Preparation and Characterisation of Alkylthio- and Phenylthio-phosphetan 1-Oxide Derivatives. Mass Spectrometric Investigations of 40 Phosphetan 1-Oxide Compounds. Differentiation of *cis*- and *trans*-Ring Methyl Groups by Aromatic Shielding

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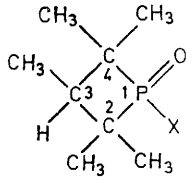
Nine new 1-alkylthio-2,2,3,4,4-pentamethylphosphetan 1-oxide derivatives, $C_8H_{16}P(O)X$, have been prepared and fully characterised by i.r. (resulting in some improved assignments), p.m.r., ^{31}P n.m.r., and especially by mass spectrometry. This last technique has been extended to cover 40 phosphetan 1-oxide compounds of various types. The breakdown pattern is shown to be essentially the same in all cases being largely governed by the fragmentation of the hydrocarbon moiety. An important rearrangement ion is observed which arises from the migration of the group on phosphorus exocyclic to the ring, X, to the hydrocarbon chain. The extent of this rearrangement depends upon the P–X bond strength and the steric crowding associated with X. The compounds $C_8H_{16}P(O)SPh$ and $C_8H_{16}P(O)SCH_2Ph$ exhibit long-range n.m.r. deshielding and shielding of the phosphetan proton and methyl groups respectively by the ring currents of the aromatic component. In the benzylthio-compound this also serves to distinguish for the first time the *cis*- and *trans*-methyl groups.

As part of his studies of the mechanism of substitution at the phosphorus atom of 2,2,3,4,4-pentamethylphosphetan 1-oxides (I) Trippett prepared the ethylthio-



(I) $C_8H_{16}P(O)X$ *trans*-HC-PO

derivative.[1] As in all nucleophilic substitutions of 1-chloro-2,2,3,4,4-pentamethylphosphetan 1-oxide (I), from which it was prepared, retention of configuration occurred. The chloride starting material is prepared from 2,4,4-trimethylpent-2-ene, phosphorus trichloride, and aluminium trichloride in a reaction which gives only the *trans*-isomer [the proton on C(3) *trans* to the oxygen on phosphorus].[2]

Trippett's method of preparing 1-ethylthio-2,2,3,4,4-pentamethylphosphetan 1-oxide used sodium ethylthiolate, generated *in situ* from ethanethiol and sodium hydride, and gave a 76% yield. Recently the use of lead thiolates has been advocated[3] for the replacement of P–Cl by P–SR [reaction (1)]. These reagents are easy to prepare[4] and give rapid reactions. In the case

$$2(\equiv P\text{–}Cl) + Pb(SR)_2 \longrightarrow 2(\equiv P\text{–}SR) + PbCl_2\downarrow \quad (1)$$

of the chloride (I) the reaction is slow and poor yields were obtained and the organothio-derivatives reported here were generally prepared by Trippett's method.

One of the reasons for preparing these thio-compounds was to study their n.m.r. spectra and this has produced some unexpected but extremely interesting results. Another reason was to study their mass spectra and we now report these for 40 compounds of the type $C_8H_{16}P(O)X$, where X is Cl, Br, NHR, NR_2, OR, and SR, as well as a few other derivatives. No systematic study of the mass spectra of the phosphetan system has so far been reported.

EXPERIMENTAL

Instruments.—Phosphorus-31 n.m.r. spectra were recorded on a Bruker HFX90 spectrometer operating at 36·43 MHz, and referenced to 85% phosphoric acid; the initial signal lock was provided by deuteriochloroform. Proton n.m.r. spectra were recorded on a Perkin-Elmer R12B spectrometer operating at 60 MHz, and referenced to tetramethylsilane. The n.m.r. data is collected in Table 2. Infrared spectra were recorded on a Perkin-Elmer PE457 spectrometer using CsBr optics. Samples were studied as liquid films and Nujol or hexachlorobutadiene mulls; chart calibration was checked against the polystyrene band at 1601 $cm.^{-1}$ The i.r. data are deposited as a Supplementary publication.† Mass spectra were recorded on an AEI MS-30 spectrometer operating with electron beam energy of 24 eV; samples were introduced as *ca.* 50% (w/w) solutions in chloroform *via* a g.l.c. Carbowax column (200—210 °C).

