Preparation and Characterization of Phosphetan Alkoxides and Aryloxides. Production of *cis*- and *trans*-Isomers from *trans*-1-Chlorophosphetan 1-Oxide

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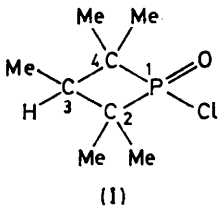
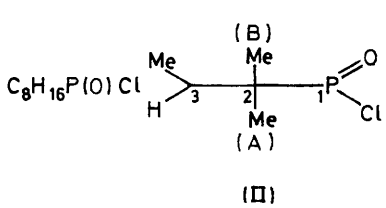
Nucleophilic substitution at the phosphorus atom in *trans*-1-chloro-2,2,3,4,4-pentamethylphosphetan 1-oxide (I) occurs with retention of configuration. We have apparently found an exception to this rule in that reaction of (I) and certain alcohols produces both *cis*- and *trans*-isomers. Seventeen alkoxides have been investigated and the products characterized by ^{1}H and ^{31}P n.m.r., i.r. and g.l.c./mass spectrometry; long-range coupling is observed in some of the compounds.

THE original discoverers of the 2,2,3,4,4-pentamethylphosphetan 1-oxides, (I), also claimed to have separated the *cis*- and *trans*-methoxy-derivatives, $C_8H_{16}P(O)OMe$, although they required a 100 ft Apiezon L g.l.c. column before they were able to separate the two isomers.[1] It has since been proved [2] that the starting material, $C_8H_{16}P(O)Cl$, is exclusively the *trans*-isomer, *i.e.* the C(3) proton is *trans* to the phosphoryl oxygen in that they are at different sides of the phosphetan ring as the side view illustrates, (II). It has also been demonstrated that nucleophilic substitution at P in $C_8H_{16}P(O)Cl$ can



(I)



(II)

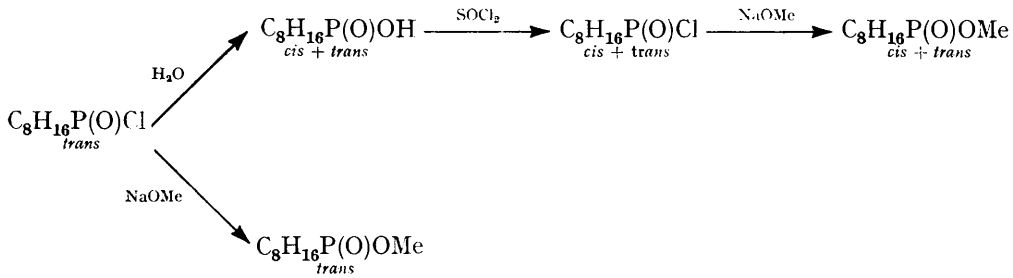
only occur with retention of configuration [3,4] so that

[1] J. J. McBride, jun., E. Jungerman, J. V. Killheffer, and R. J. Clutter, *J. Org. Chem.*, 1962, **27**, 1833.
[2] Mazhar-ul-Haque, *J. Chem. Soc.* (*B*), 1970, 934.
[3] W. Hawes and S. Trippett, *J. Chem. Soc.* (*C*), 1969, 1465.
[4] J. R. Corfield, R. K. Oram, D. J. H. Smith, and S. Trippett, *J.C.S. Perkin I*, 1972, 713.

trans-$C_8H_{16}P(O)Cl$ must give *trans*-$C_8H_{16}P(O)X$. The mechanism by which this is effected involves a trigonal bipyramidal (tbp) intermediate in which the phosphetan ring is constrained to an apical–equatorial posture; pseudorotation then manoeuvres the leaving group into the other apical position and the net result is retention of configuration.

The claim of McBride *et al.*[1] to have produced *cis*- and *trans*-isomers is thus contrary to accepted dogma. Other workers who have prepared $C_8H_{16}P(O)OMe$ from $C_8H_{16}P(O)Cl$ by reaction of NaOMe–MeOH [3] or MeOH–NEt_3 [5] report only the formation of one isomer. This being so, how is one to explain the original report? Up to now this aspect of the work has been politely ignored, and yet, as we shall see, they probably did produce both isomers.

