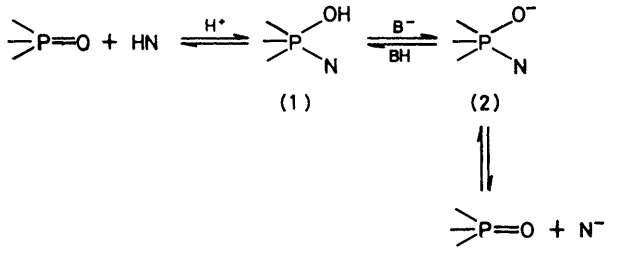
Hydroxyphosphoranes as Intermediates in the Isomerisation of *o*-Hydroxyphenyl Phosphinates

By **Graham Kemp** and **Stuart Trippett,*** Department of Chemistry, The University, Leicester LE1 7RH

The interconversions of isomeric esters of 3-methylcatechol and 1-hydroxyphosphetan 1-oxides (phosphetinic acids) have been studied by variable temperature ^{1}H n.m.r. spectroscopy (ΔG^* *ca.* 17—18 kcal mol^{-1}) and the intermediate hydroxyspirophosphoranes trapped as methoxyspirophosphoranes on treatment with diazomethane. The more stable ester from 3-methylcatechol and diphenylphosphinic acid has been obtained essentially pure; it isomerises to the less stable isomer with ΔG^* 24.4 ± 0.2 kcal mol^{-1}. No methoxyphosphorane was detected on treatment with diazomethane. The corresponding phosphinothioate esters have higher free energies of activation for interconversion and the intermediate hydrothiospirophosphoranes are not trapped with diazomethane. *P*-Hydroxy-2,2′-spirobi-(1,3,2-benzodioxaphosphole) has been obtained in solution in THF by treatment of the corresponding *P*-chloro-compound with one mole equivalent of water. With chlorotrimethylsilane and triethylamine it gave the *P*-trimethylsilyloxyphosphorane; with *o*-hydroxyphenyl *o*-phenylene phosphite (36) in DMF it gave the tris-(*o*-phenylene) phosphate anion (37) and *o*-phenylene phosphonate.

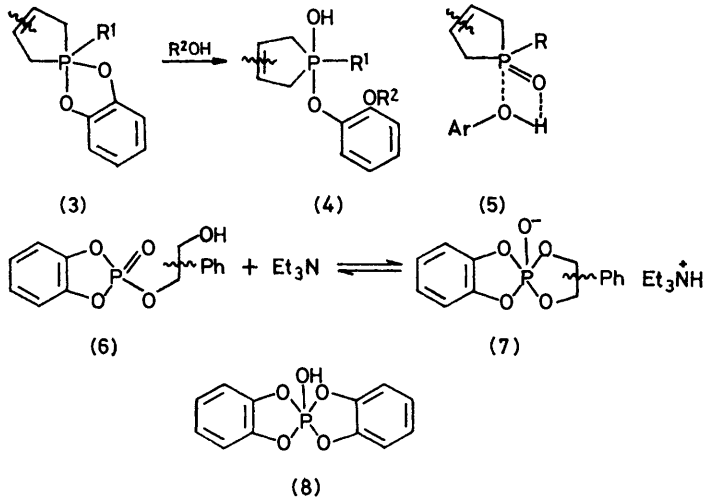
HYDROXYPHOSPHORANES (1) have long been postulated as intermediates in acid-catalysed nucleophilic substitution at phosphoryl centres and their conjugate



(1) (2)

bases (2) as the corresponding intermediates in uncatalysed substitutions.[1] In protic solvents (1) and (2) are in equilibrium. The pseudorotational possibilities open to these intermediates, and therefore both the chemical and stereochemical outcome of the substitutions, will be determined, *inter alia*, by the relative apicophilicity of the hydroxy-group—the oxy-anion is expected to be very poorly apicophilic—and by the acidity of the hydroxyphosphorane relative to the solvent. We have been concerned[2] with the relative apicophilicities of groups in 5-co-ordinate trigonal bipyramidal phosphoranes and have sought to prepare hydroxyphosphoranes in order to obtain data on the relative apicophilicity of the hydroxy-group.

Russian workers[3,4] have frequently described stable hydroxyphosphoranes; for example structure (4) was given to the products obtained by alcoholysis or hydrolysis of phosphoranes of the general formula (3).[4] From the ^{31}P chemical shifts of these compounds, typically *ca.* −75 p.p.m., it is probable that they are the strongly hydrogen-bonded complexes (5) of phospholen oxides and phenols.[5] More recently, Munoz *et al.*[6] have shown that treatment of the phosphates (6) in solution with triethylamine gives the 5-co-ordinate salts (7) which revert to (6) on acidification. Since the work described in this paper was carried out, Ramirez[7] has described the first stable hydroxyphosphorane (8) and this is referred to later.



