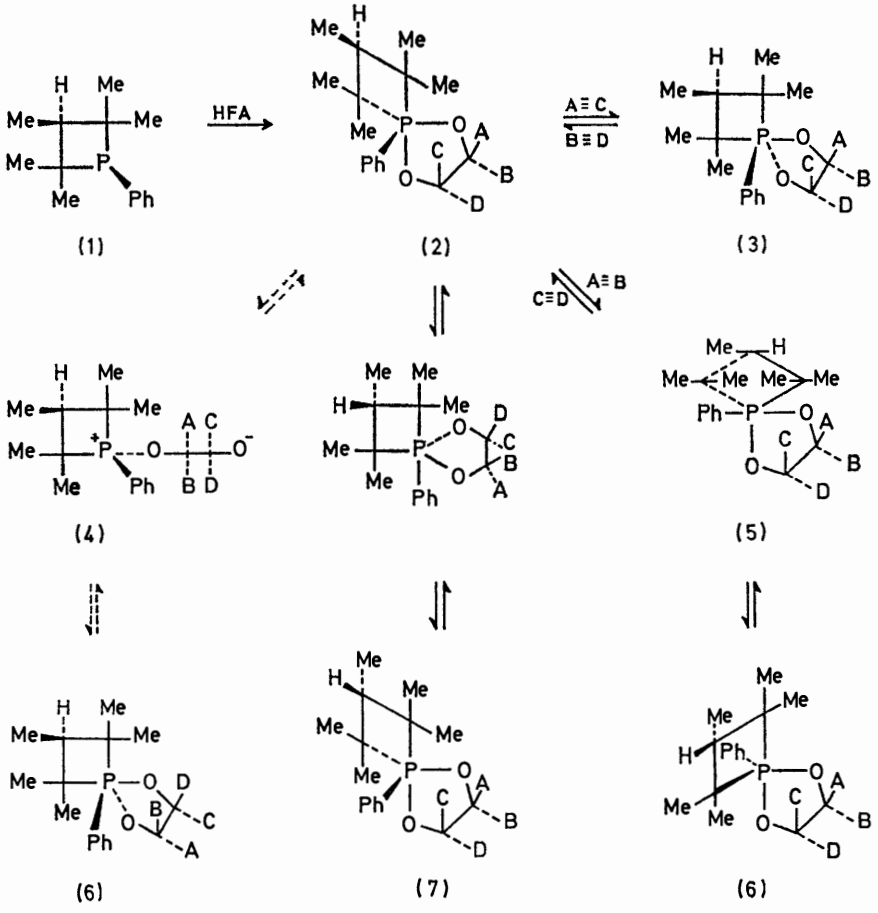
Reactions of 1-Substituted 2,2,3,4,4-Pentamethylphosphetans with Hexafluoroacetone and the ^{19}F Nuclear Magnetic Resonance Spectra of the Resulting 1,3,2-Dioxaphospholans

By **Robert K. Oram** and **Stuart Trippett,*** Department of Chemistry, The University, Leicester LE1 7RH

A series of 1-substituted 2,2,3,4,4-pentamethylphosphetans have been prepared, and converted into the corresponding 1,3,2-dioxaphospholans on treatment with hexafluoroacetone. The ^{19}F n.m.r. spectra of these adducts over a range of temperatures have given values of the free energies of activation for the pseudorotation processes which place the four-membered ring diequatorial and the 1-substituents apical. The variation in these activation energies with the nature of the 1-substituent is accounted for in terms of the relative apicophilicity of groups being a function of both electronegativity and p_π–d_π back-bonding. Some of the consequences of this hypothesis are explored. Some unusual reactions and isomerisations of the 1,3,2-dioxaphospholans and of the related 1,2-oxaphosphetans are described.

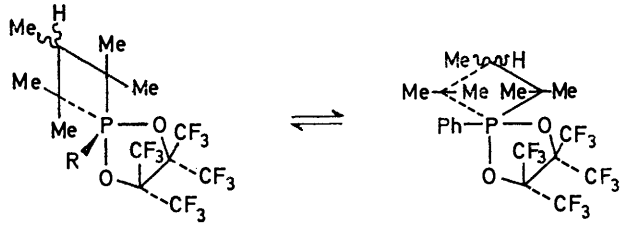
NUCLEOPHILIC substitution at phosphoryl or phosphonium centres is usually discussed [1] on the basis of the following assumptions: (*a*) substitutions proceed *via* pentacovalent intermediates which are trigonal bipyramidal in geometry; (*b*) the nucleophile enters into an apical position and the leaving group departs from an apical position; and (*c*) the intermediate may be sufficiently long-lived to undergo ligand reorganisation. Apical attack of the nucleophile can give four possible trigonal bipyramidal intermediates, and each of these can pseudorotate in three directions. In order to understand the process of substitution it is therefore necessary to be able to predict the relative stabilities of these possible intermediates and to assess the barriers to their interconversions. Two factors have been considered important in this connection: first the preference of electronegative groups for the apical positions, and secondly the preference of small-membered rings for an apical-equatorial situation, but there are few quantitative data on these factors. This paper reports our first attempts to supply these data.



[1] For reviews of the evidence on which these generalisations are based see (*a*) F. H. Westheimer, *Accounts Chem. Res.*, 1968, **1**, 70; (*b*) F. Ramirez, *ibid.*, 1968, **1**, 168; (*c*) K. Mislow, *ibid.*, 1970, **3**, 321.

Our general approach [2] involves a study of the ^1H and ^{19}F n.m.r. spectra of the 1,3,2-dioxaphospholans formed [3] from hexafluoroacetone (HFA) and 1-substituted 2,2,3,4,4-pentamethylphosphetans. The *c*-3-methyl-*r*-1-phenylphosphetan (1) with HFA gave the remarkably stable adduct (2; A—D all = CF_3), which could be recrystallised from water. The structure is supported by the ^{31}P chemical shift and by the mass spectrum. The ^1H n.m.r. spectrum, which did not vary between −60 and +160°, showed the α-methyl signals as a pair of doublets; this implies that at −60° pseudorotation between the equivalent trigonal bipyramids (2) and (3) is fast on the n.m.r. time scale. At 160° no equilibration of the *cis*- (2) and *trans*- (7) adducts occurred, showing that the pseudorotation placing the 1,3,2-dioxaphospholan ring diequatorial is of high energy. We have previously shown [4] that this pseudorotation in the corresponding 2,2,4,4-tetramethyl adduct is slow on the n.m.r. time scale at 160°. The ^{19}F n.m.r. spectrum of (2) at room temperature in *o*-dichlorobenzene consisted of two peaks, Δν 153 Hz, of equal intensity and showing fine structure. At higher temperatures these peaks smoothly and reversibly coalesced (T_c 140°). The spectrum at room temperature is consistent with the rapid pseudorotation (2) ⇌ (3) which makes A ≡ C and B ≡ D; the coalescence at 140° is due to rapid equilibration of (2) and (6) either *via* the high energy trigonal bipyramid (5) in which the four-membered ring is diequatorial or *via* dissociation of (2) to give the betaine (4) and reclosure to form (6). Either process makes A equivalent to B and C to D. However the coalescence temperature was unchanged in 1-bromonaphthalene and in ethylene glycol. Solvation in the glycol would favour formation of the betaine (4) and would be expected to lower the coalescence temperature. We therefore associate the variable temperature ^{19}F n.m.r. phenomena with the pseudorotation (2) ⇌ (5). The free energy of activation, ΔG^*, for this process at 140° is 19·6 kcal mol^{-1}.

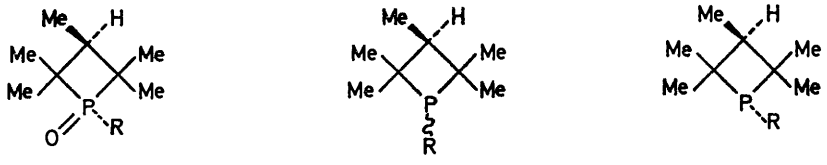
The energy difference between (2) and (5) is due to the increase in ring strain on moving the four-membered ring from an apical-equatorial to a diequatorial position, the difference in apicophilicity between Ph and CMe_2, and possible steric effects. If the phenyl group in (2) were replaced by a series of groups the strain factor and the apicophilicity of CMe_2 would remain constant and the variation in the free energy of activation for the pseudorotations (8) ⇌ (9) would be a reflection of the varying apicophilicities of the groups attached to phosphorus and possibly of varying steric effects. However two caveats have to be entered. The ΔG^* value for the process (8) ⇌ (9) is greater than the energy difference between (8) and (9) but variations in ΔG^* as R is varied will underestimate changes in the relative stabilities of (8) and (9).* Furthermore, comparison of free energies of activation determined at



(8) (9)

different coalescence temperatures is valid only if the entropies of activation are small. The available data on pseudorotation processes suggest that this is the case.[5]

Preparation of Phosphetans.—The *trans*-phosphetan oxides (10; R = Pr^i, CH_2·CMe:CH_2, *p*-BrC_6H_4, or Bu^t) were obtained from *r*-1-chloro-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide and the corresponding Grignard or organolithium reagent. 2-Methylallylmagnesium chloride gave only a low yield of the expected 1-(2-methylallyl)phosphetan oxide together with the 2-methylprop-1-enyl isomer and a dimeric phosphine oxide of unknown structure. The oxide (10; R = *p*-MeO·C_6H_4) was prepared by the general method of



(10) (11) (12)

Jungermann and McBride [6] and separated from the *cis*-isomer by column chromatography. Reduction to the phosphetans was accomplished with either phenylsilane, which in some cases (R = Bu^t, *p*-BrC_6H_4, *p*-MeO·C_6H_4) was not stereospecific, or trichlorosilane in the presence of triethylamine.

* However, calculations reported by Mislow [1c] suggest that structures such as (5) and (9; R = alkyl) are transition states rather than intermediates.

[2] Preliminary account, R. K. Oram and S. Trippett, *J.C.S. Chem. Comm.*, 1972, 554.

[3] F. Ramirez, C. P. Smith, J. F. Pilot, and A. S. Gulati, *J. Org. Chem.*, 1968, **33**, 3787.

