Spirophosphoranes derived from 3*H*-2,1-Benzoxaphospholes

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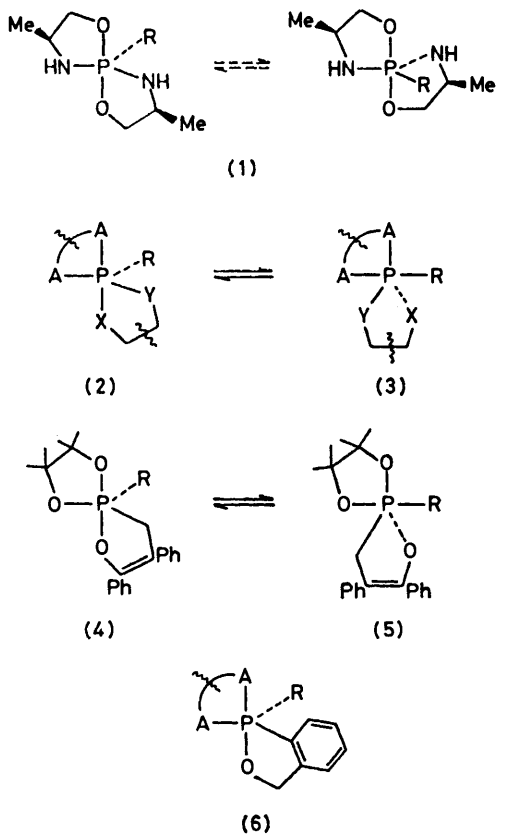
Starting from lithium *o*-lithiobenzyl alkoxides and dichlorophosphines, a series of *P*-substituted 3*H*-2-1-benzoxaphospholes has been prepared and converted into five-co-ordinate phosphoranes by addition of 4,5-dimethyl-*o*-benzoquinone or 4,4'-dimethylbenzil, or condensation with 4,5-dimethylpyrocatechol or pinacol. The variable-temperature n.m.r. spectra of these phosphoranes are discussed. In these systems phenylamino- and dimethylamino-groups have similar apicophilicities and are less apicophilic than hydrogen by some 4—5 kcal mol^{-1}.

In previous studies on the relative apicophilicities of groups attached to phosphorus in five-co-ordinate phosphoranes using dynamic n.m.r. spectroscopy we found that, relative to the phenoxy-group, the dimethylamino-group is poorly apicophilic whereas the hydrogen atom is slightly more apicophilic.[1] These results would lead one to expect a substantial difference (>6 kcal mol^{-1}) † in the relative apicophilicity of dimethylamino and hydrogen, although no direct comparison has been reported. Recent work [2] on the isomerisation of the diastereoisomers (1; R = H or NHPh) suggests that, if the isomerisations follow regular pseudorotation pathways, then there is only a 2 kcal mol^{-1} difference in apicophilicity between phenylamino and hydrogen and that this difference is determined largely by the entropy of activation for the isomerisation of (1; R = NHPh) (ΔS^* — 18.3 cal mol^{-1} K^{-1}). We have sought a system that would enable direct comparisons to be made between the apicophilicities of hydrogen, dimethylamino-, and phenylamino-groups with assurance that the processes being followed are regular pseudorotations. This paper describes our results with spirophosphoranes derived from 3*H*-2,1-benzoxaphospholes.

If pseudorotations of the generalised spirophosphoranes (2; R = H, NHPh, or NMe_2) *via* the highest-energy phosphoranes (3) are to be observable by dynamic n.m.r. spectroscopy at temperatures at which one can seek assurance that regular processes are involved, then, if X is oxygen, Y must be carbon. Only then [3] will ΔG^* for the pseudorotation of (2; R = NMe_2) be substantially below 24 kcal mol^{-1} and the corresponding coalescence temperature substantially below the working maximum of *ca.* 180 °C. Systems derived from 2-phenylacrylophenone are in this category and indeed ΔG^* for the pseudorotations of (4) *via* (5) are 14.1 ± 0.6 and 19.0 ± 0.8 kcal mol^{-1} for R = OPh or NMe_2 respectively.[4] However there appeared to be no easy route to the phosphoranes (4; R = H or NHPh) and we chose instead to look at the spirophosphoranes (6) derived from 3*H*-2,1-benzoxaphospholes.

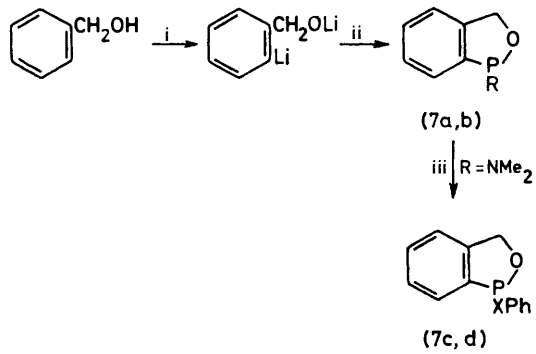
Preparation of 3H-2,1-*Benzoxaphospholes*.—The 3*H*-2,1-benzoxaphospholes (7a) and (7b) were obtained using the *o*-lithiobenzyl alcoholate of Seebach [5] as shown in Scheme 1. Treatment of (7b) with phenol at 100 °C or with an excess of aniline at 140 °C gave (7c) and (7d) respectively. An excess of aniline is required in order to inhibit the disproportionation of (7d) which occurs



above 100 °C according to Scheme 2. A similar disproportionation has recently been reported for $(PhNH)_3P$.[6]

