}0°C}}$$



+ Salts

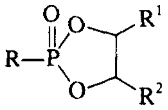
I. X = O, Y = O
II. X = NH, Y = NH
III. X = O, Y = S
IV. X = O, Y = NH

We now have synthesized several new five- and six-membered cyclic phosphorus compounds using trichloromethylphosphonyl dichloride, $\mathrm{Cl_3CP(O)Cl_2}$.

RESULTS AND DISCUSSION

2-*R*-1,3,2-dioxaphospholane-2-oxide and dioxaphosphorinane derivatives were made readily by reaction of trichloromethylphosphonyl dichloride with 1,2-, 2,3-, and 1,3-diols.

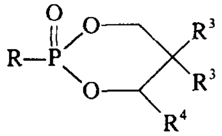
$$RP(O)Cl_2 + HO\text{—}CHR^1CHR^2\text{—}OH + 2Et_3N \xrightarrow[\text{ether}]{-20\text{-}0°C}$$



+ Ammonium Salt

	R^1	R^2
1.	Me	H
2.	CH_2Cl	H
3.	Ph	H
4.	Me	Me

$$RP(O)Cl_2 + HO\text{—}CH_2C(R^3)_2CHR^4\text{—}OH + 2Et_3N \xrightarrow[\text{ether}]{-15\text{-}0°C}$$

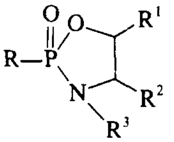


+ Salt

5. R^3 = H′, R^4 = Me 6. R^3 = Et, R^4 = H

2-*R*-1,3,2-oxazaphospholane-2-oxide derivatives were synthesized by the following procedure.

$$RP(O)Cl_2 + \text{Aminoethanols} + 2Et_3N \xrightarrow[\text{ether}]{-20\text{-}5°C}$$



$+ 2Et_3\overset{+}{N}HCl^-$

	R^1	R^2	R^3
7.	H	H	Me
8.	H	H	Et
9.	H	H	Ph
10.	H	H	CH_2Ph
11.	H	Me	H
12.	Me	H	H

Significant spectral data, elemental analysis, and physical data for the series of dioxaphospholanes and dioxaphosphorinanes, 1–6, are collected in Table I, and those of oxazaphospholanes in Table II. The mass spectral data for some heterocyclic phosphorus compounds are given in Tables III–V.

In the IR spectra, it is clear that the frequency of the P=O and P—O bond stretching vibrations are very strong absorptions in the range 1250–1320 cm^{-1} and 980–1060 cm^{-1}, respectively. The vibration of the phosphonyl group in heterocyclic molecules is 20–30 cm^{-1} higher in frequency than in their acyclic equivalents. This is presumed to be due to enhancement of the P_π-d_π double-bond character of cyclic P—X—C bonds (X; O, N, S, etc.) in the five- and six-membered ring molecules.

In general, N—H stretching vibration frequencies are apparently uninfluenced by the adjacent phosphorus atom, and the absorption bands occur in the same region

TABLE I

Spectral and Physical Data, Compounds 1–6

Compounds	mp, °C	yield, %	IR (KBr), cm^{-1}		^1H NMR($CDCl_3$), δ			anal. found (calcd)	
			P═O,	P—O	O—CH,		R^{1a}	C	H
1. 4-Methyl-1,3,2-dioxaphospholane[b]	93.5–95	52	1300	995	4.3	5.0	1.6	20.37(20.26)	2.61(2.52)
2. 4-Chloromethylene-1,3,2-dioxaphospholane	162–163	43	1315	1015	4.8	5.4	4.1	17.65(17.63)	1.82(1.78)
3. 4-Phenyl-1,3,2-dioxaphospholane	94–95	61	1305	1035	4.8	5.9	7.5	35.88(35.89)	2.75(2.69)
4. 4,5-Dimethyl-1,3,2-dioxaphospholane	116–117	40	1298	980	4.6	5.1	1.5	23.76(23.79)	3.37(3.26)
5. 4-Methyl-1,3,2-dioxaphospholane	124–125	56	1275	1055	4.8		1.5	23.78(23.79)	3.28(3.25)
6. 5,5-Diethyl-1,3,2-dioxaphosphorinane	178–179	60	1280	1040	4.6	4.8	1.8, 1.2	32.62(32.61)	4.93(4.80)

[a] R^1; Methyl, Chloromethyl, Phenyl, Ethyl.

[b] 4-Methyl-2-trichloromethyl-1,3,2-dioxaphospholane-2-oxide.

