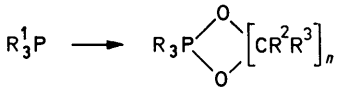
Synthesis of Phosphoranes by using *N*-Chlorodi-isopropylamine

By **Stephen Antczak, Stephen A. Bone, John Brierley,** and **Stuart Trippett,*** Department of Chemistry, The University, Leicester LE1 7RH

A wide range of cyclic and acyclic tervalent phosphorus compounds condense with 1,2- or 1,3-glycols, or with catechols, in the presence of *N*-chlorodi-isopropylamine, to give di-isopropylammonium chloride and the corresponding cyclic phosphoranes containing 1,3,2-dioxaphospholan or 1,3,2-dioxaphosphorinan rings. The variable-temperature n.m.r. spectra of a number of the new phosphoranes are recorded and interpreted in accord with previous data on relative apicophilicities of groups and ring-strain effects.

THERE is a limited number of ways of converting a tervalent phosphorus compound into the corresponding quinquecovalent 1,3,2-dioxaphospholan (1; $n = 2$) or 1,3,2-dioxaphosphorinan (1; $n = 3$). Denney [1] showed



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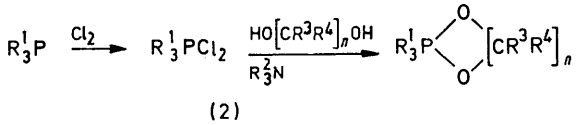

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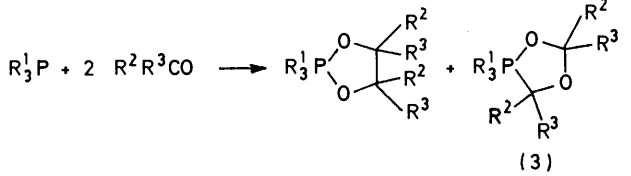


(3)

that the diethoxyphosphoranes $R_3P(OEt)_2$, obtained from tervalent phosphorus compounds and diethyl peroxide [2] or ethyl benzenesulphenate,[3] exchange the ethoxy-groups with some, but not all, 1,2- and 1,3-glycols to give the phosphoranes (1; $n = 2$ or 3). Bartlett [4] extended the peroxide reaction to the addition of tetramethyl-1,2-dioxetan to give 4,4,5,5-tetramethyl-1,3,2-dioxaphosph(v)olans directly. Treatment of dichlorophosphoranes (2) with diols in the presence of tertiary amines has had limited application.[5] Some reactive carbonyl compounds, *e.g.* hexafluoroacetone [6] and *p*-nitrobenzaldehyde,[7] with tervalent phosphorus compounds give 1,3,2-dioxaphospholans but the isomeric 1,4,2-dioxaphospholans (3) may also be formed.

We have described recently [8] the preparation of spirophosphoranes (4) by using diethyl azodiformate according to the overall equation (1). The failure of this synthesis with perfluoropinacol, and its capricious nature, made us look for other reagents capable of removing two hydrogen atoms from one molecule each of phosphorus compound and diol; this paper describes the use of *N*-chlorodi-isopropylamine for that purpose.[9]

N-Chloro-amines react with phosphines to give aminophosphonium chlorides and with phosphites to give phosphoramidates.[10] It is usually assumed that the initial reaction in both cases involves nucleophilic attack of phosphorus on chlorine. Castro [11] has used *N*-chlorodi-isopropylamine in the synthesis of alkoxyphosphonium salts according to equation (ii).

When *N*-chlorodi-isopropylamine is added to equi-

[1] B. C. Chang, W. E. Conrad, D. B. Denney, D. Z. Denney, R. Edelmann, R. L. Powell, and D. W. White, *J. Amer. Chem. Soc.*, 1971, **93**, 4004.

[2] D. B. Denney and H. M. Relles, *J. Amer. Chem. Soc.*, 1964, **86**, 84.

