The Apicophilicity of Thio-substituents in Trigonal Bipyramidal Phosphoranes

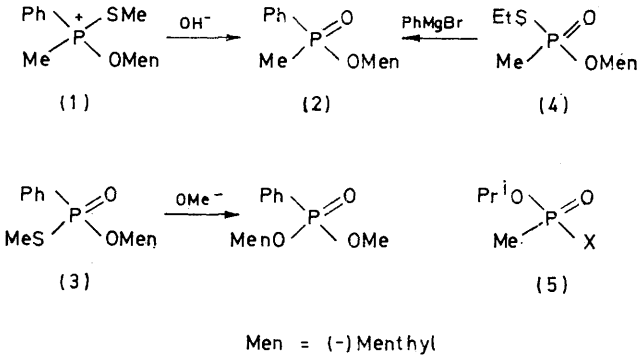
By **Stephen Bone, Stuart Trippett,* and Peter J. Whittle,** Department of Chemistry, The University, Leicester LE1 7RH

The variable temperature n.m.r. spectra of a number of five-co-ordinate spirophosphoranes having *P*-phenoxy- and *P*-phenylthio-groups have given data on the energetics of the pseudorotation processes available to these systems. It is concluded that the apicophilicities of phenoxy- and phenylthio-groups are similar, with the balance varying according to the nature of the other ligands. Further evidence is given for the high apicophilicity of the hydrogen atom. The concept of multiple turnstile rotation processes is discussed with particular reference to spirophosphoranes.

ANOMALOUS stereochemical results have been obtained in a number of displacements of alkylthio-groups at tetrahedral phosphorus(v). Thus alkaline hydrolysis of the phosphonium salt (1) gives the phosphinate (2) with retention of configuration at phosphorus [1] while methanolysis of (3) involves inversion at phosphorus.[2] Phenylmagnesium bromide and the thiophosphonate (3) give the phosphinate (2) with retention at phosphorus [3] and the thiophosphonate (5; X = SMe) reacts similarly, although with (5; X = F or Cl) the reactions proceed with inversion of configuration at phosphorus.[4] A prerequisite to understanding these anomalies is some knowledge of the relative apicophilicities of alkyl- and aryl-thio-groups, *i.e.* their preference relative to other

[1] N. J. De'ath, K. Ellis, D. J. H. Smith, and S. Trippett, *Chem. Comm.*, 1971, 714.
[2] W. B. Farnham, K. Mislow, N. Mandell, and J. Donahue, *J.C.S. Chem. Comm.*, 1972, 120.
[3] J. Donahue, N. Mandell, W. B. Farnham, R. K. Murray, K. Mislow, and H. P. Benschop, *J. Amer. Chem. Soc.*, 1971, **93**, 3792.
[4] G. R. Van den Berg, D. H. J. M. Platenburg, and H. P. Benschop, *Rec. Trav. chim.*, 1972, **91**, 929.

groups for the apical as opposed to the equatorial position in trigonal bipyramidal intermediates. In terms of both electronegativity and of the strength of lone-pair interactions from equatorial substituents,[5] as evidenced by the

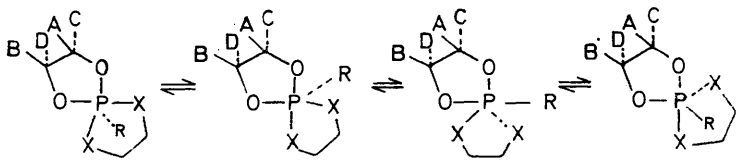


Men = (-)Menthyl

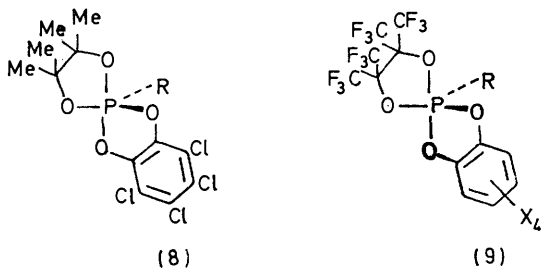
large barrier to rotation around equatorial P–S bonds,[6] one would expect sulphur to be poorly apicophilic relative to oxygen. Nevertheless, in competition, alkylthio is a much better leaving group than alkoxy [*cf.* (1) ⟶ (2)] and, if we assume departure from the apical position, this implies that there cannot be a large energy barrier to placing sulphur apical. This paper describes our attempts to assess the relative apicophilicities of arylthio- and aryloxy-groups; in the end we conclude that they have similar apicophilicities, with the balance affected by the nature of the other *P*-substituents.