Both the *cis*- and *trans*-methoxy derivatives were made by Cremer and Trivedi [5] by a different route. This used a mixture of the chloro-isomers obtained by treating the acid, $C_8H_{16}P(O)OH$, with $SOCl_2$ [see equation (1)].



(1)

Bergesen [6] reported the direct formation of *cis*- and *trans*-esters, $C_8H_{16}P(O)OEt$, from the reaction of $C_8H_{16}P(O)Cl$ and NaOEt/EtOH and claimed to separate them by partial hydrolysis—the *cis*-ester being much more reactive. He also claimed to have produced the corresponding *cis*- and *trans*-acids, $C_8H_{16}P(O)OH$, by saponification of these esters. Hawes and Trippett [7] cast doubt on this work, pointing out that isomeric acids are highly improbable (having a common anion $C_8H_{16}PO_2^-$) and stating that the p.m.r. spectrum of $C_8H_{16}P(O)OEt$ shows it to be homogeneous and that only the *trans*-ester is produced.

We now report that the reaction of *trans*-$C_8H_{16}P(O)Cl$ and alcohols in the presence of NEt_3 does in fact produce both *cis*- and *trans*-esters. On the face of it this observation contradicts the retention of configuration rule.

EXPERIMENTAL

Instruments.—N.m.r. spectra were recorded on Perkin-Elmer R12B (60 MHz) and Bruker HFX90 (90 MHz, ^1H; 36·43 MHz, ^{31}P) spectrometers. Compounds were studied in $CDCl_3$ solutions and referenced to Me_4Si (^1H) and 85% H_3PO_4 (^{31}P). I.r. spectra were measured on a Perkin-Elmer 621 instrument with CsBr optics. Compounds were studied as liquid films or mull and the charts aligned against the polystyrene peak at 1601 cm^{-1}. Mass spectra were recorded on an A.E.I. MS30 spectrometer operating at 24 eV; samples were introduced as 20—40 w/w % solutions in $CDCl_3$ *via* a g.l.c. Carbowax column (210—220 °C).

Preparation of Alkoxy- and Aryloxy-phosphetans.—The general method consisted of heating together freshly prepared $C_8H_{16}P(O)Cl$, the appropriate alcohol, and triethylamine in refluxing toluene for *ca.* 4 h, the exact time being judged by a visual assessment of the amount of precipitated Et_3N,HCl. Reactants and solvent were dried before use. The amine hydrochloride was filtered off and weighed to gauge the extent of the reaction, and then the solution of reactants was refluxed for a further span if necessary or, if the reaction was almost complete, the solvent and volatile reactants were removed on a rotary evaporator. The product was dissolved in light petroleum (b.p. 80—100°) and cooled to 0 °C whereupon any phosphetan anhydride [8] crystallized out. (The yield of this could be as high as 10% if the reaction had been performed in the open laboratory; the use of a dry N_2 atmosphere prevented its formation in significant amounts.) The resulting solution was decolourized with charcoal, if necessary, and the product allowed to crystallize if a solid or distilled under reduced pressure if a liquid. The *p*-nitrophenol derivative was recrystallized from benzene–light petroleum (3 : 1) and the 8-hydroxyquinoline derivative from diethyl ether.

The derivatives prepared by the above method, together with their yields, elemental analyses, *m/e* values, and b.p.s. or m.p.s are listed in Table 1. The alcohols 1-methylpropanol, butan-2-ol, and cyclohexanol did not react with $C_8H_{16}P(O)Cl$ under the above conditions, even after 24 h in refluxing toluene. The yield from *o*-cresol was low and the product was not separated from the unchanged starting material except for identification purposes in a g.l.c./mass spectrometer.

The 8-hydroxyquinoline derivative was outstanding in that reaction with $C_8H_{16}P(O)Cl$ occurs at room temperature as shown by the immediate precipitation of Et_3N,HCl upon mixing the reactants. The product from this reaction is 100% *trans*-isomer—no *cis*-isomer is formed if the reaction mixture is heated. The product from 2-furylmethanol decomposed on attempted purification by distillation *in vacuo*.