[3] L. L. Chang and D. B. Denney, *J.C.S. Chem. Comm.*, 1974, 84.

[4] P. D. Bartlett, A. L. Baumstark, M. E. Landis, and C. L. Lerman, *J. Amer. Chem. Soc.*, 1974, **96**, 5267.

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

[6] F. Ramirez, C. P. Smith, A. S. Gulati, and A. V. Patwardhan, *Tetrahedron Letters*, 1966, 2151.

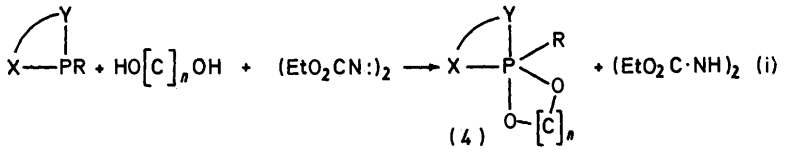
[7] F. Ramirez, S. B. Bhatia, and C. P. Smith, *Tetrahedron*, 1967, **23**, 2067.

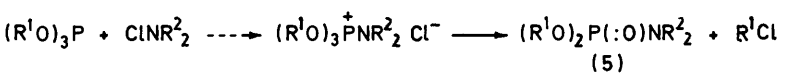
[8] S. A. Bone and S. Trippett, *J.C.S. Perkin I*, 1976, 156.

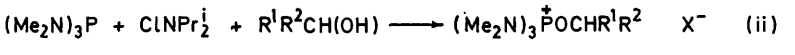
[9] For a preliminary communication on the synthesis of spirophosphoranes see S. A. Bone and S. Trippett, *Tetrahedron Letters*, 1975, 1583.

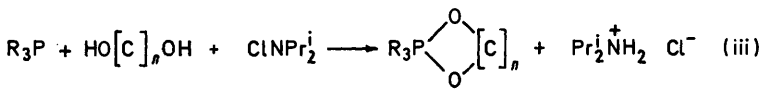
[10] K. A. Petrov and G. A. Sokolskij, *Zhur. obshchei Khim.*, 1956, **26**, 3378.

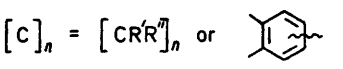
[11] B. Castro, Y. Chapleur, and R. Gross, *Tetrahedron Letters*, 1974, 2313.



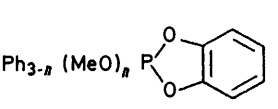




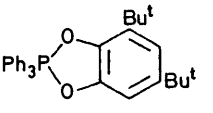




molar quantities of a tervalent phosphorus compound and a 1,2- or 1,3-diol in ether at −78 °C a precipitate of di-isopropylammonium chloride is formed. Filtration and evaporation then gives the phosphorane according to equation (iii). The high yield and ease of isolation of product are important factors in the success of the synthesis, as most phosphoranes are hydrolytically unstable and many are also thermally unstable.



(6) n = 0,1,2, or 3



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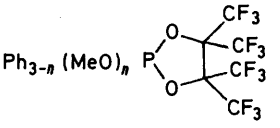
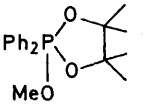


(8) n = 0 or 1



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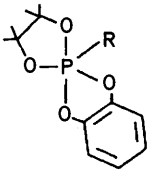
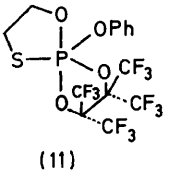


(10) R = OMe or OPh



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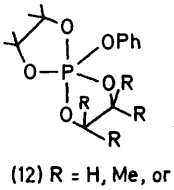
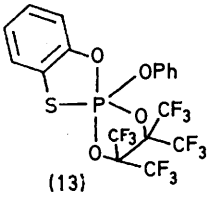


(12) R = H, Me, or CF_3



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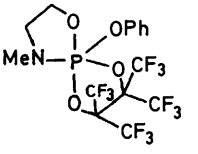

