Synthesis of Quinquevalent Phosphoranes from Phosphine Oxides

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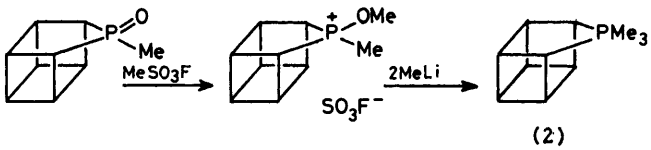
The salts obtained from phosphine oxides and trifluoromethanesulphonic anhydride give quinquevalent cyclic phosphoranes on treatment with 1,2-diols or catechols in the presence of di-isopropylamine. The method is not successful starting with cyclic phosphonic or phosphinic esters. Spirophosphoranes are obtained from phosphetan sulphides on alkylation with $[Me_3O][PF_6]$ followed by treatment with pyrocatechol, but not with perfluoropinacol, in the presence of di-isopropylamine. The spirophosphorane (25), from 2-phenyl-1,2-oxaphospholan and hexafluoroacetone, is described.

A LARGE number of methods exists for the preparation of five-co-ordinate phosphoranes starting from tervalent phosphorus compounds [1] but there is no general route

$$(CF_3)_3PO + (Me_3Si)_2O \longrightarrow (CF_3)_3P(OSiMe_3)_2 \quad (1)$$

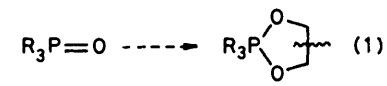


(2)

starting from phosphoryl species. Tris(trifluoromethyl)-phosphine oxide and hexamethyldisiloxane gave the phosphorane (1),[2] and the homocubylphosphorane (2) was synthesised by the route shown starting from a phosphine oxide.[3] More recently spirophosphoranes have been obtained from acyl hydrazides and phosphonic dichlorides.[4] Since in many cases oxides are more readily available than the corresponding tervalent phosphorus compounds, we have been interested in developing methods for the general conversion in equation (1), particularly as applied to 1,2-oxaphospholan 2-oxides, and this paper describes our experiments in this field.

RESULTS AND DISCUSSION

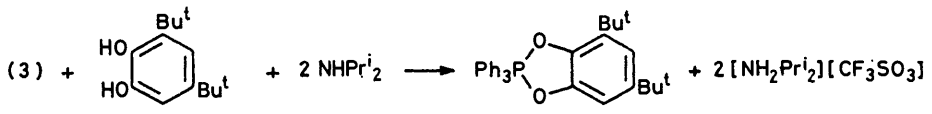
Experiments using Trifluoromethanesulphonic Anhydride.—Hendrikson and Schwartzman [5] showed that triphenylphosphine oxide and trifluoromethanesulphonic



(1)

(triflic) anhydride readily gave the salt (3) which was used in condensation reactions involving carboxylic acids and various nucleophiles. We treated the triflate (3) at −78 °C with 2,6-di-t-butylpyrocatechol and two equivalents of di-isopropylamine to give di-isopropylammonium triflate, readily precipitated by the addition of ether, and the phosphorane (4) in 92% yield. Perfluoropinacol similarly gave the phosphorane (5). Other phosphine oxides used successfully in similar condensations included methyldiphenylphosphine oxide, the phospholen oxides (6; R = Me, Et, or Ph), and the phosphetan oxides (7; R = Ph or CH_2Ph). Among other 1,2-diols used successfully were catechol, 4,5-dimethoxypyrocatechol, and pinacol. Of particular interest are the reactions involving perfluoropinacol and oxides having hydrogen on an α-carbon since in these cases reaction of hexafluoroacetone with the corresponding

$$Ph_3PO + (CF_3SO_2)_2O \xrightarrow[0\ ^\circ C]{CH_2Cl_2} [Ph_3POSO_2CF_3][CF_3SO_3] \quad (3)$$



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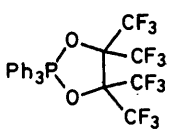

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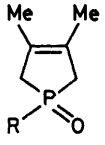
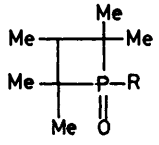


(6)



(7)

[1] 'Organophosphorus Chemistry,' ed. S. Trippett (Specialist Periodical Reports), The Chemical Society, London, 1970, and subsequent volumes.