Reaction of 1-*Hydroxyphosphetan* 1-*Oxide and Methanol.*—Phosphetan acid, $C_8H_{16}PO_2H$ (8·8 g, 0·05 mol), and methanol (6·4 g, 0·20 mol) were heated in refluxing toluene (50 cm^3)

[5] S. E. Cremer and B. C. Trivedi, *J. Amer. Chem. Soc.*, 1969, **91**, 7200.
[6] K. Bergesen, *Acta Chem. Scand.*, 1967, **21**, 1587.
[7] W. Hawes and S. Trippett, *Chem. Comm.*, 1968, 577.
[8] M. F. Crook, J. Emsley, T. B. Middleton, and J. K. Williams, *Phosphorus*, 1973, **3**, 45.

for 6 h. After removal of solvent and excess of methanol, the acid was recovered unchanged and no evidence for the formation of the methyl esters was found. The same reaction in the presence of Et_3N also failed to produce any $C_8H_{16}P(O)OMe$.

Reaction of 1-*Hydroxyphosphetan* 1-*Oxide and Trimethyl Orthoformate.*—Anhydrous $C_8H_{16}P(O)OH$ (1·76 g, 0·01 mol) and an excess of $HC(OMe)_3$ (2·12 g, 0·02 mol) were heated in refluxing toluene (80 cm^3) for 56 h. The solvent, by-products, and unchanged trimethyl orthoformate were removed on a rotary evaporator to give a colourless oil (1·8 g, 0·01 mol, 100%) which p.m.r. and g.l.c./mass spectrometry showed to be an equimolar mixture of *cis*- and *trans*-1-methoxy-2,2,3,4,4-pentamethylphosphetan 1-oxide.

In a similar reaction using triethyl orthoformate it was found expedient to wash the original solution with water (3 × 40 cm^3) before removal of the solvent on a rotary evaporator; the yield of $C_8H_{16}P(O)OEt$ (80%) was likewise shown to be an equimolar mixture of the *cis*- and *trans*-isomers. Purification of the product by distillation under reduced pressure did not change the isomer ratio in favour of either isomer.

Preparation of 1-*Hydroxyphosphetan* 1-*Oxide Salts.*—Solutions of $C_8H_{16}PO_2H$ (0·01M) were neutralized with solutions of metal hydroxides or carbonates and the water evaporated to give the corresponding phosphetan salts which were dried at 130°. Li, Na, K, Rb, Cs, Ca, Sr, and Mn^{II} salts were white, $C_8H_{16}PO_2Ag$ darkened on exposure to light, and $(C_8H_{16}PO_2)_2Ni$ was bright blue. Attempts to prepare $(C_8H_{16}PO_2)_3Al$ were unsuccessful.

DISCUSSION

The *cis*- and *trans*-isomers of $C_8H_{16}P(O)OMe$ and $C_8H_{16}P(O)OEt$ are produced in equal amounts by treating the acid with the corresponding trialkyl orthoformate. This reaction, based on that described for preparing hypophosphite esters, $H_2P(O)OR$,[9] gives excellent yields in a one-step process and the product mix is that expected from $C_8H_{16}PO_2H$ which is a strong acid and therefore cannot exist as separate *cis*- and *trans*-isomers. The p.m.r. spectrum of a *cis*–*trans*-mixture permits the two sets of signals to be clearly distinguished for the important protons.

In order to make the *cis*-isomer Cremer and Trivedi used a two-step process [equation (1)]; a product ratio of 2 *trans* : 3 *cis*-$C_8H_{16}P(O)OMe$ was obtained. This ratio, if significant, points to a tendency for the *cis*-isomer to predominate and suggests that one of the steps in reaction (1) involves *trans* to *cis* conversion. Our work shows that this is probably the second step, *i.e.* *trans*-$C_8H_{16}P(O)Cl$ can give *cis*-$C_8H_{16}P(O)OMe$ when treated with MeOH–Et_3N.

