Apicophilicity of the Ethylthio-group in Trigonal Bipyramidal Phosphoranes

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The variable-temperature n.m.r. spectra of a number of five-co-ordinate spirophosphoranes having *P*-ethoxy- and *P*-ethylthio-groups have given data on the energetics of the pseudorotation processes available to the systems. It is concluded that the apicophilicities of ethoxy- and ethylthio-groups are similar. The spirophosphoranes were obtained from 2-substituted 1,3,2-dioxaphospholans by addition to biacetyl, 3-benzylidenepentane-2,4-dione, or 2-phenylacrylophenone, or by condensation with 1,2-diols in the presence of *N*-chlorodi-isopropylamine.

FROM a study by variable temperature n.m.r. of the pseudorotation processes available to a number of five-co-ordinate spirophosphoranes having *P*-phenoxy- and *P*-phenylthio-groups, we concluded previously [1] that the apicophilicities of phenoxy- and phenylthio-groups, *i.e.* their preference relative to other groups for the apical as opposed to the equatorial position in trigonal bipyramidal phosphoranes, are similar, with the balance varying according to the nature of the other *P*-substituents. We now report on the relative apicophilicities of ethoxy- and ethylthio-groups, of more direct relevance to the unusual stereochemistry sometimes observed [2] in nucleophilic

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

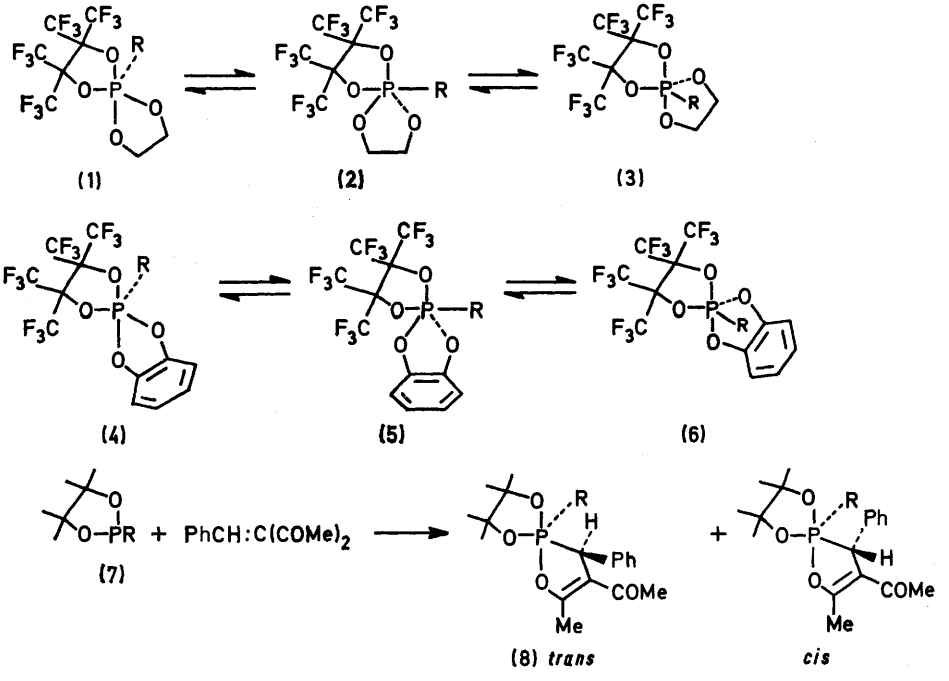
[2] N. J. De'ath, K. Ellis, D. J. H. Smith, and S. Trippett, *Chem. Comm.*, 1971, 714; J. Donahue, N. Mandell, W. B. Farnham, R. K. Murray, K. Mislow, and H. P. Benschop, *J. Amer. Chem. Soc.*, 1971, **93**, 3792.

substitutions at phosphorus bearing both alkoxy- and alkylthio-substituents. DeBruin [3] has concluded from experiments on the hydrolysis of alkoxy(alkylthio)-phosphetanium salts that alkoxy- and alkylthio-groups have similar kinetic apicophilicities, and our results support this view. As before, we have studied the variable-temperature n.m.r. spectra of a range of spirophosphoranes: detailed discussion of the pseudorotations available to spirophosphoranes and of the assumptions behind the interpretation of the n.m.r. data is given in a previous paper.[1]