(3) (4) (5)

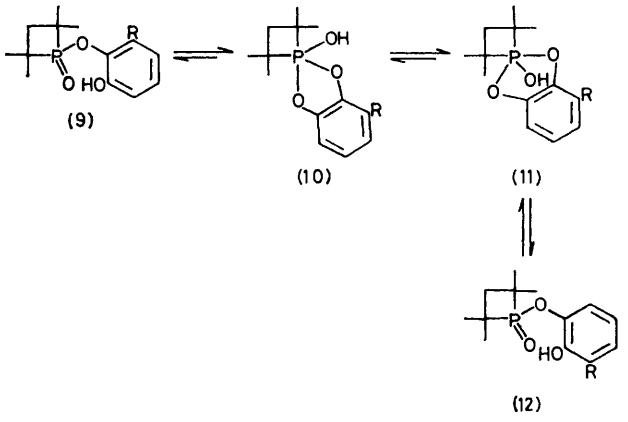
(6) (7)

(8)

Catechol Esters of Phosphetinic Acids.†—Small-membered rings are known to stabilise 5-co-ordinate phosphoranes either because they relieve some of the crowding round the central phosphorus atom or because of the

† Although adherence to the IUPAC rules would name these compounds as 1-hydroxyphosphetan 1-oxides, for ease in reading the name phosphetinic acid is used in the Discussion section.

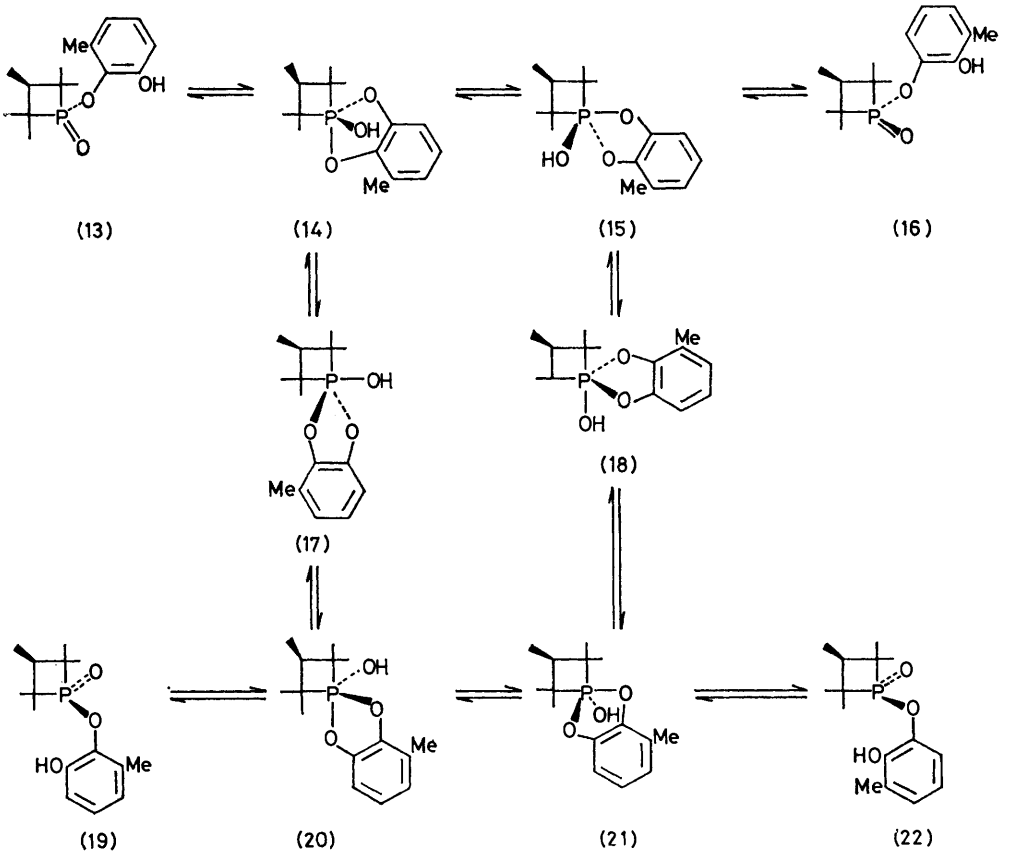
relief of ring-strain when such a ring containing a tetrahedral phosphorus moves to occupy an apical–equatorial



position of a trigonal-bipyramidal phosphorane.[8] Phosphetan and benzo-1,3,2-dioxaphosphole rings are particularly good at this and one might expect a spirohydroxyphosphorane containing these rings to have exceptional stability. We accordingly looked at the catechol esters of phosphetinic acids.[9]

the two isomers (9; R = Me) and (12; R = Me). In 1-bromonaphthalene these showed aromatic methyl signals at δ 2.38 and 2.16 p.p.m. in a ratio of 2.7 : 1 which coalesced reversibly at 67—70 °C corresponding to a free energy of activation for the equilibrium (9) ⇌ (12; R = Me) of about 17.5 kcal mol^{-1}. Above this temperature the phosphetan methyls gave two doublets which remained sharp up to 180 °C showing that migration of the 3-methylcatechyl residue from one side of the ring to the other, *via* phosphoranes having an apical hydroxy-group such as (17) and (18) below, was slow on the n.m.r. time-scale at 180 °C. In agreement with this, the n.m.r. spectrum of the corresponding catechol ester (9 or 12; R = H) showed two sets of methyl signals at 180 °C in 1-bromonaphthalene. Equilibration of the isomers (9) and (12) involves the hydroxyphosphoranes (10) and (11). As often found in phosphetan chemistry, the ^{1}H n.m.r. spectra of solutions in deuteriochloroform of the isomers (9) and (12; R = H or Me) show only one doublet for the two pairs of α-methyl groups; their magnetic non-equivalence is revealed only in an aromatic solvent.

