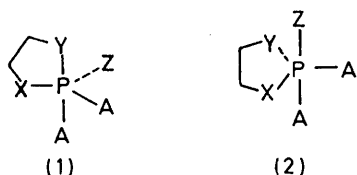


Strain Factors in Quinquecovalent Phosphoranes. Sulphur-containing Rings and Six-membered Rings

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

Variable-temperature n.m.r. spectroscopy on a range of spirophosphoranes has given data on the increase in energy when five-membered rings containing sulphur attached to phosphorus move from a diequatorial to an apical-equatorial position in a trigonal-bipyramidal phosphorane. The results have been compared with those from the corresponding oxygen-containing systems and the remarkable similarity has been explained in terms of compensating lone-pair orientation and strain terms. Lone-pair orientation effects are also important in determining the preference of six-membered rings containing heteroatoms attached to phosphorus for an apical-equatorial as oppose to a diequatorial disposition in trigonal bipyramidal phosphoranes.

PREVIOUSLY¹ we analysed the preference of five-membered rings for an apical-equatorial (1) as opposed to a diequatorial disposition (2) in trigonal bipyramidal



phosphoranes in terms of three factors: (a) an increase in angle strain on increasing the ring angle at phosphorus from 90 to 120°, (b) a change in apicophilicity in the groups occupying the apical positions, and (c) the preference of lone-pairs on equatorial heteroatoms for the equatorial plane. In these terms the difference in energy between (1) and (2) can be expressed as equation (i),

$$\Delta E = S + R^X + R^Y + \Delta A(Y - Z) \quad (i)$$

where R^X and R^Y are the energies of rotation around equatorial XP and YP bonds, respectively, and $\Delta A(Y - Z)$ is the difference in apicophilicity between the groups Y and Z determined in acyclic systems when lone-pairs are free to adopt their preferred orientations. This

analysis gives good agreement with experimental data for oxygen- and/or nitrogen-containing five-membered rings when S (saturated) = 8 kcal mol⁻¹, S (unsaturated) = 10 kcal mol⁻¹, R^N = 10 kcal mol⁻¹, and R^O is estimated at 5 kcal mol⁻¹. This paper is concerned with the similar preferences of five-membered sulphur-containing rings and of six-membered rings in general.

Five-membered Rings containing Sulphur attached to Phosphorus.—The barrier to rotation around equatorial PS bonds is known² to be comparable to that around equatorial PN bonds³ and considerably greater than in the case of PO bonds.⁴ Furthermore, the groups RO and RS are known to have similar apicophilicities.⁵ It follows from equation (i) that if X or Y is changed from oxygen to sulphur, and if we assume that the strain term is unchanged, then the energy difference between (1) and (2) would be expected to increase by the difference in the rotational energies round equatorial PO and PS bonds, *i.e.* by ca. 4–5 kcal mol⁻¹.

The pseudorotational pathways open to a spirophosphorane can be illustrated by reference to the hexafluoroacetone adduct (3; A–D all CF₃). The most stable conformers of this molecule are probably the topomers (3) and (8),⁶ although (5) and (6), with apical

¹ S. A. Bone, S. Trippett, and P. J. Whittle, *Tetrahedron Letters*, 1974, 1795.

² S. C. Peake and R. Schmutzler, *Chem. Comm.*, 1968, 1662; *J. Chem. Soc. (A)*, 1970, 1049.