The spirophosphorane (1; R = OEt) was obtained from 2-ethoxy-1,3,2-dioxaphospholan and perfluoropinacol by the *N*-chlorodi-isopropylamine method.[4] Its ^{19}F n.m.r. spectrum in 1-bromonaphthalene at room temperature contained two signals of equal intensity which coalesced reversibly at 116 ± 2 °C. The free energy of activation of the process associated with this coalescence, the pseudorotation (1) ⇌ (3) *via* the high-energy phosphorane (2; R = OEt), is 20.1 ± 0.2 kcal mol^{-1}. The ^{19}F n.m.r. spectrum of the corresponding ethylthio-spirophosphorane (1; R = SEt), prepared by the same route, showed a similar coalescence at 121 ± 2 °C with an associated free energy of activation of 19.1 ± 0.2 kcal mol^{-1}. Clearly in this system ethylthio is slightly more apicophilic than ethoxy.

A similar situation was revealed in the spirophosphoranes (4; R = OEt or SEt), also obtained by using perfluoropinacol and *N*-chlorodi-isopropylamine. The free energies of activation for the pseudorotations (4) ⇌ (6), *via* the high-energy phosphoranes (5; R = OEt or SEt), were 22.1 and 21.4 ± 0.2 kcal mol^{-1}, respectively.

Bernard and Burgada [5] have shown that the 1,3,2-dioxaphospholans (7; R = OMe or NMe_2) condense with 3-benzylidenepentane-2,4-dione to give mixtures of isomeric spirophosphoranes from which the major, *trans*-isomers (8) can readily be obtained crystalline, and have reported on the variable-temperature n.m.r. spectra of these. We have prepared the series of adducts from (7; R = OMe, OEt, OBu^t, OPh, SEt, or NMe_2); in each case, except with R = SEt, the *trans*-isomer was obtained crystalline from ether. The ethylthio-adduct (8; R = SEt) was obtained from the reaction as predominantly the *trans*-isomer but subsequently crystallised from light petroleum as the *cis*-isomer. At room temperature in chlorobenzene solution the methyl groups of the dioxaphospholan rings of the *trans*-isomers give rise to four widely spaced signals in the 100 MHz proton n.m.r. spectra, *e.g.* with R = OBu^t at δ 0.11, 0.81, 0.99, and 1.25. As the temperature is increased the two inner signals coalesce and at higher temperatures the two outer signals coalesce. Both coalescences have the same free energy of activation, the difference in coalescence temperature being due to the large difference in frequency between the coalescing signals.



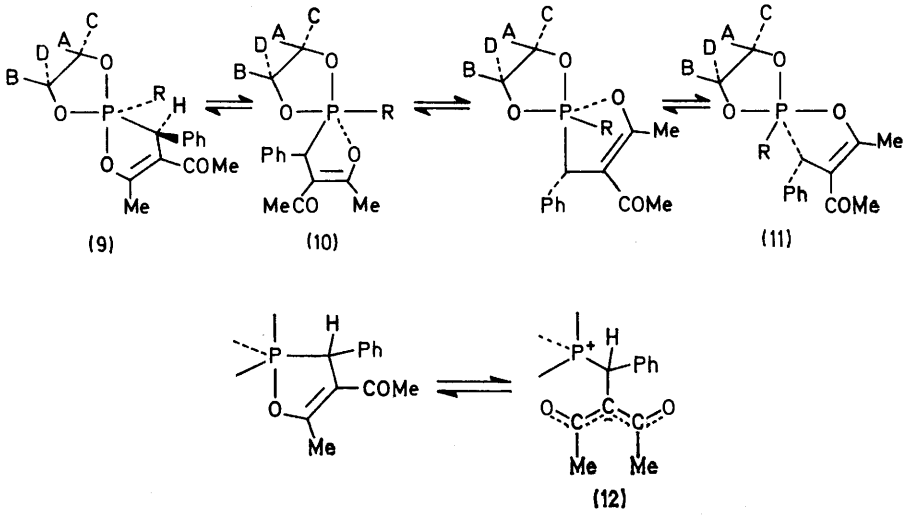
Equivalence of pairs of methyl groups is achieved when the pseudorotations (9) ⇌ (11), *via* the high-energy phosphorane (10) having the oxaphospholen ring diequatorial and R apical, become rapid on the n.m.r. time-scale. The methyl groups A and B in structure (9) occupy the same positions as D and C, respectively, in (11). Changes in the free energy of activation for this equivalence will reflect changes in the apicophilicity of the groups R. Pseudorotations involving placing the dioxaphospholan ring diequatorial cannot lead to equivalence of any of the methyl groups on this ring, but do lead