(3200–3300 cm^{-1}) as those in normal amides. The P—N—C bonds are characterized by two stretching vibrations with frequencies ranging from 645–857 cm^{-1} and 800–1150 cm^{-1}. The nomenclature (ν_1, ν_2) is used in view of the existing uncertainty as to the exact origin of these two bands.

The ^1H NMR spectra of the P—O—CH protons in dioxaphospholanes and those of P—N—CH in oxazaphospholanes exhibit signals at δ4.0–6.1 and δ3.5–4.2, respectively, and the peaks are very complex owing to the phosphorus nucleus.

The protons in both the NCH_3 and NH grouping are coupled with the phosphorus nucleus and generally give rise to well-defined doublets. The amine protons in 4,4-dimethyl-1,3,2-oxazaphospholane (11) appear at δ5.2 and the $J_{P\text{-}H}$ value is 17.2 Hz; the coupling constant of the P—N—Me group is 8.5 Hz.

In ^1H NMR spectra of heterocyclic molecules containing a phosphorus atom, observed chemical shifts are quite sensitive to changes in molecular structure, and intramolecular shielding contributions are generally reduced by the interposition of a heteroatom (N,O,S); i.e., the observed chemical shifts of P—O—CH, P—N—CH, and P—S—CH are δ4.0–5.8, δ3.2–4.1, and δ3.2–3.6, respectively. Evidently, the nature of the heteroatom is of primary importance in the behavior of P—X—CH coupling and chemical shifts. As the influence of molecular geometry and other similar factors lessen, the correlations are mainly governed by the inductive effect of the heteroatoms.

STUDY OF MASS SPECTRA

The mass spectra of phosphonyl compounds have been rather little studied.[6,7] Their characterization by mass spectrometry has not been of importance probably owing

TABLE II

Spectral, Physical Data and Yields of Oxazaphospholanes

Products	mp, °C	yield, %	IR (KBr), cm^{-1} P=O,	P—N	$(\upsilon_1, \upsilon_2)^a$	^1H NMR($CDCl_3$), δ O—CH,	N—CH	anal. found (calcd) C	H	N
7. N-Methyl-1,3,2-oxazaphospholane[b]	94–95	43	1290	945	710	4.4	3.6	20.29(20.21)	3.02(2.98)	5.96(5.92)
8. N-Ethyl-1,3,2-oxazaphospholane	98–99	35	1288	945	705	4.4	3.5	23.78(23.74)	3.71(3.56)	5.51(5.51)
9. N-Phenyl-1,3,2-oxazaphospholane	140–141	45	1292	950	685	4.6	4.0	36.02(35.97)	3.31(3.2)	4.60(4.6)
10. N-Benzyl-1,3,2-oxazaphospholane	95–96	46	1290	935	695	4.4	3.5	38.34(38.32)	3.57(3.51)	4.48(4.47)
11. 4,4-Dimethyl-1,3,2-oxazaphospholane	136–137	43	1275	945 3235(N-H)	—	4.38	5.2(N-H)	23.85(23.80)	3.59(3.56)	5.57(5.54)
12. 5-Methyl-1,3,2-oxazaphospholane	146–147	41	1258	935 3220(N-H)	755	5.1	3.6	20.45(20.51)	2.92(2.84)	5.84(5.8)

[a] The P-N-X bonds are characterized by two stretching vibrations (υ_1, υ_2).

[b] N-Methyl-2-trichloromethyl-1,3,2-oxazaphospholane-2-oxide.

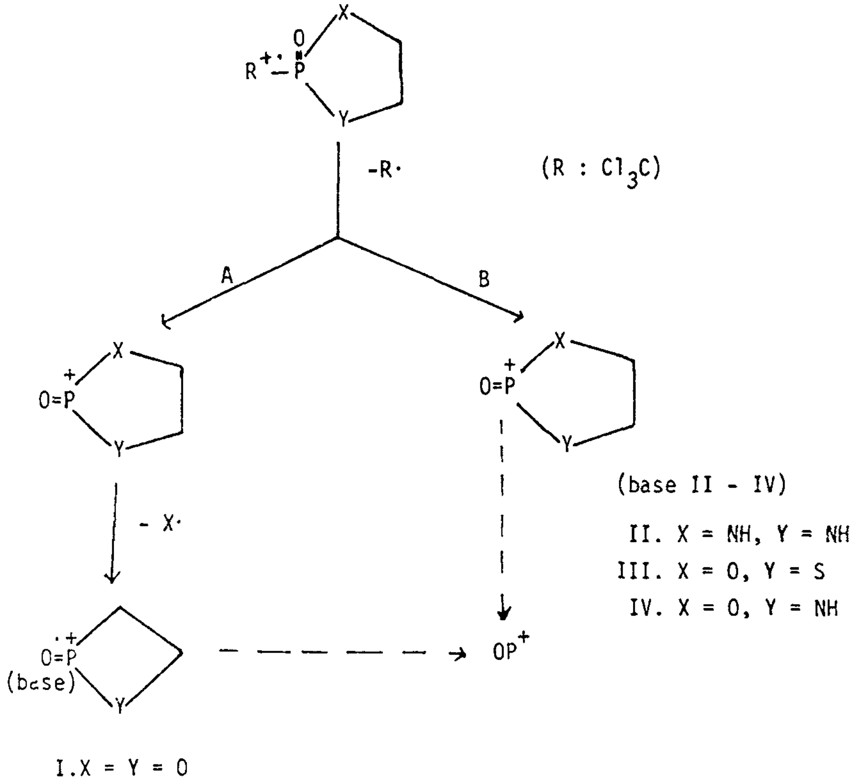
to their relatively high reactivity and ready conversion to other molecules, such as phosphates, which may be identified easily by other methods.