Materials.—Only freshly prepared 1-chloro-2,2,3,4,4-pentamethylphosphetan 1-oxide was used after recrystallisation from light petroleum (b.p. 80/100 °C). The thiols were standard laboratory reagents supplied by Koch–Light Ltd. (Bu^nSH, Bu^iSH, Bu^sSH, Bu^tSH, PhSH, $PhCH_2SH$, $HSCH_2CO_2Me$); B.D.H. Ltd. (MeSH, Pr^iSH); and Aldrich Chemical Co. Ltd. (EtSH, Pr^nSH). These thiols and all solvents (AnalaR or distilled laboratory grade) were dried before use. The preparation of the amino-phosphetan derivatives have been described previously.[5] The preparation of the alkoxy-derivatives *etc.* will be reported at a later date.

Preparation of Thiophosphetan Derivatives from Sodium Thiolates.—The thiol was dissolved in ether and the requisite amount of sodium hydride was added to it. After being stirred for 2·5 h at room temperature the mixture

† Supplementary publication No. 20844 (13 pp.) Details of Supplementary publications are given in Notice to Authors No. 7, *J.C.S. Dalton*, 1972, Index Issue.

[1] J. R. Corfield, R. K. Oram, D. J. H. Smith, and S. Trippett, *J.C.S. Perkin I*, 1972, 713.

[2] J. J. McBride, jun., E. Jungermann, J. V. Killheffer, and R. J. Clutter, *J. Org. Chem.*, 1962, **27**, 1833.

[3] R. A. Shaw and M. Woods, *Phosphorus*, 1971, **1**, 41 and 191.

[4] R. A. Shaw and M. Woods, *J. Chem. Soc.* (*A*), 1971, 1569.

[5] J. Emsley and J. K. Williams, *J.C.S. Dalton*, 1973, 1576.

was added to an ice-cooled solution of 1-chloro-2,2,3,4,4-pentamethylphosphetan 1-oxide (0·05 or 0·10 mol) in ether during 20 min after which it was refluxed for 2 h. After the mixture had been cooled an equal volume of water was added to it and the organic layer was separated and extracted twice with small amounts of water. Drying of the ethereal solution (Na_2SO_4) and removal of the solvent gave the crude product which was purified by distillation under reduced pressure or recrystallisation from light petroleum (b.p. 80/100 °C).

Preparation of 1-*Ethylthio*-2,2,3,4,4-*pentamethylphosphetan* 1-*Oxide from Lead Ethylthiolate*.—The phosphetan chloride (I; X = Cl; 9·70 g, 0·05 mol) was added to a suspension of lead ethylthiolate (9·60 g, 0·025 mol) in dry toluene (100 cm^3). Five drops of Sterox ND, a surface-activating agent, were added and the whole was stirred vigorously whilst refluxing for 14 h under an atmosphere of oxygen-free nitrogen. The yellow colour of lead ethylthiolate did not fade completely, indicating a quantitative reaction, although it became noticeably paler. The solution was filtered to remove unchanged lead ethylthiolate and precipitated lead chloride, and the solvent distilled on a rotary evaporator to give a colourless oil (8·2 g). ^1H N.m.r. spectroscopy showed this to contain 46% of the desired product; distillation under reduced pressure gave 3·1 g (0·014 mol, 28% yield) of product.

In a similar reaction with lead n-butylthiolate a colourless oil was obtained which p.m.r. showed to be *ca.* 40% 1-(n-butylthio)-2,2,3,4,4-pentamethylphosphetan 1-oxide; distillation under reduced pressure gave 2·3 g (0·010 mol, 20% yield) of product.