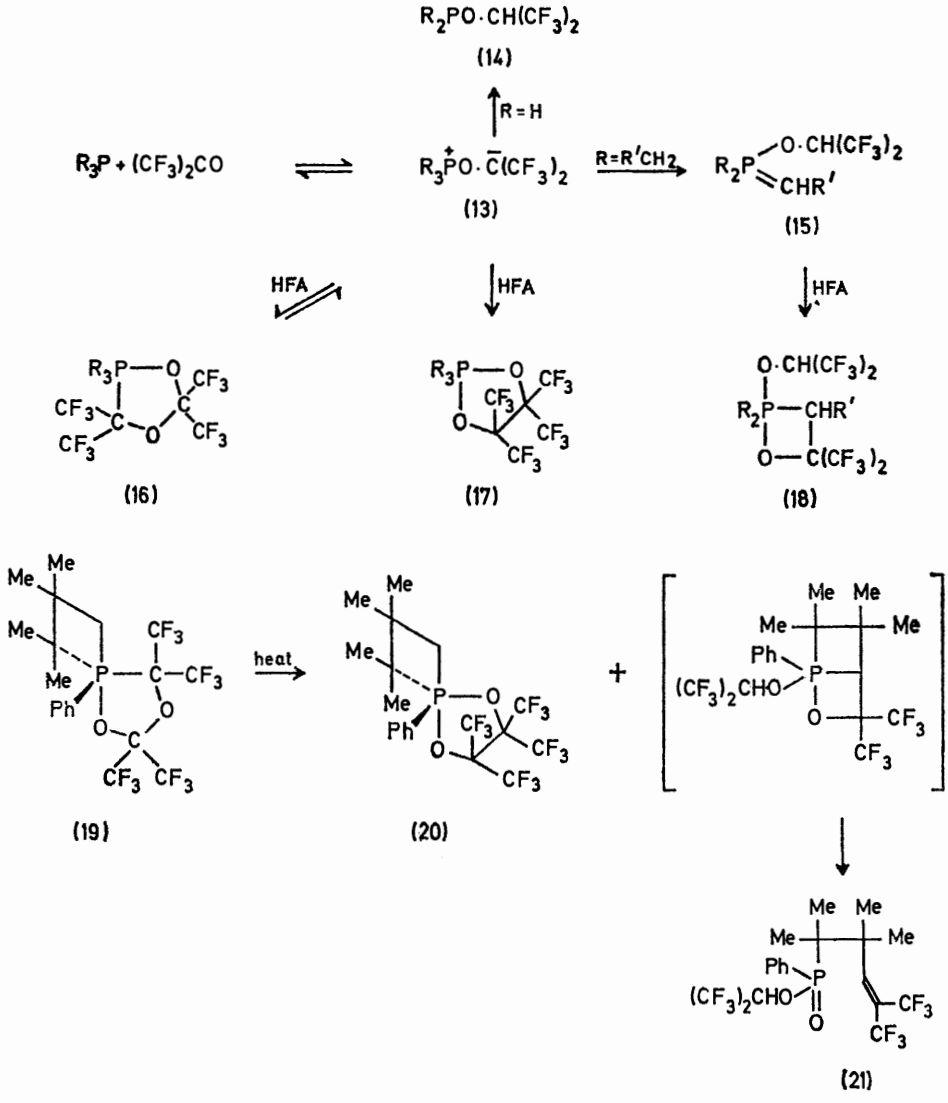
[4] A. E. Duff, R. K. Oram, and S. Trippett, *Chem. Comm.*, 1971, 1011.

[5] *E.g.* D. Gorenstein, *J. Amer. Chem. Soc.*, 1970, **92**, 644; A. Klaebe, J.-F. Brazier, F. Mathis, and R. Wolf, *Tetrahedron Letters*, 1972, 4367.

[6] E. Jungermann and J. J. McBride, *J. Org. Chem.*, 1961, **26**, 4182; E. Jungermann, J. J. McBride, J. V. Kilheffer, and R. J. Clutter, *ibid.*, 1962, **27**, 1833.

The phosphetans (11; R = NMe_2, $N[CH_2]_4$, OPh, or SPh) were obtained by nucleophilic substitution of the 1-chlorophosphetan (a mixture of *trans*- and *cis*-isomers) which is known to involve inversion of configuration at phosphorus.[7] The resulting phosphetans were initially 1 : 3 mixtures of *trans*- and *cis*-isomers which slowly equilibrated to favour the *trans*-isomer. With the 1-phenylthiophosphetan equilibration of isomers was rapid and the product isolated was a stable 1 : 1 isomer mixture.

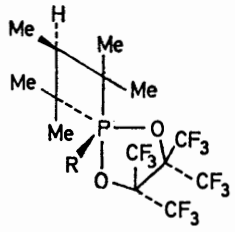
Reactions of Phosphetans with Hexafluoroacetone.—Phosphines react with HFA to give initially the 1 : 1 adducts (13).[3,8] With secondary phosphines [8] transfer of a proton can then give the phosphinites (14), whereas with phosphines having hydrogen on an α-carbon atom [9,10] transfer of this relatively acidic proton leads to the ylides (15), which react with another molecule of HFA to give the 1,2-oxaphosphetans (18). The 1 : 1 adducts (13) with a second molecule of HFA give the thermodynamically favoured 1,3,2-dioxaphospholans (17) although the initial 1 : 2 adducts are probably the 1,4,2-dioxaphospholans (16). We find that the 1,4,2-dioxaphospholan (19) formed from 2,2,3,3-tetramethyl-1-phenylphosphetan is stable at room temperature; in refluxing benzene it gives the 1,3,2-dioxaphospholan (20) and the phosphinate (21), formed *via* a 1,2-oxaphosphetan.



1,3,2-Dioxaphospholans (23) were obtained without complication and as single isomers from the pure *trans*-phosphetans (12; R = Ph, Pr^i, or $CH{:}CMe_2$) and from the *cis*-1-phenylphosphetan, and as mixtures of *cis*- (22) and *trans*- (23) isomers from the mixed isomers of the phosphetans (11; R = NMe_2, $N[CH_2]_4$, OPh, Bu^t,

[7] J. R. Corfield, R. K. Oram, D. J. H. Smith, and S. Trippett, *J.C.S. Perkin I*, 1972, 713.
[8] R. F. Stockel, *Chem. Comm.*, 1968, 1594.
[9] F. Ramirez, C. P. Smith, and J. F. Pilot, *J. Amer. Chem. Soc.*, 1968, **90**, 6726.
[10] Mazhar-Ul-Haque, C. N. Caughlan, F. Ramirez, J. F. Pilot, and C. P. Smith, *J. Amer. Chem. Soc.*, 1971, **93**, 5229.

p-BrC_6H_4, or *p*-$MeO{\cdot}C_6H_4$). Chromatography of the adducts from (11; R = NMe_2) gave the pure *trans*-isomer (23; R = NMe_2). The 1-phenylthiophosphetan (11;



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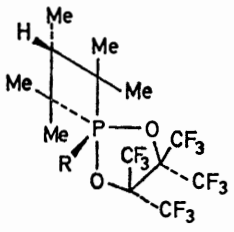
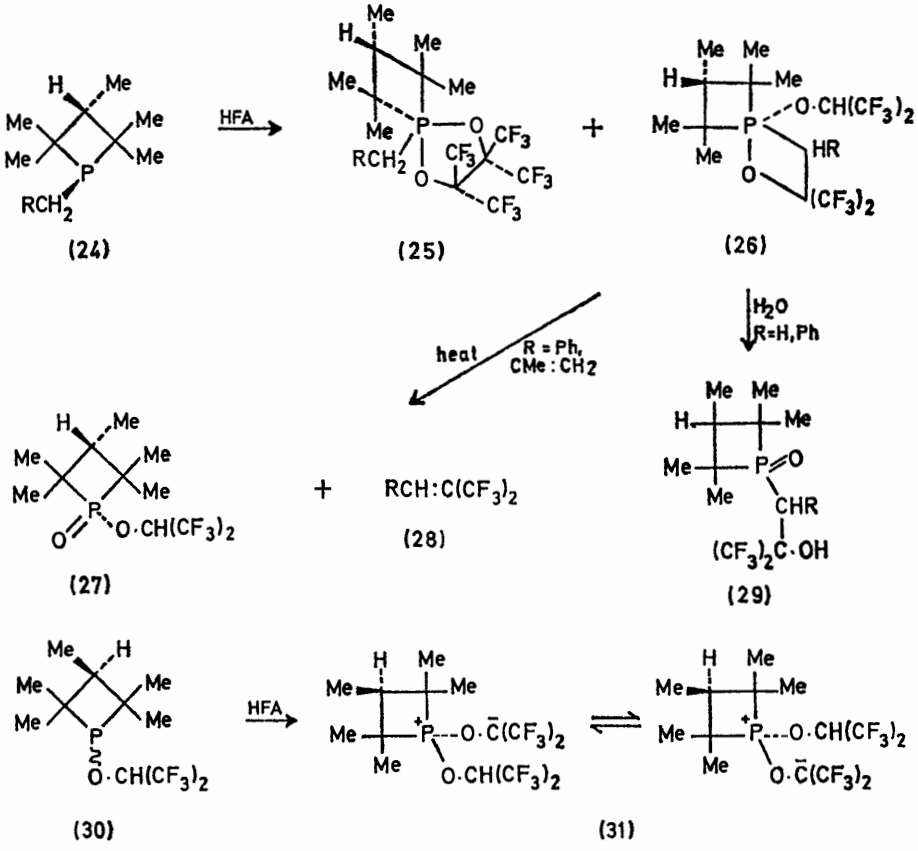


(23)

R = SPh) did not react with HFA under normal conditions; without solvent and at room temperature for 10 days only diphenyl disulphide was isolated.

the olefin (28; R = Ph) and the *cis*-phosphinate (27). With the 1-(2-methylallyl)phosphetan (24; R = $CMe{:}CH_2$) only the phosphinate (27) and the olefin (28; R = $CMe{:}CH_2$) were isolated. The exclusive formation of 1,2-oxaphosphetans from the phosphetans (24; R = Ph or $CMe{:}CH_2$) is in accord with the increased acidity of the transferred α-protons.

