The Stereochemistry of Nucleophilic Substitution at Phosphorus in P^{III} and P^{V} Phosphetans

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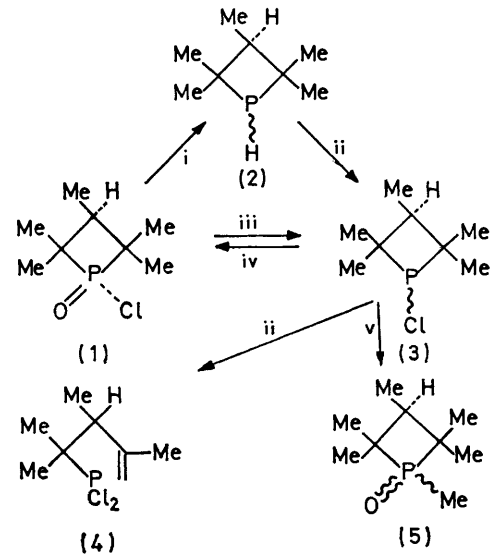
Nucleophilic substitution of the chlorine atom in 1-chloro-2,2,3,4,4-pentamethylphosphetan occurs with inversion of configuration at phosphorus. Several stereochemical cycles based on this compound and involving phosphetan 1-oxides and 1-sulphides are described. They support the generalisation that nucleophilic substitution of electronegative groups in phosphetan oxides and sulphides occurs with retention of configuration at phosphorus.

We have previously presented evidence to show that nucleophilic substitution of electronegative groups at the phosphorus atom of 2,2,3,4,4-pentamethylphosphetan 1-oxides proceeds with retention of configuration at phosphorus,[1,2] and in a preliminary communication [3] have described the nucleophilic substitution, with inversion of configuration at phosphorus, of the chlorine atom of 1-chloro-2,2,3,4,4-pentamethylphosphetan. This paper gives full details of the preparation and reactions of this last compound and describes an interlocking pattern of substitutions, involving both isomeric series of pentamethylphosphetan 1-oxides and 1-sulphides, which fully supports the foregoing generalisations.[4]

Reduction of *r*-1-chloro-2,2-*t*-3,4,4-pentamethylphosphetan 1-oxide (1) with trichlorosilane in ether or with phenylsilane at 120° gave the secondary phosphine (2). When freshly and carefully distilled this showed PH absorption in the n.m.r. at τ 6·28 (J_{PH} 170 Hz), but this was absent in old or impure samples, presumably because of rapid exchange with protonic impurities. The n.m.r. spectrum was consistent with the presence of only one isomer. The low coupling constant indicates a high degree of p^3 hybridisation of the phosphorus atom,[5] probably in order to relieve strain in the four-membered ring. With 1 mol. equiv. of chlorine, the secondary phosphine (2) gave the 1-chlorophosphetan (3), which was more readily obtained directly from the oxide (1) by reduction with a polymethylsiloxane at 160°. This reduction gave a mixture of the secondary phosphine (2) and the 1-chlorophosphetan (3), which could be separated by distillation or converted entirely into the latter by treatment with an amount of chlorine equivalent to the content of (2). An excess of chlorine had to be avoided, as the chlorophosphetan (3) underwent ring opening on treatment with chlorine [6] to give the dichlorophosphine (4).

Every sample of the chlorophosphetan (3) prepared contained the same proportions of geometrical isomers as shown by the n.m.r. spectrum. The major isomer was *r*-1-chloro-2,2,*t*-3,4,4-pentamethylphosphetan: oxidation of the mixture with hydrogen peroxide gave a 74% yield of pure (1). Treatment of the crude product from this oxidation with methylmagnesium iodide gave a mixture of isomeric 1-methyl oxides (5) in the ratio of 3·8 : 1, the *trans*-isomer predominating, and a mixture of isomers in the same proportions was obtained directly from (3) by treatment with sodium methoxide in methanol. The



Reagents: i, $HSiCl_3$ or $PhSiH_3$; ii, Cl_2; iii, $[MeSiHO]_n$; iv, H_2O_2; v, MeOH–MeO^- or H_2O_2 then MeMgI

last reaction involves rearrangement of the intermediate phosphinites; as reactions of compound (1) with Grignard reagents proceed with retention of configuration at phosphorus it follows that substitution of the chlorine atom of (3) with methoxide leads to inversion at phosphorus.