[3] K. E. DeBruin, A. G. Padilla, and M. T. Campbell, *J. Amer. Chem. Soc.*, 1973, **95**, 4681.

[4] S. A. Bone and S. Trippett, *Tetrahedron Letters*, 1975, 1583.

[5] D. Bernard and R. Burgada, *Compt. rend.*, 1972, **274C**, 288.

to equilibration of *cis*- and *trans*-isomers. Slow formation of the equilibrium concentration of the *cis*-isomers was observed in the above n.m.r. experiments but, as expected,[6] equilibration of *cis*- and *trans*-isomers was slow on the n.m.r. time-scale in the temperature range studied.



Data on the variable-temperature n.m.r. spectra of the 3-benzylidenepentane-2,4-dione adducts (8) are contained in Table 1. As in the spirophosphoranes (1) and (4) above, ethoxy- and ethylthio-groups have comparable apicophilicities. The low apicophilicity of the dimethylamino-group and the relative apicophilicities of methoxy and phenoxy-groups agree with previous conclusions.

TABLE 1

N.m.r. data [a] on the 3-benzylidenepentane-2,4-dione adducts (8)

	Inner pair of Me signals			Outer pair of Me signals		
R	$\Delta\nu$/ Hz	T_c/ °C [b]	ΔG^*/ kcal mol^{-1} [c]	$\Delta\nu$	T_c [b]	ΔG^* [c]
MeO	14.5	66	17.6	100.5	89	17.4
EtO	14	80	18.3	108	100	18.0
Bu^{t}O	19	57	16.9	114.5	75	16.7
PhO	15.5	52	16.8	112	67	16.3
EtS	35	85	18.0	112	100	17.9
Me_2N	17.5	>150	>22	98.5	>150	>20.5

[a] 100 MHz in *o*-dichlorobenzene. [b] ±3 °C. [c] ±0.2 kcal mol^{-1}.

In their classical work on 3-benzylidenepentane-2,4-dione adducts of acyclic tervalent phosphorus species, Gorenstein and Westheimer [7] identified an 'irregular' process having a free energy of activation in the 20—21 kcal mol^{-1} region involving dissociation of the adducts to the dipolar species (12). Such a process would be expected to have a much higher energy barrier in the case of the spirophosphoranes (8) because of increased strain in the dioxaphospholan rings on changing to tetrahedral geometry round phosphorus. *P*-Dimethylamino-groups stabilise the betaines (12),[8] and the lack of coalescence observed at high temperatures with the adduct (8; R = NMe_2) encourages the view that dissociation is not a significant factor in the variable-temperature n.m.r. experiments on the spirophosphoranes (8) reported above.

From the above data on the pseudorotation processes of the spirophosphoranes (1), (4), and (8) we conclude that ethoxy- and ethylthio-groups have comparable apicophilicities.

In the search for systems that would give reliable data on the relative apicophilicities of ethoxy- and ethylthio-groups many spirophosphoranes were prepared which did not give the required information, either because of thermal instability or because their n.m.r. spectra did not show the expected multiplicity in any of the solvents investigated. Some of these systems are now described briefly.