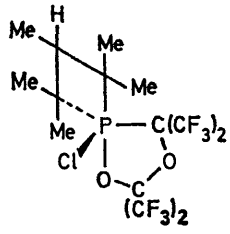
The pentamethylphosphetan (11; R = H) with HFA gave a highly crystalline 1 : 2 adduct whose ^{19}F n.m.r. spectrum at room temperature consisted of two sharp singlets, in the ratio of 3 : 4, separated by only 0·3 p.p.m. This rules out a 1,4,2-dioxaphospholan structure and suggests a mixture of isomeric 1,3,2-dioxaphospholans. The adduct decomposed slowly at room temperature and rapidly at 70° to give HFA and the phosphinite (30) as a mixture of isomers in the ratio of 3 : 4. This phosphinite reacted slowly with an excess



Chromatography of the crude product from the *trans*-1-methylphosphetan (24; R = H) gave the 1,3,2-dioxaphospholan (25; R = H) and the phosphetan oxide (29; R = H) formed by hydrolysis on the column of the 1,2-oxaphosphetan (26; R = H). The 1,2-oxaphosphetan (26; R = Ph) was the only product isolated from the *trans*-1-benzylphosphetan (24; R = Ph), and HFA. The ^1H n.m.r. spectrum showed the presence of only one of the four possible isomers and hydrolysis gave the alcohol (29; R = Ph) as a single isomer. Above 70° the 1,2-oxaphosphetan (26; R = Ph) gave of HFA at room temperature to give the expected 1,3,2-dioxaphospholan [22 or 23; R = $O{\cdot}CH(CF_3)_2$] as an apparently pure isomer of unknown geometry. The loss of stereospecificity in the formation of this adduct is presumably due to proton transfer in the intermediate (31).

The chlorophosphetan (11; R = Cl) with HFA gave a crystalline 1 : 2 adduct which decomposed at room temperature to regenerate chlorophosphetan of unchanged isomeric composition. The ^{19}F n.m.r. spectrum of the adduct showed two equal signals separated by 17

p.p.m. Together with the high solubility of the adduct in pentane, this suggests the covalent 1,4,2-dioxaphospholan structure (32).



(32)

Discussion of the ^{19}F N.m.r. Data.—The Table contains data on the variable temperature ^{19}F n.m.r. spectra of the 1,3,2-dioxaphospholans (8) together with the free energies of activations for the pseudorotations (8) ⇌ (9) obtained by application of the Gutowsky–Holm equation. Two related points are immediately apparent. First the apicophilicities of the carbon substituents are in the reverse order of their electronegativities, and secondly there is remarkably little difference in the apicophilicities of isopropyl and dimethylamino, two groups of similar size. These observations, together with the calculations of Ugi and his co-workers [11] which show that p_π–d_π back-bonding in a trigonal bipyramidal phosphorane is more effective from equatorial than from apical positions, led us to propose in our preliminary communication [2] that apicophilicity is a balance between electronegativity, increase in which favours occupation of the apical position, and ability to back-bond into phosphorus *d*-orbitals, increase in which favours occupation of the equatorial positions. At about the same time Hoffmann, Howell, and Muetterties [12] put forward a similar hypothesis on the basis of their calculations.

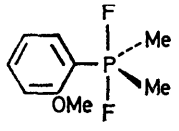
The application of these ideas to the interpretation of the above data implies considerable back-bonding from equatorial nitrogen. Hoffmann, Howell, and Muetterties [12] have predicted that such bonding is maximal with the filled *p*-orbital in either the equatorial or the apical plane with overlap from the equatorial plane being the greater, and have related this [13] to the barriers of 5—12 kcal mol^{-1} to rotation round equatorial P–N bonds observed in a variety of aminophosphoranes.[14] Similar slow rotation has been observed in alkylthio- and arylthio- [15] but not in aryloxy-phosphoranes.[16] This would lead one to expect a considerable difference in apicophilicity between sulphur and oxygen both on the grounds of electronegativity and of the extent of p_π–d_π back-bonding.

Also implied in this interpretation is considerable back-bonding from equatorial phenyl, which might be manifested by a barrier to rotation round the equatorial *P*-aryl bond. We have been unable to find evidence for this in the low temperature ^{19}F and ^1H n.m.r. spectra of the aryldifluorodimethylphosphoranes (33) and (34) prepared from the phosphine sulphides and antimony trifluoride. Slowing of *P*-aryl bond rotation should lead to non-equivalence either of the fluorine atoms, if the aryl ring prefers the apical plane, or of the methyl groups if the aryl ring prefers the equatorial plane. At −90° (^{19}F) and −80° (^1H) there was no evidence of this; the barrier to rotation in these compounds must therefore be less than about 9 kcal mol^{-1}. Solubility difficulties prevented study at lower temperatures.

N.m.r. data for the adducts (22) and/or (23)

R [a]:	Ph(*cis*)	Ph	CH:CMe$_2$	Pr^i	Me	NMe$_2$	N[CH$_2$]$_4$	OPh [b]	O·CH(CF$_3$)$_2$	H [b]
^{19}F T_c	140 [c]	>180 [e]	135 [d]	93 [d]	85 [d]	63 [e]	60 [e]	−77 [f]	*f, g*	*f, h*
								−85		
Δν/Hz	153	133	219	83	166	92	73	*ca.* 220		
Δ*G**/kcal mol^{-1}	19·6	>22	19·1	17·8	16·9	16·2	16·2	*ca.* 9		
Electronegativity [j]		2·49	2·37	2·28	2·27	2·40		2·68	3·74 [k]	2·2

[a] *trans* to 3-Me except as shown. [b] Mixture of *cis* and *trans*. [c] 1-Bromonaphthalene. [d] *o*-Dichlorobenzene. [e] Toluene. [f] $CFCl_3$. [g] Sharp singlet at −80°; broad at −125°. [h] Sharp singlet at −115°. [j] Ref. 20. [k] For O·CF_3.



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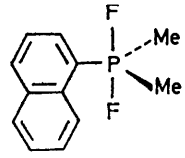


(34)

The ^{19}F spectra of (33) and (34) were both temperature- and concentration-dependent. At high concentrations (1 : 1) a single broad absorption 10 p.p.m. wide was observed at 10°. Lowering the concentration at this temperature or lowering the temperature at this concentration resulted in a change to two absorptions corresponding to PF coupling to two identical apical fluorine atoms. Increasing the temperature led to considerable narrowing of the absorption. In the ^1H n.m.r. spectra at room temperature only PCH coupling was observed; FPCH coupling developed as the temperature was lowered. These effects were unchanged in the presence of sodium fluoride and are probably due to intermolecular fluorine exchange as observed

[11] P. Gillespie, P. Hoffmann, H. Klysacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem. Internat. Edn.*, 1971, **10**, 687.

[12] R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1972, **94**, 3047.

[13] E. L. Muetterties, P. Meakin, and R. Hoffmann, *J. Amer. Chem. Soc.*, 1972, **94**, 5674.

[14] M. J. C. Hewson, S. C. Peake, and R. Schmutzler, *Chem. Comm.*, 1971, 1454.

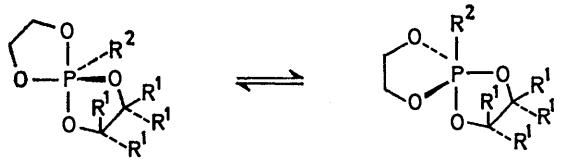
[15] S. C. Peake and R. Schmutzler, *J. Chem. Soc.* (*A*), 1970, 1049.

[16] S. C. Peake, M. Fild, M. J. C. Hewson, and R. Schmutzler, *Inorg. Chem.*, 1971, **10**, 2723.

by Cowley and his co-workers [17] in trifluorodimethyl- and difluorotrimethyl-phosphoranes.

The variable temperature ^{19}F n.m.r. spectra of the *cis*- and *trans*-*p*-bromophenyl adducts analogous to (2) and (7) were virtually identical with those of the phenyl adducts. The corresponding *p*-methoxyphenyl adducts were thermally unstable and no reliable n.m.r. data could be obtained. It might be expected that p_π–d_π back-bonding from phenyl would be sensitive to substituent effects but we have been unable to find any clear evidence on this in the literature.

Unlike the other 1,3,2-dioxaphospholans described in this paper, that obtained from the pentamethylphosphetan (11; R = H) was sensitive to the presence of water. It may therefore be that the observed ^{19}F n.m.r. data and the implied very high apicophilicity of hydrogen are due to an irregular process such as betaine formation. This interpretation is supported by the ready thermal decomposition of this adduct to give the



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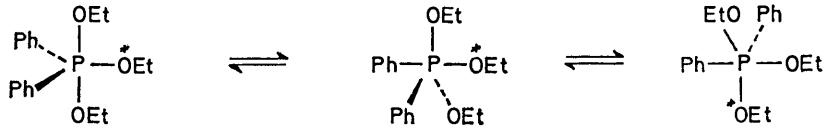
phosphetan (30), but a high apicophilicity for hydrogen is certainly consistent with calculations on H_2PF_3 [11] and with data on other phosphoranes which suggest that hydrogen is more apicophilic than oxygen. Thus the coalescence temperatures observed for the pseudorotations (35) ⇌ (36) are 37° (R^1 = Me, R^2 = H) [18] and 172° (R^1 = H, R^2 = OMe).[19]

In comparing the relative apicophilicities of groups derived from ^{19}F n.m.r. data for the 1,3,2-dioxaphospholans (8) with those obtained from data on other phosphoranes it must be remembered that both electronegativity [20] and, in particular, p_π–d_π bonding are dependent on the nature of the other substituents attached to phosphorus. It would therefore be unreasonable to expect one general scale of relative apicophilicities to apply in all circumstances. The difference of at least 13 kcal mol^{-1} in the activation energies for placing phenyl and phenoxy apical in the phosphetan–HFA adducts underestimates the difference in apicophilicity of the groups in this environment. However data on the pseudorotations (37) ⇌ (38) ⇌ (39) [21] and (40) ⇌ (41) [22] suggest that here the difference in apicophilicity is less than 12 kcal mol^{-1}. Gorenstein [23] has shown that there is little difference in apicophilicity between ethoxy and phenoxy. Until more data are available it will not be possible to assess how serious a difficulty is presented by changes in apicophilicity with environment.