The structures of (7a—d) have been established by ^1H and ^{31}P n.m.r. spectroscopy, mass spectrometry, elemental analysis, and conversion into the corresponding *P*-sulphides (8a—d). The ^1H n.m.r. spectra show a multiplet for the oxaphosphole ring hydrogens which can be analysed as the AB part of an ABX spectrum, showing that the two hydrogen atoms are non-equivalent (owing to the presence of the chiral phosphorus centre) and are coupled to phosphorus. The very different

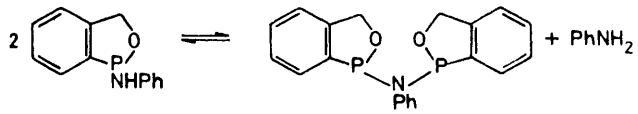
† 1 cal = 4.184 J.



a; R = Ph
b; R = NMe_2
c; R = OPh
d; R = NHPh

SCHEME 1 Reagents: i, BuLi, tetramethylethylenediamine; ii, $RPCl_2$ (R = Ph or NMe_2); iii, PhXH (X = O or NMe), 100—140 °C

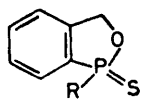
POCH coupling constants ($^3J_{PH}$, 0.5—1.5 and 14—16 Hz) found for the non-equivalent hydrogen atoms of (7a—d) are interesting in connection with the still open question of which factors influence the magnitude of



δ_P 136·5 and 134·3 p.p.m.

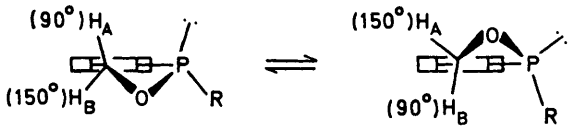
SCHEME 2

POCH coupling constants. Kainosho [7] and others [8] have found evidence for a Karplus-type dihedral angle dependence, whereas Bentrude [9] has found that $^3J_{POCH}$ depends both on the dihedral angle and on the orientation of the lone pair on phosphorus. In the case of (7)



(8)

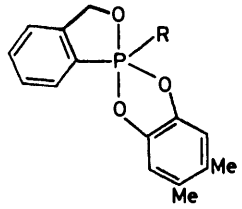
the most probable conformations are a planar ring or two fast interconverting conformers with oxygen out of the plane (*O*-flap envelope conformations, Figure).



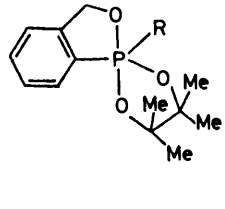
Probable conformations of (7) (one enantiomer shown). The numbers are approximate POCH dihedral angles, estimated from Dreiding models.

Unless the envelope conformations are very unevenly populated (which is considered unlikely) H_A and H_B experience the same time-averaged POCH dihedral angle (120°). This means that any dihedral angle dependence of $^3J_{PH}$ cancels out, and that the large difference in $^3J_{PH}$ found for (7a—d) is solely an effect of the phosphorus lone pair orientation. The hydrogen atom *trans* to the lone pair is tentatively assigned to the one with the small coupling constant, H_A, in accordance with the results of Bentrude for 1,3,2-dioxaphospholans ($^3J_{PH}$, *trans*, 1—2 Hz, *vs.* 9—10 Hz for the *cis*-hydrogen).

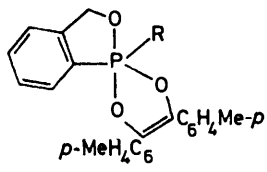
Preparation of Phosphoranes.—The phosphoranes (9a—d) were obtained from the corresponding tervalent



(9a-e)



(10c-e)



(11b,d)

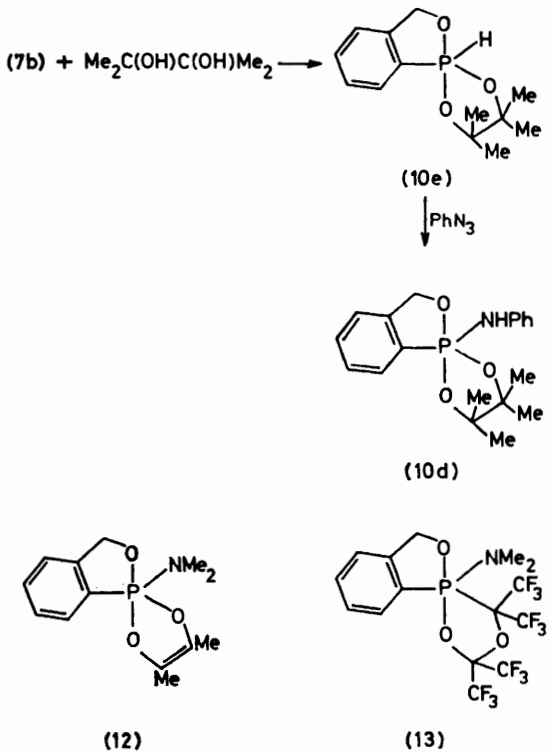
a; R = Ph
b; R = NMe_2
c; R = OPh
d; R = NHPh
e; R = H

species either by addition of freshly prepared 4,5-dimethyl-*o*-benzoquinone or by treatment with 4,5-dimethylpyrocatechol in the presence of *N*-chlorodiisopropylamine.[10] The latter method using pinacol worked well with (7c) to give (10c) but with (7a) and (7b) the condensations were sluggish and pure phosphoranes could not be isolated. The *P*H-spirophosphoranes (9e) and (10e) were obtained from (7b) and 4,5-dimethylpyrocatechol or pinacol respectively. Treatment of (10e) with phenyl azide gave (10d).