Preparation of 1-*Chloro*-2,2,3,4,4-*pentamethylphosphetan* 1-*Sulphide*.—Phosphorus trichloride (13·8 g, 0·10 mol) and anhydrous aluminium trichloride (13·3 g, 0·010 mol) were added to dichloromethane (100 cm^3) and the mixture was cooled to −5 °C. 2,4,4-Trimethylpent-2-ene (11·2 g, 0·10 mol) was added with stirring during 15 min and the stirring continued for a further 90 min while the temperature increased to ambient. Hydrogen sulphide (0·125 mol) was bubbled through the solution for 40 min and water (100 cm^3) was then added, the temperature being kept below 20 °C. The main product was the 1-oxide but *ca.* 2% of 1-chloro-2,2,3,4,4-pentamethylphosphetan 1-sulphide was formed. This was identified by g.l.c.–mass spectrometry.

In a similar reaction but with phosphorus tribromide and aluminium tribromide a yield of *ca.* 2% of 1-bromo-2,2,3,4,4-pentamethylphosphetan 1-sulphide was obtained, again identified by combined g.l.c.–mass spectrometry.

Attempted Reaction of Potassium Hydrogen Sulphide and 1-*Chloro*-2,2,3,4,4-*pentamethylphosphetan* 1-*Oxide*.—Attempts to prepare the phosphetan thio-acid, $C_8H_{16}P(O)SH \rightleftharpoons C_8H_{16}P(S)OH$, from KSH and $C_8H_{16}P(O)Cl$ in ether solution were unsuccessful.

Phosphetan Acid Anhydride.—In a previous paper [6] the ubiquitous production of the anhydride, $C_8H_{16}P(O)OP(O)C_8H_{16}$, in phosphetan chloride substitution reactions was commented upon. In some of the reactions described above small amounts of the anhydride were also formed. In particular the products of the reactions of lead ethylthiolate and sodium n-butylthiolate with 1-chloro-2,2,3,4,4-pentamethylphosphetan 1-oxide were shown, by g.l.c.–mass spectrometry to contain small traces of two anhydride isomers.

RESULTS AND DISCUSSION

An attempt to prepare 1-chloro-2,2,3,4,4-pentamethylphosphetan 1-sulphide by replacing water with hydrogen sulphide in the preparative reaction gave only 2% of the desired product (2). Production of

$$C_8H_{16} + PCl_3/Al_2Cl_6 \longrightarrow C_8H_{16}\overset{+}{P}Cl_2\overset{-}{A}lCl_4 \xrightarrow{H_2S} C_8H_{16}P(S)Cl \quad (2)$$

the bromophosphetan also proceeded with a very low yield. A simple route to phosphetan 1-sulphides is still unavailable, though other methods are possible.[7]

The alkyl- and arylthio-phosphetan 1-oxides (I; X = SR) have been prepared for a large number of substituents by reaction (3) and some of their physical properties and elemental analyses are shown in Table 1.

$$C_8H_{16}P(O)Cl + RSH + NaH \xrightarrow{\text{ether}} C_8H_{16}P(O)SR \quad (3)$$

The lead thiolate method (1) gave poor results. The nature of the alkyl group did not appreciably affect the substitution reaction as judged by the relative yields of the four butylthio-isomers.

N.m.r. Spectra; Table 2.—The ^{31}P n.m.r. signals fall within a narrow range. The peaks are broad or partially resolved multiplets with half-peak-height widths of *ca.* 100 Hz. The shift order is Ph < Et < Bu^n < $CHMeCH_2Me$ < Me < Bu^t < CH_2CHMe < CH_2Ph < Pr^n < Pr^i which relates to no obvious order of electron-releasing effect. The multiplet of some bands permits the coupling constants between phosphorus and the methyl groups on adjacent ring carbon atoms to be measured.

The ^1H n.m.r. spectra are much more interesting. The signals from the protons of the phosphetan moiety fall in the same region of the spectrum each time except for the benzylthio-derivative which is discussed more fully below. The positions of the signals from the protons of the thio-group vary considerably. The $^3J_{PSCH}$ coupling constant can be obtained from the spectra of $C_8H_{16}P(O)SMe$ (9·5 Hz) and $C_8H_{16}P(O)SCH_2Ph$ (9·0 Hz) both of which show doublets for these protons. Similar values were reported for $^3J_{POCH}$ of $C_8H_{16}P(O)OMe$.[8] The signal from the protons of the t-butyl group of $C_8H_{16}P(O)SBu^t$ is a singlet, showing $^4J_{PSCCH_3}$ to be very small. The $^3J_{HCCH}$ of the thio-fragments are *ca.* 7 Hz which produces almost coincident overlapping multiplets in some spectra. The carbon atoms of the framework have been numbeed (II) to aid identification in Table 2.