A similar conclusion emerged from the reaction of the chlorophosphetan (3) with benzylamine. Oxidation of the crude product gave a mixture of isomeric phosphinamides in the ratio of 3·8 : 1, the *cis*-isomer (6) predominating. This mixture could be separated by column chromatography. As benzylamine and the phosphinic chloride (1) gave the *trans*-phosphinamide (7) with retention of configuration at phosphorus,[1] it follows that substitution of the chlorine atom of (3) with benzylamine leads to inversion at phosphorus. Similar results were obtained with aniline.

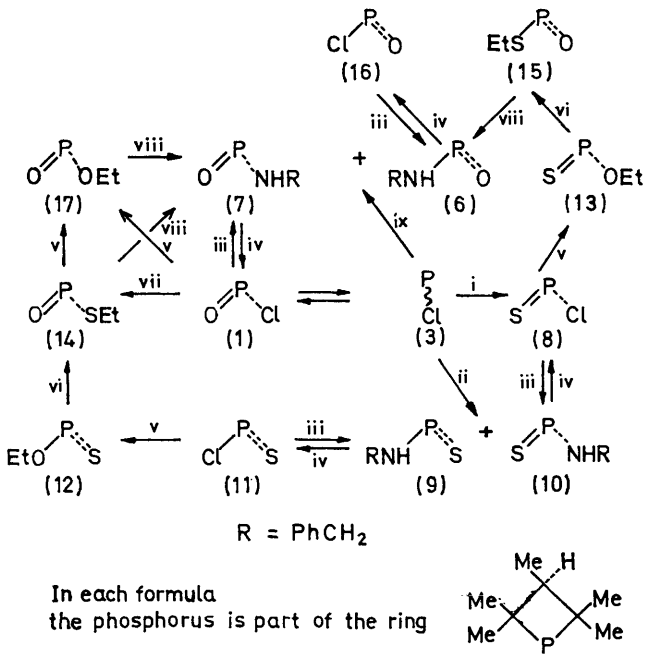
On the other hand, treatment of the chlorophosphetan

[1] W. Hawes and S. Trippett, *J. Chem. Soc.* (*C*), 1969, 1465.
[2] J. R. Corfield, N. J. De'ath, and S. Trippett, *Chem. Comm.*, 1970, 1502.
[3] D. J. H. Smith and S. Trippett, *Chem. Comm.*, 1969, 855.
[4] For a review of other work on the stereochemistry of substitutions in phosphetans see K. Mislow, *Accounts Chem. Res.*, 1970, **3**, 321.
[5] S. L. Manatt, G. L. Juvinal, R. I. Wagner, and D. D. Elleman, *J. Amer. Chem. Soc.*, 1966, **88**, 2689.
[6] J. R. Corfield, M. J. P. Harger, R. K. Oram, D. J. H. Smith, and S. Trippett, *Chem. Comm.*, 1970, 1350.

(3) with phenyl-lithium in ether gave, after oxidation, a mixture of *cis*- and *trans*-1-phenylphosphetan 1-oxides in the ratio of 65 : 35. The loss of stereospecificity was due to equilibration of the 1-phenylphosphetans in the presence of phenyl-lithium; this was demonstrated in a separate experiment. The equilibrium composition was similar to that established thermally.[7]

Several stereochemical interconversion cycles involving the chlorophosphetan (3) are now described. They are all consistent with a general pattern of nucleophilic substitution in (3) with inversion at phosphorus and nucleophilic substitution in phosphetan 1-oxides and 1-sulphides with retention at phosphorus. We have previously[8] presented evidence in support of the configurations assigned to the phosphetan 1-oxides based on the changes in their n.m.r. spectra in the presence of tris(dipivalomethanato)europium(III).