Our approach has involved a study of the pseudorotation processes of a variety of spirophosphoranes having a range of *P*-substituents. It can be illustrated by consideration of the pseudorotations of the phosphorane (6), in which A—D are identical groups. At low temperatures there will be rapid pseudorotation between the topomers (6a) and (6b); such processes, involving trigonal bipyramids of identical energies, have never been slowed on the n.m.r. time-scale. Group A in (6a) has exactly the same environment as B in (6b) and similarly C in (6a) is equivalent to D in (6b). Consequently, with the equilibration (6a) ⇌ (6b) rapid on the n.m.r. time-scale, the groups A—D will give rise to two signals of equal intensity in an n.m.r. spectrum of (6). These two signals will coalesce when equilibration of (6a) with (6c) is rapid on the n.m.r. time-scale, for A and B in (6a) have the same environment as C and D, respectively, in (6c). This equilibration is achieved *via* the high-energy trigonal bipyramid (7) in which a five-membered ring is forced to occupy an unfavourable diequatorial position. If the assumption is made [7] that high-energy trigonal bipyramids can be approximated to the transition states between topomeric trigonal bipyramids, then the activation energy for the process (6a) ⇌ (6c) is a measure of the difference in energy between (6a) and (7) and the variation in this energy of activation as the group R varies is a measure of the changing apicophilicity of R.

The free energies of activation were obtained by use of the Gutowsky–Holm equation. This is often subject to large errors but has been shown [8] to be reliable in the case of processes involving coalescing singlets of equal intensities. Comparison of ΔG^* values determined in this way at different coalescence temperatures is valid only if the corresponding ΔS^* values are very small. Pseudorotations are expected to have small entropies of activation and whenever these have been determined by line-shape analysis [9] or by conventional kinetic methods [10] they have been within experimental error of zero.



The experimental limitations of this approach to the assessment of the relative apicophilicities of arylthio- and aryloxy-groups can be illustrated by reference to the systems (8) and (9).

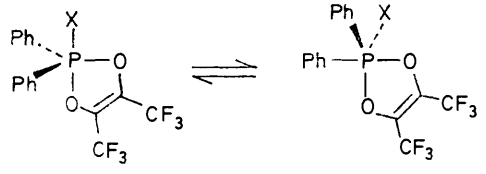


The spirophosphoranes (8; R = Cl, OMe, NMe_2, OPh, or SPh) were obtained from tetrachloro-*o*-benzoquinone and the corresponding 1,3,2-dioxophospholans. They are all crystalline, have the expected positive ^{31}P chemical shifts relative to 85% H_3PO_4, and show two equal-intensity peaks in their ^1H n.m.r. spectra at room

[5] R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1972, **94**, 3047.
[6] E. L. Muetterties, P. Meakin, and R. Hoffmann, *J. Amer. Chem. Soc.*, 1972, **94**, 5674: M. J. C. Hewson, S. C. Peake, and R. Schmutzler, *Chem. Comm.*, 1971, 1454.
[7] R. R. Holmes, *Accounts Chem. Res.*, 1972, **5**, 296.
[8] D. Kost, E. H. Carlson, and M. Raban, *Chem. Comm.*, 1971, 656; W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, 1971, **93**, 6205.
[9] *E.g.* D. Gorenstein, *J. Amer. Chem. Soc.*, 1970, **92**, 644.
[10] A. Klaebe, J.-F. Brazier, F. Mathis, and R. Wolf, *Tetrahedron Letters*, 1972, 4367.

temperature. These peaks in the spectrum of the adduct (8; R = OPh) coalesce reversibly at 106 °C (ΔG^* 20·5 kcal mol^{-1}), a process which is associated with speeding up of the pseudorotation, analogous to (6a) ⇌ (6c), involving a high-energy trigonal bipyramidal intermediate having the dioxaphospholen ring diequatorial and the phenoxy-group apical. As expected, in view of the large difference in apicophilicity (*ca.* 8 kcal mol^{-1}) between dimethylamino and phenoxy,[11] no coalescence was observed in the ^{1}H n.m.r. spectrum of (8; R = NMe_2) up to 180 °C. However, with both (8; R = SPh) and (8; R = OMe) decomposition occurred before coalescence of the methyl signals was observed. The highest temperatures attainable before the onset of rapid decomposition, 130 and 110 °C respectively, show that in this system both phenylthio and methoxy are less apicophilic than phenoxy.

The low coalescence temperature (51 °C) for the methyl signals of the chlorophosphorane (8; R = Cl) implies that chloro is *ca.* 3 kcal mol^{-1} more apicophilic than phenoxy, in direct contrast to the situation in the hexafluorobiacetyl adducts (10) where the free energies of activation for the pseudorotations (10) ⇌ (11) are 12·6 (X = OPh) and 12·0 kcal mol^{-1} (X = Cl),[12] *i.e.* phenoxy is more apicophilic than chloro. Although both chlorophosphoranes contain five-co-ordinate phosphorus, as shown both by their positive ^{31}P chemical shifts and by their n.m.r. spectra, the observed coalescence in either



(10) (11)