Biacetyl Adducts.—The 1,3,2-dioxaphospholans (7; R = OMe, OEt, OPr^i, OBu^t, OPh, or SEt) reacted exothermically with biacetyl in the absence of solvent to give the spirophosphoranes (13). In solution at room temperature the adducts (R = SEt or OPh) decomposed rapidly and were not satisfactorily characterised. In the usual n.m.r. solvents at room temperature all except the t-butoxy-adduct showed only one signal for the dioxaphospholan methyl groups. In 1-bromonaphthalene both the methoxy- and the t-butoxy-adduct showed two signals of equal intensity for these methyl groups, which coalesced reversibly at higher temperatures when the pseudorotations (13) ⇌ (15), *via* the high-energy phosphoranes (14), became fast on the n.m.r. time-scale. The free energies of activation for these processes were 21.2 ± 0.3 and 23.0 ± 0.3 kcal mol^{-1} for the methoxy- and t-butoxy-adducts respectively.

The degeneracy of chemical shift of the dioxaphospholan methyl groups in the spirophosphoranes (13;

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

[7] D. Gorenstein and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1970, **92**, 634; D. Gorenstein, *ibid.*, p. 644.

[8] F. Ramirez, *Accounts Chem. Res.*, 1968, **1**, 168.

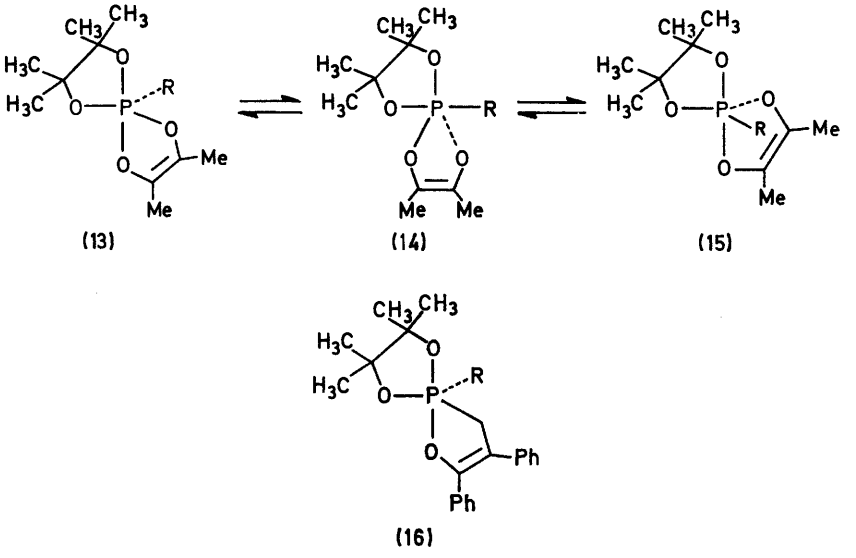
R = OMe, OEt, or OPr^i) could be removed in *o*-dichlorobenzene solution by using the shift reagent tris(dipivaloylmethanato)europium(III) [Eu(dpm)$_3$]. For example the single peak at δ 1.17 due to the four ring-methyl groups of the adduct (13; R = OMe) became two signals of equal intensity at δ 1.65 and 2.45 in the presence of a molar equivalent of Eu(dpm)$_3$. Attempts were made to obtain the free energies of activation of the pseudorotations (13) ⇌ (15) from the variable-temperature n.m.r. spectra in the presence of shift reagent [*cf.* the work of Cheng and Gutowsky [9] on the variable temperature ^{1}H n.m.r. of dimethylformamide in the presence of Eu(fod)$_3$] but the results were not clear-cut and for the adduct (13; R = OMe) the derived Δ*G** value was 1.5 kcal mol^{-1} larger than that obtained in the absence of shift reagent. For further details of this work the thesis of White [10] should be consulted.

Benzil adducts of the 1,3,2-dioxaphospholans (7) were not further investigated when that from (7; R = OEt) showed a single peak for the four ring-methyl groups in all solvents investigated.