However, we recognized that the EI mass spectra of five- and six-membered phosphonyl compounds were quite simple and it appeared to us that mass spectrometry is a useful method for the structural study of heterocyclic molecules containing a phosphorus atom.

Cleavage of the P—C bond is known to be a facile process in the EI mass spectra of phosphonyl compounds.[7] The first step is also cleavage of the P—C bond in heterocyclic phosphonyl molecules, and the resulting cyclic phosphonium ions, in most spectra of cyclic phosphorus molecules containing P—N and P—S bonds, are base peaks. On the other hand, they are abundant peaks in the spectra of dioxaphospholanes and dioxaphosphorinanes, but they are not base peaks because the P—O bond is weakened under electron-impact. It was observed that ring contraction, which resulted from loss of oxygen from the five-membered phosphonium ions, occurred in the dioxaphospholanes.

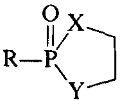
The principal fragmentation pathways of the five-membered cyclic molecules and dioxaphosphorinanes under EI were proposed in the following schemes (I–IV).

As shown in Scheme I, the general decomposition pathways may be of two types: path A and B. In case of dioxaphospholane (X=Y=O), type A is the dominant process, involving ring contraction. With other five-membered cyclic phosphonyl



SCHEME I

TABLE III

Mass spectral data of  compounds

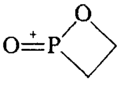
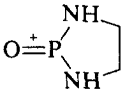
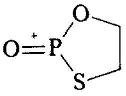
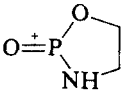
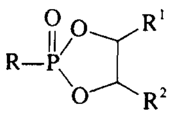
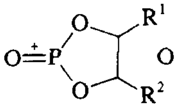
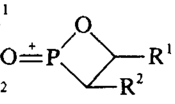
Molc. Type	$M^{+\bullet}$		Base Peak		P=O, %
	m/e	%	m/e	formula	
a. X = O, Y = O	225	0.1	91		39.7
b. X = NH, Y = NH	222	0.1	105		3.3
c. X = O, Y = S	240	3.2	123		19.9
d. X = O, Y = NH	223	—	106		24.9