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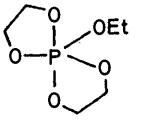

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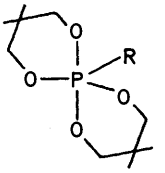
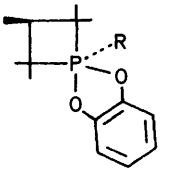
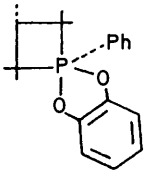


(16) R = Me, CH_2Ph, or Ph



(17) R = CH_2Ph or Ph

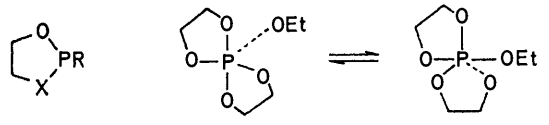


(18)

The synthesis works well with 1,2-glycols, including ethylene glycol, pinacol, and perfluoropinacol, 1,3-glycols, and catechols. The range of tervalent phosphorus compounds so far used successfully includes acyclic and cyclic phosphines, phosphinites, phosphonites, phosphites, phosphoramidites, and phosphorothioites. Among the phosphoranes so far prepared are compounds (6)—(18); in all cases the phosphoranes were formed according to equation (iii) with the right-hand ring as drawn derived from the diol.

Several of the phosphoranes derived from perfluoropinacol, *e.g.* (11) and (14), have not hitherto been accessible. Both the 1,3,2-oxathiaphospholan (19; X = S, R = OPh) and the 1,3,2-oxazaphospholidine (19; X = NMe, R = OPh) with hexafluoroacetone give 1,4,2-dioxaphospholans (3). However the outcome of reactions of tervalent phosphorus compounds with hexafluoroacetone is not predictable and the 1,3,2-oxathiaphospholan (19; X = S, R = NMe_2) gives the 1,3,2-dioxaphospholan.

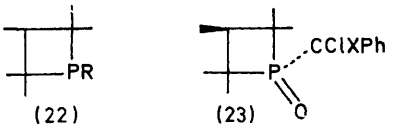
Many of the other phosphoranes are much more easily prepared than by existing methods. The previous route to the adduct (9) involved the use of a 1,2-dioxetan, and the addition of catechols avoids the use of *o*-quinones with the attendent problems of polymerisation. The method appears to give higher yields and purer phosphoranes than does the exchange method.[1] Thus the phosphorane (15) from 2-ethoxy-1,3,2-dioxaphospholan and ethylene glycol was readily crystallised without prior distillation. In our hands, the ^1H n.m.r. spectrum in 1-bromonaphthalene of the ring protons of (15) simplified to a doublet at about 125 °C, more in accord with the expected [12] energy barrier (18 kcal mol^{-1}) to the pseudorotation (20) ⇌ (21) than the coalescence temperature of 172 °C reported by Denney.[1]



(19) (20) (21)

The *trans*- and *cis*-isomers of the 1-phenylphosphetan (22; R = Ph) with catechol and *N*-chlorodi-isopropylamine gave the isomeric phosphoranes (17; R = Ph) and (18), respectively. These undergo equilibration on heating; the kinetics of this process will be reported elsewhere. The *trans*-1-benzylphosphetan (22; R = CH_2Ph) similarly gave the *trans*-phosphorane (17; R = CH_2Ph), but with perfluoropinacol as the diol only the phosphine oxides (23; X = H or Cl) were isolated.