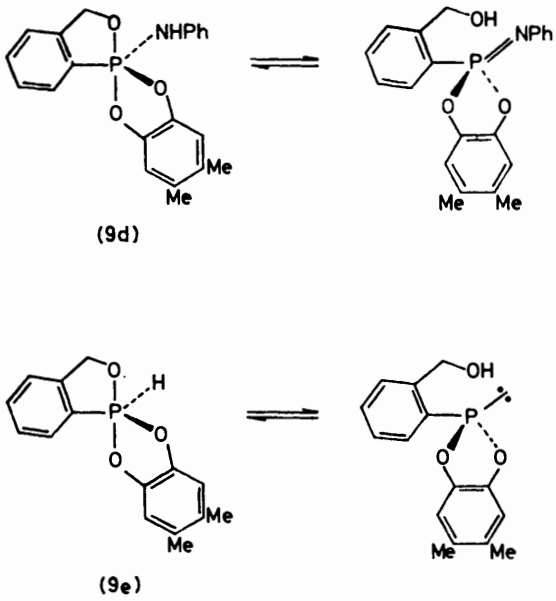
With 4,4′-dimethylbenzil (7b) and (7d) gave (11b) and (11d) respectively. With biacetyl (7b) gave a phosphorane (12) which showed only one signal for the ring methyl groups in the ^1H n.m.r. spectrum; other condensations with biacetyl were therefore not investigated. Hexafluoroacetone condensed with (7b) to give what is probably, from its ^{19}F n.m.r. spectrum, the 1,3,4-dioxaphospholan (13).

Variable-temperature N.M.R. Spectra.—The ^1H n.m.r. spectra of the phosphoranes (9b), (9d), and (9e) at room temperature in 1-bromonaphthalene showed two signals for the aryl methyl groups. These signals coalesced reversibly at higher temperatures leading to free energies of activation for the causative processes, at the relevant coalescence temperatures, of 21.8, 22.5, and 17.1 kcal mol^{-1}, respectively. Entropies of activation for regular pseudorotation processes are usually assumed to be small

and it is on this basis that comparisons of ΔG^* values determined at different coalescence temperatures are made. With (9d) and (9e) the most likely irregular processes leading to equivalence of the methyl groups

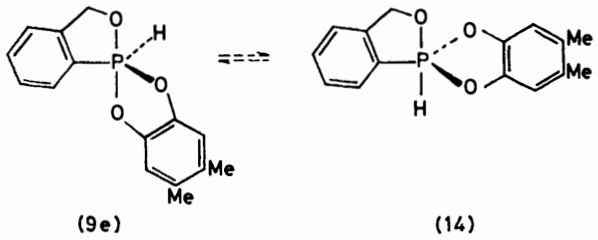


involve the ring openings shown in Scheme 3.[11] Besides leading to equivalence of the methyl groups these would also lead to loss of PNH or PH coupling with the same activation energy. However, the NH doublet of (9d), due to coupling to phosphorus ($^2J_{PH}$ 11.2 Hz), is virtually unchanged at the coalescence temperature of the methyl



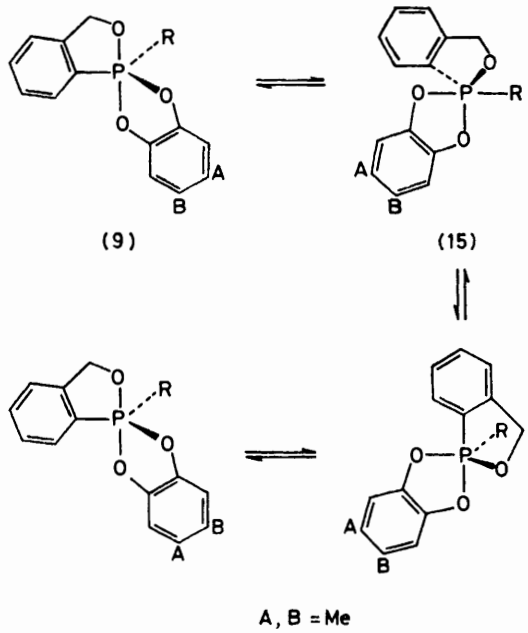
SCHEME 3

signals (143 °C) and is still a doublet, although broadened, at 175 °C. Similarly the PH doublet of (9e), which shows fine structure due to coupling to the oxaphosphole ring hydrogen atoms, preserves this fine structure at the coalescence temperature (*ca.* 50 °C) of the aryl methyl groups. Changes to the fine structure do occur at higher temperatures accompanied by a simplification of the multiplet for the oxaphosphole ring hydrogen atoms; at 140 °C this becomes a doublet. However, the PH coupling and the fine structure are still present at this temperature. These changes are probably associated with the pseudorotations (9e) ⇌ (14) which place the



1,3,2-dioxaphosphole ring diequatorial and lead to equivalence of the ring hydrogens. Pseudorotations *via* (14) would be expected [3] to have higher energies of activation than those *via* (15) discussed below.