The p.m.r. spectra of the products of the reaction of *trans*-$C_8H_{16}P(O)Cl$ and aliphatic alcohols (including amongst these benzyl alcohol and 2-furylmethanol which are aliphatic with respect to the alcohol moiety) clearly show these to be a mixture of *cis*- and *trans*-isomers, the latter predominating. These were separated and identified by g.l.c./mass spectrometry giving identical spectra containing the molecular ion (see Table 1) in all cases. The yield of *cis*-isomer was *ca.* 10—20% of the total although in the case of n-propanol it reached 35%. Isopropyl alcohol, on the other hand, gave less than 1%, undetectable in the p.m.r. spectrum, but identified by g.l.c./mass spectrometry; the data are summarized in Table 2. The isomers are distinguished by the positions of the 2,2,4,4-methyl protons and those of the POCH grouping both of which give signals in regions of the spectrum free of interference from other signals. The 3-methyl region is obscured in the alkoxy-derivatives by the protons of the ester group and the 3-H(A) is barely discernible. Long-range shielding effects are observed in

TABLE 1

Preparation, identification, and properties of alkoxy- and aryloxy-derivatives of 2,2,3,4,4-pentamethylphosphetan 1-oxide, $C_8H_{16}P(O)OR$

R	Molar scale	Time h	Temp. °C	Yield (g)	Yield (%)	B.p. (t/°C (mmHg)) or [m.p. t/°C]	M (m/e)	Elemental analyses [a] (%) C	H	P
Me	0·15	5	95	19·0	80	75—77(5) [b]	190	54·2(56·8)	10·5(10·0)	15·6(16·3)
Et	0·15	5	95	26·2	84	112(10) [c]	204	58·6(58·8)	10·3(10·3)	15·3(15·2)
Pr^n	0·15	5	95	27·6	82	98—100(2·6)	218	58·9(60·7)	10·8(10·6)	13·6(14·2)
Pr^i	0·15	5	95	29·0	86	102—104(3·0)	218	60·7(60·7)	10·4(10·6)	14·0(14·2)
Bu^n	0·15	5	95	28·3	79	134—136(3·0)	232	62·0(62·2)	10·7(10·8)	13·0(13·4)
Me_2CHCH_2	0·15	5	95	28·8	81	140—144(3·6)	232	61·8(62·2)	10·8(10·8)	13·1(13·4)
Ph	0·05	4	110	11·1	88	176—178(3·6)	252	66·6(66·7)	8·2(8·3)	12·1(12·3)
$PhCH_2$	0·05	4	110	11·0	82	170—173(3·0)	266	67·6(67·7)	8·6(8·6)	11·6(11·6)
p-$MeOC_6H_4$	0·05	5	110	12·3	87	[102—104]	282	63·8(63·8)	8·2(8·2)	10·5(11·0)
m-$MeOC_6H_4$	0·05	5	110	9·8	70	[85—86]	282			
8-Quinolyl	0·05	2	20	13·8	91	[105]	303	67·4(67·3)	7·4(7·3)	10·0(10·2) [d]
p-ClC_6H_4	0·05	3	110	13·8	93	[94—95]	286	58·8(58·6)	7·0(7·0)	10·6(10·8) [e]
2-Furylmethyl	0·05	2	110	10·1	79	[f]	256	60·9(60·9)	8·3(8·2)	12·1(12·1)
p-MeC_6H_4	0·05	4	110	11·8	89	[87—88]	266	67·7(67·7)	8·6(8·6)	11·6(11·6)
m-MeC_6H_4	0·05	4	110	11·1	76	183—185(1·8)	266			
o-MeC_6H_4	0·05	16	101	2·2 [g]	12	—	266			
p-$NO_2C_6H_4$	0·05	3	110	11·9	80	[118—120]	297	56·5(56·6)	6·4(6·7)	10·5(10·4) [h]

[a] Calculated values in parentheses. [b] W. Hawes and S. Trippett, *J. Chem. Soc.* (*C*), 1969, 1465. [c] K. Bergesen, *Acta Chem. Scand.*, 1967, **21**, 1587. [d] N, 4·6% (4·6). [e] Cl, 12·6% (12·4). [f] Decomposes. [g] Estimated from p.m.r. spectrum. [h] N, 4·6% (4·7).