The spirophosphoranes obtained from the 1,3,2-oxazaphospholidines (19; X = NMe, R = OPh, SPh, or NMe_2) and 3-methylcatechol were *ca.* 1 : 1 mixtures of the isomers (24) and (26). Separate *N*-methyl and/or aryl-methyl signals were observed for the two isomers in 1-bromonaphthalene at room temperature. The signals coalesced at higher temperatures. The derived free energies of activation for pseudorotations *via* the highest-energy trigonal bipyramids (25) were 20.0 ± 0.3 (R = OPh) and 21.7 ± 0.3 (R = SPh) kcal mol^{-1}, in agreement with previous data on similar



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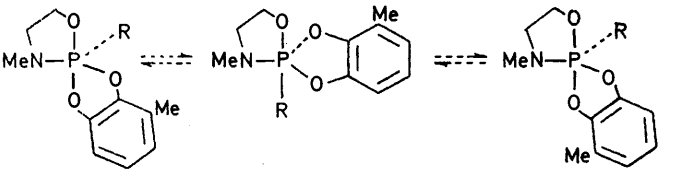
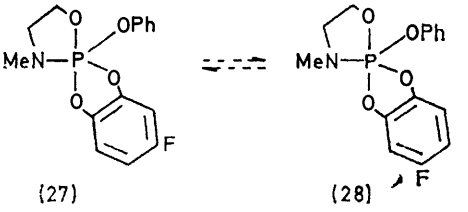


(24) (25) (26)

pseudorotations.[5,12] As expected from the lower apicophilicity of the dimethylamino-group relative to phenoxy,[13] equilibration of the isomers (24) and (26) (R = NMe_2) was slow on the n.m.r. time-scale at 180 °C.

The spirophosphorane obtained from the 1,3,2-oxazaphospholidine (19; X = NMe, R = OPh) and 4-fluorocatechol was similarly a 1 : 1 mixture of isomers



(27) (28)

(27) and (28) showing different ^{19}F n.m.r. signals. Coalescence of these at 168 ± 2 °C corresponded to a free energy of activation for interconversion of the isomers *via* a highest-energy phosphorane analogous to (25) of 20.3 ± 0.3 kcal mol^{-1}.

EXPERIMENTAL

^1H N.m.r. spectra were obtained at 60 MHz for solutions in $CDCl_3$ unless otherwise stated. ^{31}P N.m.r. spectra were obtained at 24.3 MHz for solutions in $CDCl_3$; chemical shifts upfield from external 85% H_3PO_4 are quoted as positive.

General Directions for the Preparation of Phosphoranes by using N-Chlorodi-isopropylamine.—A solution of the glycol or catechol (5 mmol) in ether (10 ml) was added slowly to a solution of the tervalent phosphorus compound (5 mmol) in ether (25 ml) maintained at −78 °C. *N*-Chlorodi-isopropylamine [14] (0.68 g) in ether (10 ml) was then added slowly and the mixture kept at −78 °C for ½ h and then set aside overnight at room temperature. Filtration followed by evaporation gave the crude phosphorane, which was crystallised from or extracted with light petroleum. In this way the following phosphoranes were prepared.

[12] S. A. Bone, S. Trippett, M. W. White, and P. J. Whittle, *Tetrahedron Letters*, 1974, 1795.

[13] S. Trippett and P. J. Whittle, *J.C.S. Perkin I*, 1973, 2302.

[14] H. Bock and K.-L. Kompa, *Chem. Ber.*, 1966, **99**, 1347.