For all but one of the spectra the signals from the methyl protons (8,9,11,12) occur as a pair of doublets centred at δ 1·33—1·35 [$^3J_{PCCH_3}$ = 18 Hz] and

[6] J. Emsley and T. B. Middleton, unpublished results.
[7] J. R. Corfield and S. Trippett, *J. Chem. Soc.* (*C*), 1971, 334.
[8] S. E. Cremer and B. C. Trivedi, *J. Amer. Chem. Soc.*, 1969, **91**, 7200.

TABLE 1

Syntheses and characterisation of the thio-derivatives of 2,2,3,4,4-pentamethylphosphetan 1-oxide, $C_8H_{16}P(O)SR$

R	Method of preparation [a]	Yield [b] (%)	B.p./°C(mmHg) or [M.p./°C]	M [c]	Elemental analyses [d](%) C	H	P	S
Me	A	61(46)	125/2·5	206	52·6 (52·4)	9·25 (9·2)	15·1 (15·05)	
Et	A	86(69)	115—117(1·0) [e]	220				
	B	45 [f](28)	118—121(1·2)					
Pr^n	A	100(78)	170—172(4·0)	234	56·55 (56·4)	10·05 (9·85)	13·2 (13·25)	13·85 (13·7)
Pr^i	A	68(37)	164—166(2·0)	234	56·4 (56·4)	9·7 (9·85)	13·2 (13·25)	
Bu^n	A	87(62)	156—158(4·0)	248	58·05 (58·05)	10·25 (10·1)	12·65 (12·5)	13·0 (12·9)
	B	40 [f](20)	151—153(3·2)					
CH_2CHMe_2	A	77(46)	154—156(1·3)	248	58·1 (58·05)	9·8 (10·1)	12·25 (12·5)	12·65 (12·9)
$CHMeCH_2Me$	A	66(44)	136—138(2·0)	248	58·6) (58·05)	10·2 (10·1)	12·3 (12·5)	12·6 (12·9)
Bu^t	A	90(75)	135(0·9)	248	58·5 (58·05)	10·35 (10·1)	13·0 (12·5)	12·9 (12·9)
Ph	A	88(62)	[88—89] [g]	268	62·8 (62·7)	7·61 (7·65)	11·25 (11·55)	11·9 (11·95)
CH_2Ph	A	78(59)	[102—103] [g]	282	63·95 (63·85)	8·1 (8·15)	10·85 (11·0)	11·05 (11·35)

[a] A, sodium thiolate method; B, lead thiolate method. [b] Yield after purification in brackets. [c] Confirmed by mass spectrometry. [d] Calculated values in brackets. [e] Lit.,[1] 104—106 (0·6 mmHg): [f] Estimated from p.m.r. spectrum. [g] Recrystallised from light petroleum (b.p. 80/100 °C).

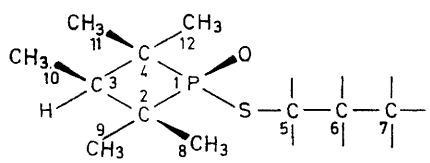
TABLE 2

The n.m.r. spectra of the thio-derivatives of 2,2,3,4,4-pentamethylphosphetan 1-oxide, $C_8H_{16}P(O)SR$, (II)