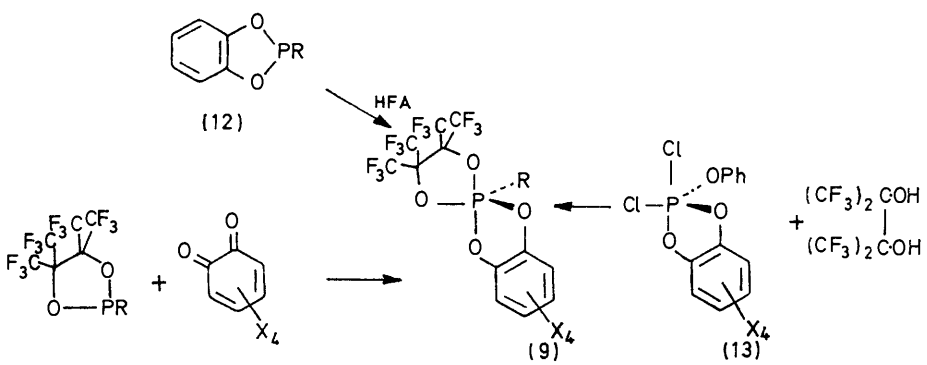
case could be due to an irregular process associated with the presence of nucleophilic impurities, *e.g.* chloride ions. If this were so the 'true' coalescence temperature associated with the relevant pseudorotation would be higher than that actually observed, and the two experiments would be in better agreement, for an increased coalescence temperature in (8; R = Cl) reduces the apicophilicity of chloro relative to phenoxy whereas an increased coalescence temperature for (10; R = Cl) increases the apicophilicity of chloro relative to phenoxy.

N.m.r. data for spirophosphoranes

Compound	^{31}P [a]	^{19}F [c,d] δ [b]	^{19}F [c,d] T_c/°C	^{19}F [c,d] ΔG^*/kcal mol^{-1} [e]
(9) X = H R = Me_2N	27·2	6·27 [f] 7·17	>160	
H PhO	32·9	5·53 [f] 6·80	152	20·5
Cl Ph	9·2	4·58 5·23		
Cl Me_2N	29·8	5·73 6·83	>160	
Cl PhO	32·9	5·27 5·68	152	21·8
(15) R = PhO	31·3	5·70 6·30	74	17·4
PhS	3·4	4·24 4·76	69	17·3
(20) R = Me_2N	29·6	4·56	0	
PhO	36·4	4·35 7·16	155	20·4
PhS	13·6	4·70 5·50	116	19·4
$(CF_3)_2CHO$	36·3	4·83 7·55	155	20·4
(22) R = PhO	39·0	4·47 [g]		
p-BrC_6H_4O	39·5	4·77 [g]		
PhS	14·0	7·40 8·60	180	22·4
Me_2N	24·0	5·50 6·90	>180	
H	28·3 (d, *J* 860 Hz)	5·93 6·26	92	18·8

		^{1}H [d] $\Delta\nu$/Hz	^{1}H [d] T_c/°C	^{1}H [d] ΔG^*/kcal mol^{-1}
(8) R = Me_2N	29·3	10	>180	
MeO	30·3	6	dec.>110	
PhO	38·9	5·6	106	20·5
PhS	10·5	9	dec.>130	
Cl	13·6	3	51 [h]	17·8
(18) R = PhO	37·2	3·5	101	20·5
PhS	12·9	3·5	104	20·7

[a] P.p.m. relative to 85% H_3PO_4. [b] P.p.m. relative to internal $PhCF_3$. [c] 56·4 MHz unless otherwise stated. [d] In 1-bromo-naphthalene. [e] Calculated from the Gutowsky-Holm equation. [f] 94 MHz. [g] In light petroleum–ether (1 : 1). [h] In CCl_4.



(12) (9) (13)

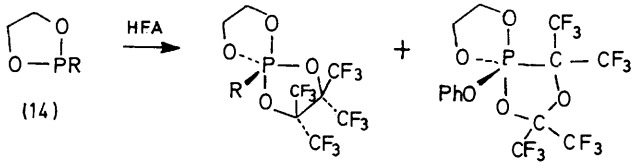
coalescence temperature in (8; R = Cl) reduces the apicophilicity of chloro relative to phenoxy whereas an

The limitation in the case of the spirophosphoranes (9) is one of synthesis. Of the dioxaphospholens (12;

[11] R. K. Oram and S. Trippett, *J.C.S. Perkin I*, 1973, 1300; S. Trippett and P. J. Whittle, *ibid.*, p. 2302.

[12] J. I. Dickstein and S. Trippett, *Tetrahedron Letters*, 1973, 2203.

R = OPh, SPh, or NMe_2) only the last reacted with hexafluoroacetone (HFA), to give the adduct (9; X = H, R = NMe_2). This was also obtained in low yield from *o*-benzoquinone and the corresponding 1-dimethylamino-

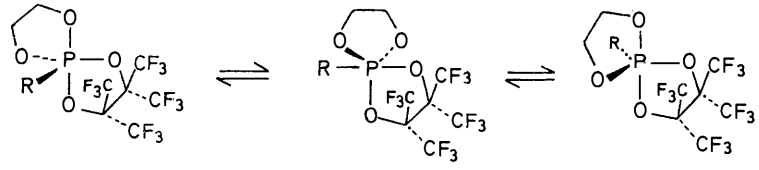


(14) (15) (16)

1,3,2-dioxaphospholan, and (9; X = H, R = OPh) was obtained from the dichlorophosphorane (13; X = H) and perfluoropinacol in the presence of pyridine, but neither method was successful in the preparation of (9; X = H, R = SPh). Similarly, compounds (9; X = Cl, R = Ph or NMe_2) were obtained by using tetrachloro-*o*-benzoquinone, and the dichlorophosphorane route gave (9; X = Cl, R = OPh), but (9; X = Cl, R = SPh) could not be prepared. The n.m.r. behaviour of these phosphoranes is given in the Table.