Methylenedeoxybenzoin (2′-Phenylacrylophenone) Adducts.—The reaction [11] of methylenedeoxybenzoin with the 1,3,2-dioxaphospholans (7; R = OMe, OBu^t, OPh, or NMe$_2$) in benzene at 60 °C for 72 h gave the adducts (16) as viscous oils which slowly crystallised at room temperature but could not be recrystallised, partly because of their extreme sensitivity to moisture. Attempts to prepare the analogous *P*-ethylthio- and *P*-phenylthio-adducts failed, probably because of the relatively vigorous conditions required for the additions.

The pseudorotation pathways available to the spirophosphoranes (16) are analogous to those of the benzylideneacetylacetone *trans*-adducts (9) described above. At low temperature the four ring-methyl groups gave rise to four separate signals in the n.m.r. spectra; at higher temperatures, when pseudorotation involving placing the oxaphospholen ring diequatorial became fast on the n.m.r. time-scale, these coalesced in pairs. However, the signals were so close together that accurate observation of the coalescences was not possible and the derived free energies of activation (Table 2) are correspondingly less reliable.

1,4,6,9-*Tetraoxa-5-phosphaspiro*[4.4]*nonanes.*—Besides the spirophosphoranes (1) and (4) described above



several other examples of this system were prepared by the *N*-chlorodi-isopropylamine method. They are shown in Table 3 together with their n.m.r. data.

TABLE 2

N.m.r. data on the 2′-phenylacrylophenone adducts (16)

R	Δν/Hz [a]	T_c/°C	Δ*G**/kcal mol^{-1}
MeO [b]	8 and 11	23 ± 5	15.5 ± 0.6
Bu^{t}O [c]	13 and 19.5	21 ± 5	15.1 ± 0.6
PhO [c]	13 and 15	0 ± 5	14.1 ± 0.6
Me$_2$N [c]	3 and 6	80 ± 10	19.0 ± 0.8

[a] 100 MHz. [b] In CH_2Cl_2. [c] In PhCl.

EXPERIMENTAL

^{1}H N.m.r. spectra were determined at 60 MHz for solutions in $CDCl_3$ unless otherwise stated. ^{31}P N.m.r. spectra were determined at 40.5 MHz for solutions in $CDCl_3$ unless otherwise stated, and shifts are quoted relative to external 85% H_3PO_4. ^{19}F N.m.r. spectra were determined at 94.1 MHz and shifts are quoted relative to internal $PhCF_3$. Positive shifts are upfield from the reference in both cases.

5-*Ethoxy*-2,2,3,3-*tetrakistrifluoromethyl*-1,4,6,8-*tetraoxa*-5-*phosphaspiro*[4.4]*nonane* (1; R = OEt).—Perfluoropinacol (10 mmol) in ether (10 ml) was added to a stirred solution of 2-ethoxy-1,3,2-dioxaphospholan (10 mol) in ether (15 ml) at −78 °C, followed dropwise by *N*-chlorodi-isopropylamine (10 mmol) in ether (10 ml) at the same temperature. The mixture was then allowed to warm to room temperature and set aside overnight. Amine hydrochloride was filtered off and the filtrate evaporated. Crystallisation of the residue from light petroleum at −20 °C gave the title *phosphorane*

[9] H. N. Cheng and H. S. Gutowsky, *J. Amer. Chem. Soc.*, 1972, **94**, 5505.

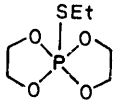
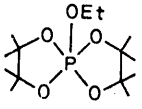
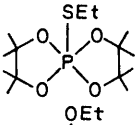
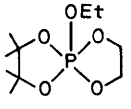
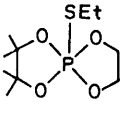
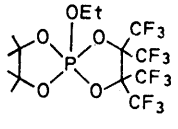
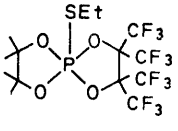
[10] M. W. White, Ph.D. Thesis, University of Leicester, 1975.

[11] A. P. Stewart and S. Trippett, *Chem. Comm.*, 1970, 1279.