TABLE IV

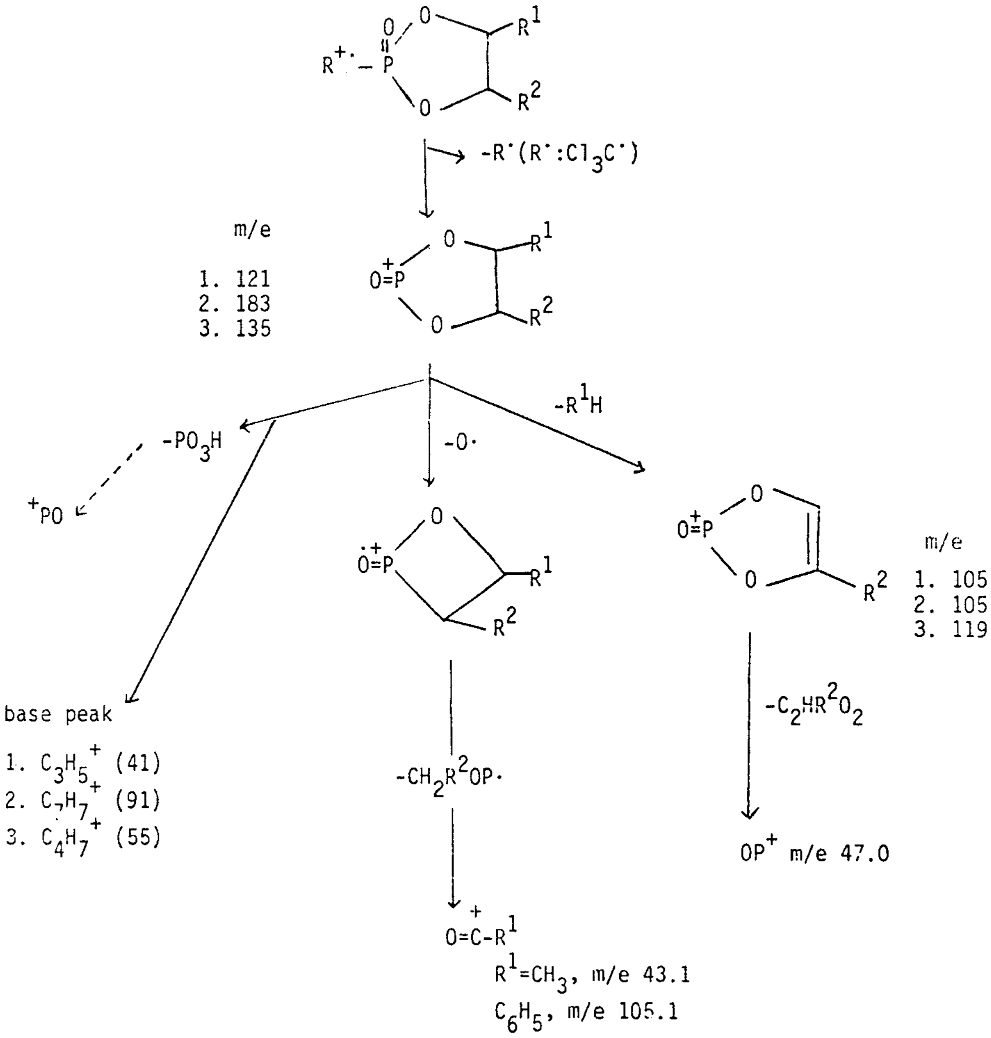
Mass Spectral Data of Dioxaphospholanes

		$M^{+\bullet}$						Base Peak	$^{b}O{=}P^{+}$
R^1	R^2	m/e	%	m/e	%	m/e	%	m/e	%
a. Me	H	238	0.5	121	24.1	105	56.2	41 $C_3H_5^+$	32.1
b. CH_2Cl	H	237 ($-Cl^{\bullet}$)	1.7	155	94.2	139	100.0	139[a]	51.8
c. Ph	H	300	1.0	183	66.4	165	72.2	91 $^{+}CH_2Ph$	14.2
d. Me	Me	—	—	135	41.9	119	23.1	55 $C_4H_7^+$	22.1

[a] 4-Chloromethyl-1,3,2-dioxaphospholane: four-membered cyclic phosphonium ion is base peak.
[b] $O{=}P^+$: m/e 47.

compounds containing P—N and P—S bonds, which give base peaks resulting from cleavage of the P—C bond, type B is the dominant process.

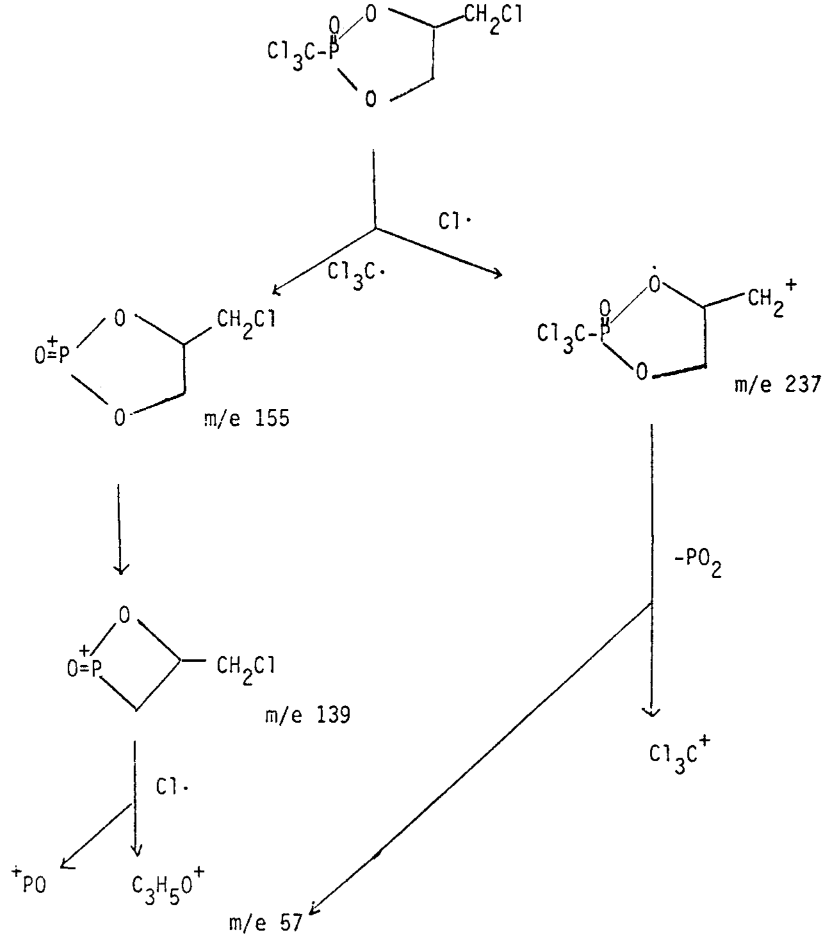
Scheme II shows a proposed decomposition pathway with ions derived from dioxaphospholanes on electron-impact. 4-Chloromethylene-2-trichloromethyl-1,3,2-dioxaphospholane (2) decomposed to give $C_3H_5ClO_2P^{+\bullet}$ (base), $C_3H_5ClO_2P^{+\bullet}$, and