In an attempt to observe the expected increase in apicophilicity of the dimethylamino-group on protonation, the *trans*-adduct (23; R = NMe_2) was dissolved in hexafluoropropan-2-ol (pK_a 9·3). Rapid and complete replacement of the amino-group occurred to give the hexafluoroisopropoxy-adduct as a single isomer identical with that obtained from the phosphinite (30) and HFA. If this involved nucleophilic substitution at phosphorus *via* a six-co-ordinate species it would be expected [24] to occur with inversion of configuration and lead to the *cis*-isomer [22; R = O·CH$(CF_3)_2$]. It was not possible to establish the stereochemistry of the replacement because of the proton transfer possibilities in the intermediate (31) already mentioned. Attempted displacements of dimethylamino with methoxy and with phenylthio under both acidic and basic conditions were unsuccessful. The phenoxy-adduct (8; R = OPh) was unchanged in hexafluoropropan-2-ol.



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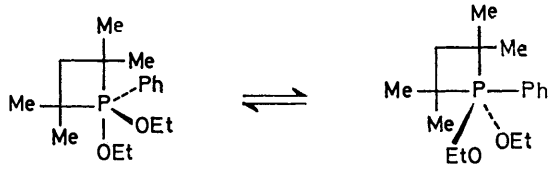
When treated in chloroform solution at room temperature with 2 mol. equiv. of hexafluoroprop-2-ol, the 1,2-oxaphosphetan (26; R = Ph) slowly isomerised and after 18 h equilibrium was established with a second



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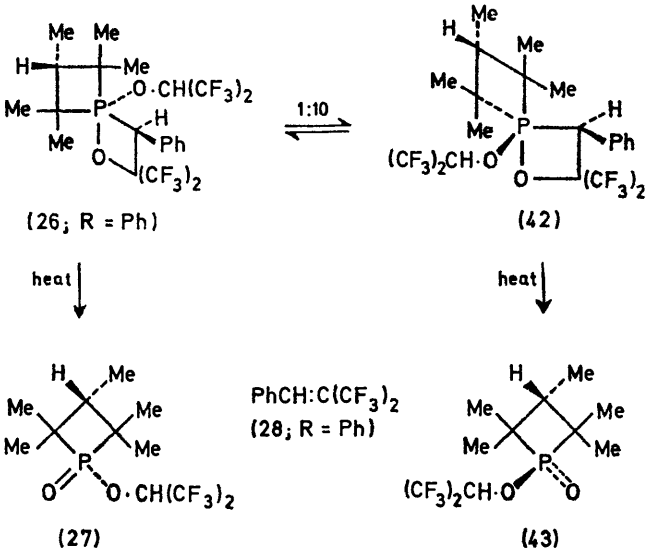
1,2-oxaphosphetan in a ratio of 1 : 10. Thermolysis of the equilibrium mixture gave the olefin (28; R = Ph) and a mixture of the phosphinites (27) and (43) in which

[17] T. A. Furtsch, D. S. Dierdorf, and A. H. Cowley, *J. Amer. Chem. Soc.*, 1970, **92**, 5759.
[18] D. Houalla, R. Wolf, D. Gagnaire, and J. B. Robert, *Chem. Comm.*, 1969, 443.
[19] B. C. Chang, W. E. Conrad, D. B. Denney, D. Z. Denney, R. Edelman, R. L. Powell, and D. W. White, *J. Amer. Chem. Soc.*, 1971, **93**, 4004.
[20] J. E. Hewey, *J. Phys. Chem.*, 1965, **69**, 3284; 1966, **70**, 2086.
[21] D. B. Denney, D. Z. Denney, B. C. Chang, and K. L. Marsi, *J. Amer. Chem. Soc.*, 1969, **91**, 5243.
[22] D. Z. Denney, D. W. White, and D. B. Denney, *J. Amer. Chem. Soc.*, 1971, **93**, 2066.
[23] D. Gorenstein, *J. Amer. Chem. Soc.*, 1970, **92**, 644.
[24] F. Ramirez, G. V. Loewengart, E. A. Tsolis, and K. Tasake, *J. Amer. Chem. Soc.*, 1972, **94**, 3531.

the *trans*-isomer (43) predominated. The original isomer is therefore assigned a *cis* relationship between the hexafluoroisopropoxy-group and the 3-methyl, and the new isomer (42) a corresponding *trans* relationship. This is consistent with equilibration involving



nucleophilic substitution at phosphorus [24] rather than acid-catalysed opening of the 1,2-oxaphosphetan ring.[25] Nucleophilic substitution would also imply a change in relationship between the hexafluoroisopropoxy-group and the phenyl at the 3-position of the 1,2-oxaphosphetan ring. This is supported by a downfield shift of 0·73 p.p.m. in the ^{1}H n.m.r. signal from the hexafluoroisopropoxy-group during the isomerisation, consistent with a change in relationship from *trans* to *cis* as shown in the formulae (26) and (42).

EXPERIMENTAL

^{19}F N.m.r. spectra were determined at 56·4 MHz; chemical shifts are relative to internal $PhCF_3$. ^{31}P N.m.r. spectra were obtained at 24·3 MHz in benzene unless otherwise stated; chemical shifts are relative to external 85% H_3PO_4. ^{1}H N.m.r. spectra were determined at 60 MHz. Mass spectral data for compounds marked with an asterisk are available in Supplementary Publication No. SUP 20697 (19 pp., 1 microfiche).†

Preparation of Phosphetan Oxides from r-1-*Chloro*-2,2,t-3,4,4-*pentamethylphosphetan* 1-*Oxide and Organometallic Reagents.*—Isopropylmagnesium bromide (0·11 mol) in ether (75 ml) was added slowly to a stirred solution of the chlorophosphetan oxide (19·4 g) in ether (100 ml). The mixture was refluxed for 18 h and then cooled in ice while 0·1N-hydrochloric acid (50 ml) was cautiously added. The ether was removed under reduced pressure and the residue extracted with dichloromethane. The extract was washed with dilute sodium hydroxide and with saturated aqueous sodium chloride, dried, and evaporated to give r-1-*isopropyl*-2,2-t-3,4,4-*pentamethylphosphetan* 1-*oxide** (18 g), m.p. 136—138° (from cyclohexane), τ 7·88 (1H, dq, *J* 1·5 and 7 Hz), 8·72 (6H, dd, J_{PH} 14 Hz), 8·74 (6H, d, *J* 15 Hz), 8·76 (6H, d, *J* 17 Hz), and 9·12 3H(, dd, *J* 7 and 1·5 Hz) (the isopropyl methine signal could not be identified) (Found: C, 65·1; H, 11·3; P, 15·0. $C_{11}H_{23}OP$ requires C, 65·35; H, 11·4; P, 15·35%).

In a similar way *p*-bromophenylmagnesium bromide gave r-1-(p-*bromophenyl*)-2,2,t-3,4,4-*pentamethylphosphetan* 1-*oxide** (66%), m.p. 172—174° (from light petroleum), τ 1·83—2·5 (4H, m), 7·93 (1H, dq, *J* 1·5 and 7 Hz), 8·58 (6H, d, *J* 17 Hz), 8·88 (6H, d, *J* 20 Hz), and 8·97 (3H, dd, *J* 1·5 and 7 Hz) (Found: C, 67·35, H, 6·2; P, 9·65. $C_{14}H_{20}BrOP$ requires C, 67·15; H, 6·35; P, 9·85%), and t-butyl-lithium gave 2,2,t-3,4,4-*pentamethyl*-r-1-*t-butylphosphetan* 1-*oxide** (76%), m.p. 150—151° (from light petroleum), τ 8·00—8·33 (1H, m), 8·67 (6H, d, *J* 16·5 Hz), 8·68 (9H, d, *J* 13·5 Hz), and 9·13 (3H, dd, *J* 1·5 and 7 Hz) (Found: C, 66·85; H, 11·5; P, 14·15. $C_{12}H_{25}OP$ requires C, 66·65; H, 11·55; P, 14·35%).

Crystallisation of the crude product from 2-methylallylmagnesium chloride from ether–light petroleum gave 2,2,t-3,4,4-*pentamethyl*-r-1-(2-*methylallyl*)*phosphetan* 1-*oxide** (8%), m.p. 127—128°, $\nu_{max.}$ 1639, 1236, 1181, 1160, 1139, 890, and 671 cm^{-1}, τ 4·98br (2H, s), 7·35 (2H, d, *J* 11 Hz), 8·02br (3H, s), 8·40 (1H, dq, *J* 1·5 and 7 Hz), 8·81 (12H, d, *J* 17 Hz), and 9·14 (3H, dd, *J* 1·5 and 7 Hz) (Found: C, 67·2; H, 10·9; P, 14·7. $C_{12}H_{23}OP$ requires C, 67·3; H, 10·75; P, 14·5%). The mother liquors were chromatographed on basic alumina. Elution with ether–light petroleum (1 : 1) gave 2,2,t-3,4,4-*pentamethyl*-r-1-(2-*methylprop*-1-*enyl*)*phosphetan* 1-*oxide** (20%), m.p. 110—112° (from light petroleum), $\nu_{max.}$ 1633, 1228, 1179, 1148, 1010, 848, and 642 cm^{-1}, τ 4·47 (1H, d, *J* 26 Hz), 7·92 (3H, d, *J* 12 Hz), 7·94 (3H, d, *J* 10 Hz), 8·47 (1H, dq, *J* 8 and 18 Hz), and 9·13 (3H, d, *J* 8 Hz) (Found: C, 67·5; H, 10·9; P, 15·05. $C_{12}H_{23}OP$ requires C, 67·3; H, 10·75; P, 14·5%). Elution with ether–methanol (100 : 1) gave an unidentified phosphine oxide* (25%), m.p. 168—170° (from dichloromethane–light petroleum), $\nu_{max.}$ 1642, 1230, 1181, 1155, 1136, 891, 821, 688, and 650 cm^{-1}, τ 4·67 (1H, d, *J* 27 Hz), 7·17 (2H, d, *J* 10 Hz), 7·47 (3H, s), 8·1 (2H, d, *J* 9 Hz), 8·42—9·0 (24H, m), and 9·11 (6H, dq, *J* 1 and 7 Hz) (Found: C, 67·1; H, 10·8; P, 14·5. Calc. for $C_{24}H_{46}O_2P_2$: C, 67·3; H, 10·75; P, 14·5%).