(68%), m.p. 45—47°, δ 1.26 (3 H, dt, *J* 7 and 2 Hz), 4.0 (4 H, d, *J* 15 Hz), and 3.78—4.32 (2 H, m), ^{31}P +28.8 p.p.m., ^{19}F +3.51 (6 F, m) and +3.72 (6 F, m), *m/e* 468, 439, 438, 423, 421, 411, 410, 399, 380, 371, 311, and 265 (Found: C, 25.7; H, 2.1; P, 6.55. $C_{10}H_9F_{12}O_5P$ requires C, 25.65; H, 1.9; P, 6.65%).

TABLE 3

Yields and n.m.r. data of 1,4,6,9-tetraoxa-5-phosphaspiro-[4.4]nonanes

Compound [a]	Yield (%)	^{31}P [b]		^{1}H or ^{19}F [c]
	57	7.3	δ	1.0—1.52 (3 H, m), 2.64 (2 H, dq, *J* 7 and 1.5 Hz), and 3.90 (8 H, s)
	82	42.4	δ	1.22 (24 H, s), 1.30—1.54 (3 H, m), and 4.05 (2 H, m) (in 1-bromonaphthalene [d] the ring methyl groups gave two equal intensity signals, Δν 5 Hz; the compound decomposed before coalescence of these signals)
	85	23.0	δ	1.22 (12 H, s), 1.24 (12 H, s), 1.32—1.55 (3 H, m), and 2.35—3.12 (2 H, m) (in CCl_3Br, Δν 4.5 Hz; decomposed before coalescence)
	76	34.9	δ	1.22 (12 H, s), 1.25—2.42 (3 H, m), 3.64 (4 H, d, *J* 14 Hz), and 3.78—4.14 (2 H, m) (in 1-bromonaphthalene [d] the ring methyl groups gave two equal intensity signals, Δν 8 Hz, T_c 92 ± 2 °C, ΔG^* 19.4 ± 0.2 kcal mol^{-1})
	78	10.5	δ	1.22 (12 H, s), 1.28—2.56 (3 H, m), 2.32—2.94 (2 H, m), and 3.80 (4 H, d, *J* 14 Hz) (the methyl groups gave one signal in all solvents investigated)
	81	37.1	δ	1.24 (12 H, s), 1.32—1.48 (3 H, m), and 4.06 (2 H, q, *J* 7 Hz) (a single ^{19}F absorption was observed in all solvents investigated)
	80	7.2	δ	1.28 (6 H, s), 1.30 (6 H, s), 1.44 (3 H, t, *J* 2 Hz), and 2.36—3.12 (2 H, m) [^{19}F (1-bromonaphthalene) +3.06 and +4.52 p.p.m.; no coalescence up to 180 °C]

[a] In each case the right-hand ring as drawn was derived from the 1,2-diol; none of the compounds was obtained crystalline. [b] P.p.m. to high field of external 85% H_3PO_4. [c] ^{1}H N.m.r. in $CDCl_3$ at 60 MHz unless otherwise stated. [d] 100 MHz.

In a similar way the following spirophosphoranes and those listed in Table 3 were obtained. Evaporation of the ethereal filtrate, extraction of the residue with light petroleum and evaporation of the extract gave the phosphorane. They all showed the molecular ion and the expected fragmentation in their mass spectra. 5-*Ethylthio*-2 2,3,3-*tetrakistrifluoromethyl*-1,4,6,8-*tetraoxa*-5-*phosphaspiro*[4.4]*nonane* (78%) showed δ 1.12—1.44 (3 H, m), 2.46—3.22 (2 H, m), and 4.00 (4 H, d, *J* 15 Hz), ^{31}P +2.5 p.p.m., ^{19}F +2.60 (6 F, m) and +3.60 (6 F, m); P-*ethoxy*-4',4',5',5'-*tetrakistrifluoromethyl*-1,3,-2-*benzodioxaphosphole*-2-*spiro*-2'-[1,3,2]*dioxaphospholan* (4; R = OEt) (85%), δ 1.04—1.58 (3 H, m), 3.84—4.56 (2 H, m), and 6.90—7.04 (4 H, m), ^{31}P +30.7 p.p.m., ^{19}F +4.73 (6 F, m) and +5.60 (6 F, m) (T_c 180 ±2 °C); the P-*ethylthio-analogue* (4; R = SEt) (82%) showed δ 1.08—1.54 (3 H, m), 2.42—3.32 (2 H, m), and 6.82 (4 H, m), ^{31}P +1.0 p.p.m., ^{19}F +3.94 (6 F, m) and +4.86 (6 F, m) (T_c 163 ±2 °C).