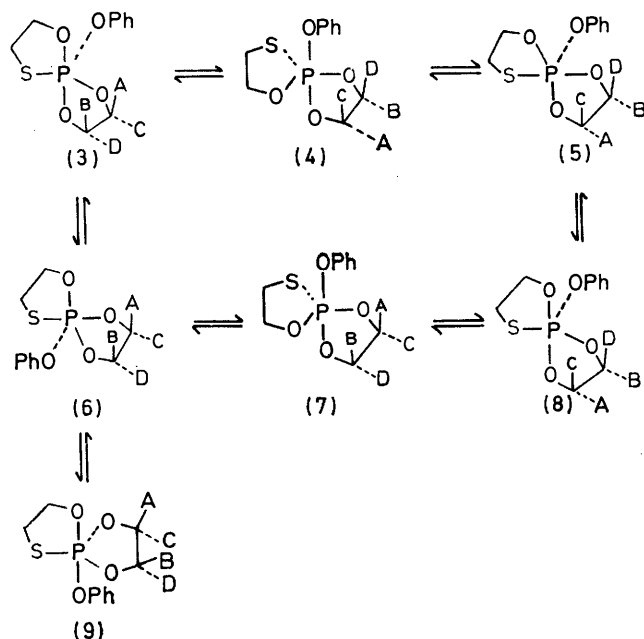
³ E. L. Muetterties, P. Meakin, and R. Hoffmann, *J. Amer. Chem. Soc.*, 1972, **94**, 3047.

⁴ D. U. Robert, D. J. Costa, and J. G. Riess, *J.C.S. Chem. Comm.*, 1973, 745.

⁵ S. A. Bone, S. Trippett, and P. J. Whittle, *J.C.S. Perkin I*, 1974, 2125.

⁶ E. Duff, D. R. Russell, and S. Trippett, *Phosphorus*, 1974, **4**, 203.

sulphur, will be of only slightly higher energy and the pseudorotations (3) \rightleftharpoons (6) and (5) \rightleftharpoons (8) will be



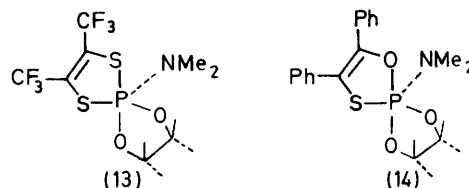
rapid on the n.m.r. time-scale at accessible temperatures. These pseudorotations do not make any of the CF_3 groups equivalent, and at room temperature the ^{19}F n.m.r. spectrum would be expected to show four equal signals. At higher temperatures the pseudorotations *via* the high-energy phosphoranes (4) and (7), having diequatorial oxathiaphospholan rings, will become rapid on the n.m.r. time-scale, leading to equivalence of the CF_3 groups A and D, and B and C, and to simplification of the n.m.r. spectrum to two signals. Pseudorotations *via* high-energy phosphoranes such as (9) with a diequatorial tetrakis(trifluoromethyl)dioxaphospholan ring are known to be slow on the n.m.r. time-scale at 180 °C;⁵ if rapid they would lead to equivalence of the CF_3 groups A and B, and C and D. As before,⁵ the assumption is made that high-energy phosphoranes with diequatorial rings can be regarded as equivalent to transition states between low-energy phosphoranes. The free energy of activation for the process leading to simplification of the ^{19}F n.m.r. spectrum is therefore a measure of the energy difference between (4) and (3).

Table I gives the free energies of activation for placing various five-membered sulphur-containing rings diequatorial with phenoxy moving to an apical position and compares these with the values in the corresponding systems where sulphur has been replaced by oxygen. The change from sulphur to oxygen does not affect the

energy of activation significantly, a surprising result in view of the prediction made earlier. However, that prediction was based on the assumption that the strain factor would remain constant, which is probably not the case; sulphur is much more able than oxygen to accommodate angle strain. Pell and Pilcher⁷ have shown, from heats of combustion, that tetrahydrofuran has 3.7 kcal mol⁻¹ more strain than tetrahydrothiophen, a difference which increases to 5.9 kcal mol⁻¹ in the corresponding 'etans and to 7.5 kcal mol⁻¹ in the 'irans. The increase in R^X and/or R^Y in equation (i) on changing X and/or Y from oxygen to sulphur, due to the greater energy of rotation round equatorial PS than round PO bonds, is therefore being offset by a decrease in the strain term, S, due to the greater ability of sulphur to accommodate the increase in angle strain.