[9] S. J. Fitch, *J. Amer. Chem. Soc.*, 1964, **86**, 61.

some instances between the (A) methyls of the phosphetan [see (II)] and the aromatic ring of the ester.[10]

With the exception of phenol itself, none of the aryl alcohols gave the *cis*-isomer.

How then do the *cis*-isomers arise in these reactions? The likely explanations in order of decreasing probability are (i) *via* the acid $C_8H_{16}PO_2H$, (ii) *via* alkyl group migration, or (iii) *via* nucleophilic substitution involving inversion of configuration.

The first of these seems most attractive because we have shown that direct esterification of $C_8H_{16}P(O)OH$ atmospheric moisture, *etc.*, is not the source of the *cis*-isomer.

The second possibility, migration of the alkyl group from its oxygen atom to that of the phosphoryl group, would convert one isomer into the other. Migration within a single molecule or mutually between two molecules might occur. The rearrangements within hexa-alkoxytriphosphazenes are of this type except migration is from O to N; migration increases with temperature and is more extensive for the lower alkyl homologues and is not observed for aryl compounds.[11]

TABLE 2

Nuclear magnetic resonance spectra of alkoxy- and aryloxy-derivatives of 2,2,3,4,4-pentamethylphosphetan 1-oxides, $C_8H_{16}P(O)OR$

	trans-Isomers									*cis*-Isomers						
	2,2,4,4-methyls H				3-methyl-H		3-H	P(O)OCH		2,2,4,4-methyls-H						
	H(A) [a]		H(B) [a]							H(A) [a]		H(B) [b]		P(O)OCH		Ratio of *cis* : *trans* isomers observed
	δ/ p.p.m.	J [b]/ Hz	δ/ p.p.m.	J [b]/ Hz	δ/ p.p.m.	J [c]/ Hz	δ/ p.p.m.	δ/ p.p.m.	J [d] Hz	^{31}P δ/ p.p.m.[e]	δ/ p.p.m.	J [b]/ Hz	δ/ p.p.m.	J [b]/ Hz	δ/ p.p.m.	J [d]/ Hz	
Me	1·20 [f]	18·5	1·24 [f]	19	*h*	*h*	*h*	3·79 (d) [g]	10	55·08	1·13 [f]	18·5	1·33	18·5	3·75 (d)	10	1 : 7·3
Et	1·19	18·5	1·23	19	*h*	*h*	*h*	4·15 (dq)	7	56·03	1·13	18·5	1·30	18·5	4·11 (dq)	7	1 : 6·3
Pr^n	1·20	18·5	1·22	19	*h*	*h*	*h*	4·04 (dt)	6·5	56·23	1·13	18·5	1·33	18·5	4·00 (dt)	6·5	1 : 1·9
Pr^i	1·18	18·5	1·23	19	*h*	*h*	*h*	4·78 (sept)	6·5	55·96							1 : 100
Bu^n	1·20	18·5	1·23	19	*h*	*h*	*h*	4·08 (dt)	6·5	56·35	1·13	18·5	1·32	18·5	4·04 (dt)	6·5	1 : 4·7
Me_2CHCH_2–	1·19	18·5	1·23	19	*h*	*h*	*h*	3·83 (dd)	6·5	56·46	1·13	18·5	1·32	18·5	3·80 (dd)	6·5	1 : 5·6
Ph	1·27	19·0	1·29	20	0·91	7·2	1·80			57·04	1·20	21	1·36	18·5			1 : 6·7
$PhCH_2$	1·16	18·5	1·25	19	0·84	7·2	1·55	4·98 (d)	8	58·84	1·00	17	1·32	21·5	5·08 (d)	8	1 : 9·5
p-$MeOC_6H_4$	1·30	18·5	1·32	20	0·94	7·2	1·70			56·88							
m-$MeOC_6H_4$	1·27	19·0	1·30	20	0·95	7·2	1·70			56·72							
8-Quinolyl	1·37	20·0	1·43	18·5	0·98	7·8	1·86			58·68							
p-ClC_6H_4	1·27	19·0	1·30	20	0·95	7·2	1·69			58·02							
2-Furylmethyl	1·08	11·85	1·23	19	0·86	7·2	1·50	4·97	9	59·50	1·07	19	1·20	19	5·05 (d)	9	1 : 4·9
p-MeC_6H_4	1·27	19·0	1·30	20	0·93	7·2	1·67	(d)		56·72							
m-MeC_6H_4	1·27	19·0	1·30	20	0·92	7·2	1·71			57·53							
o-MeC_6H_4 [i]	1·27	18·5	1·30	20						57·04							
p-$NO_2C_6H_4$	1·35	19·5	1·37	20	0·98	7·2	1·80			60·80							