Treatment of the chlorophosphetan (3) with sulphur

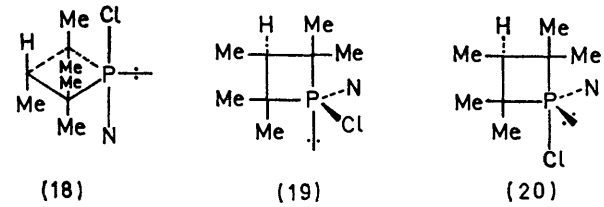


Reagents: i, S_8; ii, $PhCH_2{\cdot}NH_2$ then S_8; iii, $PhCH_2{\cdot}NH_2$; iv, $HCl{-}C_6H_6$; v, EtOH–EtO^-; vi, EtI; vii, Et_2O–EtSNa; viii, $LiNH{\cdot}CH_2Ph$; ix, $PhCH_2{\cdot}NH_2$ then H_2O_2

gave a mixture of isomeric phosphinothioic chlorides from which the *trans*-isomer (8) was readily obtained by chromatography on alumina. Treatment of (3) with benzylamine followed by sulphur gave a mixture of isomeric phosphinothioic amides separable by chromatography into the *cis*- (9) and *trans*- (10) forms. The minor isomer (10) was the same as that obtained from the phosphinothioic chloride (8) and benzylamine. This isomer re-formed the *trans*-phosphinothioic chloride (8) when treated with hydrogen chloride in benzene;[9] the major isomer (9) gave the *cis*-phosphinothioic chloride (11) under these conditions. Benzylamine and (11) re-formed the *cis*-phosphinothioic amide (9), and ethanolic sodium ethoxide and (11) gave the *cis*-ester (12), isomeric with the *trans*-ester (13) obtained from the *trans*-phosphinothioic chloride (8). Pistschimuka reactions on these isomeric *cis*- and *trans*-*O*-ethyl esters gave the *trans*- (14) and *cis*- (15) *S*-ethyl esters, respectively. These were also obtained from the respective *trans*- (1) and *cis*- (16) phosphinic chlorides on treatment with sodium ethanethiolate. The *cis*-phosphinic chloride (16) was formed from the *cis*-phosphinic amide (6) and hydrogen chloride in benzene.

The ethylthio-group of the *trans*-*S*-ethyl ester (14) was slowly displaced by ethoxy on treatment with ethanolic sodium ethoxide at room temperature, the product (17) being the same as that obtained directly from the *trans*-phosphinic chloride and ethoxide. With *N*-lithiobenzylamine the *trans*-*S*-ethyl ester (14) gave the *trans*-phosphinic amide (7), whereas the *cis*-*S*-ethyl ester (15) gave only the *cis*-phosphinic amide (6).

Nucleophilic substitution at phosphorus in the chlorophosphetan (3) with inversion of configuration requires either apical attack of the nucleophile to give the intermediate (18) or equatorial attack to give the intermediate (19). Equatorial attack at tetrahedral phosphorus has not so far been identified, and there is no obvious reason why (19) should be formed in preference to (20), which would lead to retention of configuration at phosphorus and would be more stable than (19) on stereoelectronic



(electronegativity) grounds. On the other hand, in (18) the four-membered ring spans two equatorial positions. In substitutions at phosph(v)etans this would involve at least 20 kcal mol^{-1} of ring strain compared with the intermediate in which the ring spanned an apical and an equatorial position.[2,10] However because of lone-pair repulsion in structure (18) the ring strain is probably much less than this and is more than balanced by the stereoelectronic gain in having two electronegative substituents occupying apical positions.