Preparation of the spirophosphoranes (3) and (10) by the *N*-chlorodi-isopropylamine method has recently been described.⁸ 4,4,5,5-Tetramethyl-1-phenoxy-1,3,2-dioxaphospholan with perfluorobiacetyl⁹ gave (11; X = O), with 3,4-bistrifluoromethyl-1,2-dithieten¹⁰ gave (11; X = S), with monothiobenzil¹¹ gave (12; X = S), and with benzil gave (12; X = O).

As expected, in view of the poorer apicophilicity of the dimethylamino-group relative to the phenoxy-group,¹² the ^1H n.m.r. spectra of the phosphoranes (13) and (14) did not change in the range from room temperature to 175 °C.



Six-membered Rings.—Calculations¹³ have indicated a preference of the phosphorinan ring for a diequatorial position in a trigonal bipyramidal phosphorane but only limited experimental data are available on this preference. The fluorine atoms in the trifluorophosphorane (15) are still not equivalent in the ^{19}F n.m.r. spectrum at 100 °C,¹⁴ showing that ΔG^* for the pseudorotation (15) \rightleftharpoons (16) is >16 kcal mol⁻¹, whereas the barrier to the pseudorotation (17) \rightleftharpoons (18) in the corresponding five-membered trifluorophosphorane is 7–8 kcal mol⁻¹. The relief of strain in the five-membered ring on going from (17) to (18) is 8–9 kcal mol⁻¹; it follows that any change in strain in the six-membered ring on going from (15) to (16) is small and may be negative.

The introduction into the six-membered ring of heteroatoms attached to phosphorus means that lone-pair

¹¹ B. A. Arbuzov, N. A. Polezhaeva, V. V. Smirnov, and A. A. Musina, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1975, 1658.

¹² S. Trippett and P. J. Whittle, *J.C.S. Perkin I*, 1973, 2302.

¹³ P. Gillespie, P. Hoffmann, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem. Internat. Edn.*, 1971, **10**, 687.

¹⁴ E. L. Muettterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 1963, **2**, 613; R. Schmutzler, *Angew. Chem. Internat. Edn.*, 1975, **4**, 496.

⁷ A. S. Pell and G. Pilcher, *Trans. Faraday Soc.*, 1965, **61**, 71.

⁸ S. A. Bone and S. Trippett, *Tetrahedron Letters*, 1975, 1583; S. Antczak, S. A. Bone, J. Brierley, and S. Trippett, *J.C.S. Perkin I*, in the press.

⁹ J. I. Dickstein and S. Trippett, *Tetrahedron Letters*, 1973, 2203.

¹⁰ N. J. De'Ath and D. B. Denney, *J.C.S. Chem. Comm.*, 1972, 395.

orientation effects have to be taken into account. Examination of Drieding models, containing sp^2 -hybridised heteroatoms, shows that in both an apical-equatorial chair ring and in the only conformer of a diequatorial

phorus compounds. Data on their variable-temperature ^{19}F n.m.r. spectra are given in Table 2. The increasing complexity of the spectra at low temperatures (1 peak \rightarrow 2 peaks) when $X = Y$; otherwise $2 \rightarrow 4$ is

TABLE 1

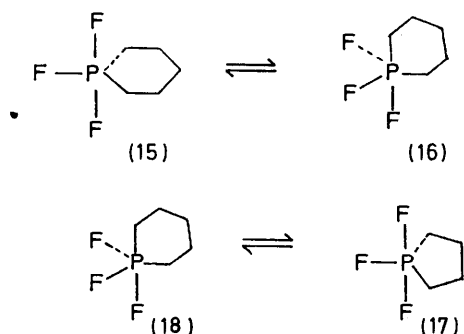
N.m.r. data ^a on spirophosphoranes

	X = S			X = O ^b		
	T_c ^c	$\Delta\nu/\text{Hz}$	ΔG^* ^d	T_c ^c	$\Delta\nu$	ΔG^* ^d
	94	94	17.7 ^e			17.4 ¹
	143	54	20.7 ^e			20.5 ¹
	136 ^b	4.5	22.3	134 ^g	2	22.9
	104	3.5	20.7 ^f	120	4.5	21.4

