Further Ring Openings and Ring Expansions of Phosphetans †

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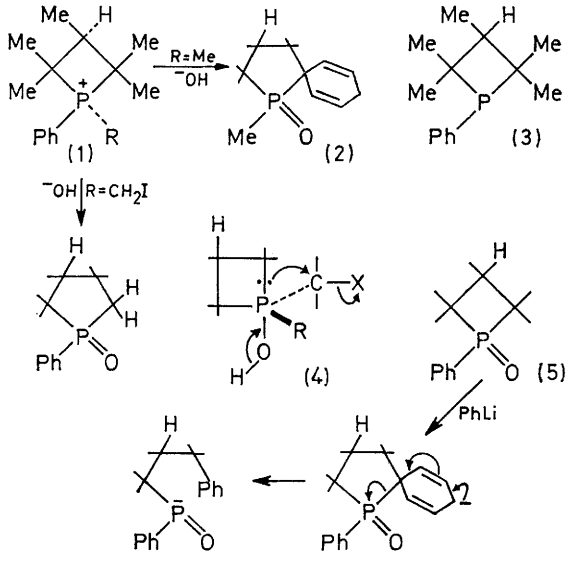
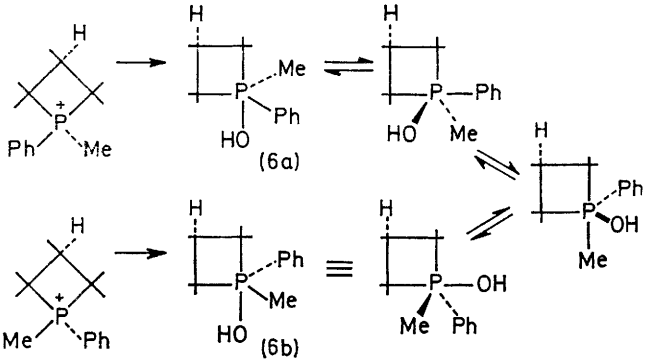
Further ring openings and ring expansions of phosphetans are described. Attempts to generate the ylide from 1,2,2,3,4,4-hexamethyl-1-phenylphosphetanium iodide led to ring opening *via* pentacovalent intermediates as also did the action of cyanide ion on this salt. Ring expansions of 2,2,3-trimethyl- and 2,2,3,3-tetramethyl-1-phenylphosphetan on reaction with ethyl propiolate in wet ether, on reaction with dimethyl acetylenedicarboxylate, and on hydrolysis of the iodomethylphosphetanium salts, occur with migration of the methylene and/or the isopropylidene group. 2,2,3-Trimethyl- and 2,2,3,3-tetramethyl-1-phenylphosphetan oxides are readily hydrolysed with dilute alkali with ring opening to give phosphinic acids.

We previously showed [1] that alkaline hydrolysis of the phosphetanium salt (1; R = Me) occurs with ring expansion to give the oxide (2) and found similar ring expansions on hydrolysis of the iodomethyl salt (1; R = CH_2I) and on reaction of the phosphine (3) with ethyl propiolate in wet ether.[2] These ring expansions conform to the general pattern (4), where X is capable of accommodating a negative charge, and owe their origin to the preference of the four-membered ring for the apical-equatorial position in the intermediate trigonal bipyramids and to the relief of steric strain on ring expansion. In some reactions, *e.g.* that of the oxide (5) with phenyl-lithium, feed-back of the negative charge leads to opening of the expanded ring.[2,3] This paper reports other ring openings and ring expansions of various substituted phosphetans.



The reported alkaline hydrolysis of the salt (1; R = Me) was carried out on the isomer shown, *i.e.* that with phenyl and 3-methyl groups on the same side of the ring. We now find that both pure geometrical isomers of (1; R = Me) give the same ring-expanded oxide (2), the geometry of which is unknown, presumably because rapid pseudorotation leads to equilibration of the intermediates (6a) and (6b). There is spectroscopic evidence of the presence of a small amount (<3%) of a second isomer of (2) but it could not be isolated.