SCHEME II

$C_3H_5O^{+}$ as most abundant ions. It also was observed that 4-chloromethylene-2-trichlorometyl 1,3,2-dioxaphospholane (2) gives a base peak corresponding to a four-membered phosphonium ion at m/e 139, which is derived by loss of oxygen in the fragmentation pathway of the five-membered cyclic ion. In all EI spectra of other dioxaphospholanes, the dominant primary process in decomposition of ionized five-membered cyclic groups is loss of oxygen to give four-membered phosphonium ions, loss of R^1H to give dioxaphospholenes, and loss of PO_3H to give $C_3H_5^+$ at m/e 41, $C_4H_7^+$ at m/e 55, and $C_7H_7^+$ at m/e 91, which are the respective base peaks.

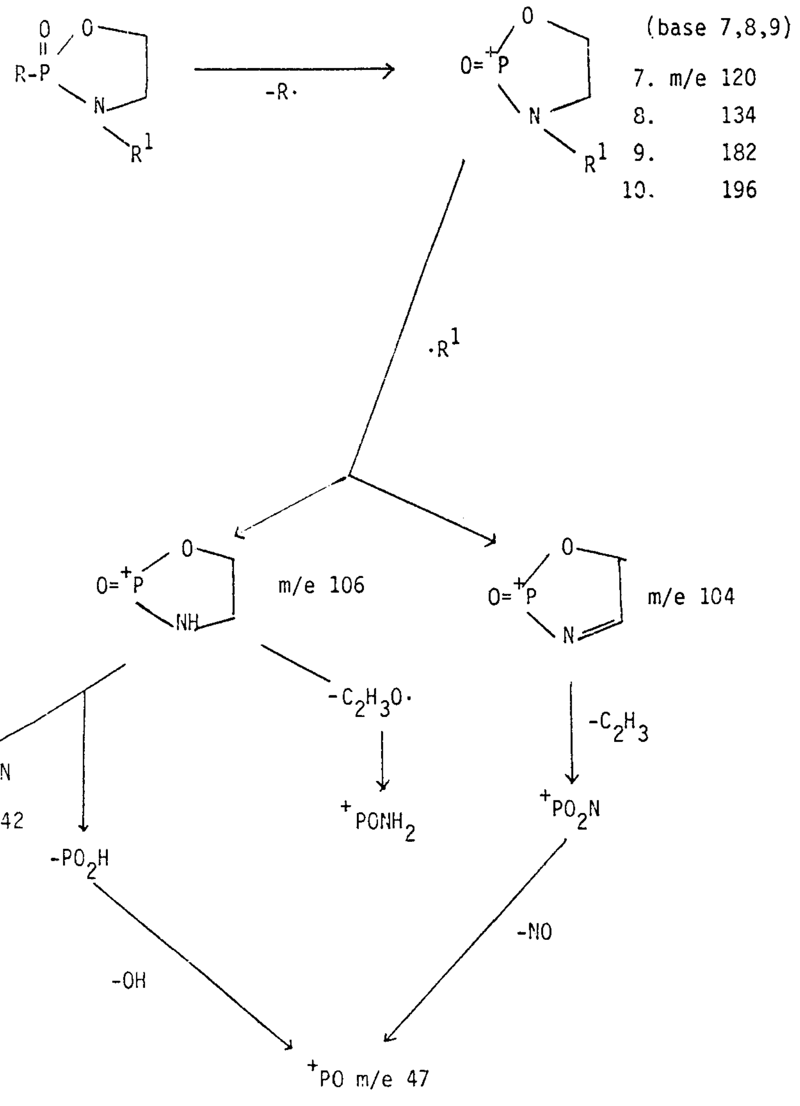
The six-membered heterocyclic phosphonyl compounds, 4-methyl-1,3,2-dioxaphosphorinane-2-oxide (5) and 5,5-diethyl-1,3,2-dioxaphosphorinane (6), are similar