^a In 1-bromonaphthalene unless otherwise stated. ^b Two signals coalesce to one. ^c ± 2 °C. ^d ± 0.3 kcal mol⁻¹; calculated by using the Gutowsky Holm equation. ^e ^{19}F at 94.1 MHz. ^f ^1H at 100 MHz. ^g In CBrCl_3 .

ring the lone-pairs on equatorial atoms are in unfavourable orientations. Only with an apical-equatorial boat

associated with slowing of the pseudorotations (19) \rightleftharpoons (20) which place the six-membered rings diequatorial. The barrier to this process clearly depends on the nature of the atom which remains equatorial, showing that lone-pair orientation effects are playing a significant part, although changes in the rotational energy round the



ring is it possible for the lone-pair on the equatorial atom to be in the favoured equatorial plane.

From the low-temperature ^1H n.m.r. spectra of several phosphoranes containing 1,3,2-dioxaphosphorinane rings Denney ¹⁵ concluded that this ring has a preference for an apical-equatorial position.

The adducts (19) were prepared by the addition of hexafluoroacetone to the appropriate trivalent phosphorus compounds.

TABLE 2
 ^{19}F N.m.r. data ^a on the spirophosphoranes (19)

X	Y	T_c ^b	$\Delta\nu/\text{Hz}$	ΔG^* ^c
O	O	-140	100	5.9
MeN	O	-70	102	9.2
MeN	MeN	< -140		< 6

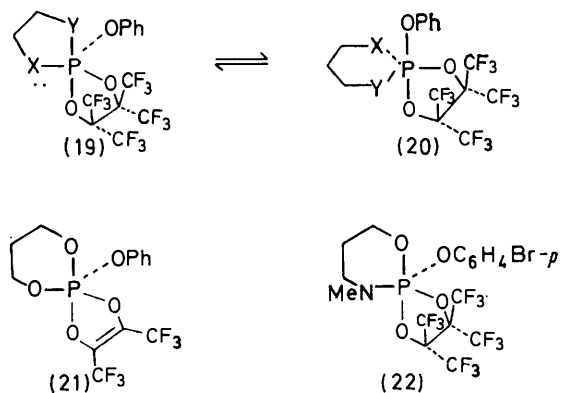
^a In ether-light petroleum. ^b ± 3 °C. ^c ± 0.3 kcal mol⁻¹.

equatorial bond are not fully reflected in the height of the barrier.

The barrier to rotation round equatorial PO bonds is known ⁴ to be < 8 kcal mol⁻¹ and we ¹ have estimated a value of 5 kcal mol⁻¹ on the basis of strain data in five-membered phosphoranes. The barrier to equivalence

¹⁵ 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.

of the CF_3 groups in (19; $\text{X} = \text{Y} = \text{O}$) of 5.9 kcal mol⁻¹ might therefore be associated, not with the pseudorotation (19) \rightarrow (20), but with slowing of rotation round the P-OPh bond. In order to assess this possibility the spirophosphorane (21) was prepared from hexafluorobiacyl and 2-phenoxy-1,3,2-dioxaphosphorinane and its low-temperature ¹⁹F n.m.r. spectrum examined. The



spectrum remained a sharp singlet down to -145°C , showing that even at this temperature rotation round the equatorial P-OPh bond is rapid on the n.m.r. time-scale and supporting the association of the non-equivalence of the CF_3 groups of (19; $\text{X} = \text{Y} = \text{O}$) at low temperatures with slowing of the pseudorotation (19) \rightleftharpoons (20).