1-p-*Methoxyphenyl*-2,2,3,4,4-*pentamethylphosphetan* 1-*Oxides.*—2,4,4-Trimethylpent-2-ene (4·5 g) in dichloromethane (50 ml) was added slowly to a stirred solution of dichloro-*p*-methoxyphenylphosphine (8·4 g) and aluminium chloride (5·2 g) in dichloromethane (100 ml) at 10°. After 1 h the solution was added slowly to an ice–water slurry (1 kg). The organic layer was washed with dilute sodium hydroxide and with water, dried, and evaporated. The residue was chromatographed on basic alumina (100 g). Elution with ether–light petroleum (1 : 1) gave r-1-p-*methoxyphenyl*-2,2,t-3,4,4-*pentamethylphosphetan* 1-*oxide** (10%), m.p. 151—153° (from light petroleum), τ 1·9—3·0 (4H, m), 6·17 (3H, s), 8·62 (6H, d, *J* 16 Hz), 8·80 (6H, d, *J* 24 Hz), and 9·00 (3H, d, *J* 7 Hz) (Found: C, 67·5; H, 8·7; P, 11·6. $C_{15}H_{23}O_2P$ requires C, 67·65; H, 8·65; P, 11·65%). Elution with ether–methanol (100 : 1) gave the cis-*isomer* (15%), m.p. 113—115° (from light petroleum), τ 1·93—3·07 (4H, m), 6·17 (3H, s), 7·72 (1H, q, *J* 7 Hz), 8·65 (6H, d, *J* 16 Hz), 8·82 (6H, d, *J* 19 Hz), and 9·00 (3H, d, *J* 7 Hz) (Found: C, 67·9; H, 8·65; P, 11·6%).

† For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

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Reduction of Phosphetan Oxides.—(i) *By use of phenylsilane.* Phenylsilane (0·05 mol) was added in three portions to the phosphetan oxide (0·05 mol) at room temperature. The mixture was heated to 100° over 2 h and then distilled under reduced pressure. In this way the following 1-substituted 2,2,3,4,4-pentamethylphosphetans were obtained: *trans*-(2-methylprop-1-enyl) (85%), b.p. 76—78° at 2 mmHg, τ 3·8 (1H, m), 7·40 (1H, q, *J* 8 Hz), 8·08 (3H, s), 8·13 (3H, s), 8·73 (6H, d, *J* 19 Hz), 9·00 (6H, d, *J* 6 Hz), and 9·27 (3H, d, *J* Hz), ^{31}P δ −32·5 p.p.m.; *trans*-(2-methylallyl) (50%), b.p. 64—65° at 1·8 mmHg, τ 5·1—5·4br (2H, s), 7·43 (1H, q, *J* 7 Hz), 7·42—7·65br (2H, s), 8·23 (3H, s), 8·88 (6H, d, *J* 18 Hz), 9·07 (6H, d, *J* 6 Hz), and 9·33 (3H, d, *J* Hz); t-butyl as a 3 : 2 mixture of isomers (97%), b.p. 84—86° at 1 mmHg, τ 7·43 (q, *J* 7 Hz; minor isomer) and 7·92 (dq, *J* 1·5 and 6·5 Hz; major isomer); *p*-bromophenyl as a 3 : 2 mixture of isomers, b.p. 117—118° at 0·25 mmHg, τ 7·23 (q, *J* 7 Hz; major isomer), and 7·68 (dq, *J* 3 and 7 Hz; minor isomer); *p*-methoxyphenyl as a 4 : 3 mixture of isomers (62%), b.p. 117—119° at 0·5 mmHg, τ 7·12 (q, *J* 7 Hz; minor isomer) and 7·47 (dq, *J* 3 and 7 Hz; major isomer).

(ii) *By use of trichlorosilane.* Trichlorosilane (0·015 mol) in toluene (10 ml) was added slowly to a stirred solution of triethylamine (0·015 mol) and the phosphetan oxide (0·015 mol) in toluene at 0°. After 0·5 h 5N-sodium hydroxide (30 ml) was added dropwise. The organic layer was washed with saturated aqueous sodium chloride, dried, and used directly in the reactions with HFA. Reduction under these conditions was stereospecific.

2,2,3,4,4-*Pentamethylpyrrolidin*-1-*ylphosphetan.*— Pyrrolidine (2·1 g) in pentane (10 ml) was added slowly to a stirred solution of 1-chloro-2,2,3,4,4-pentamethylphosphetan [7] (1·8 g) in pentane (25 ml) at 0° and the mixture was set aside at room temperature for 24 h. Filtration and removal of solvent under reduced pressure gave the crude pyrrolidin-1-ylphosphetan (2·0 g), τ 6·5—7·0 (4H, m), 7·33—8·5 (4H, m), 8·70 (6H, d, *J* 4 Hz), 8·85 (6H, d, *J* 20 Hz), and 9·15 (3H, d, *J* 8 Hz) for the major isomer and τ 6·6—7·07 (4H, m), 7·38 (1H, q, *J* 7·5 Hz), 8·03—8·4 (4H, m), 8·91 (6H, d, *J* 6 Hz), and 9·27 (3H, d, *J* 7·5 Hz) for the minor isomer. On keeping at 100° for 3 h the isomer ratio changed from 3 : 1 to 3 : 4. Hydrogen peroxide (20 vol; 20 ml) and the phosphetan (0·11 g; isomer ratio 3 : 4) in dichloromethane (20 ml) were stirred together for 2 h. The organic layer was washed with water and dried and distilled to give 2,2,3,4,4-*pentamethylpyrrolidin*-1-*ylphosphetan* 1-*oxide* * (80%), b.p. 90—95° at 0·5 mmHg, τ 6·67—7·2 (4H, m), 8·17—8·67 (4H, m), 8·78 (6H, d, *J* 16·5 Hz), 8·88 (6H, d, *J* 16·5 Hz), and 9·28 (3H, d, *J* 7·5 Hz) for the major isomer; the minor isomer showed τ 8·74 (6H, d, *J* 17 Hz) and 8·93 (6H, d, *J* 17 Hz); isomer ratio 3 : 2 (Found: C, 62·7; H, 10·9; N, 6·05. $C_{12}H_{24}NOP$ requires C, 62·9; H, 10·75; N, 6·15%).

r-1-*Dimethylamino*-2,2,t-3,4,4-*pentamethylphosphetan* 1-*Oxide.*—Dimethylamine (4·0 g) in hexane (20 ml) was added slowly to a stirred solution of the chlorophosphetan oxide (7·8 g) in hexane (25 ml) at −20°; the mixture was set aside at this temperature for 24 h and filtered. Solvent was removed under reduced pressure and the residue, in dichloromethane (40 ml), extracted with 0·05N-hydrochloric acid (3 × 25 ml). The combined extracts were rapidly made alkaline with aqueous sodium hydroxide and extracted with dichloromethane. The extract was dried and evaporated and the residue distilled to give r-1-*dimethylamino*-2,2,t-3,4,4-*pentamethylphosphetan* 1-*oxide* * (12%), b.p. 85—90° at 1 mmHg, m.p. 42—47°, τ 7·62 (6H, d, *J* 10 Hz), 8·3 (1H, q, *J* 7 Hz), 8·73 (6H, d, *J* 18·5 Hz), 8·94 (6H, d, *J* 17 Hz), and 9·3 (3H, d, *J* 7 Hz), ^{31}P δ − 74 p.p.m. (Found: C, 58·9; H, 10·85; N, 6·65. $C_{10}H_{22}NOP$ requires C, 59·15; H, 10·85; N, 6·9%).

r-1-*Dimethylamino*-2,2,t-3,4,4-*pentamethylphosphetan.*— Dimethylamine (5·4 g) was added slowly to a stirred solution of 1-chloro-2,2,3,4,4-pentamethylphosphetan (5·3 g) in pentane (50 ml) at −20°; the mixture was set aside at room temperature for 24 h and filtered. Distillation gave *r*-1-dimethylamino-2,2,*t*-3,4,4-pentamethylphosphetan (66%), b.p. 71—73° at 6 mmHg, τ 7·32 (6H, d, *J* 8·5 Hz), 8·3—8·6 (1H, m), 8·74 (6H, d, *J* 5 Hz), 8·80 (6H, d, *J* 20 Hz), and 9·22 (3H, dd, *J* 1 and 8 Hz), ^{31}P δ −106 p.p.m.

The phosphetan (0·2 g) in dichloromethane (40 ml) was stirred with hydrogen peroxide (20 vol; 20 ml) for 0·5 h; the organic layer was dried and evaporated. Distillation gave *r*-1-dimethylamino-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide (0·1 g), b.p. 90—95° at 1·5 mmHg, m.p. 40—50°, identical (i.r. and n.m.r. spectra) with an authentic sample.

2,2,3,4,4-*Pentamethyl*-1-*phenylthiophosphetan.*— Sodium benzenethiolate (4·0 g) was added over 20 min to a stirred solution of 1-chloro-2,2,3,4,4-pentamethylphosphetan (5·5 g) in ether (100 ml); the mixture was stirred at room temperature for 18 h and filtered. Distillation gave 2,2,3,4,4-pentamethyl-1-phenylthiophosphetan (6·0 g), b.p. 108—110° at 0·2 mmHg, as a mixture of isomers in the ratio of 55 : 45, τ (major isomer) 2·3—3·0 (5H, m), 7·43 (1H, q, *J* 8 Hz), 8·63 (6H, d, *J* 8·5 Hz), 8·80 (6H, d, *J* 14 Hz), and 9·27 (3H, d, *J* 8 Hz), τ (minor isomer) 7·87 (1H, dq, *J* 1·5 and 7 Hz), 8·72 (6H, d, *J* 12·5 Hz), 8·86 (6H, d, *J* 11 Hz), and 9·17 (3H, d, *J* 7 Hz), ^{31}P δ −99 p.p.m.