SCHEME III

to dioxaphospholanes (1–4) in EI mass spectra. Both dioxaphosphorinanes give large peaks at m/e 135 ($C_4H_8O_3P^+$) and at m/e 177 ($C_7H_{14}O_3P^+$), which again indicates the tendency for fragmentation to give six-membered phosphonium ions by cleavage of the P—C bond, even in the six-membered ring molecules.

The decomposition pathways of the oxazaphospholanes are described in Scheme IV. Each of the two primary processes involves loss of R^1—H (R^1; methyl, ethyl, phenyl, and benzyl) and loss of $R^{\ddagger}$, implying that a prior, or possibly concerted, hydrogen migration from five-membered phosphonium ions to yield oxazaphospholene ion ($C_2H_3NO_2P^+$ m/e 104) and oxazaphospholane ion ($C_2H_5NO_2P^+$ m/e 106), respectively, could be occurring in *N*-substituted-1,3,2-oxazaphospholane-2-oxides. The five-membered phosphonium ions, which are derived from cleavage of the P—C bond, are base peaks in most mass spectra of the oxazaphospholanes. On the other hand, the mass spectrum of *N*-benzyloxazaphospholane shows that cleavage of the C—N bond in the N—$CH_2C_6H_5$ group gives the base peak at m/e 91 ($C_7H_7^{\ddagger}$), in contrast to the corresponding oxazaphospholanes. It was assumed that this unexpected result is due to the stability of the initially formed benzyl ion.



SCHEME IV

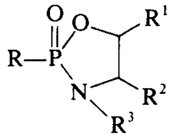
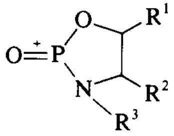
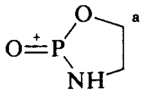
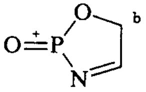
In addition, from the EI spectra of 4,4-dimethyl-1,3,2-oxazaphospholane-2-oxide and 5-methyl-1,3,2-oxazaphospholane, it is observed that cleavage of the P—C bond is a facile process and gives peaks at m/e 134 ($C_4H_9NO_2P^+$) and 120 ($C_3H_7NO_2P^+$), which are the respective base peaks. It is evident that the P—N bond is more stable than the P—O bond under electron impact.

The molecular ions are generally of low abundance in all the compounds, and the spectra of the 4,5-methyl- and 4-chloromethylene-1,3,2-dioxaphospholane-2-oxide do not show an M^+ peak. The ion at m/e 47 (P^+=O) is an abundant ion in all the EI mass spectral data and the peak at m/e 117 (Cl_3C^+) also is present in all the mass spectra, although their abundance varies considerably.

These results suggest that mass spectrometry is a convenient method for the

TABLE V

Mass spectral data of oxazaphospholanes

				$M^{+\cdot}$						$O{=}P^+$
	R^1	R^2	R^3	m/e	%	m/e	(base)	%	%	%
a.	H	H	Me	237	3.1	120		1.2	5.3	19.7
b.	H	H	Et	253	0.9	134		42.5	3.4	18.7
c.	H	H	Ph	299	10.2	182		1.2	46.0	25.3
d.	H	H	CH_2Ph	—	—	196	(56.0%)[c]	—	8.4	16.9
e.	Me	H	H	237	0.7	120		—	—	17.2
f.	H	(Me_2)	H	236 $(-CH_3)$	14.5	134		—	—	32.0

[a] m/e 106,
[b] m/e 104,
[c] base m/e 91 ($^+CH_2Ph$).

characterization of five- and six-membered heterocyclic molecules obtained from alkylphosphonyl dichlorides.

EXPERIMENTAL

The starting material, trichloromethylphosphonyl dichloride, was prepared by the reported method[8] in this laboratory. All the chemicals used were of reagent grade and purified prior to use, if necessary, by known methods.

All the melting points were obtained in open capillaries with a Thomas Hoover capillary melting point apparatus and are uncorrected.

^{1}H NMR spectra were taken on a Varian T-60A spectrometer with tetramethylsilane (TMS) as internal standard and $CDCl_3$ as a solvent. Chemical shifts from TMS are reported on the δ scale.