R	^{31}P n.m.r. spectra δ [a] p.p.m.	Multiplicity [b]	J_{PCCH_3} (Hz)	^{1}H N.m.r. spectra $\delta(CH_3,10)$ [c,d]	$\delta(CH_3,8,11)$ [e,d]	$\delta(CH_3,9,12)$ [f,d]	$\delta(CH,3)$ [g,d]	$\delta(CH,5)$	$\delta(CH,6)$ [d]	$\delta(CH,7)$ [d]
Me	75·41	3		0·89	1·35	1·28	1·72	2·33 (3H, d)		
Et	74·52	9	20·59	0·89	1·35	1·27	1·70	2·98 (2H, dt)	1·39 (3H, t)	
Pr^n	76·83	3		0·91	1·35	1·29	*h*	2·88 (2H, m)	*j*	*j*
Pr^i	78·08	5	20·59, 17·64	0·89	1·34	1·26	1·70	3·60 (1H, sex [i])	1·45 (6H, d)	
Bu^n	75·17	1		0·89	1·33	1·26	*h*	2·88 (2H, m)	*j*	*j*
CH_2CHMe_2	75·90	1		0·88	1·34	1·27	*h*	2·71 (2H, dd)	1·91 (1H, m)	1·04 (6H, d)
$CH(Me)CH_2Me$	75·25	11	20·59, 17·64	0·89	1·34	1·27	*h*	3·49 (1H, m)	*j*	*j*
Bu^t	75·57	11	20·59, 17·64	0·88	1·33	1·28	*h*		1·58 (9H, s)	
Ph	72·18	9	20·59, 17·64	0·89	1·33	1·27	1·89		7·69 (2H, m)	7·32 (3H, m)
CH_2Ph	76·06	11	20·59, 17·64	0·87	1·32	1·08	1·70	4·09 (2H, d)	7·34 (5H, m)	

[a] 85% H_3PO_4. [b] Number of peaks clearly discernible. [c] (3H, dd, $^4J_{PCCCH_3}$, 1·5 Hz; $^3J_{HCCH_3}$, 7 Hz). [d] Me_4Si. [e] (6H, d, $^3J_{PCCH_3}$, 18 Hz). [f] (6H, d, $^3J_{PCCH_3}$, 20·5 Hz). [g] (1H, dq, $^3J_{HCCP}$, 3·5 Hz, $^3J_{HCCH_3}$, 7 Hz). [h] Hidden beneath thiol protons. [i] Overlapping septet less smallest peaks. [j] Too complex for interpretation.

δ 1·27—1·29 [$^3J_{PCCH_3}$ = 20·5 Hz] (Me_4Si). Although the *cis*- (8,11) and *trans*- (9,12) methyl groups give



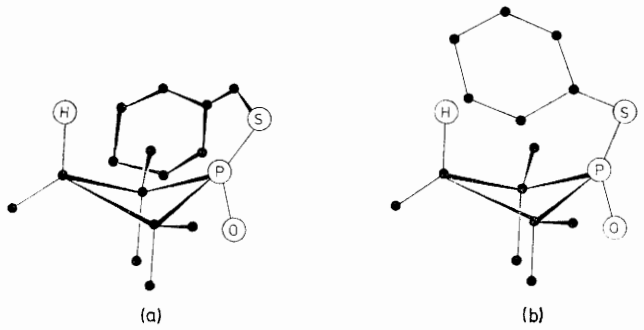
(II)

signals at different δ values, and show different coupling there has so far been no way of deducing which is which in the spectrum. The spectrum of $C_8H_{16}P(O)SCH_2Ph$ however now permits such an assignment to be made. In this one of the pair of doublets is shifted upfield, being centred at δ 1·08, the other doublet remaining unchanged in position. The coupling constant is unaffected in either case.

This changed shift in the spectrum of the benzylthio-compound is characteristic of the increased shielding which can arise from ring currents associated with aromatic systems. Protons favourably placed above and below such rings experience an apparently weaker magnetic field. In this compound the $-SCH_2Ph$ group

must be able to position itself in such a way as to influence the methyl groups on the same side of the ring. Construction of a model shows that this is possible and is illustrated diagramatically in Figure (a). Thus, for the first time, the *cis*- and *trans*-methyl groups can be distinguished.