From catechol. *P*-Methoxy-4′,4′,5′,5′-tetramethyl-1,3,2-benzodioxaphosphole-2-spiro-2′-[1,3,2]dioxaphospholan (10; R = OMe) (71%), m.p. and mixed [8] m.p. 80—81.5°; the *P*-phenoxy-analogue (10; R = OPh) (80%), m.p. and mixed [5] m.p. 81—81.5°; P-*methoxy*-PP-*diphenyl*-1,3,2-*benzodioxaphosphole* (6; $n = 1$) (84%), m.p. 84—85°; δ 3.3 (3 H, d, J 11 Hz), 6.6—6.8 (4 H, m), and 7.1—8.0 (10 H, m), ^{31}P +19 p.p.m. (Found: C, 70.35; H, 5.4; P, 9.3. $C_{19}H_{17}O_3P$ requires C, 70.4; H, 5.3; P, 9.55%); the *triphenyl analogue* (6; $n = 0$) (62%), m.p. 75° (decomp.), δ 6.5—6.8 (4 H, m) and 7.0—7.8 (15 H, m), ^{31}P 22.9; the dimethoxyphenyl analogue (6; $n = 2$) (90%), not crystalline, δ 3.79 (6 H, d, J 12 Hz) and 7.0—8.35 (10 H, m), ^{31}P +29.5 p.p.m.; the trimethoxy-analogue (6; $n = 3$) (24%), not crystalline, δ 3.86 (9 H, d, J 14 Hz) and 7.14 (4 H, s), ^{31}P (CCl_4) +51.6 p.p.m.; P-r-*phenyl*-2′,2′,t-3′,4′,4′-*pentamethyl*-1,3,2-*benzodioxaphosphole*-2-*spiro*-1′-*phosphetan* (17; R = Ph) (83%), m.p. 124—125°, δ 0.85 (3 H, dd, J 2 and 7 Hz), 1.26 (6 H, d, J 19 Hz), 1.44 (6 H, d, J 16 Hz), 1.9 (1 H, m), 6.62 (4 H, s), and 7.14—7.86 (5 H, m), ^{31}P +5.7 p.p.m. (Found: C, 73.2; H, 7.6; P, 9.5. $C_{20}H_{25}O_2P$ requires C, 73.2; H, 7.6; P, 9.5%); the c-3′-*analogue* (18) (80%), m.p. 65—67°, δ 0.84 (3 H, dd, J 2 and 4 Hz), 1.40 (6 H, d, J 15 Hz), 1.20 (6 H, d, J 18 Hz), 2.02 (1 H, m), 6.5 (4 H, s), and 7.0—7.7 (5 H, m), ^{31}P +1.9 p.p.m. (Found: C, 72.9; H, 7.7%); and the P-r-*benzyl*-t-3′-*analogue* (17; R = CH_2Ph) (64%), m.p. 140—141°, δ 0.82 (3 H, dd, J 2 and 7 Hz), 1.30 (6 H, d, J 16 Hz), 1.35 (6 H, d, J 18 Hz), 3.28 (2 H, d, J 7 Hz), 6.34 (4 H, s), and 6.82 (5 H, s), ^{31}P +4.2 p.p.m. (Found: C, 73.55; H, 7.9; P, 8.95. $C_{21}H_{27}O_2P$ requires C, 73.7; H, 7.9; P, 9.1%).

From 3,5-*di-t-butylcatechol.* 4,6-*Di-t-butyl*-PPP-*triphenyl*-1,3,2-*benzodioxaphosphole* (7) (70%), m.p. 146—148°, δ 1.13 (9 H, s), 1.15 (9 H, s), 6.55—6.7 (2 H, m), and 7.0—7.6 (15 H, m), ^{31}P +21.9 p.p.m. (Found: C, 79.7; H, 7.4; P, 6.3. $C_{32}H_{35}O_2P$ requires C, 79.65; H, 7.3; P, 6.4%).

From pinacol. *P*-Methoxy-*PP*-diphenyl-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (9) (79%),[4] m.p. 133°, δ 1.11 (12 H, s), 3.25 (3 H, d, J 12 Hz), and 7.5—8.5 (10 H, m), ^{31}P +45 p.p.m.; and 2,2,3,3,7,7,8,8-octamethyl-5-phenoxy-1,4,6,9-tetraoxa-5-phosphaspiro[4.4]nonane (12; R = Me) (89%), m.p. below room temperature (the m.p. reported in ref. 9 is incorrect), spectral properties identical with those reported.[8]

From ethylene glycol. 2,2,3,3-Tetramethyl-5-phenoxy-1,4,6,9-tetraoxa-5-phosphaspiro[4.4]nonane (12; R = H) (80%), b.p. 120° at 0.2 mmHg, having the spectral properties recorded; [8] and 5-ethoxy-1,4,6,9-tetraoxa-5-phosphaspiro-[4.4]nonane (15) (79%),[1] m.p. 36—38°, ^{31}P +27.9 p.p.m.