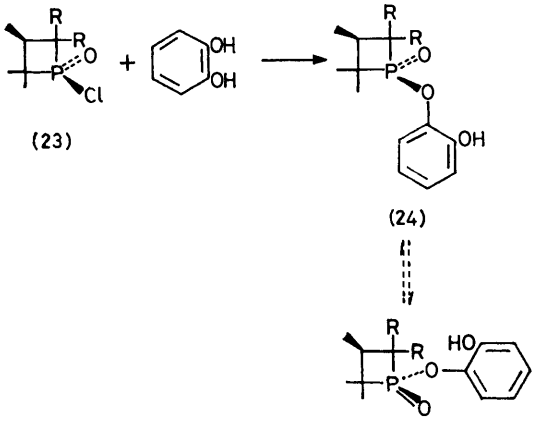
Similarly the *trans*-3-methylcatechol ester (13) of 2,2,3,4,4-pentamethylphosphetinic acid in solution in



1-Chloro-2,2,4,4-tetramethylphosphetan 1-oxide with 3-methylcatechol gave a crystalline phosphinate with a sharp melting point. Although probably one isomer in the crystalline state, its solutions contained a mixture of

1-bromonaphthalene consisted of a 1.8 : 1 equilibrium of the isomers (13) and (16) with a barrier to interconversion of about 17.5 kcal mol^{-1} (T_c 76—80 °C, Δν 38 Hz). Even after being heated to 180 °C there was no evidence

in the n.m.r. spectrum for the presence of either of the *cis*-isomers (19) or (20). At first sight this was surprising for the pseudo-rotations of (14) and (15) to (20) and (21) respectively would be expected to have ΔG^* of only *ca.* 20 kcal mol^{-1} assuming that the apicophilicity of the hydroxy- is similar to that of the ethoxy-group.[10] However, the equilibrium concentration of (14) and (15) could be very low and the effective barrier between (13) and (19) could be as high as *ca.* 38 kcal mol^{-1} (*i.e.* 17.5 + 20). In order to investigate this barrier, the *cis*-phosphetinic chloride (23; R = Me), obtained from



(23) (24) (25)

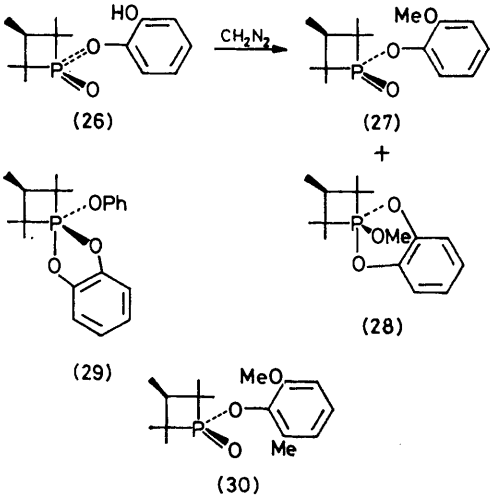
the acid and an excess of thionyl chloride at room temperature as a 3 : 1 mixture with the *trans*-isomer, was treated with catechol and triethylamine. However only the *trans*-ester (25; R = Me) was obtained. As expected,[11] esterification of the phosphetinic chlorides is stereospecific and the 3 : 1 *cis* : *trans*-mixture of chlorides gave with phenol a 3 : 1 mixture of *cis*- and *trans*-phenates. Clearly there is an easy pathway on the normal preparative time-scale from the *cis*-esters (19) and (24; R = Me) to the *trans*-isomers (13) and (25; R = Me) and the equilibria are very largely in favour of the *trans*-isomers.

Previous experience [12] had shown that, in contrast to the preference for *trans*-isomers shown in the 2,2,3,4,4-pentamethylphosphetan series, 2,2,3-trimethylphosphetan compounds are usually obtained as mixtures of isomers. The crystalline catechol ester of 2,2,3-trimethylphosphetinic acid was similarly a 2 : 1 mixture of the isomers (24; R = H) and (25; R = H) but we were unable by slow crystallisation to obtain a mixture sufficiently different in composition from that of the equilibrium mixture to allow the free energy of activation for the interconversion of the isomers to be determined.

When solutions of the above catechol or 3-methylcatechol esters of phosphetinic acids in ether were treated with diazomethane, the formation of small amounts of methoxyphosphoranes could be seen from the characteristic *P*OMe doublets in the ^{1}H n.m.r. spectra of the crude products. Heteronuclear decoupling showed that these doublets were associated with ^{31}P chemical shifts in the expected range for methoxyspirophosphoranes such as (28). The phosphoranes concentrated in the mother-liquors when the major products, *o*-methoxyphenyl esters, were crystallised. Thus the catechol ester (26) of 2,2,3,4,4-pentamethylphosphetinic acid with diazomethane gave the phosphetinate (27) and some 5% of the methoxyphosphorane (28), obtained essentially pure by rapid t.l.c. of the mother-liquors on silica. The ^{31}P chemical shift of (28), −6.4 p.p.m. (to *low* field of external 85% H_3PO_4), compares with that of −6.2 p.p.m. for the phenoxyphosphorane (29). The methoxyphosphorane (28) is shown as the initially formed *cis*-isomer which equilibrates rapidly with the *trans*-isomer with ΔG^* *ca.* 23 kcal mol^{-1} as shown by variable temperature n.m.r. spectroscopy. Presumably (28) arises from methylation of hydroxyphosphoranes analogous to (14) and (15). Similar trapping of hydroxyphosphoranes as methoxyphosphoranes occurred, in the yields indicated, when solutions of the esters (13 + 16; 12%), (9; R = Me; 5%), and (9; R = H; 10%) were treated with diazomethane.