Subsequent to the work described above we have determined the structure of the spirophosphorane (22) by X-ray analysis.¹⁶ The apical-equatorial perhydrooxazaphosphorine ring is a boat conformer with the lone-pair of the planar nitrogen in the equatorial plane, emphasising the importance of lone-pair orientation effects in determining the stable conformers of phosphoranes. If the most stable conformer of an apical-equatorial 1,3,2-dioxaphosphorinane ring is also the boat form, then (a) the energy barrier of 5.9 kcal mol⁻¹ for pseudorotation of (19; $\text{X} = \text{Y} = \text{O}$) is that for moving a boat 1,3,2-dioxaphosphorinane ring from an apical-equatorial to a higher energy diequatorial position, and (b) since an apical-equatorial chair 1,3,2-dioxaphosphorinane ring would be of higher energy than a similarly positioned boat-form, it is not possible to predict the preferred location of a chair 1,3,2-dioxaphosphorinane ring in a trigonal bipyramidal phosphorane. Clearly these considerations are relevant to the mechanism of nucleophilic substitution at phosphoryl centres in 1,3,2-dioxaphosphorinanes, and they will be discussed in detail elsewhere.

EXPERIMENTAL

¹⁹F N.m.r. spectra were determined at 56.4 MHz and chemical shifts are quoted relative to internal PhCF_3 unless otherwise stated. ³¹P N.m.r. spectra were obtained at 24.3 MHz and chemical shifts are quoted relative to external 85% H_3PO_4 . Positive shifts are upfield from the reference

in both cases. ¹H N.m.r. spectra were obtained at 60 MHz for solutions in CDCl_3 unless otherwise stated.

5-Phenoxy-7,8-bistrifluoromethyl-2,3,3-tetramethyl-1,4-dioxo-6,9-dithia-5-phosphaspiro[4.4]non-7-ene (11; $\text{X} = \text{S}$).—3,4-Bistrifluoromethyl-1,2-dithieten (1.15 g) in dichloromethane (15 ml) was added slowly to a stirred solution of 4,4,5,5-tetramethyl-2-phenoxy-1,3,2-dioxaphospholan (1.2 g) in dichloromethane (20 ml) at -78°C , and the solution was allowed to warm to room temperature. Evaporation and crystallisation of the residue from light petroleum gave the title phosphorane (95%), m.p. $88\text{--}89.5^\circ$, *m/e* 467, 373, 240, 226, 182, 162, and 147, τ (100 MHz; 1-bromonaphthalene) 9.12 (6 H, s) and 9.18 (6 H, s), ¹⁹F (CDCl_3) -8.65 (d, *J* 0.5 Hz), ³¹P (CH_2Cl_2) -13.6 p.p.m. (Found: C, 41.3; H, 3.8; S, 13.8. $\text{C}_{16}\text{H}_{17}\text{F}_6\text{O}_3\text{PS}_2$ requires C, 41.2; H, 3.6; S, 13.7%).

In a similar way was prepared the 5-dimethylamino-analogue (14) (95%), m.p. $127\text{--}128^\circ$, τ 7.27 (6 H, d, *J* 13 Hz), 8.62 (6 H, s), and 8.80 (6 H, s), ¹⁹F (CDCl_3) -8.43 , ³¹P (CDCl_3) -10.3 p.p.m. (Found: C, 34.6; H, 4.4; N, 3.4. $\text{C}_{12}\text{H}_{18}\text{F}_6\text{NO}_2\text{PS}_2$ requires C, 34.5; H, 4.3; N, 3.4%).