Ring-opening processes are therefore not responsible for the coalescence of the aryl methyl signals in (9b), (9d), and (9e). These coalescences are associated with the pseudorotations shown in Scheme 4 involving the



SCHEME 4

high-energy phosphoranes (15). The changes in activation energy as R varies therefore reflect the relative apicophilicities of the groups R in this system. Dimethylamino- and phenylamino-groups therefore have similar apicophilicities and both are considerably less

apicophilic than hydrogen. A direct comparison with the phenoxy-group was not possible as the phenoxyphosphorane (9c) showed only one signal for the methyl groups in all the solvents investigated.

Dimethylamino- and phenylamino-groups also showed similar apicophilicities in the phosphoranes (11b) and (11d). Here the free energies of activation for coalescence of the aryl methyl signals by pseudorotations analogous to those in Scheme 4 were 21.6 and 22.0 kcal mol^{-1}, respectively, with the PNH coupling in (11d) preserved at 40 °C above the coalescence temperature.

At low temperatures the methyl groups of (10c), (10d), and (10e) showed four signals. At higher temperatures these coalesced in pairs with coalescence temperatures depending on the initial frequency separations but leading to the same activation energies. These were 15.8, 20.9, and 16.8 kcal mol^{-1} for (10c), (10d), and (10e), respectively. PH Coupling and fine splitting in (10e) were preserved above the coalescence temperature for the methyl groups and the PNH coupling in (10d) was still present at the coalescence temperature (130 °C) although the NH proton had become a broad singlet at 160 °C. In this system, hydrogen is less apicophilic relative to phenoxy than previous work had indicated but still considerably more apicophilic than the phenylamino-group.

We conclude that, in the phosphoranes described here, phenylamino and dimethylamino have similar apicophilicities and are less apicophilic than hydrogen by some 4—5 kcal mol^{-1}. The relevance of this conclusion to the unexpected parameters reported for the isomerisation of (1) will need further investigation if it is established that the latter occurs *via* a regular pseudorotation pathway.

EXPERIMENTAL

^1H and ^{31}P N.m.r. spectra were recorded on a JEOL FX 90 Q spectrometer (solvent $CDCl_3$, temperature *ca.* 25 °C unless otherwise specified). Chemical shifts are given relative to internal $SiMe_4$ for ^1H data and relative to external 85% H_3PO_4 for ^{31}P data (δ_P), and are positive for low-field shifts. N.m.r. data are given in Tables 1 and 2, except the dynamic ^1H n.m.r. data. Free energies of activation at the coalescence temperature were calculated using the Gutowsky–Holm equation; ΔG^* values were reproducible to 0.1 kcal mol^{-1} unless otherwise stated.

Mass spectra were obtained on an AEI-902 mass spectrometer at 70 eV. Since all compounds except (8a—d) and (13) are oxidisable and hydrolyse easily, manipulations were carried out under nitrogen using dry solvents and pre-dried apparatus. Small-scale preparations and recrystallisations were performed in Schlenk tubes and solid samples handled in a glove box.

1-*Phenyl*-3H-2,1-*benzoxaphosphole* (7a).—To a solution of benzyl alcohol (5.04 g, 50 mmol) and tetramethylethylenediamine (15 ml, 100 mmol) in hexane at 20 °C was added butyl-lithium in hexane (67 ml; 1.50M; 100 mmol), and the mixture was refluxed and stirred for 10 h. After addition of hexane (100 ml) and cooling in a dry ice–acetone bath, $PhPCl_2$ (9.0 g, 50 mmol) was added dropwise with stirring during 0.5 h, and the mixture stirred at −78 °C for another 0.5 h. The suspension was allowed to warm to room temperature and set aside for the solids to settle. The hexane solution was decanted off and the precipitate washed with hexane (2 × 50 ml). Evaporation of the solvent at 20—40 °C, under slightly reduced pressure, gave a brown oil which was purified by Kugelrohr distillation (b.p. *ca.* 100 °C at 0.1 mmHg). The colourless crystalline product (3.2 g, 30%; m.p. 54—61 °C) still contained some impurities (*ca.* 5% according to ^{31}P n.m.r.). An analytical sample, m.p. 62—63 °C, of the *benzoxaphosphole* (7a) was obtained by recrystallisation from hexane, *m/e* 214 (M^+, 100%), 196 (65), 167 (38), 166 (32), 165 (55), 137 (59), 109 (26), and 107 (22) (Found: C, 72.9; H, 5.25. $C_{13}H_{11}OP$ requires C, 72.9; H, 5.2%).