EXPERIMENTAL

All experiments involving tervalent phosphorus compounds were carried out under oxygen-free nitrogen. ^{31}P Chemical shifts are given relative to 85% phosphoric acid.

2,2,3,4,4-*Pentamethylphosphetan*.—Phenylsilane (3·9 g) was added to *r*-1-chloro-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide (7·0 g) at 0°; the mixture was kept at room tem-

[7] S. E. Cremer, R. J. Chorvat, C. H. Chang, and D. W. Davis, *Tetrahedron Letters*, 1968, 5799.
[8] J. R. Corfield and S. Trippett, *Chem. Comm.*, 1971, 721.
[9] K. Ellis, D. J. H. Smith, and S. Trippett, *J.C.S. Perkin I*. in the press.
[10] A. Duff, R. K. Oram, and S. Trippett, *Chem. Comm.*, 1971, 1011.

perature for 1 h and then slowly heated to 120° over a further 1 h. After 1 h at 120° distillation gave 2,2,3,4,4-*pentamethylphosphetan* (4 g), b.p. 85—90° at 110 mmHg. Redistillation through a 60 cm spinning-band column gave the pure phosphetan, b.p. 80—81° at 80 mmHg, $\nu_{max.}$ 2160 and 2260 cm^{-1}, τ 6·28 (1H, d, J_{PH} 170 Hz), 7·66 (1H, q, J 7 Hz), 8·74 (6H, d, J 11 Hz), 8·80 (6H, d, J 14 Hz), and 9·17 (3H, d, J 7 Hz), ^{31}P n.m.r. signal at −23 p.p.m.

1-*Chloro*-2,2,3,4,4-*pentamethylphosphetan*.—(*a*) A mixture of polymethylsiloxane (Hopkin and Williams MS 1107; 10 ml) and *r*-1-chloro-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide (9·7 g) was stirred and heated slowly to 160° over 1 h and kept at this temperature for a further 2 h. The volatile products (5·1 g) were then distilled at 6 mmHg into a receiver cooled in ice. Redistillation through a 60 cm spinning-band column gave 1-*chloro*-2,2,3,4,4-*pentamethylphosphetan*, b.p. 87° at 20 mmHg, τ 7·70 (1H, q, J 8 Hz), 8·75 (6H, d, J 20 Hz), 8·77 (6H, d, J 8 Hz), and 9·23 (3H, d, J 8 Hz), *m/e* 180, 178, 108, 95, 70, and 55. The minor isomer showed its presence through shoulders on the low-field parts of the doublets at τ 8·75 and 8·77.

(*b*) Chlorine (5 g) in carbon tetrachloride (6 ml) was added slowly to a stirred solution of 2,2,3,4,4-pentamethylphosphetan (10 g) in carbon tetrachloride (20 ml) at −20° and the mixture was set aside at room temperature for 2 h. Distillation gave the chlorophosphetan (9·6 g), b.p. 87° at 20 mmHg, having the same n.m.r. spectrum as the compound obtained in (*a*).

Reaction of 1-*Chloro*-2,2,3,4,4-*pentamethylphosphetan with Chlorine*.—Chlorine (0·64 g) in carbon tetrachloride (5 ml) was added to a stirred solution of the chlorophosphetan (1·6 g) in carbon tetrachloride (10 ml) at −20° and the mixture was set aside at room temperature for 3 h. Distillation gave *dichloro*-1,1,2,3-*tetramethylbut*-3-*enylphosphine* (0·9 g), b.p. 112° at 18 mmHg, τ 5·12 (2H, m), 7·43 (1H, m), 8·22 (3H, d, J 1 Hz), and 8·8 (9H, m), *m/e* 212, 101, 69, 54, and 41. The same product was obtained from phosgene and the chlorophosphetan.