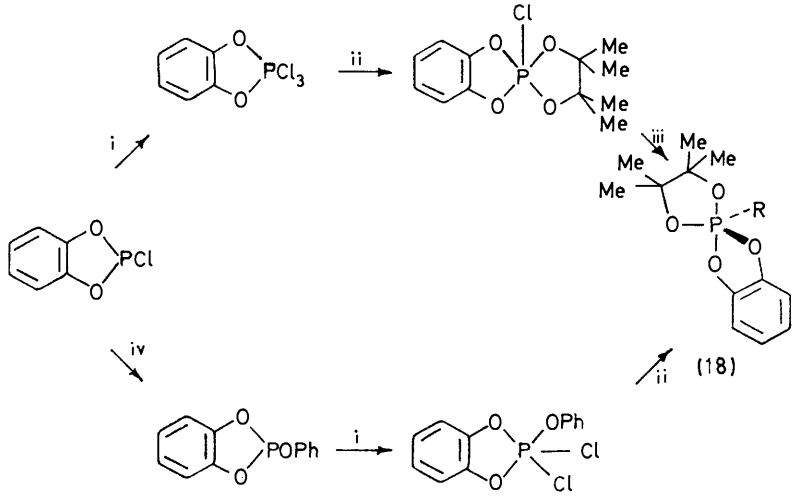
Compounds (15; R = OPh) and (16) were separated by fractional crystallisation. The ^{19}F n.m.r. spectrum of (15) consisted of two equal-intensity signals which coalesced reversibly at 74 (R = OPh) and 69 °C (R = SPh) when equilibration of the topomers (15a) and (15b), *via* the high-energy (17), became fast on the n.m.r. time-scale. The spirophosphoranes (18; R = OPh or SPh) were obtained by the chlorophosphorane route as shown in the Scheme. Their ^1H n.m.r. spectra showed two signals in the methyl region which coalesced reversibly at 101 and 104 °C, respectively, this process being associated with speeding up of the pseudorotations *via* the high-energy trigonal bipyramids (19). In both (15) and (18) there is therefore little difference in apicophilicity between phenoxy- and phenylthio-groups.

Phenylthio seems to be rather more apicophilic than phenoxy in the HFA adducts (20). Here the coalescence



(15a) (17) (15b)

temperatures in the ^{19}F n.m.r. spectra are 155 (R = OPh) and 116 °C (R = SPh) with associated ΔG^* values of 20·4 and 19·4 kcal mol^{-1}. However, this system may not be entirely reliable; the dimethylamino-compound (20; R = NMe_2) [13] showed only one signal in its ^{19}F n.m.r.



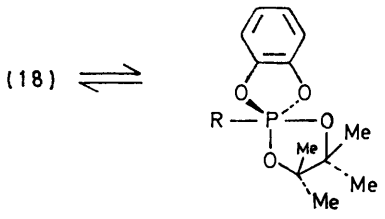
SCHEME

Reagents: i, Cl_2–CCl_4; ii, pinacol–pyridine; iii, PhSH–pyridine; iv, phenol–pyridine

Valid comparisons in apicophilicity between phenoxy- and phenylthio-groups were eventually obtained in the spirophosphoranes (15) and (18). HFA and the ethylene phosphites (14; R = OPh or SPh) gave the phosphoranes (15; R = OPh or SPh) together with the 1,4,2-dioxaphospholan (16) in the case when R = OPh. spectrum above 0 °C and, on dissolving in hexafluoropropan-2-ol, rapidly and quantitatively gave [20; R = O·CH$(CF_3)_2$], whose ^{19}F n.m.r. spectrum showed reversible coalescence of two equal signals at 155 °C. Obviously an

[13] F. Ramirez, A. S. Gulati, and C. P. Smith, *J. Amer. Chem. Soc.*, 1967, **89**, 6283.

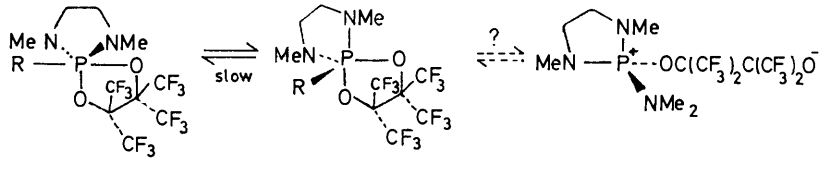
irregular process is occurring with (20; R = NMe_2); this could be reversible dissociation to a betaine and it is not possible to rule this out completely in the case of (20; R = SPh).