8-*Acetyl*-2,2,3,3,7-*pentamethyl*-r-9-*phenyl*-t-5-*t-butoxy*-1,4,6-*trioxa*-5-*phosphaspiro*[4.4]*non*-7-*ene*.—A solution of 3-benzylidenepentane-2,4-dione (0.05 mol) and 2-t-butoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (0.05 mol) in benzene (1 ml) and light petroleum (4 ml) was set aside overnight at 40 °C. Evaporation and crystallisation from ether gave the title *phosphorane*, m.p. 147—150°, δ (PhCl) 4.04 (1 H, d, *J* 22.5 Hz), 2.48 (3 H, d, *J* 1 Hz), 1.74 (3 H, s), 1.37 (9 H, s), 1.25 (3 H, s), 0.99 (3 H, s), 0.81 (3 H, s), and 0.11 (3 H, s), ^{31}P (CH_2Cl_2) +14.5 p.p.m. (Found: C, 64.7; H, 8.1. $C_{22}H_{33}O_5P$ requires C, 64.7; H, 8.15%). The *cis*-phosphorane, which was not isolated, showed δ (PhCl) 4.32 (1 H, d, *J* 25 Hz), 1.78 (3 H, d, *J* 1 Hz), 1.89 (3 H, s), 1.21 (6 H, s), and 1.11 (6 H, s).

In a similar way the following *trans*-phosphoranes were obtained: the 5-methoxy-analogue,[5] m.p. 129—133°; the 5-dimethylamino-analogue,[5] m.p. 151—155°; the 5-*phenoxy-analogue*, m.p. 149—150°, δ 7.3—6.7 (10 H, m), 4.27 (1 H, d, *J* 23 Hz), 1.90 (3 H, s), 1.65 (3 H, d, *J* 1 Hz), 1.38 (3 H, s), 1.30 (3 H, s), 1.03 (3 H, s), and 0.25 (3 H, s), ^{31}P (CH_2Cl_2) +15.9 p.p.m. (Found: C, 67.25; H, 6.9. $C_{24}H_{29}O_5P$ requires C, 67.3; H, 6.8%); the 5-*ethoxy-analogue*, m.p. 108—109°, δ 7.30 (5 H, s), 3.75—4.4 (3 H, m), 2.60 (3 H, d, *J* 1 Hz), 1.96 (3 H, s), 1.34—1.60 (3 H, m), 1.35 (3 H, s), 1.26 (3 H, s), 0.98 (3 H, s), and 0.21 (3 H, s), ^{31}P (CH_2Cl_2) +10.9 p.p.m. (Found: C, 63.2; H, 7.75; P, 7.85. $C_{20}H_{29}O_5P$ requires C, 63.15; H, 7.7; P, 8.15%). The cis-5-*ethylthio-analogue*, m.p. 136—137° (from light petroleum), was also isolated, δ (PhCl) 4.36 (1 H, d, *J* 24 Hz), 1.94—2.5 (2 H, m), 2.36 (3 H, d, *J* 1 Hz), 1.84 (3 H, s), 1.26 (3 H, s), 1.22 (3 H, s), 1.18 (3 H, s), 1.08 (3 H, s), and 0.7 (3 H, dt, *J* 3 and 8 Hz), ^{31}P (PhCl) −2.9 p.p.m. (Found: C, 60.5; H, 7.4. $C_{20}H_{29}O_4PS$ requires C, 60.6; H, 7.3%). The *trans*-ethylthio-analogue showed δ 7.08 (5 H, s), 4.08 (1 H, d, *J* 17.5 Hz), 2.38 (3 H, d, *J* 1 Hz), 1.88 (3 H, s), 1.33 (3 H, s), 1.25 (3 H, s), 0.82 (3 H, s), and 0.23 (3 H, s).