[2] R. G. Cavell and R. D. Leary, *Chem. Comm.*, 1970, 1520.

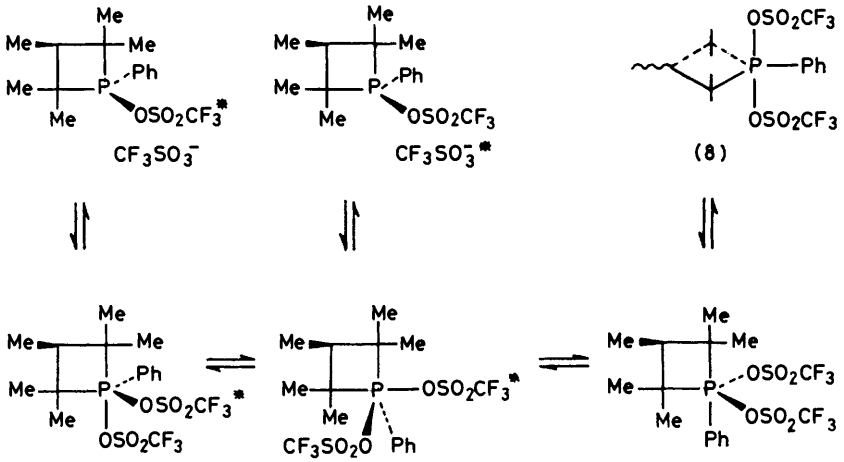
[3] E. W. Turnblom and T. J. Katz, *J. Amer. Chem. Soc.*, 1973, **95**, 4292.

[4] A. Schmidpeter and J. Luber, *Chem. Ber.*, 1977, **110**, 1124.

[5] J. B. Hendrickson and S. M. Schwartzman, *Tetrahedron Letters*, 1975, 277.

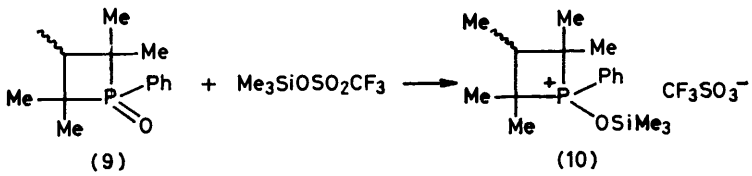
phosphines can give, not the expected 1,3,2-dioxaphospha(v)olans, but instead 1,2-oxaphospha(v)etans.[6,7]

The phosphoranes obtained from the *cis*- and *trans*-



SCHEME 1

phosphetan oxides (7; R = Ph) were identical and were derived from the *trans*-phosphine. Thus the phosphorane formed from either isomer of (7; R = Ph) and 4,5-dimethoxypyrocatechol was the same as that obtained from the *trans*-phosphetan and 4,5-dimethoxy-1,2-benzoquinone. Isomerisation took place at the phosphonium triflate stage. After treating the isomeric oxides with triflic anhydride in dichloromethane at



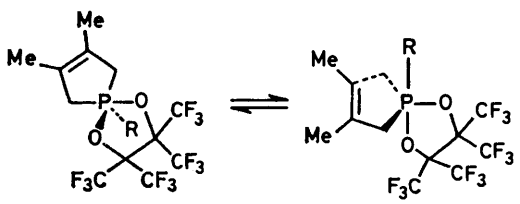
0 °C for 3 h the ^1H, ^{31}P, and ^{19}F n.m.r. spectra of the resulting solutions were identical. The ^{31}P chemical shift was solvent-dependent, being −110 p.p.m. in CH_2Cl_2 and −79 p.p.m. in $CDCl_3$, and the ^{19}F spectrum was a single sharp peak down to −97 °C. These observations suggest that the triflate groups are in rapid exchange *via* five-co-ordinate intermediates as shown in Scheme 1 for the *trans*-isomer. *cis-trans* Isomerisation probably occurs *via* the phosphorane (8) formed either directly from the salt or by pseudorotation as shown.