(19)

One further cautionary note must be entered which again highlights the dangers inherent in the interpretation of variable temperature (dynamic) n.m.r. phenomena. The spirophosphoranes (22) were obtained as stable crystalline compounds from HFA and the 1,3,2-dioxaphospholans (21; R = OPh, SPh, or NMe_2).[14] The dimethylamino-compound was unchanged in hexafluoropropan-2-ol and the two equal-intensity signals in its ^{19}F n.m.r. spectrum (solvent 1-bromonaphthalene) did not coalesce up to 180 °C, *i.e.* pseudorotation *via* the high-energy intermediate (23; R = NMe_2) is slow on the n.m.r. time-scale at this temperature. Reversible coalescence of the two signals in the ^{19}F n.m.r. spectrum of (22; R = SPh) did take place at 180 °C but the ^{19}F n.m.r. spectrum of (22; R = OPh) in a wide variety of solvents was a singlet down to at least −90 °C. Below this temperature, separation into two broad signals occurred in dichloromethane but not in ether. Clearly, in the light of the difference in apicophilicity between phenoxy and dimethylamino, and of the d.n.m.r. behaviour of (8), (9), (15), (18), and (20) (R = OPh) described above, the ^{19}F d.n.m.r. spectrum of (22; R = OPh) is totally unexpected. The compound is reasonably stable to hydrolysis with a half-life in refluxing 50% aqueous ethanol of about 1 h; its ^{31}P chemical shift is unchanged in hexafluoropropan-2-ol and the essentially trigonal bipyramidal geometry around phosphorus, as shown by *X*-ray analysis,[15] is identical in the two adducts (22; R = OC_6H_4Br-*p* or SPh). Unless this is a case of chemical shift degeneracy, we cannot account for the ^{19}F n.m.r. spectrum of (22; R = OPh).

We conclude that in five-co-ordinate phosphoranes the apicophilicities of phenoxy- and phenylthio-groups are very similar, with the balance being influenced by the nature of the other *P*-substituents. This is a surprising result. Of the three factors considered by Hoffmann [5] to affect apicophilicity, both electronegativity and lone-pair interactions would lead to sulphur being poorly apicophilic relative to oxygen. Only the third factor, the preference for the apical position of substituents with low-lying unfilled orbitals, in the case of sulphur 3*d* orbitals, could redress the balance. DeBruin [16] has recently concluded from experiments on the hydrolysis of alkoxyalkylthiophosphetanium salts that alkoxy- and alkylthio-groups have similar kinetic apicophilicities. We have so far been unable to obtain a direct comparison between these particular groups in our systems largely because of problems with thermal instability.



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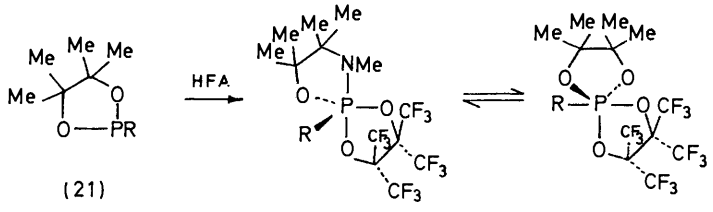


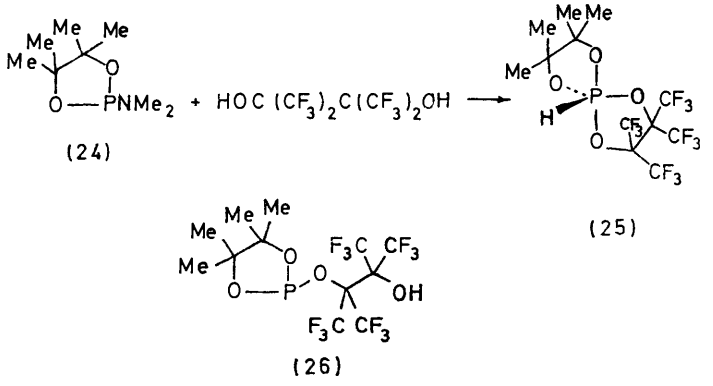
(21) (22) (23)

Perfluoropinacol and the dioxaphospholan (24; R = NMe_2) gave the spirophosphorane (25) [*i.e.* (22; R = H)], shown by its spectroscopic properties to exist in solution entirely in the five-co-ordinate form. The two signals in the ^{19}F n.m.r. spectrum coalesced at 109 °C. As the P,H-coupling and the shape of the PH proton signals were unaffected up to 160 °C this coalescence is unlikely to be due to rapid equilibration with a small amount of phosphite (26). The low coalescence temperature relative to that of (22; R = SPh) supports the assignment of a high apicophilicity to the hydrogen atom.[11]

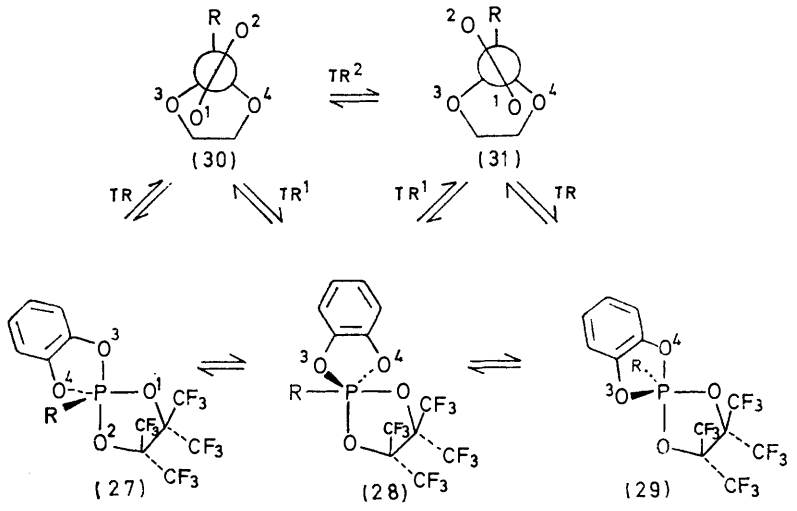
Our results in this and previous papers [11,12] have been