From perfluoropinacol. *PPP*-Triphenyl-4,4,5,5-tetrakistrifluoromethyl-1,3,2-dioxaphospholan (8; $n = 0$) (81%), m.p. 105° (decomp.); [15] the P-*methoxy*-PP-*diphenyl analogue* (8; $n = 1$) (93%), m.p. 75—76°, δ 3.45 (3 H, d, J 12 Hz) and 7.0—8.0 (10 H, m), ^{31}P +18 p.p.m. (Found: C, 41.4; H, 2.4; P, 5.7. $C_{19}H_{13}F_{12}O_3P$ requires C, 41.6; H, 2.4; P, 5.65%); 2,2,3,3-tetramethyl-5-phenoxy-7,7,8,8-tetrakistrifluoromethyl-1,4,6,9-tetraoxa-5-phosphaspiro[4.4]nonane (12; R = CF_3) (91%), m.p. and mixed [5] m.p. 105—106° (from ethanol); 5-*phenoxy*-2,2,3,3-*tetrakistrifluoromethyl*-1,4,6-*trioxa*-9-*thia*-5-*phosphaspiro*[4.4]*nonane* (11) (88%), m.p. 107—108°, δ 3.6—4.0 (4 H, m), and 7.2 (5 H, m), ^{19}F 4.36 (3 F), 5.31 (3 F), and 6.06 (6 F), ^{31}P (CH_2Cl_2) −2.7 p.p.m. (Found: C, 31.5; H, 1.7; P, 5.9. $C_{14}H_9F_{12}O_4PS$ requires C, 31.6; H, 1.7; P, 5.8%); P-*phenoxy*-4′,4′,5′,5′-*tetrakistrifluoromethyl*-1,3,2-*benzoxathiaphosphole*-2-*spiro*-2′-[1,3,2]*dioxaphospholan* (13) (83%), m.p. 93—93.5°, ^{19}F (94.1 MHz in 1-bromonaphthalene) 4.12 (3 F), 4.70 (3 F), and 6.21 (6 F), ^{31}P (CH_2Cl_2) +2.4 p.p.m. (Found: C, 37.3; H, 1.6; P, 5.4. $C_{18}H_{21}O_4PS$ requires C, 37.2; H, 1.6; P, 5.3%); and 9-*methyl*-5-*phenoxy*-2,2,3,3-*tetrakistrifluoromethyl*-1,4,6-*trioxa*-9-*aza*-5-*phosphaspiro*[4.4]*nonane* (14) (92%), m.p. 113—113.5°, δ 2.9—4.0 (4 H, m), 2.9 (3 H, d, J 10 Hz), and 6.75—7.35 (5 H, m), ^{19}F 1.22 (3 F, m), 2.97 (3 F, m), 3.72 (3 F, m), and 6.59 (3 F, m), ^{31}P +41.6 p.p.m. (Found: C, 34.45; H, 2.4; P, 2.7. $C_{15}H_{12}F_{12}NO_4P$ requires C, 34.05; H, 2.3; P, 2.65%).

From 2,2-*dimethylpropane*-1,3-*diol.* 6-*Phenyl*-3,3,9,9-*tetramethyl*-1,5,7,11-*tetraoxa*-6-*phosphaspiro*[5.5]*undecane* (16; R = Ph) (83%), m.p. 69—72°, δ 0.9 (12 H, s), 3.65 (8 H, d, J 18 Hz), and 6.1—7.9 (5 H, m), ^{31}P +48.4 p.p.m. (Found: C, 60.35; H, 8.2. $C_{16}H_{25}O_4P$ requires C, 60.0; H, 8.3%); the 6-methyl analogue (16; R = Me) (78%), decomposed on attempted distillation, δ 0.95 (12 H, s), 1.51 (3 H, d, J 17 Hz), and 3.65 (8 H, d, J 16 Hz), ^{31}P +40.0 p.p.m.; and the 6-*benzyl analogue* (16; R = CH_2Ph) (56%), m.p. 61.5—63°, δ 0.85 (12 H, s), 3.0 (2 H, d, J 12 Hz), and 3.55 (8 H, d, J 15 Hz), ^{31}P +46.2 p.p.m.