The phosphetan (0·25 g), sulphur (0·05 g), and a small crystal of aluminium chloride were refluxed in benzene (10 ml) for 12 h; the solvent was removed under reduced pressure and the residue chromatographed on basic alumina. Elution with pentane gave 2,2,3,4,4-*pentamethyl*-1-*phenylthiophosphetan* 1-*sulphide* * (0·2 g), b.p. 145° at 0·5 mmHg, as a mixture of isomers in the ratio of 3 : 2, τ (major isomer) 2·25—2·75 (5H, m), 7·25—7·87 (1H, m), 8·60 (6H, d, *J* 21 Hz), 8·68 (6H, d, *J* 22 Hz), and 9·07 (3H, dd, *J* 1·5 and 7 Hz), τ (minor isomer) 8·53 (6H, d, *J* 22 Hz), 8·60 (6H, d, *J* 21 Hz), and 9·02 (3H, dd, *J* 1·5 and 7 Hz), ^{31}P ($CHCl_3$) δ −118 p.p.m. (Found: C, 59·6; H, 7·45; S, 21·95. $C_{14}H_{21}PS_2$ requires C, 59·15; H, 7·4; S, 22·55%).

2,2,3,4,4-*Pentamethyl*-1-*phenoxyphosphetan.*— Sodium phenoxide (3·6 g) was added over 20 min to a stirred solution of 1-chloro-2,2,3,4,4-pentamethylphosphetan (5·5 g) in ether (120 ml); the mixture was stirred at room temperature for 18 h and filtered. Evaporation gave crude 2,2,3,4,4-pentamethyl-1-phenoxyphosphetan (6·9 g) as a mixture of isomers in the ratio of 2 : 1, τ (major isomer) 2·63—3·33 (5H, m), 8·10 (1H, dq, *J* 2 and 7 Hz), 8·78 (6H, d, *J* 13 Hz), 8·90 (6H, d, *J* 11·5 Hz), and 9·19 (3H, d, *J* 7 Hz), τ (minor isomer) 7·18 (1H, q, *J* 7 Hz), 8·83 (6H, d, *J* 13·5 Hz), 8·93 (6H, d, *J* 14 Hz), and 9·28 (3H, d, *J* 7 Hz). The equilibrium isomer ratio, attained after 6 days at 0°, was 1 : 2.

Reaction of 2,2,3,3-*Tetramethyl*-1-*phenylphosphetan with Hexafluoroacetone.*—Hexafluoroacetone (15 ml) was condensed into a stirred solution of the phosphetan (7·3 g) in pentane (50 ml) at −78°; the mixture was kept at −78°

for 0·5 h and then allowed to warm to 0°. Removal of solvent under reduced pressure gave 2′,2′,3′,3′-*tetramethyl*-1′-*phenyl*-3,3,5,5-*tetrakistrifluoromethyl*-1,4,2-*dioxaphospholan*-2-*spiro*-1′-*phosphetan* (19) (18 g), m.p. 64—68° (decomp.), τ 1·62—2·65 (5H, m), 6·70 (2H, d, *J* 20 Hz), 8·42 (3H, d, *J* 21 Hz), 8·83 (3H, d, *J* 20 Hz), 9·03 (3H, s), and 9·60 (3H, s), ^{19}F δ +1·47 (3H, m), +2·60 (3F, m), +14·57 (3F, m), and +17·58 p.p.m. (3F, m).

A solution of this adduct (5·4 g) in benzene (100 ml) was refluxed for 0·5 h; the solvent was removed under reduced pressure and the residue chromatographed on basic alumina (180 g). Elution with pentane gave 2′,2′,3′,3′-*tetramethyl*-1′-*phenyl*-4,4,5,5-*tetrakistrifluoromethyl*-1,3,2-*dioxaphospholan*-2-*spiro*-1′-*phosphetan* * (20) (3·9 g), m.p. 61—65° (from methanol), τ 1·75—2·67 (5H, m), 6·82 (2H, d, *J* 19 Hz), 8·58 (3H, d, *J* 19 Hz), 8·82 (3H, d, *J* 20 Hz), 9·05 (3H, s), and 9·57 (3H, d, *J* 2 Hz), ^{19}F δ +3·85 (6F, m), +5·57 (3F, m), and +6·49 p.p.m. (3F, m), ^{31}P δ +0·2 p.p.m. (Found: C, 42·15; H, 3·35; F, 42·45. $C_{19}H_{19}F_{12}O_2P$ requires C, 42·35; H, 3·55; F, 42·35%). Elution with ether–pentane (1 : 9) gave *hexafluoroisopropyl* 5,5,5-*trifluoro*-4-*trifluoromethyl*-1,1,2,2-*tetramethylpent*-3-*enyl*(*phenyl*)-*phosphinate* * (1·0 g), b.p. 100—105° at 0·05 mmHg, τ 1·88—2·67 (5H, m), 2·83 (1H, s), 4·82 (1H, m, *J* 5 Hz), 8·62 (3H, d, *J* 21 Hz), 8·63 (3H, d, *J* 19 Hz), 8·63 (3H, s), and 8·70 (3H, s), ^{19}F δ −9·47 (3F, q, *J* 8 Hz), +0·49 (3F, q, *J* 8 Hz), and +9·93 p.p.m. (6F, d, *J* 5 Hz) (Found: C, 42·55; H, 3·65; F, 42·55. $C_{19}H_{19}F_{12}O_2P$ requires C, 42·35; H, 3·55; F, 42·35%).

Reaction of Phosphetans with Hexafluoroacetone.—Hexafluoroacetone (10 ml) was condensed into a stirred solution of the phosphetan (0·015 mol) in toluene (20 ml) at −78°. After 0·5 h at −78° the solution was allowed to warm to 0° and evaporated under reduced pressure. The residue was chromatographed on basic alumina and the 1,3,2-dioxaphospholans (8) were eluted with pentane. In this this way the following *adducts* were obtained: (22; R = Ph) * (95%), m.p. 95—97° (from methanol), τ 1·83—2·83 (5H, m), 8·60 (6H, d, *J* 17 Hz), 8·65 (6H, d, *J* 19 Hz), and 9·28 (3H, dd, *J* 1·5 and 7 Hz), ^{19}F δ +2·89 (6F, m) and +5·65 p.p.m. (6F, m), ^{31}P δ −3·4 p.p.m. (Found: C, 43·45; H, 3·7; F, 41·0. $C_{20}H_{21}F_{12}O_2P$ requires C, 43·5; H, 3·8; F, 41·3%); (23; R = Ph) * (85%), m.p. 45—50° (from aqueous methanol), τ 1·83—2·67 (5H, m), 7·78 (1H, q, *J* 8 Hz), 8·33 (6H, d, *J* 17 Hz), 8·63 (6H, d, *J* 19 Hz), and 9·43 (3H, d, *J* 8 Hz), ^{19}F δ +3·2 (6F, m) and +5·79 p.p.m. (6F, m), ^{31}P δ −7·7 p.p.m. (Found: C, 43·3; H, 3·8; F, 41·1. $C_{20}H_{21}F_{12}O_2P$ requires C, 43·5; H, 3·8; F, 41·3%); (22; R = Pr^i) * (84%), m.p. 76—76·5° (from methanol), τ 7·5—8·0 (2H, m), 8·78 (6H, d, *J* 17·5 Hz), 8·80 (6H, dd, *J* 7 and 17 Hz), 8·89 (6H, d, *J* 19 Hz), and 9·43 (3H, dd, *J* 1·5 and 6·5 Hz), ^{19}F δ +3·00 (6F, m) and +4·47 p.p.m. (6F, m), ^{31}P δ −19·5 p.p.m. (Found: C, 39·35; H, 4·45; F, 44·4. $C_{17}H_{23}F_{12}O_2P$ requires C, 39·4; H, 4·45; F, 44·0%); (22; R = $CH{:}CMe_2$) * (52%), m.p. 80—82° (from methanol), τ 4·25 (1H, d, *J* 25 Hz), 8·20 (3H, s), 8·32 (3H, s), 8·72 (6H, d, *J* 18 Hz), 8·92 (6H, d, *J* 20 Hz), and 9·45 (3H, dd, *J* 1·5 and 6 Hz), ^{19}F δ +2·29 (6F, m) and +6·40 p.p.m. (6F, m), ^{31}P δ +0·5 p.p.m. (Found: C, 41·15; H, 4·45; F, 42·3. $C_{18}H_{23}F_{12}O_2P$ requires C, 40·75; H, 4·35; F, 43·0%); (22; R = NMe_2) * (50%), m.p. 65—75° (from pentane), b.p. 90—95° at 0·5 mmHg, τ 7·48 (1H, q, *J* 7 Hz), 7·50 (6H, d, *J* 11 Hz), 8·58 (6H, d, *J* 20 Hz), 8·92 (6H, d, *J* 20·5 Hz), and 9·40 (3H, d, *J* 7 Hz), ^{19}F δ +4·50 (6F, m) and +6·14 p.p.m. (6F, m), ^{31}P δ −15·5 p.p.m. (Found: C, 37·15; H, 4·3; F, 44·2. $C_{16}H_{22}F_{12}NO_2P$ requires C, 37·0; H, 4·6; F, 43·9%).