The solutions formed from trimethylsilyl triflate and *cis*- or *trans*-phosphetan oxides (9; R = Ph) in dichloromethane at 0 °C had n.m.r. spectra consistent with formation of the isomeric triflates (10) which did not interconvert. However, treatment of these solutions with diols and base gave only the starting phosphetan oxides, presumably *via* nucleophilic attack at silicon.

The *trans*-benzylphosphetan oxide (7; R = CH_2Ph) with triflic anhydride and pyrocatechol in the presence of base gave a phosphorane identical to that previously obtained from the *trans*-benzylphosphetan by using *N*-chlorodi-isopropylamine.[8] However, no phosphorane was obtained using perfluoropinacol.

The ^{19}F n.m.r. spectra of the phosphorane (11; R = Ph) in CH_2Cl_2 at room temperature contained a single peak. On cooling this showed a reversible splitting into two equal signals ($\Delta\nu$ 136 Hz) with T_c −78 ± 2 °C corresponding to ΔG^* for the pseudorotation (11; R = Ph) ⇌ (12; R = Ph) of 9.0 ± 0.2 kcal mol^{-1}.

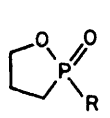
The same phenomena in the ^{19}F n.m.r. spectrum of (11; R = Me) had T_c −125 ± 2 °C and $\Delta\nu$ 22 Hz, leading to a value of ΔG^* for the pseudorotation (11; R = Me) ⇌



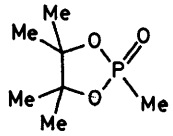
(12; R = Me) of 7.3 ± 0.2 kcal mol^{-1}. The small difference in apicophilicity between methyl and phenyl, with the former being the more apicophilic, agrees with earlier results.[9] The values of ΔG^* for the pseudorotation of (11; R = Ph) compares with that of 9.6 kcal mol^{-1} previously found for the corresponding phosphorane derived from pinacol.[10]

[6] F. Ramirez, C. P. Smith, and J. F. Pilot, *J. Amer. Chem. Soc.*, 1968, **90**, 6726.
[7] R. K. Oram and S. Trippett, *J.C.S. Perkin I*, 1973, 1300.
[8] S. Antczak, S. A. Bone, J. Brierley, and S. Trippett, *J.C.S. Perkin I*, 1977, 278.
[9] S. A. Bone, S. Trippett, and P. J. Whittle, *J.C.S. Perkin I*, 1977, 437.
[10] M. W. White, Ph.D. Thesis, University of Leicester, 1975.

The above synthesis of phosphoranes from phosphine oxides and 1,2-diols by using triflic anhydride could not be extended to the cyclic phosphonates or phosphinates (13)—(15).



(13) R = Ph or OEt



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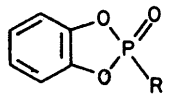


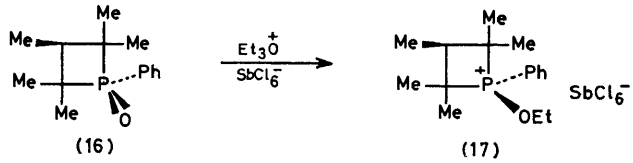
(15) R = Me or Ph

Experiments using Alkoxy- or Alkylthio-phosphetanium Salts.—Alkylation of the phosphetan oxide (16) with triethyloxonium hexafluoroantimonate gave the salt (17). However all attempts to convert this into a spirophosphorane by treatment with a 1,2-diol or pyrocatechol in the presence of a variety of bases gave only starting oxide.

Methylation of the isomeric phosphetan sulphides (18) with trimethyloxonium hexafluorophosphate gave the *cis*- and *trans*-salts (19). With pyrocatechol and one equivalent of di-isopropylamine these gave the phosphoranes (20) with complete stereospecificity as shown by monitoring the reactions using ^{31}P n.m.r. spectroscopy. Presumably these reactions involve the intermediate phosphoranes (21). The overall retention of configuration at phosphorus suggests that further reactions involve dissociation of these to the salts (22) rather than phosphorane formation *via* six-co-ordinate species unless ring-closure to these takes place entirely *syn* rather than *anti* to the methylthio-group.