The major product from (13 + 16) and diazomethane was (30), derived from (13) and identical to the ester obtained from 2-methoxy-6-methylphenol. This emphasises that the yield of methylated product does not necessarily reflect the equilibrium concentration of the corresponding hydroxy-species.

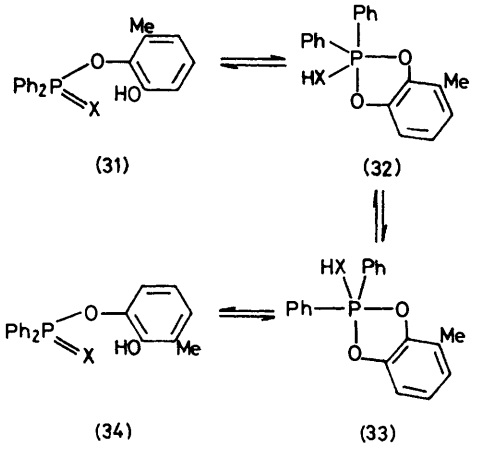
Besides the uncatalysed isomerisations of the phosphetinate esters of 3-methylcatechol described above, the same processes are subject to both acid and base catalysis. Thus, in the presence of one mole equivalent



(26) (27) (28) (29) (30)

of either triethylamine or trifluoroacetic acid in deuteriochloroform the esters (13 + 16) showed only one ^{31}P signal at room temperature corresponding to the weighted average of the signals due to (13) and (16). One cannot be absolutely certain that the same sort of catalysis is not operating in the ' uncatalysed ' isomerisations, but the reproducibility of these with various samples of ester and the consistency in the results obtained with different esters make this unlikely.

Catechol Esters of Diphenylphosphinic Acid.—If isomerisation of phosphetinates of 3-methylcatechol such as (13) and (16) involves hydroxyphosphoranes, then one would expect the corresponding isomerisations of cyclic phosphinate esters to have much higher free energies of activation because in these there would be no relief of ring-strain on forming the spirophosphorane.

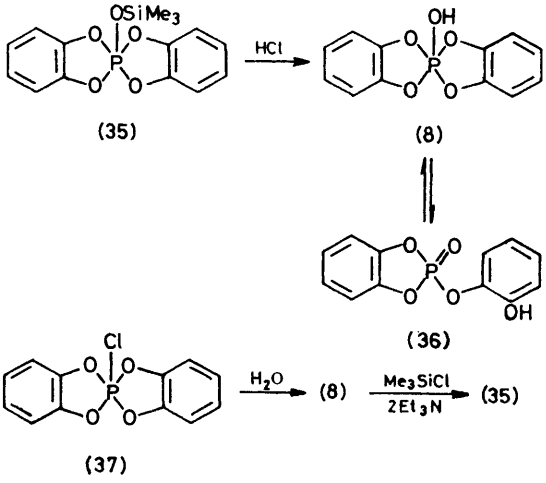


The major isomer of the diphenylphosphinates of 3-methylcatechol (31 or 34; X = O) was obtained almost pure by slow crystallisation from dichloromethane–light petroleum. Isomerisation was sufficiently slow to allow establishment of the 1.83 : 1 equilibrium ratio of isomers to be followed conveniently in solution at 30 °C by monitoring the aromatic methyl signals in the ^{1}H n.m.r. spectrum. The resulting ΔG^* of 24.2 ± 0.2 kcal mol^{-1} for the conversion of the major into the minor isomer *via* the hydroxyphosphoranes (32; X = O) and (33; X = O) is some 7 kcal mol^{-1} higher than with the phosphetinic esters. This correlates well with the acceleration in rate of about 10^6 observed [13] in the alkaline hydrolysis of phosphetanium salts relative to their acyclic analogues where the rate-limiting steps also involve the formation of hydroxyphosphoranes from 4-co-ordinate phosphorus centres. No methoxyphosphoranes could be detected when the diphenylphosphinates of 3-methylcatechol were treated in solution with diazomethane.

Catechol Esters of Phosphinothioic Acids.—Isomeric esters from 3-methylcatechol and phosphinothioic acids would be expected to interconvert *via* hydrothiophosphoranes analogous to the hydroxyphosphoranes discussed above. In practice the barriers to isomerisation are considerably higher in the case of the sulphur analogues. Thus the isomeric esters from 2,2,3,4,4-pentamethylphosphetinothioic acid and 3-methylcatechol have ΔG^* for isomerisation of 22.5 ± 0.5 kcal mol^{-1} (T_c, for the aromatic methyls in 1-bromonaphthalene, 160 °C; $\Delta\nu$ 19 Hz) and ΔG^* for isomerisation of the minor into the major isomer of the diphenylphosphinothioates (31; X = S) and (34; X = S), *via* the hydrothiophosphoranes (32; X = S) and (33; X = S), is 28.3 ± 0.2 kcal mol^{-1}. The minor isomer from (31; X = S) and (34; X = S) was isolated pure by crystallisation and establishment of the equilibrium mixture followed by ^{1}H n.m.r. spectroscopy at 70 °C in benzene. No evidence for the formation of methylthiophosphoranes could be found in the ^{1}H n.m.r. spectra of the products from the action of diazomethane on the above thioesters of 3-methylcatechol.