The following 1,3,2-*dioxaphospholans* were obtained as mixtures of *trans*- (22) and *cis*- (23) isomers: (R = Bu^t) * (25%), m.p. 60—75° (decomp.) (from pentane), τ (major isomer) 8·25 (1H, dq, *J* 2 and 7 Hz), 8·52 (9H, d, *J* 14·5 Hz), 8·63 (6H, d, *J* 19 Hz), 8·67 (6H, d, *J* 17 Hz), and 9·63 (3H, dd, *J* 7 and 22 Hz), τ (minor isomer) τ 8·46 (6H, d, *J* 21 Hz), 8·63 (6H, d, *J* 19 Hz), and 8·68 (9H, d, *J* 14·5 Hz); ratio of isomers 5 : 2, ^{19}F δ +1·33 (6F, m) and +3·04 p.p.m. (6F, m), ^{31}P δ (CH_2Cl_2) −5 p.p.m. (this compound could not be obtained analytically pure); (R = *p*-BrC_6H_4) * (95%), m.p. 85—95° (from aqueous methanol), τ (major isomer) 1·9—2·6 (4H, m), 7·57—8·10 (1H, m), 8·55 (6H, d, *J* 18 Hz), 8·60 (6H, d, *J* 19·5 Hz), and 9·23 (3H, dd, *J* 7 and 2 Hz), τ (minor isomer) 8·37 (6H, d, *J* 17 Hz), 8·67 (6H, d, *J* 20 Hz), and 9·42 (3H, d, *J* 7·5 Hz); ratio of isomers 72 : 28, ^{19}F δ +3·41 (6F, m) and +6·23 p.p.m. (6F, m), ^{31}P δ −3·7 and −6·3 p.p.m. (Found: C, 38·25; H, 3·3; F, 35·95. $C_{20}H_{21}BrF_{12}O_2P$ requires C, 38·05; H, 3·15; F, 36·15%); (R = *p*-MeO·C_6H_4) * (10%), m.p. 43—61° (from aqueous methanol), τ (major isomer) 1·83—3·17 (4H, m), 6·40 (3H, s), 7·70 (1H, dq, *J* 1·5 and 7 Hz), 8·45 (6H, d, *J* 20 Hz), 8·83 (6H, d, *J* 21 Hz), and 9·47 (3H, dd, *J* 1·5 and 7 Hz), τ (minor isomer) 6·38 (3H, s), 8·60 (6H, d, *J* 18 Hz), and 8·80 (6H, d, *J* 21 Hz), the other signals being obscured by those from the major isomer; ratio of isomers 3 : 2, ^{19}F δ +3·07 (6F, m) and +5·88 p.p.m. (6F, m), ^{31}P δ −5 p.p.m. (Found: C, 43·1; H, 3·6; F, 39·0. $C_{21}H_{23}F_{12}O_3P$ requires C, 43·3; H, 3·95; F, 39·15%); (R = $N[CH_2]_4$) * (74%), m.p. 108—118° (from pentane), τ (major isomer) 6·33—6·83 (4H, m), 8·0—8·33 (4H, m), 8·63 (6H, d, *J* 21 Hz), 8·68 (6H, d, *J* 22 Hz), and 9·13 (3H, dd, *J* 1·5 and 6 Hz), τ (minor isomer) 8·49 (6H, d, *J* 19·5 Hz), 8·72 (6H, d, *J* 20 Hz), and 9·23 (3H, dd, *J* 1·5 and 6 Hz); ratio of isomers 2 : 1, ^{19}F δ +3·97 (6F, m) and +5·3 p.p.m. (6F, m), ^{31}P δ −11·2 p.p.m. (Found: C, 39·5; H, 4·25; F, 41·6. $C_{18}H_{24}F_{12}NO_2P$ requires C, 39·65; H, 4·4; F, 41·85%); (R = OPh) * (95%), b.p. 125° at 0·5 mmHg, m.p. 40—60°, τ (major isomer) 2·5—3·0 (5H, m), 8·72 (6H, d, *J* 22·5 Hz), 8·92 (6H, d, *J* 22 Hz), and 9·39 (3H, d, *J* 7 Hz), τ (minor isomer) 8·50 (6H, d, *J* 21 Hz), and 8·92 (6H, d, *J* 22 Hz); ratio of isomers 2 : 1, ^{19}F δ +4·9 p.p.m., ^{31}P δ −16 p.p.m. (Found: C, 42·55; H, 3·85; F, 40·2. $C_{20}H_{21}F_{12}O_3P$ requires C, 42·25; H, 3·7; F, 40·15%).

Reaction of r-1,2,2-t-3,4,4-*Hexamethylphosphetan with Hexafluoroacetone*.—The crude product was chromatographed on basic alumina. Elution with pentane gave the 1,3,2-*dioxaphospholan* (22; R = Me) (62%), b.p. 89—95° at 0·5 mmHg, τ 7·45 (1H, q, *J* 7 Hz), 8·27 (3H, d, *J* 9 Hz), 8·70 (6H, d, *J* 19 Hz), 8·80 (6H, d, *J* 21 Hz), and 9·22 (3H, d, *J* 7 Hz), ^{19}F δ +3·69 (6F, m) and +6·70 p.p.m. (6F, m), ^{31}P δ −6·2 p.p.m. (Found: C, 36·45; H, 3·9; F, 47·8. $C_{15}H_{19}F_{12}O_2P$ requires C, 36·75; H, 3·9; F, 46·5%). Elution with pentane–ether (20 : 1) gave 2,2,t-3,4,4-*pentamethyl*-r-1-(3,3,3-*trifluoro*-2-*hydroxy*-2-*trifluoromethylpropyl*)-*phosphetan* 1-*oxide* * (12%), m.p. 125—127° (from light petroleum), τ 1·93 (1H, s, collapsed on the addition of one drop of D_2O), 7·67 (2H, d, *J* 9 Hz), 8·37 (1H, dq, *J* 2 and 7 Hz), 8·55 (6H, d, *J* 18 Hz), 8·57 (6H, d, *J* 20 Hz), and 9·05 (3H, dd, *J* 2 and 7 Hz), ^{19}F δ +15·34 p.p.m. (s) (Found: C, 42·9; H, 5·6; F, 35·4. $C_{12}H_{19}F_6O_2P$ requires C, 42·35; H, 5·6; F, 35·55%).

Reaction of r-1-*Benzyl*-2,2,t-3,4,4-*pentamethylphosphetan*

with Hexafluoroacetone.—The crude product was chromatographed on basic alumina. Elution with pentane gave the 1,2-oxaphosphetan (26; R = Ph) (68%), τ 2·5—2·83br (5H, s), 4·13 (1H, d, *J* 14 Hz), 5·0—5·67 (1H, m), 7·75 (1H, q, *J* 8 Hz), 8·38 (3H, d, *J* 24 Hz), 8·66 (3H, d, *J* 20 Hz), 8·78 (3H, d, *J* 22 Hz), 8·88 (3H, d, *J* 20 Hz), and 9·05 (3H, d, *J* 8 Hz), ^{19}F δ +7·67 (3F, q, *J* 9 Hz), +9·52 (3F, m), +10·3 (3F, m), and +12·2 p.p.m. (3F, q, *J* 9 Hz), ^{31}P δ −10·2 p.p.m.

A solution of the 1,2-oxaphosphetan (2·9 g) in benzene (50 ml) was refluxed for 0·5 h and evaporated at 0° and 10 mmHg. Distillation of the residue gave r-1-(*hexafluoroisopropoxy*)-2,2,c-3,4,4-*pentamethylphosphetan* 1-*oxide* * (92%), b.p. 85—87° at 0·1 mmHg, m.p. 63—66°, τ 4·63 (1H, septet, *J* 6 Hz), 8·18 (1H, dq, *J* 2 and 7 Hz), 8·67 (6H, d, *J* 21 Hz), 8·80 (6H, d, *J* 20 Hz), and 9·02 (3H, dd, *J* 1·5 and 7 Hz), ^{19}F δ +11·0 p.p.m. (d, *J* 6 Hz) (Found: C, 40·55; H, 5·15; F, 34·85. $C_{11}H_{17}F_6O_2P$ requires C, 40·5; H, 5·2; F, 34·95%), and, in a trap at −78°, 3,3,3-trifluoro-1-phenyl-2-trifluoromethylpropene,* $\nu_{max.}$ 1662, 1402, 1300, 1282, 1238, 1187, 1155, 978, 837, 747, 714, and 690 cm^{-1}, τ 2·35br (1H, s) and 2·62 (5H, s), ^{19}F δ −3·0 (3F, q, *J* Hz) and +0·5 p.p.m. (3F, q, *J* 7 Hz).

The 1,2-oxaphosphetan (1·45 g) and water (50 ml) containing 2N-hydrochloric acid (0·1 ml) were kept at 80° for 2 h and then extracted with dichloromethane. The extract was dried and evaporated and the residue heated at 100° and 0·1 mmHg for 1 h. Crystallisation of the residue from light petroleum gave 2,2,t-3,4,4-*pentamethyl*-r-1-(3,3,3-*trifluoro*-2-*hydroxy*-1-*phenyl*-2-*trifluoromethylpropyl*)*phosphetan* 1-*oxide* * (25%), m.p. 144—147°, τ 2·07 (1H, s, collapsed on the addition of one drop of D_2O), 2·33—2·83 (5H, m), 6·27 (1H, d, *J* 3 Hz), 7·93 (1H, q, *J* 7·5 Hz), 8·47 (3H, d, *J* 19·5 Hz), 8·73 (3H, d, *J* 18 Hz), 9·05 (3H, d, *J* 18 Hz), 9·06 (3H, d, *J* 7·5 Hz), and 9·57 (3H, d, *J* 17·5 Hz), ^{19}F δ +8·74 (3F, q, *J* 12 Hz) and +12·6 p.p.m. (3F, dq, *J* 5 and 12 Hz) (Found: C, 51·7; H, 5·7; F, 34·2. $C_{18}H_{23}F_6O_2P$ requires C, 51·95; H, 5·55; F, 34·5%).

Reaction of 2,2,t-3,4,4-*Pentamethyl*-r-1-(2-*methylallyl*)-*phosphetan with Hexafluoroacetone*.—The crude product was chromatographed on basic alumina. Elution with pentane gave 5,5,5-trifluoro-2-methyl-4-trifluoromethylpenta-1,3-diene * (30%), $\nu_{max.}$ 1687, 1637, 1480, 1330, 1265, 1240, 1209, 1112, 962, 886, and 753 cm^{-1}, τ 2·50 (1H, q, *J* 7 Hz), 4·90 (1H, s), 5·03 (1H, s), and 8·23 (3H, s), ^{19}F δ −3·71, (3F, dq, *J* 7 and 7 Hz) and +0·83 p.p.m. (3F, q, *J* 7 Hz). Elution with ether–pentane (1 : 20) gave *r*-1-(hexafluoroisopropoxy)-2,2,*c*-3,4,4-pentamethylphosphetan 1-oxide (60%), m.p. and mixed m.p. 62—64°, identical (i.r. and n.m.r. spectra) with an authentic sample.