No reaction occurred between the salts (19) and perfluoropinacol in the presence of base. Since perfluoropinacol and pyrocatechol have similar acidities, this might suggest a six-co-ordinate intermediate, formation of which was inhibited in the case of perfluoropinacol by steric factors.

The major objective of the above work, which was not achieved, was the synthesis of spirophosphoranes from the readily available 1,2-oxaphospholan oxides (23) in order to determine, from variable-temperature n.m.r. measurements, the barrier to placing the 1,2-oxaphospholan ring in a diequatorial position.[11] The spirophosphorane (25) was eventually made by the route shown in Scheme 2 but it decomposed to give the



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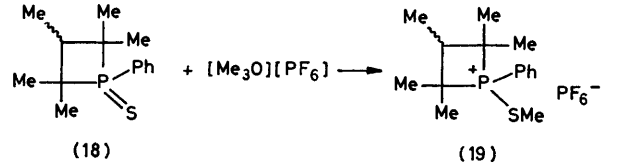
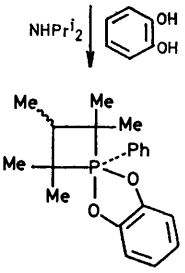
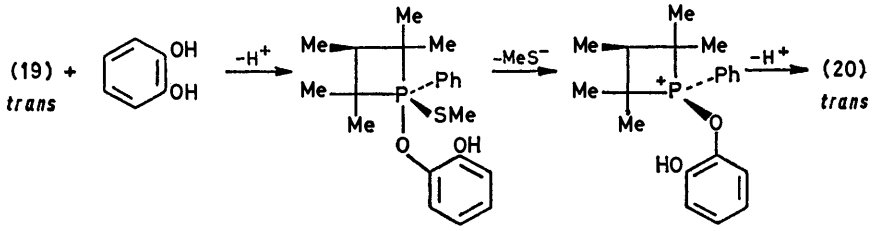


(18) (19)



(20)

phosphonate (26) before simplification of its ^{19}F n.m.r. spectrum occurred. *N*-Chlorodi-isopropylamine was found to be a better reagent for oxidative ring-closure of the secondary phosphine (24) than the recommended diphenyl disulphide.[12]



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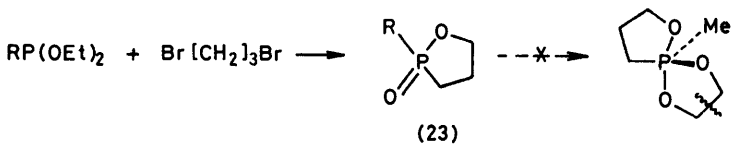


(23)

EXPERIMENTAL

^1H N.m.r. spectra were obtained at 60 MHz for solutions in $CDCl_3$. ^{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.

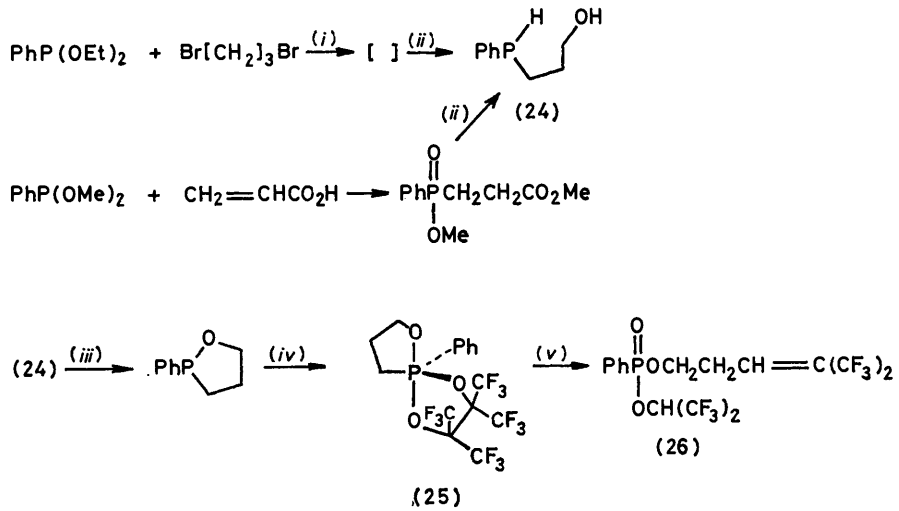
General Directions for the Preparation of Phosphoranes from Phosphine Oxides by using Trifluoromethanesulphonic Anhydride.—The anhydride (5 mmol) in dichloromethane (5 ml) was added slowly to the phosphine oxide (5 mmol) in