1-*Phenyl*-3H-2,1-*benzoxaphosphole* P-*sulphide* (8a) was obtained from (7a) and sulphur in $CHCl_3$ (exothermic), m.p. 116.5—117.5 °C (from CCl_4) (Found: C, 63.2; H, 4.5; S, 13.2. $C_{13}H_{11}OPS$ requires C, 63.4; H, 4.45; S, 13.0%).

1-*Dimethylamino*-3H-2,1-*benzoxaphosphole* (7b).—Compound (7b) was prepared in the same way as (7a) using Me_2NPCl_2 (7.3 g, 50 mmol) instead of $PhPCl_2$. The crude product was purified by Kugelrohr distillation followed by vacuum distillation through a 15-cm Vigreux column, to give the *dimethylamino-compound* (7b) as a colourless oil (4.6 g, 50%), b.p. 53—54 °C at 0.10 mmHg, *m/e* 181 (M^+, 66%), 166 (3), 137 (100), 136 (23), 109 (18), and 107 (7) (Found: C, 59.8; H, 6.9; N, 7.8; P, 16.7. $C_9H_{12}NOP$ requires C, 59.7; H, 6.7; N, 7.7; P, 17.1%).

TABLE 1

N.m.r. data for the 3*H*-2,1-benzoxaphospholes (7a—d) and their *P*-sulphides (8a—d) ($CDCl_3$; *ca.* 25 °C)

		CH_2OP (ABX system)					
Compound	δ_P	$\delta(H_A)$	$\delta(H_B)$	$^2J_{AB}$	$^3J_{PH(A)}$	$^3J_{PH(B)}$	Other signals
(7a)	120.2	5.43	5.32	13.4	0.7	14.1	7.2—7.6 (ArH, m)
(7b)	135.9	5.40	5.13	13.9	0.5	14.7	2.49 (Me, d, $^3J_{PH}$ 9.0), 7.2—7.6 (ArH, m)
(7c)	162.7	5.48	5.25	14.1	1.5	15.7	6.9—7.4, 7.7—7.8 (ArH, m)
(7d)	108.5	5.43	5.18	14.1	0.6	15.8	4.99 (NH, d, $^2J_{PH}$ 9.1), 6.8—7.7 (ArH, m)
(8a)	97.1	5.59	5.50	13.7	5.0	9.3	7.3—7.9 (ArH, m)
(8b)	94.8	5.28			7.7 [b]		2.73 (Me, d, $^3J_{PH}$ 12.1)
		4.75	4.64	13.9	5.1	9.8 [c]	7.2—7.8 (ArH, m)
(8c)	94.8	5.31	5.20	13.9	13.9	3.3	6.9—8.0 (ArH, m)
(8d)	83.6	5.37	5.26	14.1	5.6	10.1	5.76 (NH, d, $^2J_{PH}$ 8.9), 6.5—7.9 (ArH, m)

[a] δ_P Values are in p.p.m.; *J* values in Hz. [b] Pseudo-doublet. [c] In C_6D_6.

1-*Dimethylamino*-3H-2,1-*benzoxaphosphole* P-*sulphide* (8b) was obtained from (7b) and sulphur in $CHCl_3$ (exothermic), m.p. 101—103 °C (from hexane) (Found: C, 50.8; H, 5.8; N, 6.6; P, 14.5. $C_9H_{12}NOPS$ requires C, 50.7; H, 5.7; N, 6.6; P, 14.5%).

1-*Phenoxy*-3H-2,1-*benzoxaphosphole* (7c).—An attempt to prepare (7c) in the same way as (7a) using $PhOPCl_2$

TABLE 2

N.m.r. data for the spirophosphoranes (9)—(13) ($CDCl_3$; *ca.* 25 °C) [a]

Compound	δ_P	CH_2OP (ABX system) $\delta(H_A)$	$\delta(H_B)$	$^2J_{AB}$	$^3J_{PH(A)}$	$^3J_{PH(B)}$	C–Me	Other signals
(9a)	−12.4	5.17	5.26	14.3	9.0	7.4	2.12 2.15	6.76, 6.80, 7.2—8.0, 8.3—8.5 (ArH)
(9b)	−20.1	4.99	4.85	14.3	8.7	7.9	2.14 2.18	2.73 (NMe, d, $^3J_{PH}$ 10.6) 6.74, 7.2—7.6, 8.0—8.3 (ArH)
(9c)	−18.3	4.88	4.44	14.6	12.3	6.5	2.20	6.7—7.7, 8.2—8.4 (ArH)
(9d)	−27.4	4.92	4.59	14.3	5.7	10.8	2.15 2.17	5.05 (NH, d, $^2J_{PH}$ 11.6), 6.65, 6.78, 6.9—7.6, 8.0—8.2 (ArH)
(9e)	−15.4	5.17	5.06	14.7	0.7	18.6 [b]	2.11 2.16	8.62 (PH, d,[b] $^1J_{PH}$ 788.0) 6.71, 7.2—7.7, 8.0—8.2 (ArH)
(10c)	−28.1	4.71	3.99	14.5	13.1	4.6	1.27—1.45 (m, br)	6.8—7.6, 8.1—8.4 (ArH)
(10d)	−39.0	4.76	4.33	14.3	9.2	6.7	1.16 1.23 1.36	4.85 (NH, d, $^2J_{PH}$ 7.3) 6.8—7.4, 8.0—8.3 (ArH)
(10e)	−33.1	5.03	4.88	14.5	2.4	13.2 [c]	1.08 1.24 1.31 1.35	7.83 (PH, d,[c] $^1J_{PH}$ 731.0), 7.2—7.6, 8.0—8.2 (ArH)
(11b)	−24.2	5.01	4.85	14.2	9.0	7.6	2.31 2.36	2.77 (NMe, d, $^3J_{PH}$ 10.6) 7.0—7.6, 8.0—8.3 (ArH)
(11d)	−32.6	4.92	4.63	14.3	6.5	10.3	2.29 2.31	5.00 (NH, d, $^2J_{PH}$ 10.8), 7.0—7.5, 8.0—8.2 (ArH)
(12)	−24.4	4.92	4.77	14.3	9.8	6.5	1.87	2.69 (NMe, d, $^3J_{PH}$ 10.5), 7.1—7.5, 7.9—8.2 (ArH)
(13)	−13.7	4.97	4.68	13.9	13.9	5.0	*d*	2.71 (NMe, d, $^3J_{PH}$ 11.0), 7.1—7.6, 7.8—8.1 (ArH)