2,2,3,3-Tetramethyl-5-phenoxy-7,8-diphenyl-1,4,6-trioxa-9-thia-5-phosphaspiro[4.4]non-7-ene (12; $\text{X} = \text{S}$).—A solution of monothiobenzil, generated from sodium *S*-(α -phenylphenacyl) thiosulphate (1.1 g), in dichloromethane (25 ml) was added slowly to a stirred solution of 4,4,5,5-tetramethyl-2-phenoxy-1,3,2-dioxaphospholan (0.75 g) in dichloromethane (15 ml) at -78°C . The blue colour of the monothiobenzil was immediately discharged. Evaporation, and crystallisation of the residue from light petroleum gave the title phosphorane (32%), m.p. $140\text{--}141^\circ$, *m/e* 466, 366, 256, and 210, τ 2.65–3.7 (15 H, m), 8.42 (3 H, s), 8.53 (3 H, s), 8.60 (3 H, s), and 8.65 (3 H, s) (Found: C, 66.1; H, 5.9. $\text{C}_{26}\text{H}_{29}\text{O}_4\text{PS}$ requires C, 66.9; H, 5.8%).

In a similar way was prepared the 5-dimethylamino-analogue (15) (63%), m.p. 156° (decomp.) (from ether), *m/e* 417, 317, 290, 257, 252, 210, and 207, τ 2.95 (10 H, m), 7.34 (6 H, d, *J* 11 Hz), 8.80 (9 H, s), and 8.91 (3 H, s) (in 1-bromonaphthalene at 100 MHz the methyl groups gave four signals of equal intensity at τ 8.85, 8.93, 8.97, and 9.11), ³¹P (CDCl_3) $+22$ p.p.m. (Found: C, 63.3; H, 6.9; N, 3.3. $\text{C}_{22}\text{H}_{28}\text{NO}_3\text{PS}$ requires C, 63.3; H, 6.7; N, 3.3%).

2,2,3,3-Tetramethyl-5-phenoxy-7,8-bistrifluoromethyl-1,4,6,9-tetraoxa-5-phosphaspiro[4.4]non-7-ene (11; $\text{X} = \text{O}$).—Hexafluorobiacyl (1.0 g) was passed into a solution of 4,4,5,5-tetramethyl-2-phenoxy-1,3,2-dioxaphospholan (1.2 g) in ether (30 ml) at 0°C and the solution set aside at room temperature for 1 h. Evaporation then gave the title phosphorane (95%), m.p. $58.5\text{--}60.5^\circ$, *m/e* 434, 419, 377, 361, 341, 334, and 317, τ 2.67–3.35 (5 H, m) and 8.67 (12 H, s), ¹⁹F (94.1 MHz; CDCl_3) 2.6 (s) p.p.m., ³¹P (ether) $+37$ p.p.m. (Found: C, 44.3; H, 4.1; P, 7.05. $\text{C}_{16}\text{H}_{17}\text{F}_6\text{O}_5\text{P}$ requires C, 44.25; H, 3.9; P, 7.15%).

A similar reaction gave 5-phenoxy-2,3-bistrifluoromethyl-1,4,6,10-tetraoxa-5-phosphaspiro[4.5]dec-2-ene (88%), m.p. $70\text{--}75^\circ$ (sealed tube) (from hexane), τ 2.50–3.23 (5 H, m), 5.82 (4 H, dt, *J* 17 and 7 Hz), and 8.0 (2 H, q, *J* 7 Hz), ¹⁹F (ether) $+71$ p.p.m. (relative to internal CFCl_3), ³¹P $+51$ p.p.m., *m/e* 392, 373, 334, 299, 259, and 254.

2,2,3,3-Tetramethyl-5-phenoxy-7,8-diphenyl-1,4,6,9-tetraoxa-5-phosphaspiro[4.4]non-7-ene (12; $\text{X} = \text{O}$).—Benzil (0.7 g) was dissolved in a solution of 4,4,5,5-tetramethyl-2-phenoxy-1,3,2-dioxaphospholan (0.8 g) in ether (2 ml) with

¹⁶ J. H. Barlow, S. A. Bone, D. R. Russell, and S. Trippett, unpublished work.

gentle warming and the solution set aside at room temperature overnight. Filtration and crystallisation from light petroleum gave the title *phosphorane* (77%), m.p. 122.5–123.5°, *m/e* 450, 350, and 274, τ 3.0 (15 H, s), and 8.6 (12 H, s), ^{31}P (CH_2Cl_2) +40.2 p.p.m. (Found: C, 69.35; H, 6.1; P, 6.9. $\text{C}_{26}\text{H}_{27}\text{O}_5\text{P}$ requires C, 69.35; H, 6.0; P, 6.8%).