P-*Hydroxy*-2,2′-*spirobi*-(1,3,2-*benzodioxaphosphole*).—Ramirez [7] has recently described the preparation of the stable hydroxyspirophosphorane (8) by the action of hydrogen chloride on the silyloxyphosphorane (35) in dichloromethane. In solution in acetone or acetonitrile the hydroxyphosphorane is in equilibrium with the phosphate (36); at room temperature equilibration is rapid on the n.m.r. time-scale but at −48 °C both ^{31}P resonances can be detected. Methylation of (8) with diazomethane gave the corresponding methoxyphosphorane.

We had independently obtained (8) by hydrolysis of the chlorospirophosphorane (37). When one mol. equiv. of water was added to a solution of (37) in THF at −90 °C, the ^{31}P signal at +11.9 p.p.m. was immediately replaced by a single sharp signal at +29.0 p.p.m. This signal broadened on warming the solution to room temperature, when it was centred on +26 p.p.m., and this behaviour was reversible. These phenomena were not affected by the presence of one mol. equiv. of triethylamine but the addition of two mol. equiv. gave a sharp signal at +27.4 p.p.m., even at room temperature. The addition of chlorotrimethylsilane to this

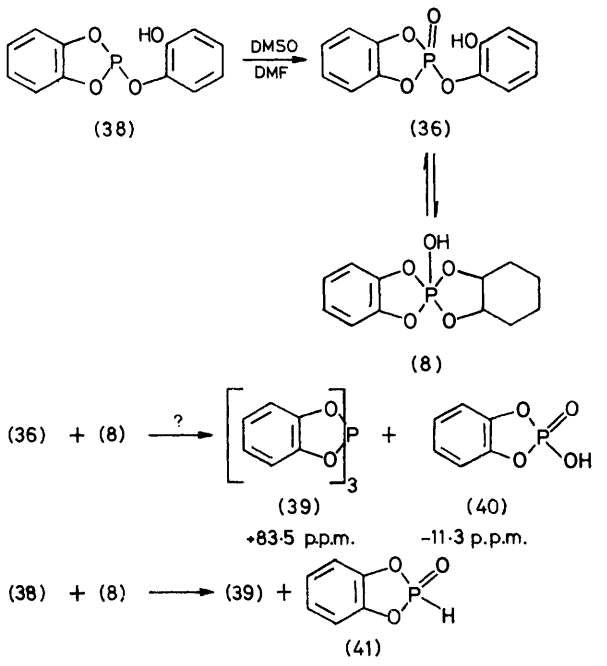


solution gave the major ^{31}P signal at +30.4 p.p.m. and from the resulting solution the trimethylsilyloxyphosphorane (35) was isolated and characterised. In contrast to the situation with acetone or acetonitrile solutions, there was no evidence for the presence of the phosphate (36) in solutions of the hydroxyphosphorane (7) in THF.

The hydroxyphosphorane (8) is extremely readily hydrolysed. Addition of an excess of water to the chlorophosphorane (37) in THF gave major ^{31}P absorptions at +9.3 and +4.0 p.p.m. After 18 h only the

latter remained. The absorptions are probably due to bis-(*o*-hydroxyphenyl) phosphate and *o*-hydroxyphenyl phosphate respectively.

Munoz *et al.*[14] have postulated that the formation of the hexaco-ordinate anion (39) in the oxidation of the phosphite (38) with DMSO in DMF involves the reaction of the intermediate (36) with its isomer (8) to give (39) and the acid (40). Certainly, dilution with DMF of a solution of (8) in THF did lead to the formation of (39) but there was no accompanying ^{31}P signal at −11.3 p.p.m. ascribable to (40). However, on addition of a



solution of the phosphite (38) in DMF to a solution of (8), formed in the absence of base, in THF the ^{31}P signals due to (38) and (8) were immediately replaced by those due to (39) and to the phosphonate (41; −1.6 p.p.m., J_{PH} 687 Hz). This phosphonate, unlike its acyclic analogues, is rapidly oxidised by DMSO to the acid (40) and it may be that the formation of (39) from (38) in DMF–DMSO involves reaction of (8) with (38).

EXPERIMENTAL

^1H N.m.r. spectra were obtained at 60 MHz for solutions in deuteriochloroform unless otherwise stated. Phosphetan C-3-methine protons are usually obscured by other resonances and are not quoted. ^{31}P N.m.r. spectra were obtained at 40.1 MHz for solutions in $CDCl_3$; chemical shifts upfield from external 85% H_3PO_4 are quoted as positive.

1-(2-*Hydroxyphenoxy*)-2,2,4,4-*tetramethylphosphetan* 1-*Oxide* (9; R = H).—1-Chloro-2,2,4,4-tetramethylphosphetan 1-oxide (3.62 g) in tetrahydrofuran (10 ml) was added slowly to a stirred solution of catechol (2.2 g) and triethylamine (2.0 g) in the same solvent (40 ml) and the mixture refluxed overnight. Filtration and removal of solvent then gave an oil (6.03 g) which was chromatographed on alumina. Elution with chloroform gave the *oxide* (9; R = H) (60%), m.p. 123—124° (from light petroleum), δ 1.47 (12 H, d, *J* 19 Hz), 1.71 (2 H, d, *J* 28 Hz), 6.70—7.20 (4 H, m), and 9.37 (1 H, s), δ_P −59.9 p.p.m. (Found: C, 61.5; H, 7.5; P, 12.2. $C_{13}H_{19}O_3P$ requires C, 61.4; H, 7.5; P, 12.2%).