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

[12] M. Grayson and C. E. Farley, *Chem. Comm.*, 1967, 830.

dichloromethane (10 ml) at 0 °C and the mixture set aside at 0 °C until the reaction was complete (15 min to 3 h, depending on the oxide). The mixture was then cooled to −78 °C and the diol or pyrocatechol (5 mmol) and di-isopropylamine (10 mmol) in ether (20 ml) added slowly with rapid stirring. After 30 min the resulting solution was allowed to warm to room temperature and ether (15 ml) added to precipitate di-isopropylammonium triflate. Filtration and evaporation of the filtrate then gave the crude phosphorane which was extracted with or crystallised from light petroleum (b.p. 40—60 °C). In this way the following phosphoranes were prepared.

From perfluoropinacol. *PPP*-Triphenyl-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxaphospholan (5) (71%), m.p. 103 °C (decomp.);[13] the P-*methyl*-PP-*diphenyl-analogue* (51%), m.p. 95.5 °C (decomp.); δ_H 2.5 (3 H, d, *J* 11 Hz) and



SCHEME 2 (*i*) 190 °C, 4 h; (*ii*) $LiAlH_4$; (*iii*) $NPr^i{}_2Cl$, −78 °C, ether; (*iv*) $(CF_3)_2CO$; (*v*) 140 °C

m.p. and mixed m.p. 124—125 °C; and the *P-r*-benzyl analogue (51%),[8] m.p. 139—141 °C.

From 3,5-di-t-butylpyrocatechol. 4,6-Di-t-butyl-*PPP*-triphenyl-1,3,2-benzodioxaphosphole (4) (92%),[8] m.p. 146—147 °C.

From 4,5-dimethoxypyrocatechol. P-r-*Phenyl*-5,6-*dimethoxy*-2′,2′,t-3′,4′,4′-*pentamethyl*-1,3,2-*benzodioxaphosphole*-2-*spiro*-1′-*phosphetan* (63%), m.p. 93.5—94.5 °C, δ_H 0.8—1.13 (4 H, m), 1.22 (6 H, d, *J* 14 Hz), 1.48 (6 H, d, *J* 11 Hz), 3.69 (6 H, s), 6.49 (2 H, s), and 7.2—7.8 (5 H, m), δ_P −0.1 (Found: C, 68.0; H, 7.5; P, 8.0. $C_{22}H_{29}O_4P$ requires C, 68.0; H, 7.5; P, 8.0%).