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 °C. After 0.5 h at –78 °C the solution was allowed to warm to room temperature and set aside for 1 h. Evaporation, and crystallisation of the residue then gave the following phosphoranes in nearly quantitative yields: *5-phenoxy-2,2,4,4-tetrakis(trifluoromethyl)-1,3,6-trioxa-9-thia-5-phosphaspiro[4.4]nonane* (13), m.p. 110–112°, *m/e* 532, 513, 472, 463, 451, and 439, τ 2.8 (5 H, s) and 5.4–7.5 (4 H, m), ^{19}F 4.1 (6 F, m) and 17.1 (6 F, m) p.p.m., ^{31}P –11 p.p.m. (Found: C, 31.7; H, 1.5; F, 43.8. $\text{C}_{14}\text{H}_9\text{F}_{12}\text{O}_4\text{PS}$ requires C, 31.6; H, 1.7; F, 43.9%); *5-phenoxy-2,2,3,3-tetrakis(trifluoromethyl)-1,4,6,10-tetraoxa-5-phosphaspiro[4.5]decane* (20; X = Y = O), m.p. 93–97° (sealed tube), *m/e* 530, 511, 473, 461, 437, 397, and 345, τ 2.53–3.35 (5 H, m), 5.32–6.42 (4 H, m), and 7.52–

8.42 (2 H, m), ^{19}F (ether–light petroleum) 4.78 (s) p.p.m., ^{31}P +68 p.p.m. (Found: C, 33.6; H, 2.0; P, 5.9. $\text{C}_{15}\text{H}_{11}\text{F}_{12}\text{O}_5\text{P}$ requires C, 34.0; H, 2.1; P, 5.85%); *10-methyl-5-phenoxy-2,2,3,3-tetrakis(trifluoromethyl)-1,4,6-trioxa-10-aza-5-phosphaspiro[4.5]decane* (20; X = NMe, Y = O), m.p. 98.5–99° (from ethanol), *m/e* 543, 524, 474, 450, 422, 350, 211, and 118, τ 2.65–3.25 (5 H, m), 5.75–7.87 (4 H, m), 7.10 (3 H, d, *J* 10 Hz), and 7.93–8.55 (2 H, m), ^{19}F (ether–light petroleum) 3.94 (6 F, m) and 5.39 (6 F, m) p.p.m., ^{31}P +58 p.p.m. (Found: C, 35.5; H, 2.4; F, 41.8; P, 5.7. $\text{C}_{16}\text{H}_{14}\text{F}_{12}\text{NO}_4\text{P}$ requires C, 35.35; H, 2.6; F, 42.0; P, 5.7%); and *6,10-dimethyl-5-phenoxy-2,2,3,3-tetrakis(trifluoromethyl)-1,4-dioxa-6,10-diaza-5-phosphaspiro[4.5]decane* (20; X = Y = NMe), m.p. 50–52°, *m/e* 556, 537, 487, 463, 240, 224, 166, and 147, τ 2.56–3.14 (5 H, m), 6.66–7.62 (4 H, m), 7.40 (6 H, d, *J* 12 Hz), and 8.04–8.32 (2 H, m), ^{19}F (light petroleum) 4.88 (s) p.p.m., ^{31}P +37 p.p.m. (Found: C, 37.0; H, 3.0; F, 41.3; P, 5.7. $\text{C}_{17}\text{H}_{17}\text{F}_{12}\text{N}_2\text{O}_3\text{P}$ requires C, 36.7; H, 3.1; F, 41.0; P, 5.6%).

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