This ester (0.7 g) was dissolved in ether (25 ml) and diazomethane (prepared from 2.14 g of *N*-methyl-*N*-nitroso-*p*-toluenesulphonamide) in ether (15 ml) was added and the solution set aside at room temperature overnight. Evaporation and crystallisation of the residue from light petroleum gave 1-(2-*methoxyphenoxy*)-2,2,4,4-*tetramethylphosphetan* 1-*oxide* (74%), m.p. 118—119°, δ 1.37 (6 H, d, *J* 19 Hz), 1.43 (6 H, d, *J* 20 Hz), 1.64 (2 H, d, *J* 28 Hz), 3.87 (3 H, s), and 6.70—7.53 (4 H, m), δ_P −55.1 p.p.m. (Found: C, 62.9; H, 7.8; P, 11.3. $C_{14}H_{21}O_3P$ requires C, 62.7; H, 7.9; P, 11.5%). The mother-liquors showed absorption at δ 3.7 (d, J_{PH} 12 Hz) which decoupled when irradiated at 24 290 585 Hz corresponding to δ_P −3.5 p.p.m.

In a similar way the following esters were prepared and methylated.

1-[2-*Hydroxy*-3(6)-*methylphenoxy*]-2,2,4,4-*tetramethylphosphetan* 1-*oxide* (9, 12; R = Me) (48%) had m.p. 148—149°, δ 1.43 (12 H, d, *J* 19 Hz), 1.67 (2 H, d, *J* 28 Hz), 2.25 (3 H, s), 6.68—7.16 (3 H, m), and two broad singlets at 8.81 and 9.71 (total 1 H), δ_P −57.5 and −62.1 p.p.m. (Found: C, 62.6; H, 8.0. $C_{14}H_{21}O_3P$ requires C, 62.7; H, 7.9%). Methylation gave a 2-*methoxyphenyl ester* (92%), m.p. 104—105°, δ 1.43 (6 H, d, *J* 20 Hz), 1.47 (6 H, d, *J* 19 Hz), 1.63 (2 H, d, *J* 28 Hz), 2.30 (3 H, s), 3.86 (3 H, s), and 6.67—7.20 (3 H, m), δ_P −54.2 p.p.m. (Found: C, 64.0; H, 8.2; P, 10.8. $C_{15}H_{23}O_3P$ requires C, 63.8; H, 8.2; P, 11.0%). The mother-liquors showed absorption at δ 3.6 (d, J_{PH} 12 Hz); δ_P −2.9 p.p.m.

r-1-(2-*Hydroxyphenoxy*)-2,2,t-3,4,4-*pentamethylphosphetan* 1-*oxide* (26) (81%) had m.p. 114—115°, δ 1.05 (3 H, dd, *J* 1 and 7 Hz), 1.33 (6 H, d, *J* 21 Hz), 1.37 (6 H, d, *J* 20 Hz), 6.73—7.47 (4 H, m), and 9.28 (1 H, br, s), δ_P −61.5 p.p.m. (Found: C, 62.7; H, 7.9; P, 11.3. $C_{14}H_{21}O_3P$ requires C, 62.7; H, 7.9; P, 11.5%). Methylation gave the *o-methoxyphenyl ester* (27) (90%), m.p. 151—152°, δ 0.97 (3 H, dd, *J* 1 and 7 Hz), 1.33 (12 H, d, *J* 19 Hz), 3.86 (3 H, s), and 6.68—7.47 (4 H, m), δ_P −58.4 p.p.m. (Found: C, 64.05; H, 8.3; P, 10.9. $C_{15}H_{23}O_3P$ requires C, 63.8; H, 8.2; P, 11.0%). The mother-liquors showed absorption at δ 3.6 (d, J_{PH} 12 Hz; δ_P −6.4 p.p.m.). Rapid t.l.c. on silica, eluting with ether, gave the methoxyphosphorane essentially pure, δ 0.82 (3 H, dd, *J* 1 and 7 Hz), 1.24 (6 H, d, *J* 20 Hz), 1.26 (6 H, d, *J* 20 Hz), 3.60 (3 H, d, *J* 12 Hz), and 6.75—6.98 (4 H, m), *m/e* 282, 212, 197, 170, and 139.

r-1-[2-*Hydroxy*-3(6)-*methylphenoxy*]-2,2,t-3,4,4-*pentamethylphosphetan* 1-*oxide* (13, 16) (55%) had m.p. 165—166°, δ 0.98 (3 H, dd, *J* 1 and 7 Hz), 1.36 (6 H, d, *J* 20 Hz), 1.40 (6 H, d, *J* 21 Hz), 2.30 (3 H, br, s), 6.40—7.23 (3 H, m), and two broad singlets at 8.85 and 9.68 (total 1 H), δ_P −61.1 and −64.3 p.p.m. (Found: C, 63.9; H, 8.3. $C_{15}H_{23}O_3P$ requires C, 63.8; H, 8.2%). Methylation gave the 2-*methoxy*-6-*methylphenyl ester* (30) (69%), m.p. 132—132.5°, δ 0.97 (3 H, dd, *J* 1 and 7 Hz), 1.30 (6 H, d, *J* 20 Hz), 1.40 (6 H, d, *J* 19 Hz), 2.30 (3 H, s), and 6.66—7.17 (3 H, m), δ_P −58.2 p.p.m. (Found: C, 64.8; H, 8.6; P, 10.7. $C_{16}H_{25}O_3P$ requires C, 64.85; H, 8.5; P, 10.45%). The mother-liquors showed absorption at δ 3.5 (d, J_{PH} 12 Hz; δ_P −4.75 p.p.m.).