2,2,t-3,4,4-*Pentamethyl*-1-*methylthio*-r-1-*phenylphosphetanium Hexafluorophosphate*.—Trimethyloxonium hexafluorophosphate (3.7 g) was added to a stirred solution of 2,2,*t*-3,4,4-pentamethyl-*r*-1-phenylphosphetan 1-sulphide (4.53 g) in dichloromethane (10 ml) and the mixture stirred at room temperature overnight. The resulting solution was then added slowly to ether (200 ml) with rapid stirring. Filtration gave the trans-*phosphetanium hexafluorophosphate* (96%), m.p. 136—140 °C (from acetone–ethyl acetate); δ_H[$(CD_3)_2CO$; external $SiMe_4$] 0.97 (3 H, dd, *J* 1 and 7 Hz), 1.37 (6 H, d, *J* 22 Hz), 1.4 (6 H, d, *J* 21 Hz), 1.9 (3 H, d, *J* 13 Hz), 2.33—2.93 (1 H, m), and 7.35—7.95 (5 H, m); δ_P −82.7 and +144.4 (Found: C, 43.7; H, 5.8; P, 14.7. $C_{15}H_{24}F_6P_2S$ requires C, 43.7; H, 5.9; P, 15.0%). The analogous cis-*phosphetanium hexafluorophosphate* (70%) had m.p. 129—129.5 °C, δ_H[$(CD_3)_2CO$; external $SiMe_4$] 0.73 (3 H, dd, *J* 1 and 7 Hz), 1.27 (6 H, d, *J* 22 Hz), 1.3 (6 H, d, *J* 23 Hz), 1.9 (3 H, d, *J* 13 Hz), 2.33—2.95 (1 H, m), and 7.33—7.95 (5 H, m); δ_P −82.7 and +144.4 (Found: C, 43.7; H, 5.85; P, 14.9%).

Pyrocatechol (0.55 g) and di-isopropylamine (0.51 g) in ether (20 ml) were added to a stirred solution of the above *trans*-salt (2.06 g) in dichloromethane (10 ml) at −78 °C. After 10 min, ether (10 ml) was added and the mixture allowed to warm to room temperature. Filtration, followed by evaporation to dryness of the filtrate and extraction of the residue with light petroleum gave *P-r*-phenyl-2′,2′,*t*-3′,4′,4′-pentamethyl-1,3,2-benzodioxaphosphole-2-spiro-1′-phosphetan (60%),[8] m.p. and mixed m.p. 124—125 °C; 7.37—7.95 (10 H, m), δ_P +11.4 (Found: C, 43.1; H, 2.4; P, 6.05. $C_{19}H_{13}F_{12}O_2P$ requires C, 42.9; H, 2.5; P, 5.8%); 7,8-*dimethyl*-5-*phenyl*-2,2,3,3-*tetrakis*(*trifluoromethyl*)-1,4-*dioxa*-5-*phosphaspiro*[4.4]*non*-7-*ene* (11; R = Ph) (85%), b.p. 130 °C at 0.2 mmHg; δ_H 1.5 (6 H, s), 2.78 (4 H, d, *J* 16 Hz), and 7.26—8.05 (5 H, m); δ_P −7.8 (Found: C, 41.5; H, 2.9; P, 5.9. $C_{18}H_{15}F_{12}O_2P$ requires C, 41.4; H, 2.9; P, 5.9%); the 5-*methyl analogue* (11; R = Me) (69%), b.p 105 °C at 0.2 mmHg, m.p. 44—45 °C; δ_H 1.7 (6 H, s), 1.74 (3 H, d, *J* 11 Hz), 2.33 (2 H, d, *J* 14 Hz), and 2.6 (2 H, d, *J* 19 Hz), δ_P −14.0 (Found: C, 33.9; H, 2.9; P, 7.0. $C_{13}H_{13}F_{12}O_2P$ requires C, 33.9; H, 2.9; P, 6.7%); the 5-*ethyl analogue* (11; R = Et) (66%), b.p. 110—115 °C at 0.3 mmHg; δ_H 0.97 (3 H, dt, *J* 8 and 22 Hz), 1.53 (6 H, s), and 1.6—3.0 (6 H, m), δ_P −19.1 (Found: C, 35.6; H, 3.4; P, 6.75. $C_{14}H_{15}F_{12}O_2P$ requires C, 35.5; H, 3.2; P, 6.5%); and 6,6,*r*-7,8,8-pentamethyl-*t*-5-phenyl-2,2,3,3-tetrakis(trifluoromethyl)-1,4-dioxa-5-phosphaspiro[3.4]-octane (36%), m.p. 94—95 °C.[7]