[a] δ_P Values are in p.p.m.; J values in Hz. [b] CH_2OPH is an ABMX system; further couplings $^4J_{H(A)H(M)}$ 1.2 and 2.2, $^4J_{H(B)H(M)}$ 1.2 and 0. [c] CH_2OPH is an ABMX system; further couplings $^4J_{H(A)H(M)}$ 1.8 and 2.4, $^4J_{H(B)H(M)}$ 0.9 and 0. [d] ^{19}F N.m.r.: δ_F 2.2 and 3.5 p.p.m. (m, ratio 3 : 1, ref. $PhCF_3$).

instead of $PhPCl_2$ gave an impure product in 15% yield. A better method involves the reaction of (7b) with phenol. A stirred mixture of (7b) (3.62 g, 20 mmol) and phenol (2.07 g, 22 mmol) was heated at 100 °C for 5 h. The flask was connected to a trap which allowed dimethylamine to escape. Vacuum distillation through a small Claisen head gave the *phenoxy-derivative* (7c) as a colourless oil (3.70 g, 80%), b.p. 104—105 °C at 0.05 mmHg, which crystallised upon cooling and scratching, m.p. 37—39 °C, *m/e* 230 (M^+, 39%), 137 (100), 109 (19), and 107 (8) (Found: C, 67.65; H, 4.8. $C_{13}H_{11}O_2P$ requires C, 67.8; H, 4.8%).

1-*Phenoxy*-3H-2,1-*benzoxaphosphole* P-*sulphide* (8c) was prepared from (7c) and sulphur upon heating to *ca.* 60 °C, m.p. 52—53 °C (from CCl_4–hexane, 1 : 2) (Found: C, 59.5; H, 4.1; S, 12.2. $C_{13}H_{11}O_2PS$ requires C, 59.5; H, 4.2; S, 12.2%).

1-*Anilino*-3H-2,1-*benzoxaphosphole* (7d).—A stirred mixture of (7b) (1.81 g, 10 mmol) and aniline (3.72 g, 40 mmol) was heated at 140 °C for 24 h. The flask was connected to a trap which allowed dimethylamine to escape. Most of the excess of aniline was removed at room temperature and 0.1 mmHg, and the crude, solid, *anilino-compound* (7d) recrystallised twice from ether (once with active carbon); yield 60% of colourless crystals, m.p. 104—106 °C (decomp.), *m/e* 229 (M^+, 50%), 180 (10), 137 (100), 136 (38), 109 (41), and 107 (18) (Found: C, 67.95; H, 5.5; N, 6.0. $C_{13}H_{12}NOP$ requires C, 68.1; H, 5.3; N, 6.1%).

1-*Anilino*-3H-2,1-*benzoxaphosphole* P-*sulphide* (8d) was obtained from (7d) and sulphur in $CHCl_3$ (exothermic), m.p. 143—144 °C (from CCl_4) (Found: C, 59.5; H, 4.6; N, 5.3; S, 12.1. $C_{13}H_{12}NOPS$ requires C, 59.8; H, 4.6; N, 5.4; S, 12.3%).

5,6-*Dimethyl*-P-*phenyl*-1,3,2-*benzodioxaphosphole*-2-*spiro*-1′-3′H-[2,1]*benzoxaphosphole* (9a).—A solution of (7a) (214 mg, 1 mmol) in ether (2 ml) was added to a solution of 4,5-dimethylpyrocatechol [12] (138 mg, 1 mmol) in ether (10 ml) at −78 °C. *N*-Chlorodi-isopropylamine (136 mg, 1 mmol) was then added with stirring, and the cooling bath removed. Precipitation of di-isopropylammonium chloride occurred around 0 °C, and the stirring was continued at room temperature for 2 h. Filtration and evaporation gave the crude *spiro-compound* (9a) which was recrystallised from hexane; yield 330 mg (94%), m.p. 136—138 °C (Found: C, 71.8; H, 5.4. $C_{21}H_{19}O_3P$ requires C, 72.0; H, 5.5%). In 1-bromonaphthalene–C_6D_6 (4 : 1) the CH_3 groups gave two ^1H n.m.r. singlets, $\Delta\nu_0$ 4.0 Hz (extrapolated to T_c), T_c 118 °C, $\Delta G^{\ddagger}$ 21.4 kcal mol^{-1}.