[a] See text for meaning of A and B. [b] $^3J_{PCCH_3}$. [c] $^3J_{HCCH_3}$. [d] $^3J_{POCH}$. [e] 85% H_3PO_4 (proton spectra ref. Me_4Si). [f] Doublet in all cases. [g] d, Doublet; t, triplet, *etc.* [h] Obscured by other signals. [i] Taken from unseparated reaction product—see text.

produces both isomers. That the acid can be formed in these reactions is shown by the production of the anhydride. It has been shown that reaction of the acid, or its anion, with more $C_8H_{16}P(O)Cl$ is rapid (2) and,

$$C_8H_{16}P(O)Cl + C_8H_{16}PO_2H = C_8H_{16}P(O)OP(O)C_8H_{16} + HCl \quad (2)$$

moreover, that the anhydride is not susceptible to nucleophilic attack by alcohols.[8] Any acid not consumed by reaction (2) does not react with alcohols directly under conditions of either acid or base catalysis as we have shown in the case of methanol. Thus the phosphetan acid, produced as a by-product, from

However, Cremer and Trivedi,[5] using deuteriated methanol, studied exchange processes between CD_3O^- and $C_8H_{16}P(O)OCH_3$. Exchange did occur but isomer interconversion of *trans* to *cis* or *cis* to *trans* did not occur during 24 h at 60°, or if it had occurred was below the amount detectable by their p.m.r. spectrometer. Likewise in our work we have not observed changes in isomer ratio upon heating samples to much higher temperatures than this, and therefore conclude that alkyl group migration is not the answer here.

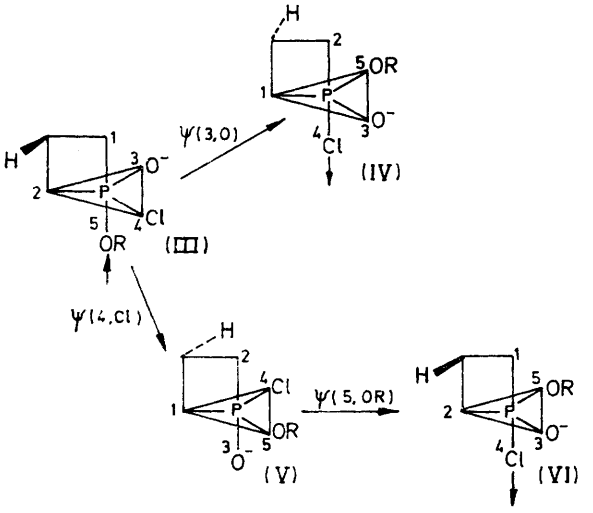
Somewhat reluctantly, since it is contrary to the general rule, we must consider the third alternative—nucleophilic substitution involving inversion of con-

[10] R. E. Ardrey, J. Emsley, A. J. B. Robertson, and J. K. Williams, *J.C.S. Dalton*, 1973, 2641.