Mass spectra were determined on a Hewlett-Packard HP5985A mass spectrometer, using 70-eV electrons, and with sample introduction via the batch inlet system at 200 ~ 250°C. Infrared spectra were recorded on a Perkin-Elmer Model 267 grating infrared spectrophotometer. Elemental analyses were obtained on a Hewlett-Packard HP185B CHN analyzer. The following abbreviations are used throughout this section; vs = very strong, s = strong, Et_3N = triethylamine, Et_2O = ethyl ether.

4-Methyl-1,3,2-Dioxaphospholane-2-oxide (1)

A solution of 4.2 g (0.02 mol) of trichloromethylphosphonyl dichloride in 20 mL of Et_2O was added dropwise to 1.5 g (0.02 mol) of 1,2-propanediol and Et_3N, 4.1 g (0.04 mol), in Et_2O, 80 mL, at −20 to −10° over a period of 30 min. The mixture was stirred for a further 1.5 hr. at 0–5°C, filtered, the filtrate evaporated, and the residual solid recrystallized from acetone to give the compound, $C_4H_6Cl_3O_3P$.

IR (KBr); 2995, 1475, 1380, 1300 vs, 1060, 1010, 995 vs, 980 s, 870 s, 780, 760 vs.
Mass spec.; m/e (rel. inten. %) 238 (0.5 $M^{+\cdot}$), 137 (21.5), 121 (24.1), 105 (56.2), 47 (32.1), 41 (100).

4-Chloromethylene-1,3,2-Dioxaphospholane-2-Oxide (2)

In a 250 ml flask with dropping funnel was placed 11.8 g (0.05 ml) of phosphonyl dichloride in 80 mL of dry Et_2O, and 5.5 g (0.05 ml) of 3-chloropropane-1,2-diol. The mixture was stirred, cooled to −20°, and then 10.1 g (0.01 mol) of Et_3N was added dropwise. During the addition, the temperature was maintained at −15 to −20°. After addition was complete, the reaction mixture was stirred for 1 hr. at 0–5° and filtered, leaving a white solid, which was suspended in water. The insoluble solid was collected and recrystallized from chloroform, to give the cyclic compound, $C_4H_5Cl_4O_2P$.

IR (KBr); 3020, 2980, 1470, 1435, 1350 s, 1315 vs, 1015 vs, 940, 905, 780 s.
Mass spec.; 241 (0.5, $C_4H_6Cl_3O_3P^+$), 155 (84.2), 141 (37.2), 139 (100), 57 (84.2), 471 (51.8).

4-Phenyl-1,3,2-Dioxaphospholane-2-Oxide (3)

The starting material (4.7 g, 0.02 mol) in Et_2O was added dropwise to a stirred suspension of 1-phenyl-1,2-ethanediol (2.7 g, 0.02 mol) and Et_3N (4.1 g, 0.04 mol) in Et_2O (80 ml) at −20°. The solution was filtered, the white solid was suspended in water, and residual solid was recrystallized from acetone to give the compound $C_9H_8Cl_3O_3P$.

IR (KBr); 3025, 2990, 1590, 1460, 1305 vs, 980 s, 880 s, 760 s, 710, 700.
Mass spec.; 301 (7.8, $M^{+\cdot}$), 183 (66.4), 165 (72.2), 105 (54.5), 91 (100), 78 (49.6), 47 (14.2).

4,5-Dimethyl-1,3,2-Dioxaphospholane-2-Oxide (4)

By a similar procedure, butane-2,3-diol and phosphonyl dichloride in Et_2O yielded the desired cycle molecule, $C_5H_8Cl_3O_3P$.

IR (KBr); 2990, 1450, 1390, 1298 vs, 1080, 1040 vs, 980 vs, 930 s, 780, 760 s.
Mass spec.; 135 (40.8), 71 (43.2), 55 (100), 47 (40.5), 29 (43.6).

4-Methyl-1,3,2-Dioxaphosphorinane-2-Oxide (5)

The same procedure as described above yielded the product, $C_5H_8Cl_3O_3P$ from 1,3-butanediol.

IR (KBr); 2980, 1480, 1275 v, 1055 vs, 990, 960 v, 880, 780, 760 s, 600.
Mass spec.; 235 (2.8, $M^{+\cdot}$), 135 (40.8), 71 (43.2), 55 (100), 47 (40.5), 29 (43.6).

5,5-Diethyl-1,3,2-Dioxaphosphorinane-2-Oxide (6)

The six-membered ring compound also was obtained from 2,2-diethyl-1,3-propanediol and phosphonyl dichloride in dry Et_2O, $C_8H_{14}Cl_3O_3P$.

IR (KBr); 2985, 1480, 1280 vs, 1085 s, 1040 vs, 980 s, 890, 840 s, 760 s, 615.
Mass spec.; 97 (59.1), 55 (100), 47 (22.5), 41 (55.2), 29 (51.4).