Oxidation of 1-*Chloro*-2,2,3,4,4-*pentamethylphosphetan*.—The chlorophosphetan (0·824 g) in dichloromethane (10 ml) was added slowly to stirred hydrogen peroxide (30%; 10 ml) at 0° and the stirring was continued for 2 h at 0°. The organic layer was then washed with water and dried. Removal of solvent and crystallisation of the residue from light petroleum gave *r*-1-chloro-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide (0·625 g), m.p. and mixed m.p. 71—73°, n.m.r. spectrum identical with that of an authentic sample.

The crude product from a similar oxidation of 5·8 g of chlorophosphetan was dissolved in dry ether (50 ml) and methylmagnesium iodide (1·5M; 22 ml) was added dropwise with stirring. The solution was refluxed for 2 h and poured into 2N-hydrochloric acid (200 ml). The organic layer was washed with water, dried, and evaporated. Chromatography of the residue on alumina (200 g) and elution with ether–methanol (19 : 1) gave a white solid (3·8 g), which was a 3·8 : 1 mixture (n.m.r. spectrum) of isomeric 1,2,2,3,4,4-hexamethylphosphetan 1-oxides in which the *r*-1,*t*-3-isomer predominated.

Reaction of 1-*Chloro*-2,2,3,4,4-*pentamethylphosphetan with Sodium Methoxide*.—Methanol (8 ml) in which sodium (0·13 g) had been dissolved was added to the chlorophosphetan (0·99 g) in methanol (5 ml); the solution was kept at room temperature for 1 h and then evaporated. The residue was extracted with dichloromethane (10 ml) and the extract filtered and evaporated to give a white solid (0·72 g) which was a 3·8 : 1 mixture (n.m.r. spectrum) of isomeric 1,2,2,3,4,4-hexamethylphosphetan 1-oxides in which the *r*-1,*t*-3-isomer predominated.

Reaction of 1-*Chloro*-2,2,3,4,4-*pentamethylphosphetan with Benzylamine*.—Benzylamine (0·7 g) in carbon tetrachloride (5 ml) was added slowly to the chlorophosphetan (0·58 g) in carbon tetrachloride (5 ml) at room temperature and the mixture, after 4 h, was slowly added to hydrogen peroxide (30%; 10 ml) at 0° with stirring. After being stirred for 1 h at room temperature the organic layer was washed with water, dried, and evaporated. The residue was chromatographed on basic alumina (50 g). Elution with ether containing 1% methanol gave r-1-*benzylamino*-2,2,c-3,4,4-*pentamethylphosphetan* 1-*oxide*, m.p. 146° (from dichloromethane–light petroleum), τ 2·77 (5H, s), 5·9 (2H, t, J 9 Hz), 8·81 (6H, d, J 18 Hz), and 9·02 (6H, d, J 17 Hz), *m/e* 265, 195, 106, 91, 58, and 43 (Found: C, 67·8; H, 9·2; N, 5·4. $C_{15}H_{24}NOP$ requires C, 67·9; H, 9·1; N, 5·3%). Continued elution gave the *trans*-isomer,[1] m.p. and mixed m.p. 160—161°. The n.m.r. spectrum of the crude product before chromatography showed it to be a 3·7 : 1 mixture of isomers in which the *cis* predominated.

Reaction of 1-*Chloro*-2,2,3,4,4-*pentamethylphosphetan with Phenyl-lithium*.—Phenyl-lithium (1 equiv.) in ether (15 ml) was added slowly to the chlorophosphetan (1·39 g) in ether (10 ml) at 0°; the mixture was stirred at room temperature for 2 h and then added slowly to hydrogen peroxide (30%; 10 ml) at 0°. The organic layer was washed with water and dried and evaporated. The residue was chromatographed on basic alumina (60 g). Elution with ether–methanol (20 : 1) gave a white solid (1·30 g) whose n.m.r. spectrum showed it to be a 65 : 35 mixture of 2,2,3,4,4-pentamethyl-1-phenylphosphetan 1-oxides in which the *cis*-isomer predominated.