[11] B. W. Fitzsimmons, C. Hewlett, and R. A. Shaw, *J. Chem. Soc.*, 1964, 4459.

figuration. The extent to which it occurs depends upon several factors but primarily it is a feature of alkoxy- rather than aryloxy-substitution.

The tbp intermediate produced by nucleophilic attack of the alkoxy-group entering at an apical position is shown and the atoms of the tbp positions numbered, (III). The phosphetan ring atoms and the *trans*-H only are shown. Pseudorotation about the phosphoryl bond, $\psi(3, O)$, produces (IV) from which configuration the Cl can now escape leaving behind the *trans*-isomer of $C_8H_{16}P(O)OR$, *i.e.* retention of configuration has occurred. This is the general route and the operation can be



summed up as $15 \xrightarrow{\psi(3,\,O)} \overline{24}$ (in which the numbers refer to the apical atoms and the bar denotes anticlockwise numbering of the equatorial atoms [12]).

For substitution and inversion of configuration to occur it is necessary to rearrange the tbp of (III) to that of (VI) prior to loss of Cl from the leaving position. The shortest route from (III) to (VI) is through (V):

$$\underset{\text{(III)}}{15} \xrightarrow{\psi(4,\,Cl)} \underset{\text{(V)}}{23} \xrightarrow{\psi(5,OR)} \underset{\text{(VI)}}{\overline{14}}$$

This explanation seems so simple that one is led to ask why it does not occur more often. The answer lies in the relative apicophilicities of the P=O and P–Cl bonds and the latter is the more apicophilic so that (III) ⟶ (IV) is favoured.* For (III) ⟶ (V) to happen there must be some factor present which increases the apicophilicity of P=O relative to P–Cl to such an extent as to make $\psi(4,Cl)$ a viable alternative to $\psi(3,O)$.

One of the tenets of pseudorotation is that the more electronegative a group the more apicophilic it is. However experimentally observed orders of apicophilicity do not bear this out. For example, the apicophilicity in five-co-ordinate phosphetans is $Me_2N <$ OR (R = Me, Et, Pr^i) < SMe < Cl,[14] which is decidedly not the order of relative electronegativity.

Electronegativity is not a property which has much use in this context. Hinze and Jaffé [15] have shown that it can vary widely for a particular element according to its valence state, and in any case the atoms in a molecule tend to the same electronegativity.[16,17] This being so it is hardly surprising that it bears little relationship to relative apicophilicity.

A more fruitful approach is one which links apicophilicity to the ability of a group to act as a π-donor,[18] so that the stronger this is the more the group prefers the equatorial position and the less apicophilic it will be. (A π-donor is defined as a substituent with one or two high-lying occupied molecular orbitals.) In the same paper 3*d* orbital participation was briefly discussed and it was also established that, contrary to the common view, equatorial π-bonding between phosphorus and ligand is more efficient than axial π-bonding. This last point is in our belief the key to the problem.

We should like to propose that p_π–d_π bonding between the group and the phosphorus atom determines relative apicophilicities. Or rather, that since p_π–d_π bonding is better when the group is equatorially placed, it is relative *equatoriophilicities* that are the driving force to pseudorotational rearrangements. This kind of bonding is strongest in P=O where it is needed to satisfy formal valence requirements, and the same is true of the P=N bonding in the phosphonitriles.[19]

In other bonds there is also a component of the bonding formed by the donation of a non-bonding electron pair on the ligand into an empty 3*d* phosphorus orbital, *i.e.* $p_\pi \rightarrow d_\pi$ bonding. This type of bonding is especially prevalent in P–N bonds as witnessed by the restricted rotation about these formally single bonds.[20] Even the P=O bond probably has a further component of $p_\pi \rightarrow d_\pi$ bonding.