[14] E. A. Duff, M.Sc. Thesis, University of Leicester, 1972.
[15] J. A. Howard and D. R. Russell, unpublished results quoted in J. A. Howard, D. R. Russell, and S. Trippett, *J.C.S. Chem. Comm.*, 1973, 856.
[16] K. E. DeBruin, A. G. Padilla, and M.-T. Campbell, *J. Amer. Chem. Soc.*, 1973, **95**, 4681.

interpreted in terms of Berry pseudorotation (BPR) processes. In view of the continuing advocacy [17] of the alternative turnstile rotation (TR) it is of interest to consider their interpretation in these terms. Basically it is not important to us exactly how one trigonal bipyramid is converted into the next with the exchange of the 30° [2 + 3] species (30) and (31), shown in Newman projection; the TR^2 route from (27) to (29) would proceed *via* (30) and (31) but by-passing (28), with (30) and (31) equilibrating directly by a 60° rotation of the two relative to the three. Along the TR^2 route there is no significant change in angle-strain and this route appears to offer a



two apical for two equatorial substituents, *i.e.* whether by a single BPR or by a TR^1 process. What is important is the feasibility of multiple TR routes which bypass high-energy trigonal bipyramids and in particular, in this context, those which are of high energy because of a diequatorial small ring. This can be illustrated by reference to the pseudorotation of the spirophosphoranes



(27) [*i.e.* (9; X = H)] in which final equivalence of the four CF_3 groups on the n.m.r. time-scale is achieved by rapid equilibration of the trigonal bipyramids (27) and (29). The BPR route from (27) to (29) proceeds *via* (28), which is of high energy because of strain in the diequatorial ring. The TR^1 route also proceeds *via* (28) and lower-energy path from (27) to (29) than either the BPR or the TR^1 route. Nevertheless, the observed barrier to equivalence of the CF_3 groups in (27; R = OPh) is 21 kcal mol^{-1}, which must contain a considerable strain factor. This example could be multiplied many times over and at present we know of no compelling evidence for multiple TR processes.

[17] P. Gillespie, F. Ramirez, I. Ugi, and D. Marquarding, *Angew. Chem. Internat. Edn.*, 1973, **12**, 91.

EXPERIMENTAL

^{19}F N.m.r. spectra were determined at 56·4 MHz and chemical shifts are relative to internal $PhCF_3$. ^{31}P N.m.r. spectra were obtained at 24·3 MHz for solutions in tetrahydrofuran unless otherwise stated; chemical shifts are relative to external 85% H_3PO_4. Positive shifts are upfield from the reference in both cases All experiments involving P^{III} compounds were carried out under oxygen-free nitrogen.