The same mixture of isomeric oxides (1·8 g) was obtained when *r*-1-phenyl-2,2,*t*-3,4,4-pentamethylphosphetan (2·1 g) in ether at room temperature was treated with phenyl-lithium (1 equiv.) and the reaction mixture worked up as before.

r-1-*Chloro*-2,2,t-3,4,4-*pentamethylphosphetan* 1-*Sulphide*.—Sulphur (0·6 g) was added slowly to chlorophosphetan (3·25 g) and aluminium chloride (0·12 g) at room temperature; the mixture was slowly heated to 80° and then dissolved in dichloromethane (40 ml). The solution was washed with water, dried, and evaporated. The residue was chromatographed on basic alumina (120 g). Elution with light petroleum gave r-1-*chloro*-2,2,t-3,4,4-*pentamethylphosphetan* 1-*sulphide* (2·6 g), m.p. 118—120° (from light petroleum), τ 7·75 (1H, m), 8·64 (6H, d, J 22 Hz), 8·70 (6H, d, J 25 Hz), and 9·07 ($3H_{III}$ dd, J 1 and 7 Hz), *m/e* 210, 140, 97, 95, and 70, ^{31}P n.m.r. signal at −137 p.p.m. (Found: C, 45·5; H, 7·7; P, 14·6; S, 15·4. $C_8H_{16}ClPS$ requires C, 45·6; H, 7·6; P, 14·7; S, 15·2%).

Reaction of r-1-*Ethoxy*-2,2,t-3,4,4-*pentamethylphosphetan* 1-*Sulphide with Ethyl Iodide*.—Ethanol (5 ml) in which sodium (0·164 g) had been dissolved was added slowly to the *trans*-phosphinothioic chloride (8) (1·49 g) in ethanol (5 ml) at room temperature; the solution was refluxed for 1 h and poured into water. The aqueous solution was extracted (3 ×) with dichloromethane and the combined extracts were dried and evaporated. Distillation of the residue gave r-1-*ethoxy*-2,2,t-3,4,4-*pentamethylphosphetan* 1-*sulphide* (1·38 g), b.p. 61° at 0·2 mmHg, τ 5·90 (2H, m), 7·93 (1H, m), 8·83 (6H, d, J 20 Hz), and 8·87 (6H, d, J 20 Hz), ^{31}P n.m.r. signal at −120·6 p.p.m. (Found: C, 54·5; H,

9·6; S, 14·45. $C_{10}H_{21}OPS$ requires C, 54·5; H, 9·6; S, 14·55%).

This compound (0·69 g) and ethyl iodide (3 ml) were heated in a sealed tube at 120° for 6 h; the product was dissolved in dichloromethane (20 ml), washed with dilute aqueous sodium thiosulphate and water, and dried. Evaporation of solvent and distillation of the residue gave r-1-*ethylthio*-2,2,c-3,4,4-*pentamethylphosphetan* 1-*oxide* (0·64 g), b.p. 80—82° at 0·25 mmHg, τ 7·29 (2H, m), 8·14 (1H, m), 8·82 (6H, d, *J* 18 Hz), and 8·97 (6H, d, *J* 21 Hz), ^{31}P n.m.r. signal at −74·6 p.p.m. (Found: C, 54·35; H, 9·7; P, 14·0; S, 14·4. $C_{10}H_{21}OPS$ requires C, 54·5; H, 9·6; P, 14·1; S, 14·55%).

r-1-*Benzylamino*-2,2,t-3,4,4-*pentamethylphosphetan* 1-*Sulphide*.—Benzylamine (2·25 g) in ether (20 ml) was added slowly to the *trans*-chlorophosphetan sulphide (1·98 g) in ether; the solution was refluxed for 1 week, then washed with 2N-hydrochloric acid and with water and dried. Evaporation and crystallisation of the residue from light petroleum gave r-1-*benzylamino*-2,2,t-3,4,4-*pentamethylphosphetan* 1-*sulphide* (2·6 g), m.p. 105—106°, τ 2·67 (5H, s), 5·67 (2H, d, *J* 5 Hz), 7·23br (1H, s), 7·7—8·1 (1H, m), 8·75 (6H, d, *J* 19 Hz), 8·80 (6H, d, *J* 16 Hz), and 9·07 (3H, dd, *J* 2 and 8 Hz), *m/e* 281, 249, 211, 179, 168, 136, 106, 97, and 91 (Found: C, 63·9; H, 8·5; N, 5·05. $C_{15}H_{24}NPS$ requires C, 64·1; H, 8·5; N, 5·0%).