From pyrocatechol. P-*Phenyl*-3′,4′-*dimethyl*-1,3,2-*benzodioxaphosphole*-2-*spiro*-1′-*phosphol*-3′-*ene* (80%), m.p. 122—123 °C, δ_H 1.63 (6 H, s), 2.73 (2 H, d, *J* 16 Hz), 2.82 (2 H, d, *J* 17 Hz), 6.74 (4 H, s), and 7.26—7.9 (5 H, m); δ_P −1.1 p.p.m. (Found: C, 72.4; H, 6.35; P, 10.25. $C_{18}H_{19}O_2P$ requires C, 72.5; H, 6.4; P, 10.4%); *P-r*-phenyl-2′,2′,*t*-3′,4′,4′-pentamethyl-1,3,2-benzodioxaphosphole-2-spiro-1′-phosphetan (77% from *trans*-oxide, 61% from *cis*),[8]

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

°C. In a similar way the *cis*-salt gave the *cis*-phosphorane (73%),[8] m.p. 65—67 °C, identical to a sample prepared by using *N*-chlorodi-isopropylamine.

5-Phenyl-2,2,3,3-tetrakistrifluotomethyl-1,4,6-trioxa-5-phosphaspiro[4.4]*nonane* (25).—Diethyl phenylphosphonite (12.5 g) and 1,3-dibromopropane (10.1 g) were heated together, at a temperature rising from 120 to 190 °C during 4 h. The residue was dissolved in tetrahydrofuran (100 ml) and added slowly to lithium aluminium hydride (5.0 g) in ether (400 ml) with stirring and the mixture set aside at room temperature overnight. Water (10 ml) was then cautiously added, the mixture refluxed for 1 h, and then dried over $MgSO_4$. Filtration and distillation then gave 3-hydroxypropyl(phenyl)phosphine (28%),[14] b.p. 118—120 °C at 0.3 mmHg, δ 1.43—2.07 (4 H, m), 3.3 (1 H, s), 3.57 (2 H, t, *J* 6 Hz), 4.17 (1 H, d, *J* 210 Hz), and 7.15—8.90 (5 H, m). The same phosphine was obtained in 29% yield by a similar reduction of methyl 2-methoxycarbonylethylphenylphosphinate.

3-Hydroxypropyl(phenyl)phosphine (2.7 g) in ether (20 ml) and *N*-chlorodi-isopropylamine (2.2 g) in ether (20 ml) were added simultaneously over 1 h to ether at −78 °C with vigorous stirring. The mixture was then allowed to warm to room temperature. Filtration and distillation then gave 2-phenyl-1,2-oxaphospholan (20%),[12] b.p. 110—120 °C at 0.3 mmHg, δ_P −110.4.

Liquid hexafluoroacetone (1 ml) was allowed to distil slowly into a stirred solution of the above oxaphospholan (0.5 g) in ether (15 ml) at −78 °C and the solution allowed to warm up to room temperature overnight. Evaporation and crystallisation of the residue from light petroleum gave the *title phosphorane* (25) (47%), m.p. 90—91 °C, δ_H 1.3—2.2 (2 H, m), 2.3—2.9 (2 H, m), 3.5—4.4 (2 H, m), 7.3—7.6 (3 H, m), and 7.8—8.3 (2 H, m), δ_P +3.8 (Found: C, 36.1; H, 2.4; P, 6.4. $C_{15}H_{11}F_{12}O_3P$ requires C, 36.2; H, 2.2; P, 6.6%).

When kept at 140 °C for 1 h this phosphorane gave 4,4-bistrifluoromethylbut-3-enyl 2,2,2-trifluoro-1-(trifluoromethyl)ethyl phenylphosphonate (26); δ_H 2.63—3.15 (2 H, m), 4.37 (2 H, dd, *J* 6 and 7 Hz), 5.4 (1 H, t, *J* 6 Hz), 6.9 (1 H, dt, *J* 1 and 7 Hz), and 7.3—8.1 (5 H, m); δ_P (1-bromonaphthalene) −11.0; δ_F (1-bromonaphthalene) −4.5 (3 F, q, *J* 7 Hz), +1.5 (3 F, q, *J* 7 Hz), and +10.65 (6 F, d, *J* 6 Hz) relative to internal $PhCF_3$.

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[14] K. Isslieb and H.-R. Roloff, *Chem. Ber.*, 1965, **98**, 2091.