Attempts to generate the methylene ylide from the salt (1; R = Me) by use of either sodamide in liquid ammonia or butyl-lithium failed because of ring-opening reactions of pentacovalent intermediates formed by nucleophilic attack on phosphorus. After hydrolysis and methylation with diazomethane of the product from the sodamide reaction, three crystalline compounds were isolated: the secondary phosphine oxide (7) and two diastereoisomers of the methyl phosphinate (8). These arise from the intermediate phosphorane (9) as shown. Treatment with methyl iodide of the product from the butyl-lithium reaction gave the phosphonium salt (10), formed *via* a similar sequence of reactions. Formation of products derived from intermediate pentacovalent phosphoranes has previously been noted [4] in the action of alkyl-lithiums on acyclic phosphonium salts.

A different type of ring opening occurred when the salt (1; R = Me) was treated with potassium cyanide; the products, isolated after oxidation, were the diastereoisomers of the tertiary alcohol (11). In neither case was the molecular ion observed in the mass spectrum. Dehydration of the major isomer gave the expected olefin. If the formation of the tertiary alcohols (11) involves the pentacovalent intermediate (12) the powerful inductive effect of the nitrile group induces ring opening

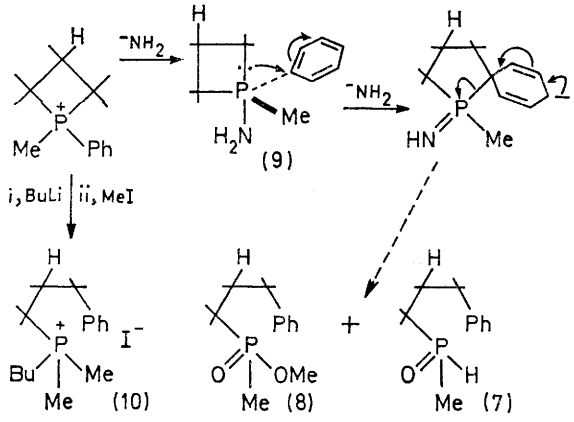
† *Note added in proof.* The stereochemical assignments in this paper should be reversed; see S. E. Cremer, *Chem. Comm.*, 1970, 616.

[1] S. E. Fishwick, J. Flint, W. Hawes, and S. Trippett, *Chem. Comm.*, 1967, 1113.

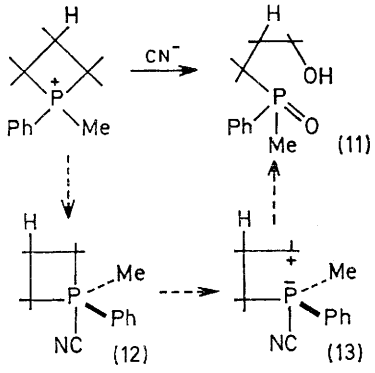
[2] W. Hawes and S. Trippett, *J. Chem. Soc.* (*C*), 1969, 1465.

[3] S. E. Cremer and R. J. Chorvat, *Tetrahedron Letters*, 1968, 413.

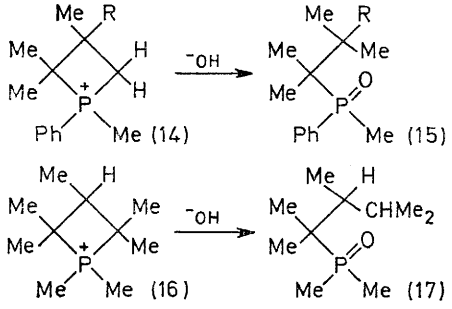
[4] D. Seyferth, J. K. Heeren, and W. B. Hughes, *J. Amer. Chem. Soc.*, 1962, **84**, 1764.