r-1-*Benzylamino*-2,2,c-3,4,4-*pentamethylphosphetan* 1-*Sulphide*.—Benzylamine (25·4 g) in dichloromethane (100 ml) was added slowly to a stirred solution of chlorophosphetan (18·2 g) in dichloromethane (150 ml); the mixture was stirred at room temperature for 2 h and evaporated. The residue in benzene (100 ml) was cooled to 0° and stirred during the addition of sulphur (3·75 g) in small portions. The mixture was refluxed for 1 h, diluted with benzene (200 ml), washed with 2N-hydrochloric acid and water, and dried. Removal of solvent gave a white solid (30·9 g). This (15 g) was chromatographed on basic alumina (760 g). Elution with ether–light petroleum (1 : 1) gave *r*-1-benzylamino-2,2,*t*-3,4,4-pentamethylphosphetan 2-sulphide, m.p. and mixed m.p. 105—106°. Continued elution with the same solvent gave r-1-*benzylamino*-2,2,c-3,4,4-*pentamethylphosphetan* 1-*sulphide*, m.p. 83—84° (from dichloromethane–light petroleum), τ 2·57 (5H, s), 5·62 (2H, d, *J* 11 Hz), 5·80br (1H, s), 7·73—8·27 (1H, m), 8·78 (6H, d, *J* 21 Hz), and 8·93 (6H, d, *J* 18 Hz), *m/e* 281, 224, 178, 168, 136, 120, 106, 97, and 91 (Found: C, 63·8; H, 8·55; N, 5·15. $C_{15}H_{24}NPS$ requires C, 64·05; H, 8·5; N, 5·0%).

r-1-*Chloro*-2,2,c-3,4,4-*pentamethylphosphetan* 1-*Sulphide*.—A solution of the *cis*-phosphinothioic amide (9) (0·8 g) in benzene (20 ml) was saturated with dry hydrogen chloride and heated in a sealed tube at 120° for 8 h. The resulting suspension was filtered and the filtrate evaporated to give r-1-*chloro*-2,2,c-3,4,4-*pentamethylphosphetan* 1-*sulphide* (0·7 g), m.p. 121—122° (sealed capillary; from light petroleum), τ 7·73—8·17 (1H, m), 8·62 (6H, d, *J* 25 Hz), 8·58 (6H, d, *J* 18 Hz), and 8·98 (3H, dd, *J* 1 and 7 Hz). In a similar way the *trans*-phosphinothioic amide (8) gave an almost quantitative yield of the *trans*-phosphinothioic chloride (6), m.p. and mixed m.p. 118—120°.

Reaction of r-1-*Ethoxy*-2,2,c-3,4,4-*pentamethylphosphetan* 1-*Sulphide with Ethyl Iodide*.—Ethanol (10 ml) in which sodium (0·055 g) had been dissolved was added slowly to the *cis*-phosphinothioic chloride (9) (0·5 g) in ethanol (15 ml); the solution was refluxed for 1 h and diluted with dichloromethane (100 ml). The resulting solution was washed with water, dried, and evaporated. Distillation gave r-1-*ethoxy*-2,2,c-3,4,4-*pentamethylphosphetan* 1-*sulphide* (0·31 g), b.p. 100° (bath temp.) at 0·2 mmHg, τ 8·82 (6H, d, *J* 22 Hz), 8·80 (3H, t, *J* 8 Hz), 8·88 (6H, d, *J* 18 Hz), and 9·15 (3H, dd, *J* 2 and 7 Hz).