Also surprising is the downfield shift observed in the spectrum of $C_8H_{16}P(O)SPh$ for the signal from the proton attached to C(3) of the phosphetan ring. This generally is observed as a quartet at *ca.* δ 1·70 but is found at δ 1·89 in the phenylthio-derivative. It is tempting to attribute this shift to deshielding caused by the proton being near to, and in the plane of, the benzene ring. This is feasible if the –SPh group adopts a configuration like that of Figure (b), in which the



Stereochemical diagrams of (a) $C_8H_{16}P(O)SCH_2Ph$, showing interaction between the *cis*-methyls of the phosphetan ring and the benzene ring, and (b) $C_8H_{16}P(O)SPh$, showing interaction between the phosphetan ring proton, H, and the benzene ring

phenyl group lies perpendicular to the phosphetan ring. Again a stereo-model of this compound shows that such a configuration is possible. In this compound the methyl groups (9,12) are not in a position to experience the effects of ring currents. The interaction between the phosphetan ring and other aromatic systems attached to the phosphorus atom is being studied.

*Infrared Spectra.**—The thiophosphetan 1-oxides represent a rare bonding combination at phosphorus of the type $C_2P(O)SR$ (*i.e.* thiophosphinic compounds) a class which is noticeably absent from the thorough compilation of P–S infrared data by Chittenden and Thomas.[9]

As in other phosphetan spectra [5,6,10] the methyl vibrations of the ring and thio-groups provide the strongest bands. The phosphoryl stretching mode, ν(P=O), is at 1194—1203 cm^{-1} which is exactly where the formula of Chittenden and Thomas [11] predicts it to be.

The i.r. spectra of the thio-derivatives are interesting on two counts: first as confirmation of the vibrations proposed as ' characteristic phosphetan modes ' in earlier work [5,6] and especially with regard to ν_{as}(CPC) and ν_s(CPC); and secondly in establishing P–S–C frequencies, and to demonstrate whether this combination has a correlatable range in the spectrum. Consideration of these two points shows there to be bands in the spectra common to all these compounds.

The phosphetan modes in the thio-compounds (I; X = SR) fall at 1230—1239, 929—935, 745—756, 650—670, 640—650, 556—569, 533—544, and 393—404 $cm.^{-1}$ These eight bands are the same as those recorded previously but with the additional observation that the band at 533—544 cm^{-1} has undergone an upward shift of *ca.* 15 cm^{-1} compared with the amino-compounds, showing its susceptibility to substitution at the phosphorus centre. The location of the other frequencies is remarkably constant for the various substituents attached to phosphorus except for the ν_{as}(CPC) band at 1230—1239 cm^{-1}, although the difference between the positions for the amino- and thio-derivatives is small.

Other bands common to all the spectra of the thio-derivatives are at 1164—1182, 985—990, 502—510, and 463—470 $cm.^{-1}$ The last two ranges are the *two* bands of the ν(P–S) which are often, but inexplicably, associated with this bond,[9] their separation being *ca.* 40 cm^{-1} as in other P–S compounds. The two bands at 1164—1182 and 985—990 cm^{-1} are reminiscent of the 1150—1160 and 940—957 cm^{-1} bands of the amino-derivatives. Extensive coupling is expected in both cases and it is unwise to label either the lower or the higher range as a particular vibration.

The spectra (SUP 20844) contain many peaks characteristic of alkylthio-groups [12] and there is also a set of bands at 760—769 cm^{-1} appearing as shoulders to the nearby phosphetan band. These are observed in all the P–S–C (aliphatic) derivatives and may be assigned to an S–C bond mode.

*Mass Spectrometry.**—The thio-, together with the amino-,[5] alkoxy-[6] and other miscellaneous compounds were subjected to mass spectrometric investigation. Some of the compounds given in the Supplementary publication and listed here are reported for the first time and details of their preparation and properties will be published on another occasion.

The halogen derivatives (**1**)—(**4**), being the simplest molecules, and because of the characteristic isotopic patterns of the halogens, allowed a fragmentation scheme to be determined. At low *m/e* values (<112) the spectrum of each compound is dominated by the ions arising from the hydrocarbon moiety, one of these giving rise to the base peak. In the spectra of both the oxides and the sulphides the relative abundances of the molecular ions from the 1-chloro-compounds are greater than those from the 1-bromo-compounds. This is in contrast to the alkyl halides in which the relative

* See Supplementary Publication No. 20844 details, p. 2641.