Reaction of P^{III} *Compounds with Hexafluoroacetone.*—

Hexafluoroacetone (22 mmol) was condensed into a solution of the P^{III} compound (10 mmol) in ether (30 ml) at −78°. After 0·5 h at −78° the solution was allowed to warm to room temperature and set aside for 1 h. Evaporation, and crystallisation or distillation of the residue then gave the following adducts: P-*dimethylamino*-4′,4′,5′,5′-*tetrakistrifluoromethyl*-1,3,2-*benzodioxaphosphole*-2-*spiro*-2′-1′,3′,2′-*dioxaphospholan* (9; X = H, R = NMe_2), m.p. 74—77° (from light petroleum), τ 2·88 (4H, s) and 7·10 (6H, d, *J* 11 Hz) (Found: C, 32·45; H, 2·0. $C_{14}H_{10}F_{12}NO_4P$ requires C, 32·6; H, 1·95%); 5-*phenylthio*-2,2,3,3-*tetrakistrifluoromethyl*-1,4,6,9-*tetraoxa*-5-*phosphaspiro*[4.4]*nonane* (15; R = SPh), m.p. 67—69° (from light petroleum), τ 2·52 (5H, m) and 5·6—6·4 (4H, m) (Found: C, 31·8; H, 1·95; F, 42·9; P, 5·5. $C_{14}H_9F_{12}O_4PS$ requires C, 31·6; H, 1·7; F, 42·85; P, 5·8%); 2,2,3,3-*tetramethyl*-5-*phenylthio*-7,7,8,8-*tetrakistrifluoromethyl*-1,4,6,9-*tetraoxa*-5-*phosphaspiro*[4.4]*nonane* (22; R = SPh), m.p. 102—103° (from light petroleum), τ 2·26 (5H, m), 8·70 (6H, s), and 8·85 (6H, s) (Found: C, 36·7; H, 2·9; S, 5·4·5. $C_{18}H_{17}F_{12}O_4PS$ requires C, 37·6; N, 3·1; S, 6·1%); the 5-*dimethylamino-analogue* (22; R = NMe_2), m.p. 72—73° (from light petroleum), τ 7·2 (6H, d, *J* 10 Hz), 8·8 (6H, 2), and 9·0 (6H, s) (Found: C, 32·8; H, 3·55; N, 3·0. $C_{14}H_{18}F_{12}NO_4P$ requires C, 32·1; H, 3·45; N, 2·7%); the 5-*phenoxy-analogue* (22; R = OPh), m.p. 105—106° (from ethanol), τ 2·4—3·07 (5H, m), 8·73 (6H, s), and 8·93 (6H, s) (Found: C, 37·85; H, 3·0; F, 39·7; P, 5·7. $C_{18}H_{17}F_{12}O_5P$ requires C, 37·75; H, 3·0; F, 39·85; P, 5·4%); the 5-p-*bromophenoxy-analogue* (22; R = OC_6H_4Br-*p*), m.p. 82—90° (from ethanol), τ 2·47 (2H, d, *J* 9 Hz), 2·93 (2H, d, *J* 9 Hz), 8·70 (6H, s), and 8·88 (6H, s) (Found: C, 33·6; H, 2·55; F, 35·2; Br, 12·2. $C_{18}H_{16}BrF_{12}O_5P$ requires C, 33·2; H, 2·5; F, 35·0; Br, 12·3%); 6,9-*dimethyl*-5-*phenoxy*-2,2,3,3-*tetrakistrifluoromethyl*-1,4-*dioxa*-6,9-*diaza*-5-*phosphaspiro*-[4.4]*nonane* (20; R = OPh), m.p. 69·5—71° (from light petroleum), τ 2·83 (5H, m), 6·97 (2H, s), 7·17 (2H, m), and 7·43 (6H, d, *J* 10 Hz) (Found: C, 35·5; H, 2·7; N, 5·4. $C_{16}H_{15}F_{12}N_2O_3P$ requires C, 35·4; H, 2·8; N, 5·2%); the 5-*phenylthio-analogue* (20; R = SPh), m.p. 46—52° (from light petroleum), τ 2·60 (5H, m), 7·07 (4H, m), and 7·43 (6H, d, *J* 12 Hz) (Found: C, 34·3; H, 2·6; F, 41·1; S, 6·1. $C_{16}H_{15}F_{12}N_2O_2SP$ requires C, 34·4; H, 2·7; F, 40·8; S, 5·7%); and the 5-*dimethylamino-analogue* (20; R = NMe_2), m.p. 78—82° (from light petroleum), τ 6·93 (2H, s), 7·13 (6H, d, *J* 12 Hz), 7·1 (2H, m), and 7·32 (6H, d, *J* 10 Hz) (Found: C, 29·4; H, 3·2; N, 8·7; F, 46·6. $C_{12}H_{16}F_{12}N_3O_2P$ requires C, 29·2; H, 3·3; N, 8·6; F, 46·2%). Dissolving the adduct (20; R = NMe_2) in hexafluoropropan-2-ol gave the *adduct* [20; R = $OCH(CF_3)_2$] quantitatively, m.p. 63—64° (after sublimation at 0·1 mmHg), τ 4·67 (1H, d of septets, *J* 15 and 6 Hz), 6·88 (2H, m), 7·07 (2H, s), and 7·35 (6H, d, *J* 11 Hz) (Found: C, 25·3; H, 1·9; F, 55·8. $C_{13}H_{11}F_{18}N_2O_3P$ requires C, 25·3; H, 1·8; F, 55·6%).

2-Phenoxy-1,3,2-dioxaphospholan and HFA, treated as above, gave a 1 : 2·5 mixture of (15; R = OPh) and (16), m.p. 130—135° at 0·2 mmHg, separated by fractional crystallisation from light petroleum to give 5-*phenoxy*-2,2,4,4-*tetrakistrifluoromethyl*-1,3,6,9-*tetraoxa*-5-*phosphaspiro*[4.4]*nonane* (16), m.p. 74·5—75°, ^{31}P δ +18·2 p.p.m., ^{19}F δ +4·79 (3F), 5·21 (3F), 16·95 (3F), and 18·05 (3F) (Found: C, 32·8; H, 1·8; F, 44·2; P, 6·0. $C_{14}H_9F_{12}O_5P$ requires C, 32·6; H, 1·75; F, 44·2; P, 6·0%), and a sample m.p. 45—53°, containing about 80% of (15; R = OPh), τ 2·7 (5H, m) and 5·5—6·4 (4H, m).