This ester (0·3 g) and ethyl iodide (3 ml) were heated in a sealed tube at 120° for 6 h. Dichloromethane (30 ml) was added and the solution was washed with dilute aqueous sodium thiosulphate and water and dried. Evaporation and distillation gave *r*-1-ethylthio-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide (0·28 g), b.p. 110° (bath temp.) at 0·2 mmHg, having i.r. and n.m.r. spectra identical with those of an authentic sample.

r-1-*Ethylthio*-2,2,t-3,4,4-*pentamethylphosphetan* 1-*Oxide* — The suspension formed on stirring sodium hydride (2·4 g) and ethanethiol (6·2 g) in ether (50 ml) for 2 h was added slowly to a stirred solution of *r*-1-chloro-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide (19·6 g) in ether (100 ml) at 0°; the mixture was refluxed for 1 h, filtered, and treated with water (100 ml). The organic layer was dried and evaporated and the residue distilled to give r-1-*ethylthio*-2,2,t-3,4,4-*pentamethylphosphetan* 1-*oxide* (16·7 g), b.p. 104—106° at 0·6 mmHg, τ 7·02 (2H, dq, *J* 7 and 8 Hz), 8·30 (1H, dq, *J* 4 and 7 Hz), 8·60 (3H, t, *J* 7 Hz), 8·67 (6H, d, *J* 19 Hz), 8·73 (6H, d, *J* 21 Hz), and 9·08 (3H, dd, *J* 1·5 and 7 Hz), *m/e* 220, 205, 191, 161, 150, 108, and 97 (Found: C, 54·4; H, 9·6; P, 13·9; S, 14·3. $C_{10}H_{21}OPS$ requires C, 54·5; H, 9·6; P, 14·05; S, 14·55%).

This ester (2·2 g) was added to ethanol (20 ml) in which sodium (0·23 g) had been dissolved; the solution was set aside at room temperature for 2 h. The ethanol was evaporated off and the residue partitioned between dichloromethane and water. The organic layer was dried and evaporated. The residue was shown by n.m.r. spectroscopy to contain only unchanged thio-ester (23%) and *r*-1-ethoxy-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide [1] (77%).

Reaction of r-1-*Ethylthio*-2,2,t-3,4,4-*pentamethylphosphetan* 1-*Oxide with* N-*Lithiobenzylamine*.—The *trans*-thioester (2·04 g) in ether (25 ml) was added to a solution of benzylamine (5·35 g) and butyl-lithium (2·5N; 4·0 ml) in ether (50 ml); the solution was kept at room temperature for 1 h and 2N-hydrochloric acid (10 ml) was then added. The organic layer was washed with water, dried, and evaporated. Crystallisation from dichloromethane–light petroleum gave *r*-1-benzylamino-2,2,*t*-3,4,4-pentamethylphosphetan 1-oxide (1·9 g), m.p. and mixed m.p. 159—160°.

The *cis*-thioester in the same way gave the *cis*-phosphinic amide (84%), m.p. and mixed m.p. 145—146°.

r-1-*Chloro*-2,2,c-3,4,4-*pentamethylphosphetan* 1-*Oxide*.—A suspension of *r*-1-benzylamino-2,2,*c*-3,4,4-pentamethylphosphetan 1-oxide (1·45 g) in benzene (50 ml) was saturated with dry hydrogen chloride and set aside at room temperature for 15 h. Filtration and evaporation of the filtrate gave r-1-*chloro*-2,2,c-3,4,4-*pentamethylphosphetan* 1-*oxide* (1·1 g), m.p. 55—59°, τ 8·60 (6H, d, *J* 21 Hz) and 8·77 (6H, d, *J* 23 Hz). With benzylamine (2 equiv.) in ether at room temperature the *cis*-phosphinic amide was reformed in almost quantitative yield.

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