Reaction of 2,2,3,4,4-*Pentamethylphosphetan with Hexafluoroacetone*.—The secondary phosphine (4·1 g) in pentane (40 ml) was cooled to −78° and hexafluoroacetone (25 g) was condensed into the stirred solution. After 0·5 h the temperature was allowed to rise to −20° and unchanged HFA (15·2 g) collected in a trap at −78°. Solvent was removed under reduced pressure to give the 1,3,2-dioxaphospholan (22 and 23; R = H) as a white solid (89%), m.p. 25—35° (decomp.), $\nu_{max.}$ 2244 cm^{-1}, τ 4·97 (0·5H, s) 7·63—8·17 (1H, m), 8·77 (12H, d, *J* 21 Hz), and 9·11 (3H, d, *J* 7 Hz), ^{19}F δ +9·04 (s) and +9·34 p.p.m. (s) in a ratio of 3 : 4.

A solution of the adduct (9·5 g, 0·02 mol) in benzene (100 ml) was refluxed for 2 h while HFA (3·0 g, 0·018 mol) collected in a trap at −78° connected to the condenser. Removal of solvent under reduced pressure then gave crude 1-hexafluoroisopropoxy-2,2,3,4,4-pentamethylphosphetan (81%), τ (major isomer) 5·72 (1H, d septet, *J* 6 and 7 Hz), 8·18 (1H, dq, *J* 2 and 7), 8·92 (6H, d, *J* 12 Hz), 9·03 (6H, d, *J* 18 Hz), and 9·42 (3H, d, *J* 7 Hz), τ (minor isomer) 5·72 (1H, d septet, *J* 6 and 7 Hz), 7·33 (1H, q, *J* 7 Hz), 8·90 (6H, d, *J* 20 Hz), 9·10 (6H, d, *J* 17 Hz), and 9·42 (3H, d, *J* 7 Hz), ratio of isomers 4 : 3, ^{19}F δ +11·14 (dd, *J* 6 and 7 Hz) and +11·71 p.p.m. (dd, *J* 6 and 7 Hz) in a ratio of 55 : 45. The phosphetan (3·1 g), sulphur (0·35 g), and a small crystal of aluminium chloride were refluxed in benzene (20 ml) for 12 h; the solvent was removed and the residue chromatographed on basic alumina. Elution with pentane gave 1-*hexafluoroisopropoxy*-2,2,3,4,4-*pentamethylphosphetan* 1-*sulphide* * (94%), b.p. 73—75° at 1 mmHg, τ (major isomer) 4·28 (1H, d septet, *J* 4 and 6 Hz), 8·70 (6H, d, *J* 24 Hz), 8·93 (6H, d, *J* 22 Hz), and 9·37 (3H, dd, *J* 3 and 7 Hz), τ (minor isomer) 7·78 (1H, q, *J* 7 H), 8·92 (6H, d, *J* 22 Hz), and 9·38 (3H, d, *J* 7 Hz), ^{19}F δ +10·7 (d, *J* 6 Hz) and +11·2 p.p.m. (d, *J* 6 Hz) in the ratio of 46 : 54 (Found: C, 38·15; H, 4·9; F, 33·1. $C_{11}H_{17}F_6O_2PS$ requires C, 38·6; H, 4·95; F, 33·35%).

The 1-hexafluoroisopropoxyphosphetan (4·6 g) in pentane (50 ml) was cooled to −78° and hexafluoroacetone (8 g) was condensed into the stirred solution. After 1 h the temperature was allowed to rise to −20° with a −78° condenser in place. After a further 0·5 h the excess of HFA (3 g) was collected in a trap at −78°. Solvent was removed under reduced pressure and a solution of the residue in dichloromethane (50 ml) refluxed for 1 h. Solvent was then removed and the residue kept at 30° and 0·1 mmHg for 3 h. Crystallisation of the residue from pentane at −78° gave the 1,3,2-*dioxaphospholan* * [22 or 23; R = $OCH(CF_3)_2$] (42%), m.p. 33—38°, τ 4·60 (1H, septet, *J* 6 Hz), 8·82 (6H, d, *J* 23·5 Hz), 8·88 (6H, d, *J* 23·5 Hz), and 9·46 (3H, dd, *J* 1·5 and 7 Hz), ^{19}F δ +5·06 (12 F, s) and +9·76 p.p.m. (6F, d, *J* 6 Hz), ^{31}P δ −15 p.p.m. (Found: C, 31·9; H, 2·7; F, 53·45. $C_{17}H_{17}F_{18}O_3P$ requires C, 31·8; H, 2·65; F, 53·25%).

Reaction of 1-*Chloro*-2,2,3,4,4-*pentamethylphosphetan with Hexafluoroacetone*.—Hexafluoroacetone (10 ml) was condensed into a solution of the chlorophosphetan (3·6 g) in pentane (50 ml) at −78° and the solution was kept at −25° for 3 h. On cooling to −78° the adduct crystallised as long prisms (49%), m.p. *ca.* 20°, τ 7·08 (1H, dq, *J* 1 and 7·5 Hz), 8·45 (6H, d, *J* 31 Hz), 8·60 (6H, d, *J* 28 Hz), and 9·11 (3H, d, *J* 7 Hz), ^{19}F δ +0·3 (6F, m) and +17·4 p.p.m. (6F, m). A solution of the adduct (6·0 g) in dichloromethane (40 ml) was refluxed for 4 h. Hexafluoroacetone (2·0 g) collected in a trap at −78° attached to the system. Removal of the solvent under reduced pressure gave chlorophosphetan (1·7 g) having an ^{1}H n.m.r. spectrum identical with that of the starting material.

o-*Methoxyphenyldimethylphosphine Sulphide*.—*o*-Methoxyphenylmagnesium bromide (0·05 mol) in ether (25 ml) was added slowly to a solution of dimethylphosphinothioic chloride (6·4 g) in ether (50 ml). The mixture was refluxed for 24 h and then added slowly to ice–water (250 g). The organic layer was washed with N-sodium hydroxide and evaporated and the residue was chromatographed on basic alumina (250 g). Elution with ether–light petroleum (1 : 20) gave o-*methoxyphenyldimethylphosphine sulphide* * (56%), m.p. 90—91° (from dichloromethane–light petroleum), τ 1·42—3·17 (4H, m), 6·05

(3H, s), and 7·98 (6H, d, J 14 Hz) (Found: C, 54·05; H, 6·55; P, 15·35. $C_9H_{13}OPS$ requires C, 54·0; H, 6·5; P, 15·5%).

In a similar way 1-naphthylmagnesium bromide gave *dimethyl-(1-naphthyl)phosphine sulphide* * (68%), m.p. 101—102° (from chloroform–light petroleum), τ 1·83—2·67 (7H, m) and 7·97 (6H, d, J 13 Hz) (Found: C, 65·45; H, 5·75; P, 13·85. $C_{12}H_{13}PS$ requires C, 65·5; H, 5·9; P, 14·1%).

Difluoro-(o-methoxyphenyl)dimethylphosphorane.—An intimate mixture of *o*-methoxyphenyldimethylphosphine sulphide (4·5 g) and antimony trifluoride (3·5 g) was slowly heated to 100° over 4 h at a pressure of 10 mmHg and then held under these conditions for 2 h. Distillation gave *difluoro-(o-methoxyphenyl)dimethylphosphorane* (62%), b.p. 126—128° at 1·5 mmHg, τ 2·27—3·33 (4H, m), 6·27 (3H, s), and 8·03 (6H, d, J 17·5 Hz), ^{19}F δ (at +30°) +14·2br p.p.m. (s); δ (at −50°) +7·7 p.p.m. (d, J 560 Hz) relative to internal $CFCl_3$, ^{31}P δ +16·5 p.p.m. (in $CFCl_3$).

In a similar way dimethyl-(1-naphthyl)phosphine sulphide gave *difluorodimethyl-(1-naphthyl)phosphorane* (49%), b.p. 127—132° at 0·3 mmHg, m.p. 80—90°, τ 1·5—2·83 (**7H, m**) and 7·88 (6H, d, J 21 Hz), ^{19}F δ +5·6 p.p.m. (d, J 697 Hz) relative to internal $CFCl_3$, ^{31}P δ +17 p.p.m. (in $CFCl_3$).

Reaction of the 1,3,2-*Dioxaphospholan* (22; R = NMe_2) *with* 1,1,1,3,3,3-*Hexafluoropropan-2-ol.*—The adduct (22; R = NMe_2) (0·25 g) was stirred with hexafluoropropan-2-ol (0·34 g) at 0° for 5 min and the excess of the latter was removed under reduced pressure to give the 1,3,2-dioxaphospholan [22 or 23; R = $O{\cdot}CH(CF_3)_2$] (0·36 g), m.p. 37—40°, identical (i.r. and ^1H, ^{19}F, and ^{31}P n.m.r. spectra) with the adduct obtained from the hexafluoroisopropoxyphosphetan.

Reaction of the 1,2-*Oxaphosphetan* (26; R = Ph) *with* 1,1,1,3,3,3-*Hexafluoropropan-2-ol.*—A solution of the 1,2-oxaphosphetan (0·55 g) in deuteriochloroform (1 ml) containing hexafluoropropan-2-ol (0·17 g) was set aside at room temperature. After 18 h equilibrium was established with an isomer (ratio 1 : 10) which showed the following characteristic absorptions: τ 2·78 (5H, s), 4·10 (1H, d, J 8 Hz), and 4·66 (1H, d septet, J 7 and 6·5 Hz).

The equilibrium mixture of isomers in deuteriochloroform was kept at 60° for 24 h. ^1H N.m.r. then showed the presence of the *cis-* and *trans*-isomers of 1-hexafluoroisopropoxy-2,2,3,4,4-pentamethylphosphetan 1-oxide in the ratio of 1 : 10. The *trans*-isomer showed τ 4·73 (1H, septet, J 6 Hz), 8·73 (6H, d, J 21 Hz), 8·75 (6H, d, J 19 Hz), and 9·05 (3H, d, J 8 Hz).

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