N-*Methyl-1,3,2-Oxazaphospholane-2-Oxide* (7)

In a 250 mL three-necked flask with glass joints, equipped with a sealed mechanical stirrer, a low-temperature thermometer, and a dropping funnel, 11.7 g (0.05 mol) of trichloromethyl dichloride was dissolved in a solution of 50 ml of Et_2O, and the solution was cooled to −20°C. To the cooled solution, 2-(methylamino)ethanol (3.7 g, 0.05 mol) was added dropwise with stirring over a period of 40 min. The reaction mixture was stirred an additional hour, and the temperature was allowed to rise to O°C, and the mixture was filtered with suction. After the ether was removed from the filtrate, the residual solid was recrystallized from a solution of acetone-chloroform, to give the five-membered cyclic compound, $C_4H_7Cl_3NO_2P$.

IR (KBr); 2975, 1485, 1290 vs, 1220, 1040 s, 945 vs, 1010 vs, 870 s, 760 s, 705, 630.
Mass spec.; 241 (1.0, $M^{+\cdot}$), 120 (100), 57 (8.7), 47 (9.7), 42 (54.4).

N-*Ethyl-1,3,2-Oxazaphospholane-2-Oxide* (8)

To a solution of the phosphonyl dichloride in ether, a solution of Et_3N and 2-ethylaminoethanol in ether was added dropwise. The mixture was stirred at 0°C for 2 hr, filtered and the filtrates evaporated. The solid was recrystallized from chloroform-Et_2O below O°C to give the product, $C_5H_9Cl_3NO_2P$.

IR (KBr); 2985, 1470, 1385 s, 1288 vs, 1220, 1010 s, 945 vs, 775 s, 775 s, 750, 630.
Mass spec.; 253 (0.9, $M^{+\cdot}$), 134 (100), 106 (42.2), 104 (3.4), 47 (16.1), 42 (19.2).

N-*Phenyl-1,3,2-Oxazaphospholane-2-Oxide* (9)

The reaction of the phosphonyl dichloride with 2-anilinoethanol in the presence of Et_2N gave, after the usual work-up, the cyclic compound, $C_9H_9Cl_3NO_2P$.

IR (KBr); 3025, 2950, 1600, 1500 s, 1480, 1292 vs, 1040 vs, 970, 950 s, 875, 830 s, 760 s, 685.
Mass spec.; 299 (10.2 $M^{+\cdot}$), 182 (100), 119 (37.2), 106 (2.1), 104 (46.0), 77 (56.3), 47 (25.3).

N-*Benzyl-1,3,2-Oxazaphospholane-2-Oxide* (10)

The same procedure as described above yielded, from *N*-benzylethanolamine, the product, $C_{16}H_{11}Cl_3NO_2P$, which was recrystallized from chloroform-ether.

IR (KBr); 3080, 3030, 2990, 2875, 1980, 1960, 1900, 1880, 1815, 1500, 1460, 1385 s, 1290 vs, 1175 s, 1120 s, 1015 vs, 970 s, 935 s, 835 s, 760 vs, 693, 620.
Mass spec.; 196 (56.0), 153 (8.1), 91 (100), 65 (38.1), 47 (16.9).

4,4-Dimethyl-1,3,2-Oxazaphospholane-2-Oxide (11)

Essentially the same procedure as in experiment 7 yielded from, 2-amino-2-methyl-1-propanol, the cyclic molecule, $C_5H_9Cl_3NO_2P$.

IR (KBr); 3235 s, 2995, 1475, 1370 s, 1340, 1275 vs, 1000 vs, 945, 880, 820, 775, 755 s.
Mass spec.; 251 (1.6 $M^{+\cdot}$), 237 (15.3), 134 (100), 55 (27.4), 47 (28.0), 42 (28.7).

5-Methyl-1,3,2-Oxaxaphospholane-2-Oxide (12)

A mixture of 1-amino-2-propanol (3.8 g, 0.05 mol) and Et_3N (10.1 g, 0.1 mol) in 40 mL of Et_2O was added dropwise at −20° to a stirred solution of phosphonyl dichloride (11.7 g, 0.05 mol) in 50 mL of ether. After 1 hr., $Et_3N.HCl$ was filtered and solvent evaporated. The residue was recrystallized from acetone-chloroform to give $C_4H_7Cl_3NO_2P$.

IR (KBr); 3320 s, 2995, 1450, 1360, 1258 vs, 1050 vs, 960, 930 s, 780 s, 755.
Mass spec.; 237 (0.7 $M^{+\cdot}$), 120 (100), 76 (50.0), 56 (66.8), 47 (17.2).

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