[9] R. A. Chittenden and L. C. Thomas, *Spectrochim. Acta*, 1964, **20**, 1679.

[10] Unpublished spectra of the authors.

[11] L. C. Thomas and R. A. Chittenden, *Spectrochim. Acta*, 1964, **20**, 467.

[12] A. Menefee, D. O. Alford, and C. B. Scott, *J. Org. Chem.*, 1957, **22**, 792.

abundance of the molecular ions decrease in the order I, Br, Cl, F.

In the case of a phosphorus atom attached to halogen, interaction of the outermost *p* orbitals of the halogen with the 3*d* orbitals of the phosphorus might lead to the more ready loss of one of the lone-pair electrons on the halogen atom and also increase the strength of the P–X bond. Because of the energies of the orbitals involved this interaction should be greater for chlorine, this leading to the relative abundances observed for the molecular ions.

List of 2,2,3,4,4-pentamethylphosphetan 1-oxides and 1-sulphides, $C_8H_{16}P(X)Y$, investigated by mass spectrometry (see SUP 20844)

No.	X	Y	No.	X	Y
(1)	O	Cl	(21)	O	OMe
(2)	O	Br	(22)	O	OEt
(3)	S	Cl	(23)	O	OPr^n
(4)	S	Br	(24)	O	OPr^i
(5)	O	NHEt	(25)	O	OBu^n
(6)	O	$NHPr^n$	(26)	O	OCH_2CHMe_2
(7)	O	$NHBu^n$	(27)	O	OPh
(8)	O	NHPh	(28)	O	OCH_2Ph
(9)	O	$NHCH_2Ph$	(29)	O	$OP(O)C_8H_{16}$‡
(10)	O	NHC_2N_3H*	(30)	O	SMe
(11)	O	$NHCH_2CH_2NHP(O)C_8H_{16}$	(31)	O	SEt
(12)	O	$NH(CH_2)_3NMe_2$	(32)	O	SPr^n
(13)	O	$NH(CH_2)_3NEt_2$	(33)	O	SPr^i
(14)	O	$NH(CH_2)_3NBu^n_2$	(34)	O	SBu^n
(15)	O	NC_5H_{10}†	(35)	O	SCH_2CHMe_2
(16)	O	NMe_2	(36)	O	SBu^t
(17)	O	NEt_2	(37)	O	$SCHMeCH_2CH_3$
(18)	O	NBu^n_2	(38)	O	SPh
(19)	O	$N(CH_2CHMe_2)_2$	(39)	O	SCH_2Ph
(20)	O	OH	(40)	O	SCH_2CO_2Me

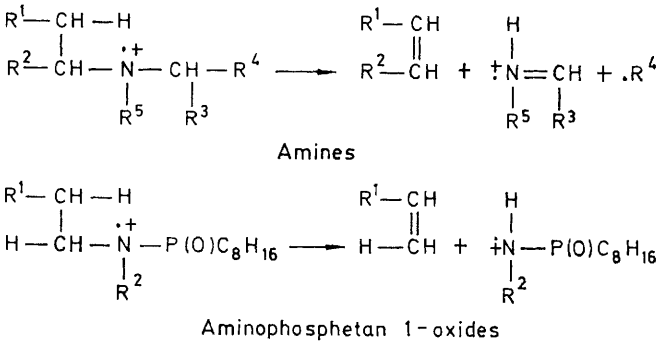
* 3-Amino-1,2,4-triazole derivative. † Piperidino-derivative. ‡ Phosphetan anhydride.

The molecular ions of the 1-sulphides are of greater relative abundance than those from the 1-oxides; this would be expected from the greater ability of the sulphur atom to stabilise the positive charge.

The majority of the ions observed arise from the loss of various hydrocarbon residues from the molecular ion, which suggests that one of the primary processes involves the breaking of one of the C–C or C–P bonds of the ring. Even so it is not possible to account for ions of *m/e* 121 and 123 in the bromine derivatives, and of *m/e* 77 and 79 in the chlorine derivatives.