Reactions of Phospholans with Tetrachloro-o-benzoquinone.—A solution of the phospholan (10 mmol) in ether (5 ml) was added slowly to a stirred solution of tetrachloro-*o*-benzoquinone (10 mmol) in ether (25 ml) at room temperature. The red colour was rapidly discharged. Solvent was then removed and the residue crystallised from light petroleum to give the following adducts in almost quantitative yields: 4′,4′,5′,5′-*tetramethyl*-P-*phenoxy*-1,3,2-*benzodioxaphosphole*-2-*spiro*-2′-1′,3′,2′-*dioxaphospholan* (8; R = OPh), m.p. 159—160° (Found: C, 44·6; H, 3·5; P, 6·7. $C_{18}H_{17}Cl_4O_5P$ requires C, 44·45; H, 3·5; P, 6·4%); the P-*phenylthio-analogue* (8; R = SPh), m.p. 150·5—151·5° (Found: C, 43·15; H, 3·45; P, 6·1. $C_{18}H_{17}Cl_4O_4PS$ requires C, 43·2; H, 3·4; P, 6·2%); the P-*dimethylamino-analogue* (8; R = NMe_2), m.p. 132—134° (Found: C, 38·45; H, 4·3; P, 7·15. $C_{14}H_{18}Cl_4NO_4P$ requires C, 38·45; H, 4·1; P, 7·1%); the P-*methoxy-analogue* (8; R = OMe), m.p. 116—118° (Found: C, 36·75; H, 3·6; P, 7·1. $C_{13}H_{15}Cl_4O_5P$ requires C, 36·8; H, 3·5; P, 7·3%); the *dodecafluoro*-P-*phenyl analogue* (9; X = Cl, R = Ph), m.p. 174—175° (Found: C, 31·4; H, 1·0; F, 33·1. $C_{18}H_5Cl_4F_{12}O_4P$ requires C, 31·5; H, 0·75; F, 33·25%); and the *dodecafluoro*-P-*dimethylamino-analogue* (9; X = Cl, R = NMe_2), m.p. 124—126° (Found: C, 25·9; H, 1·0; F, 34·7. $C_{14}H_6Cl_4F_{12}NO_4P$ requires C, 25·7; H, 1·0; F, 34·9%).

Preparation of Spirophosphoranes via *Dichlorophosphoranes.*—(*a*) A solution of chlorine (0·71 g) in carbon tetrachloride (15 ml) was added slowly to phenyl *o*-phenylene phosphite (2·32 g) in carbon tetrachloride (10 ml) with stirring at 0°. Solvent was then removed and the residue dissolved in benzene (25 ml). Pyridine (1·6 g) was added followed dropwise with cooling by a solution of pinacol (1·18 g) in benzene (10 ml). Filtration, evaporation of the filtrate, and crystallisation of the residue from light petroleum gave the *adduct* (18; R = OPh) (1·8 g), m.p. 81—81·5°. This compound was extremely readily hydrolysed. It gave the expected mass spectrum but satisfactory elemental analytical figures could not be obtained.

A similar reaction sequence using hexafluoropinacol gave the *adduct* (9; X = H, R = OPh) (70%), m.p. 59—60° (from light petroleum) (Found: C, 38·1; H, 1·85; F, 40·1. $C_{18}H_9F_{12}O_5P$ requires C, 38·3; H, 1·6; F, 40·3%).

(*b*) Tetrachloro-*o*-benzoquinone (2·5 g) was added to phenyl phosphorodichloridite (1·95 g) in ether (30 ml) and the solution refluxed for 0·5 g. Solvent was then removed and the colourless solid suspended in benzene (30 ml). Pyridine (1·6 g) was then added, followed dropwise with cooling by perfluoropinacol (3·34 g) in benzene (10 ml). Filtration, evaporation of the filtrate, and crystallisation of the residue from light petroleum gave the *spirophosphorane* (9; X = Cl, R = OPh) (57%), m.p. 102—103° (Found: C, 30·75; H, 1·0; F, 32·55. $C_{18}H_5Cl_4F_{12}O_5P$ requires C, 30·75; H, 0·7; F, 32·5%).

(*c*) A solution of chlorine (0·71 g) in carbon tetrachloride (10 ml) was added slowly to *o*-phenylene phosphorochloridite (1·75 g) in carbon tetrachloride (10 ml) at 0° with stirring. Solvent was then removed and the residue suspended in benzene (25 ml). Pyridine (2·4 g) was added, followed dropwise in succession by pinacol (1·18 g) in benzene (10 ml) and benzenethiol (1·1 g) in benzene (5 ml). Filtration, evaporation of the filtrate, and extraction of the residue with light petroleum gave the *spirophosphorane* (18; R = SPh) (30%), m.p. 136—137° (from light petroleum) (Found: C, 59·1; H, 5·9; P, 8·45. $C_{18}H_{21}O_4PS$ requires C, 59·35; H, 5·8; P, 8·5%).

2,2,3,3-*Tetramethyl*-7,7,8,8-*tetrakistrifluoromethyl*-1,4,6,9-*tetraoxa*-5-*phosphaspiro*[4.4]*nonane* (25)—2-Dimethylamino-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (1·9 g) was treated with perfluoropinacol (3·34 g) in benzene (20 ml) for 4 h and the solution distilled to give the *spirophosphorane*, b.p. 100—105° at 0·15 mmHg, m.p. 38—40°, τ (benzene) 3·45 (1H, d, J 830 Hz), 8·95 (6H, s), and 9·05 (6H, s) (Found: C, 29·9; H, 2·8; F, 47·2. $C_{12}H_{13}F_{12}O_4P$ requires C, 30·0; H, 2·7; F, 47·5%).

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