From 3-*methylcatechol.* The following were obtained as 1 : 1 mixtures of 4- and 7-methyl isomers: 3′,4(7)-dimethyl-*P*-phenoxy-1,3,2-benzodioxaphosphole-2-spiro-2′-[1,3,2]-oxazaphospholidine (24; R = OPh) (68%), δ 1.90 (3 H, s), 2.30 (3 H, s), 2.94 (6 H, d, J 10 Hz), 2.68—4.16 (8 H, m), and 6.48—7.28 (16 H, m) (in 1-bromonaphthalene the 4(7)-methyl groups had Δν 35 Hz, T_c 127 ± 2 °C), ^{31}P +41.2 p.p.m.; the *P*-phenylthio-analogue (24; R = SPh) (60%), δ 1.64 (3 H, s), 2.40 (3 H, s), 2.82 (6 H, d, J 10 Hz), 2.46—3.38 (4 H, m), 3.40—4.46 (4 H, m), 6.05—6.74 (6 H, m), and 6.84—7.45 (10 H, m) (in 1-bromonaphthalene the 3′-methyl groups had Δν 10 Hz, T_c 127 ± 2 °C), ^{31}P +23.4 p.p.m.; and the *P*-dimethylamino-analogue (24; R = NMe_2) (85%), δ 2.22 (3 H, s), 2.26 (3 H, s), 2.70 (12 H, d, J 11 Hz), 2.90 (6 H, d, J 10 Hz), 2.26—3.34 (4 H, m), 3.48—4.22 (4 H, m), and 6.46—6.80 (6 H, m), ^{31}P +37.9 p.p.m.

From 4-*fluorocatechol.* The product was a 1 : 1 mixture of 5- and 6-fluoro-isomers: 5(6)-fluoro-3′-methyl-*P*-phenoxy-1,3,2-benzodioxaphosphole-2-spiro-2′-[1,3,2]oxazaphospholidine (27) (60%), ^{31}P +41.3 p.p.m., ^{19}F ($CDCl_3$) +55.96 and +58.97 p.p.m., (1-bromonaphthalene; 56.4 MHz; Δν 300 Hz, T_c 168 ± 2 °C).

The only phosphetan-containing compounds isolated from the attempted reaction of perfluoropinacol with *r*-1-benzyl-2,2,*t*-3,4,4-pentamethylphosphetan were r-1-α-*chlorobenzyl*-2,2,*t*-3,4,4-*pentamethylphosphetan* 1-*oxide*, m.p. 173—174°, δ 0.9 (3 H, m), 1.20 (6 H, m), 1.52 (6 H, m), 2.16 (1 H, m), 5.2 (1 H, d, J 4 Hz), and 7.1—7.75 (5 H, m), ^{31}P −60.7 p.p.m. (Found: C, 63.2; H, 7.75; Cl, 12.6. $C_{15}H_{22}ClOP$ requires C, 63.3; H, 7.75; Cl, 12.5%), and the αα-*dichlorobenzyl analogue*, m.p. 116—116.5°, δ 0.88 (3 H, dd, J 1.5 and 7 Hz), 1.28 (6 H, d, J 16 Hz), 1.44 (6 H, d, J 17 Hz), 2.15 (1 H, m), and 7.05—7.98 (5 H, m), ^{31}P −64.8 p.p.m. (Found: C, 56.5; H, 6.5; Cl, 22.6. $C_{15}H_{21}Cl_2OP$ requires C, 56.4; H, 6.6; Cl, 22.3%)

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