It is postulated that the formation of these ions, of the type $(CH_3)_2C{=}Y^+$, Y = Cl or Br, is *via* homolytic fission of a P–C bond followed by the migration of Y to the hydrocarbon moiety and the subsequent fission of the C–C bond β to Y (hereafter referred to as Scheme 1).

Aminophosphetans.—The amino-derivatives (**5**)—(**19**) also show a fragmentation pattern that can be rationalised as above. It is also found that, where possible, the expected fission of the C–C bond β to nitrogen takes place, and an ion is observed arising from migration of a hydrogen atom on the β carbon atom of the *N*-alkyl group, to nitrogen. The process is similar to that observed in amines,[13] leading to the formation of an immonium ion and the expulsion of a neutral molecule of an alkene (Scheme 2). This process is found to be



SCHEME 2

more important in the compounds containing a tertiary nitrogen atom.

The rearrangement ion described in Scheme 1 is also observed, the intensity of the ion decreasing as the size and degree of branching of R^1 and R^2 increases, such that in (**12**), (**13**), and (**14**) it is not observed. Other rearrangement ions of the form (III) and (IV) are also

$[C_4H_9P(O)NR^1R^2]^+$ (III) $[C_3H_7P(O)NR^1R^2]^+$ (IV)

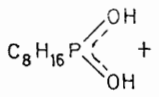
found but the rationale behind their formation is less clear. If R^1 or R^2 is H or Me they appear as such in the ions, but if they contain a C–C bond β to nitrogen, fission of this bond occurs and R^1 and/or R^2 then appear as CH_2.

This situation may be further complicated when R^2 itself contains nitrogen, as in (**12**), (**13**), and (**14**), when two C–C bonds exist β to nitrogen. In this case (III) appears at *m/e* **147**, *i.e.* $[C_4H_9P(O)NH(CH_2)_2]^+$, whereas (IV) is not observed. Not all the compounds studied show these ions but the formation of (III) would seem to be governed by steric effects in the same way as was the formation of the ion described in Scheme 1. However for ion (IV) the reverse seems to be the case. In the symmetrical diamine (**11**) fragmentation appears to take place simultaneously in both rings and the only rearrangement ion observed is that of Scheme 2, again showing the influence of steric effects in their formation. Compound (**11**) is also unusual in that the molecular ion is absent but an $(M + 1)$ ion of relative abundance 20% is found. This presumably arises from an ion-molecule reaction but has not been studied further. The $(M + 1)$ ion may involve the positioning of a proton between the two oxygen atoms attached to phosphorus, and the formation of a hydrogen-type bond.

Acid, Anhydride, and Alkoxyphosphetans.—These compounds (**20**)—(**29**) give fragmentation patterns similar to those described above, being governed mainly by

[13] R. S. Gohlke and F. W. McLafferty, *Analyt. Chem.*, 1962, **34**, 1281.

that due to the hydrocarbon moiety. The most noticeable feature of the spectrum of the acid (**20**) is the abundant $(M + 1)$ ion—this presumably being due to



(V)

the resonance-stabilised form (V). Of the rearrangement ions already mentioned only that described in Scheme 1 is important for the acid and this is explained by $E(\text{P–O}) > E(\text{P–N})$. Type (IV) ions are of very low intensity with the size of R having very little effect on their relative abundance. Type (III) ions are only observed for the butoxy-derivatives (**25**) and (**26**).

Thiophosphetans.—In the spectra of these compounds, (**30**)—(**40**), the rearrangement ion described in Scheme 1 is much more abundant, in fact it is able to account for the base peak in all cases where R is a straight-chain alkyl group or phenyl. The abundances of these rearrangement ions demonstrate clearly the effect of the size of R, and the degree of branching. Moreover, since they are also much more abundant than in any of the previous classes of compound studied, they show that the extent of rearrangement is dependent on the strength of the exocyclic phosphorus bond.

In conclusion it can be seen that the mass spectra of the phosphetan 1-oxides are largely governed by the fragmentation of the hydrocarbon moiety, but that an important rearrangement ion is observed which arises from migration of the group singly bonded to phosphorus to the hydrocarbon chain. The extent of the rearrangement depends on the strength of the bond to phosphorus and also on the steric crowding associated with this group.

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