r-1-[2-*Hydroxy*-3(6)-*methylphenoxy*]-2,2,t-3,4,4-*pentamethylphosphetan* 1-*sulphide* (46%) had m.p. 139—140°, δ(major isomer) 1.03 (3 H, dd, *J* 1 and 7 Hz), 1.37 (6 H, d,

J 22 Hz), 1.43 (6 H, d, *J* 19 Hz), 2.30 (3 H, s), 5.69 (1 H, br, s), and 6.74—7.07 (3 H, m), (minor isomer) 1.03 (3 H, dd, *J* 1 and 7 Hz), 1.34 (6 H, d, *J* 22 Hz), 1.48 (6 H, d, *J* 19 Hz), 2.25 (3 H, s), 5.69 (1 H, br, s), and 6.74—7.07 (3 H, m), δ_P −104.3 p.p.m. (Found: C, 60.6; H, 7.9; P, 10.2. $C_{15}H_{23}O_2PS$ requires C, 60.4; H, 7.8; P, 10.4%). Methylation with diazomethane (92%) or with sodium hydride-methyl iodide (57%), gave an O-2-*methoxy*-3(6)-*methylphenyl ester*, m.p. 137—138°, δ 0.97 (3 H, dd, *J* 1 and 7 Hz), 1.33 (6 H, d, *J* 22 Hz), 1.47 (6 H, d, *J* 20 Hz), 2.20 (3 H, br, s), 3.80 (3 H, s), and 6.63—7.20 (3 H, m), δ_P −106.3 p.p.m. (Found: C, 61.4; H, 8.1; P, 9.9. $C_{16}H_{25}O_2PS$ requires C, 61.5; H, 8.1; P, 9.9%).

r-1-[2-*Hydroxyphenoxy*]-2,2,c(t)-3-*trimethylphosphetan* 1-*oxide* (48%) had m.p. 102—103°, δ 0.8—1.33 (6 H, m), 1.36—1.69 (3 H, m), 1.71—3.27 (3 H, m), 6.58—7.16 (4 H, m), and 9.29 (1 H, br, s), δ_P −57.3 and −58.5 p.p.m. (Found: C, 60.1; H, 7.1; P, 12.9. $C_{12}H_{17}O_3P$ requires C, 60.0; H, 7.1; P, 12.9%).

2-*Hydroxy*-3(6)-*methylphenyl diphenylphosphinate* (31, 34; X = O) (41%) had m.p. 130—131°, δ (major isomer) 2.00 (3 H, s), 6.83—7.07 (3 H, m), 7.23—8.30 (10 H, m), and 9.84 (1 H, br, s), δ_P −37.6 p.p.m. (Found: C, 70.2; H, 5.3; P, 9.5. $C_{19}H_{17}O_3P$ requires C, 70.4; H, 5.3; P, 9.55%). Methylation gave a 2-*methoxy*-3(6)-*methylphenyl ester* (76%), m.p. 118—119°, δ 2.30 (3 H, s), 3.40 (3 H, s), 6.50—7.07 (3 H, m), and 7.17—8.23 (10 H, m), δ_P −30.7 p.p.m. (Found: C, 71.0; H, 5.7; P, 9.1. $C_{20}H_{19}O_3P$ requires C, 71.0; H, 5.7; P, 9.15%). The minor isomer of the above 2-hydroxy-3(6)-methylphenyl ester had δ 2.25 (3 H, s), 6.37—6.83 (3 H, m), 7.23—8.30 (10 H, m), and 8.97 (1 H, br, s).

O-2-*Hydroxy*-3(6)-*methylphenyl diphenylphosphinothioate* (31, 34; X = S) (40%) was crystallised from dichloromethane–light petroleum to afford the pure minor isomer, m.p. 145—146°, δ 1.74 (3 H, s), 6.40—7.03 (4 H, m), and 7.27—8.33 (10 H, m), δ_P −84.7 p.p.m. (Found: C, 67.5; H, 5.0; P, 8.8. $C_{19}H_{17}O_2PS$ requires C, 67.05; H, 5.0; P, 9.1%). The major isomer had δ 2.23 (3 H, s), 6.20—7.07 (4 H, m), and 7.20—8.27 (10 H, m). Methylation of the major isomer gave an O-2-*methoxy*-3(6)-*methylphenyl ester* (93%), m.p. 128—129°, δ 2.14 (3 H, s), 3.34 (3 H, s), 6.53—7.10 (3 H, m), 7.20—7.63 (6 H, m), and 7.78—8.29 (4 H, m), δ_P −82.3 p.p.m. (Found: C, 67.9; H, 5.5; P, 9.0. $C_{20}H_{19}O_2PS$ requires C, 67.8; H, 5.4; P, 8.75%).

2,2,r-3,4,4-*Pentamethyl*-t-1-*phenoxyphosphetan* 1-*Oxide*.—Phenol (1.79 g) was added to a stirred suspension of sodium hydride (1.4 g of a 50% dispersion in oil) in THF (60 ml). After the evolution of hydrogen had ceased, *t*-1-chloro-2,2,*r*-3,4,4-pentamethylphosphetan 1-oxide (3.65 g) was added and the solution refluxed for 16 h and cooled. Filtration and evaporation, followed by rapid chromatography on alumina using chloroform as the eluant, gave the *title oxide* (54%), m.p. 54—55°, δ 0.96 (3 H, dd, *J* 1 and 7 Hz), 1.27 (6 H, d, *J* 19 Hz), 1.31 (6 H, d, *J* 19 Hz), and 7.03—7.54 (5 H, m), δ_P −56.9 p.p.m. (Found: C, 66.7; H, 8.4; P, 12.35. $C_{14}H_{21}O_2P$ requires C, 66.65; H, 8.4; P, 12.3%).