The ability to form $p_\pi \rightarrow d_\pi$ bonding should parallel the Lewis basicity of the ligands and it is therefore not surprising that the order of apicophilicity is inversely proportional to Lewis basicity, *i.e.* N > O > S > Cl. The phosphoryl group constitutes a special case since

* Pseudorotation in phosphetans is limited by the constraint of $\widehat{CPC} = 90°$, although recently the free energies of activation for pseudorotation about the C–P,ψ(1, C), bond have been estimated as *ca.* 40—90 kJ mol^{-1}. Pseudorotation of this kind results in the ring being diequatorial, $\widehat{CPC} = 120°$, which is obviously energetically unfavourable.[13]

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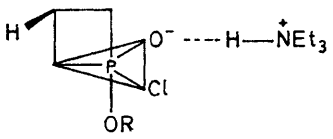
p_π–d_π bonding is paramount. The order of this bonding is thus P=O ⋙ P–NR_2 > P–OR > P–SR > P–Cl and hence apicophilicity is the reverse of this, as is found.

For the P=O to become almost as apicophilic as that of P–Cl its p_π–d_π component must be removed or considerably weakened. It is not sufficient merely to involve it in a delocalized π system linked to the incoming nucleophile RO^- although this will undoubtedly weaken the π-bonding. What is required is something akin to almost complete localization of the formal negative charge on the phosphoryl oxygen. This would be considerably facilitated by H-bonding between the phosphoryl group and the protonated base used in our system:



This H-bonding could well be of the very strong type considering the cation–anion factor and consequently the P–O bond would lose its d_π–p_π component sufficiently to make its apicophilicity about that of the chlorine. Route (III) ⟶ (V) then becomes a possible alternative although it occurs for only a small percentage of the reactants.

Apicophilicity is still a vexed question in chemistry being only a component of reactions in which many other factors must play important roles. Aryloxy-compounds, with the curious exception of the phenoxy-compound, behave as normally predicted with complete retention of configuration. In these cases there may well be much less localization of the formal negative charge on the phosphoryl oxygen as one might expect.

Infrared Spectra.—These are listed as a Supplementary publication 20924 (4 pp) * for the 16 alkyloxy- and aryloxy-derivatives. All show the modes previously reported as characteristic phosphetan vibrations: 1248—1258 [ν_{as}(CPC)], 925—935, 748—765, 665—673, 615—640, 555—563, 496—540 (multiplets), and 397—403 cm^{-1}. To these we should now like to add the strong peak at 1164—1170 cm^{-1}. Inspection of the i.r. spectra of the 40 or more compounds we have reported to date [10,20,21] shows this frequency, which we have previously misinterpreted, as common to all. In the phosphetan amides [20] it was assigned to ν(P=N) in preference to a series of bands at 940—957 cm^{-1} which should now be considered. It is weakest in the phosphetan anhydride but in the bromide and chloride it is present as medium and strong peaks respectively.[21] The Raman spectra of $C_8H_{16}P(O)Cl$ and $C_8H_{16}P(O)OP(O)C_8H_{16}$ show it to be polarized.

As an aid to assignment several phosphetan acid salts have been made. These give spectra with very sharp peaks, *e.g.* the normally broad phosphetan peak or peaks in the 500—540 cm^{-1} region appear as four sharp signals in these compounds. The salt spectra show $\nu_{as}(PO_2^-)$ at 1130—1163 cm^{-1} and $\nu_s(PO_2^-)$ at 1039—1050 cm^{-1} in accord with the ranges quoted for $R_2PO_2^-$ compounds.[22] Both peaks carry shoulders, the latter falling in the middle of the set of methyl rock vibrations and the former adjacent to the newly assigned phosphetan band which appears at 1155—1180 cm^{-1}, sometimes as a shoulder but in most instances as a clearly defined peak. The reported [22] equal intensities of the symmetric and asymmetric PO_2^- modes enabled a clear assignment to be made in most cases. All the other characteristic phosphetan modes are present in the salt spectra confirming their assignments.

In view of the 100 cm^{-1} separating $\nu_{as}(PO_2^-)$ from $\nu_s(PO_2^-)$ it seems logical to assign the new phosphetan band at *ca.* 1165 cm^{-1} to ν_s(CPC) thus complementing ν_{as}(CPC) which is found at *ca.* 1255 cm^{-1}. These bands are Raman polarized and depolarized respectively as required.[21]

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index Issue (items less than 10 pp. are supplied as full size copies).

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