P-*Dimethylamino*-5,6-*dimethyl*-1,3,2-*benzodioxaphosphole*-2-*spiro*-1′-3′H-[2,1]*benzoxaphosphole* (9b).—Compound (9b) was prepared from (7b) in the same way as (9a). Recrystallisation from hexane–toluene (8 : 1) gave the *dimethylamino-compound* (9b) in 68% yield, m.p. 126—129 °C (Found: C, 64.5; H, 6.3; N, 4.3. $C_{17}H_{20}NO_3P$ requires C, 64.3; H, 6.35; N, 4.4%). The compound was also prepared from (7b) (181 mg, 1 mmol) and 4,5-dimethyl-*o*-benzoquinone [12] (136 mg, 1 mmol) in toluene (2 ml) at 0 °C, in 72% yield. In 1-bromonaphthalene–C_6D_6 (4 : 1) the $ArCH_3$ groups gave two ^1H n.m.r. singlets, $\Delta\nu_0$ 6.7 Hz (extrapolated to T_c), T_c 133 °C, $\Delta G^{\ddagger}$ 21.8 kcal mol^{-1}.

5,6-*Dimethyl*-P-*phenoxy*-1,3,2-*benzodioxaphosphole*-2-*spiro*-1′-3′H-[2,1]*benzoxaphosphole* (9c).—Compound (9c) was prepared from (7c) in a similar way to (9a). Recrystallisation from hexane gave the *phenoxy-compound* (9c) in 66% yield, m.p. 105—108 °C (Found: C, 69.3; H, 5.4. $C_{21}H_{19}O_4P$ requires C, 68.85; H, 5.2%). The CH_3 groups gave one ^1H n.m.r. signal in 1-bromonaphthalene, $CDCl_3$, and toluene down to −70 °C.

p-*Anilino*-5,6-*dimethyl*-1,3,2-*benzodioxaphosphole*-2-*spiro*-1′-3′H-[2,1]*benzoxaphosphole* (9d).—Compound (9d) was prepared from (7d) in a similar way to (9a). Recrystallis-

ation from hexane–toluene (4 : 1) gave the *anilino-derivative* (9d) in 70% yield, m.p. 153—155 °C (Found: C, 69.4; H, 5.6; N, 3.8. $C_{21}H_{20}NO_3P$ requires C, 69.0; H, 5.5; N, 3.8%). It was also prepared from 4,5-dimethyl-*o*-benzoquinone in a similar way to (9b) in 71% yield. In 1-bromonaphthalene–C_6D_6 (4 : 1) the CH_3 groups gave two ^1H n.m.r. singlets, $\Delta\nu_0$ 5.8 Hz (extrapolated to T_c), T_c 143 °C, $\Delta G^{\ddagger}$ 22.5 kcal mol^{-1}.

5,6-Dimethyl-3H-1,3,2-benzodioxaphosphole-2-spiro-1'-3'H-[2,1]benzoxaphosphole (9e).—A stirred mixture of (7b) (181 mg, 1 mmol) and 4,5-dimethylpyrocatechol (138 mg, 1 mmol) was heated with stirring at 100 °C. Within 1 min gas was evolved and the mixture solidified. Further heating to 135 °C gave a clear liquid. After 30 min the mixture was cooled, and the crude *spiro-compound* (9e) recrystallised from hexane; yield 214 mg (78%), m.p. 131—134 °C (Found: C, 65.4; H, 5.4. $C_{15}H_{15}O_3P$ requires C, 65.7; H, 5.5%). In 1-bromonaphthalene–C_6D_6 (4 : 1) the CH_3 groups gave two ^1H n.m.r. singlets $\Delta\nu_0$ 9.2 Hz (extrapolated to T_c), T_c 52 °C, $\Delta G^{\ddagger}$ 17.1 kcal mol^{-1}. In $CDCl_3$ $\Delta\nu_0$ 4.7 Hz, T_c 46 °C, $\Delta G^{\ddagger}$ 17.2 kcal mol^{-1}.

4',4',5',5'-Tetramethyl-P-phenoxy-3H-2,1-benzoxaphosphole-1-spiro-2'-[1,3,2]dioxaphospholan (10c).—A solution of pinacol (118 mg, 1 mmol) in ether (1 ml) was added to a solution of (7c) (230 mg, 1 mmol) in ether (10 ml) at −78 °C, followed by *N*-chlorodi-isopropylamine (136 mg, 1 mmol). The cooling bath was removed, and the mixture was stirred at room temperature for 20 h. Filtration and evaporation of the solvent gave the crude product, which was contaminated with one major by-product (δ_p 29.7 p.p.m.; *ca.* 20%). Fractional recrystallisation from hexane (the by-product is less soluble) gave the *phenoxy-compound* (10c) (175 mg, 50%), m.p. 75—81 °C (Found: C, 65.9; H, 6.9. $C_{19}H_{23}O_4P$ requires C, 65.9; H, 6.7%). In $CDCl_3$ the CH_3 groups gave four ^1H n.m.r. singlets at −10 °C, $\Delta\nu_0$ 13.1 Hz, T_c 30 ± 5 °C, and $\Delta\nu_0$ 17.9 Hz, T_c 35 ± 5 °C, $\Delta G^{\ddagger}$ 15.8 ± 0.3 kcal mol^{-1}.