2,2,3,3-*Tetramethyl*-7,8-*diphenyl*-5-*t-butoxy*-1,4,6-*trioxa*-5-*phosphaspiro*[4.4]*non*-7-*ene*.—A solution of 2'-phenylacrylophenone (0.05 mol) and 4,4,5,5-tetramethyl-2-t-butoxy-1,3,2-dioxaphospholan (0.05 mol) in benzene (5 ml) was set aside at 60 °C for 72 h. Evaporation then gave the title phosphorane which crystallised slowly but could not be recrystallised or obtained analytically pure, although its spectra indicated that it was essentially pure; δ (C_6H_6) 3.22 (2 H, ABX, *J* 19.2, J_{PH} 17.2 Hz), 1.43 (9 H, s), and 1.17br (12 H, s), ^{31}P (C_6H_6) +17.1 p.p.m., *m/e* 428, 372, 355, 328, 314, 290, 272, 256, and 208.

In a similar way the following phosphoranes were obtained: the 5-methoxy-analogue, δ (CH_2Cl_2) 3.61 (3 H, d, *J* 13 Hz), 2.95 (2 H, ABX, *J* 19.5, J_{PH} 18 Hz), and 1.26br (12 H, s), ^{31}P (CH_2Cl_2) +13.5 p.p.m.; the 5-phenoxy-analogue, m.p. 125—128° (from ether), δ 7.3—6.2 (15 H, m), 3.27 (2 H, ABX, *J* 19.5, J_{PH} 18 Hz), and 1.38 (12 H, s), ^{31}P (CH_2Cl_2) +24.0 p.p.m.; and the 5-dimethylamino-analogue, δ (C_6H_6) 3.29 (2 H, d, *J* 18 Hz), 2.97 (6 H, d, *J* 10 Hz), 1.39br (6 H, s), and 1.30br (6 H, s), ^{31}P +19.5 p.p.m.

Biacetyl Adducts.—Biacetyl (0.01 mol) was added slowly to the stirred 2-substituted 4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (0.01 mol), the temperature being kept below 50 °C, and the mixture was set aside overnight at room

temperature. The following 5-substituted 2,2,3,3,7,8-hexamethyl-1,4,6,9-tetraoxa-5-phosphaspiro[4.4]non-7-enes were formed almost quantitatively but were extremely readily hydrolysed; the 5-methoxy-analogue, m.p. 55—60° (from light petroleum), δ 3.58 (3 H, d, *J* 14 Hz), 1.82 (6 H, s), and 1.27 (12 H, s) (in 1-bromonaphthalene the ring methyl groups gave two signals, Δν 4.0 ± 0.25 Hz; T_c 114 ± 5°), ^{31}P (CH_2Cl_2) +34.2 p.p.m.; the 5-ethoxy-analogue, δ (*o*-$C_6H_4Cl_2$) 3.88 (2 H, dq, *J* 7.0 and 9.5 Hz), 1.72 (6 H, s), 1.13 (3 H, dt, *J* 1 and 7.0 Hz), and 1.18 (12 H, s), ^{31}P (CH_2Cl_2) +36 p.p.m.; the 5-isopropoxy-analogue, δ (*o*-$C_6H_4Cl_2$) 4.57 (1 H, dsept, *J* 6 and 8 Hz), 1.73 (6 H, s), and 1.3—1.1 (18 H, m), ^{31}P (CH_2Cl_2) +37.8 p.p.m.; the 5-t-butoxy-analogue, m.p. 40—50°, δ (C_6H_6) 1.67 (6 H, s), 1.40 (9 H, s), 1.20 (6 H,s), and 1.17 (6 H, s), ^{31}P (CH_2Cl_2) +36.8 p.p.m.

Exposure of a solution of the 5-methoxy-analogue in ether to the atmosphere followed by evaporation and crystallisation of the residue from ether gave 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan 2-oxide,[12] m.p. 100—101°.

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[12] J. R. Cox, jun., and M. G. Newton, *J. Org. Chem.*, 1969, **34**, 2600.