In a similar way, 2-methoxy-6-methylphenol gave the t-1-(2-*methoxy*-6-*methylphenoxy*) *analogue* (68%), m.p. and mixed m.p. 132—132.5°.

Reactions with r-1-*Chloro*-2,2,c-3,4,4-*pentamethylphosphetan* 1-*Oxide*.—1-Hydroxy-2,2,3,4,4-pentamethylphosphetan 1-oxide (7.2 g) was stirred at room temperature with thionyl chloride (10 ml) and benzene (50 ml) for 4 h. Solvent and excess of reagent were then removed at room temperature under reduced pressure and finally at 1.5 mmHg. The residual 1-chlorophosphetan (*cis* : *trans* 3 : 1) in THF (20 ml) was added slowly to a stirred solution of phenol (3.95 g) and triethylamine (4.9 g) in THF (80 ml) and the solution refluxed for 16 h and cooled. Filtration and evaporation gave an oil which was chromatographed on alumina. Elution with dichloromethane gave 2,2,3,4,4-pentamethyl-1-phenoxyphosphetan 1-oxide (35%) as a mixture of *cis*- and *trans*-isomers in a ratio of 3 : 1. The *cis*-isomer had δ (100 MHz) 0.96 (3 H, dd, *J* 1 and 7 Hz), 1.21 (6 H, d, *J* 19 Hz), 1.39 (6 H, d, *J* 20 Hz), and 6.94—7.60 (5 H, m).

A similar experiment using catechol gave only the *trans*-(*o*-hydroxyphenoxy) isomer (65%), m.p. and mixed m.p. 114—115°.

P-*Trimethylsilyloxy*-2-*spirobi*-(1,3,2-*benzodioxaphosphole*).—Triethylamine (1.16 g) in THF (5 ml) was added slowly to a stirred solution of *P*-chloro-2-spirobi-(1,3,2-benzodioxaphosphole) [15] (1.62 g) in THF (40 ml) at 0 °C followed by water (0.103 g) in THF (10 ml). The ^{31}P spectrum, taken at room temperature, then showed a broad absorption at +26.4 p.p.m. Chlorotrimethylsilane (0.62 g) in THF (5 ml) was then added to the solution at 0 °C and the mixture stirred at room temperature for 1 h and filtered. Evaporation of the filtrate and crystallisation of the residue from light petroleum gave the title phosphorane, m.p. 106—112°, δ 0.14 (9 H, s) and 6.77—7.23 (8 H, m), δ_P +30.4 p.p.m. (lit.,[7] m.p. 110—112°, δ 0.15, δ_P 30.5 p.p.m.), M^+ 336.

We thank the S.R.C. for support and Dr. A. Denes for help in the phosphinothioate work.

[8/109 *Received*, 23*rd January*, 1978]

REFERENCES

[1] F. H. Westheimer, *Accounts Chem. Res.*, 1969, **1**, 70.
[2] S. Trippett, *Phosphorus and Sulphur*, 1976, **1**, 89.
[3] N. A. Razumova and A. A. Petrov, *J. Gen. Chem.* (*U.S.S.R.*), 1963, **33**, 3796; N. A. Razumova, Zh. L. Evtikov, A. K. Voznesenskaya, and A. A. Petrov, *ibid.*, 1969, **39**, 162.
[4] F. V. Bagrov and N. A. Razumova, *J. Gen. Chem.* (*U.S.S.R.*), 1970, **40**, 2557; F. V. Bagrov, N. A. Nazumova, and A. A. Petrov, *ibid.*, 1972, **42**, 782; N. A. Razumova, N. A. Kurshakova, and A. A. Petrov, *ibid.*, 1975, **45**, 686; N. A. Kurshakova and N. A. Razumova, *ibid.*, 1976, 1023.
[5] G. Aksnes and P. Albriktsen, *Acta Chem. Scand.*, 1968, **22**, 1866.
[6] C. Bui Cong, A. Munoz, M. Sanchez, and A. Klaebe, *Tetrahedron Letters*, 1977, 1587.
[7] F. Ramirez, M. Nowakowski, and J. F. Marecek, *J. Amer. Chem. Soc.*, 1977, **99**, 4515.
[8] F. Ramirez, *Accounts Chem. Res.*, 1969, **1**, 168.
[9] For a preliminary account of some of this work see G. Kemp and S. Trippett, *Tetrahedron Letters*, 1976, 4381.
[10] S. A. Bone, S. Trippett, M. W. White, and P. J. Whittle, *Tetrahedron Letters*, 1974, 1795.
[11] W. Hawes and S. Trippett, *J. Chem. Soc.* (*C*). 1969, 1465.
[12] J. R. Shutt, Ph.D. Thesis, University of Leicester, 1969.
[13] J. R. Corfield, N. J. De'ath, and S. Trippett, *Chem. Comm.*, 1970, 1502.
[14] A. Munoz, M. Gallagher, A. Klaebe, and R. Wolf, *Tetrahedron Letters*, 1976, 673.
[15] F. Ramirez, A. J. Bigler, and C. P. Smith, *Tetrahedron*, 1968, **24**, 5041.