P-Anilino-4',4',5',5'-tetramethyl-3H-2,1-benzoxaphosphole-1-spiro-2'-[1,3,2]dioxaphospholan (10d).—A stirred mixture of (10e) (254 mg, 1 mmol) and phenyl azide (240 mg, 2 mmol) was heated at 105 °C for 3 h. After cooling the flask was evacuated at 1 mmHg for 1 h. The solid crude product was recrystallised from hexane to give 240 mg (70%) of the *anilino-derivative* (10d), m.p. 115—117 °C (Found: C, 66.0; H, 6.6; N, 3.8. $C_{19}H_{24}NO_3P$ requires C, 66.1; H, 7.0; N, 4.1%). In 1-bromonaphthalene–C_6D_6 (4 : 1) the CH_3 groups gave four ^1H n.m.r. singlets, $\Delta\nu_0$ 6.6 Hz (extrapolated to T_c), T_c 116 °C, and $\Delta\nu_0$ 21.9 Hz (extrapolated to T_c, T_c 130 ± 5 °C, $\Delta G^{\ddagger}$ 20.9 kcal mol^{-1}.

4',4',5',5'-Tetramethyl-3H-2,1-benzoxaphosphole-1-spiro-2'-[1,3,2]dioxaphospholan (10e).—A stirred mixture of (7b) (906 mg, 5 mmol) and pinacol (710 mg, 6 mmol) was heated at 140 °C for 12 h. After cooling most of the excess of pinacol was removed at 1 mmHg, and the crude *spiro-compound* (10e) recrystallised from ether; yield 790 mg (62%), m.p. 98.5—101 °C (Found: C, 61.7; H, 7.85. $C_{13}H_{19}O_3P$ requires C, 61.4; H, 7.5%). In $CDCl_3$ the CH_3 groups gave four ^1H n.m.r. singlets, $\Delta\nu_0$ 6.5 Hz, T_c 42 °C, and $\Delta\nu_0$ 23.7 Hz, T_c 58 °C, $\Delta G^{\ddagger}$ 16.8 kcal mol^{-1}.

P-Dimethylamino-4',5'-bis-(p-tolyl)-3H-2,1-benzoxaphosphole-1-spiro-2'-[1,3,2]dioxaphosphole (11b) *and the P-Anilino-analogue* (11d).—Compounds (11b) and (11d) were prepared from (7b) or (7d), respectively, (1 mmol) and 4,4'-dimethylbenzil (1 mmol) in $CDCl_3$ (1 ml) at 20 °C. After 3 h the ^{31}P n.m.r. spectra showed one signal, and evaporation gave the crude products which were used directly for the n.m.r. experiments. In 1-bromonaphthalene–C_6D_6 (4 : 1) the CH_3 groups gave two ^1H n.m.r. singlets: for (11b), $\Delta\nu_0$ 5.2 Hz (extrapolated to T_c), T_c 125 °C, $\Delta G^{\ddagger}$ 21.6 kcal mol^{-1}; for (11d) $\Delta\nu_0$ 3.9 Hz (extrapolated to T_c), T_c 128 °C, $\Delta G^{\ddagger}$ 22.0 kcal mol^{-1}.

P-Dimethylamino-4,5-dimethyl-3H-2,1-benzoxaphosphole-1-spiro-2'-[1,3,2]dioxaphosphole (12).—A solution of biacetyl (86 mg, 1 mmol) in hexane (1 ml) was added during 1 h to a solution of (7b) (200 mg, 1.1 mmol) in hexane (1 ml) at 20 °C with stirring. After a further 1 h the colourless mixture was cooled to −78 °C, and the solid *spiro-compound* (12) isolated and recrystallised from hexane; yield 225 mg (80%), m.p. 95—98 °C (Found: C, 58.4; H, 7.0; N, 5.2. $C_{13}H_{18}NO_3P$ requires C, 58.4; H, 6.8; N, 5.2%). The CH_3 groups gave one ^1H n.m.r. signal in $CDCl_3$ and in 1-bromonaphthalene.

P-Dimethylamino-2',2',5',5'-tetrakistrifluoromethyl-3H-2,1-benzoxaphosphole-1-spiro-4'-[1,3,4]dioxaphospholan (13). Hexafluoroacetone (0.7 ml at −78°, 7.5 mmol) was slowly evaporated into a solution of (7b) (362 mg, 2 mmol) in ether (8 ml) at −78 °C with stirring. After 30 min the solution was heated to room temperature and the solvent removed. The solid residue was recrystallised from hexane to give 510 mg (50%) of the *dimethylamino-compound* (13), m.p. 92—94 °C (Found: C, 35.1; H, 2.4; N, 2.7. $C_{15}H_{12}F_{12}NO_3P$ requires C, 35.1; H, 2.4; N, 2.7%).

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