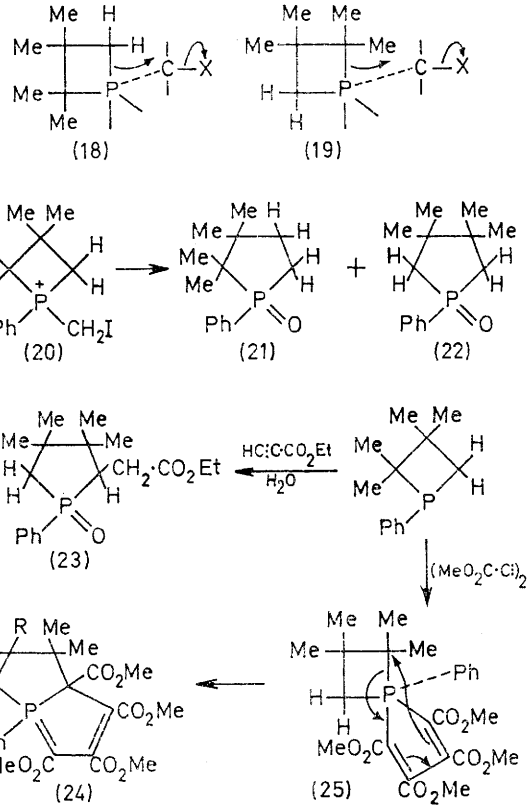
to give the carbonium ion (13) instead of the normally observed departure of an incipient anion.



Whereas the salt (1; R = Me) undergoes ring expansion on alkaline hydrolysis, Fishwick and Flint [5] showed that the corresponding 1,2,2,3-tetramethylphosphetanium salt (14; R = H) gave the ring-opened phosphine oxide (15; R = H) presumably because the $-CH_2^-$ system is more stable than $-Me_2C^-$. We find that the 1,2,2,3,3-pentamethylphosphetanium salt (14; R = Me) is hydrolysed in the same way to give the oxide (15; R = Me), and that 1,1,2,2,3,4,4-heptamethylphosphetanium iodide (16) is hydrolysed with expulsion from the intermediate of $-Me_2C^-$ to give the oxide (17).



Ring Expansions of 2,2,3,3-*Tetramethyl*-1-*phenylphosphetans*.—Ring expansions in this series occur with migration of both the CH_2 (18) and the CMe_2 (19) groups. Because the more electronegative group is apical the intermediate (18) would be expected to be more stable than (19). Reaction *via* the phosphorane (18) would be favoured if the migrating carbon developed anionic character in the transition state, while formation of the intermediate (19) could be favoured by steric factors including ease of access of the nucleophile.



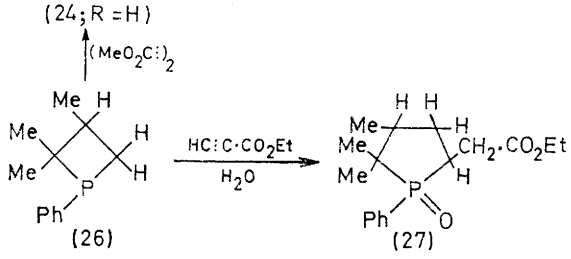
Alkaline hydrolysis of the iodomethyl salt (20) occurred with predominant migration of the methylene group to give largely the oxide (21), together with the isomeric oxide (22) (8%). However, reaction of the phenylphosphetan with ethyl propiolate in wet ether was accompanied by predominant migration of the CMe_2 group to give the oxide (23) with little of its isomer. Similarly, formation of the stable ylide (24; R = Me) from the phenylphosphetan and dimethyl acetylenedicarboxylate *via* the phosphorane (25) also involved migration of the CMe_2 group.[6]

The structures of these products of ring expansions were readily deduced from their n.m.r. spectra. Thus in the oxide (22) the methyl signals appeared as two 6H singlets, while in the oxide (21) the 3-methyl groups appeared as separate singlets but the 2-methyl groups each gave rise to a doublet, showing characteristic P–H coupling through three bonds.

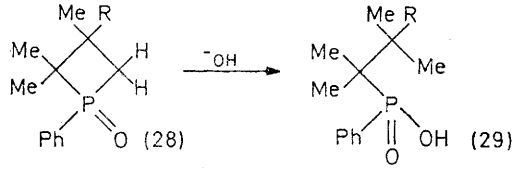
Ring Expansions of 2,2,3-*Trimethyl*-1-*phenylphosphetans*.—Here too, ring expansions involve migration of both the CH_2 and CMe_2 groups but the situation is complicated by geometrical isomerism round the ring

[5] S. E. Fishwick and J. A. Flint, *Chem. Comm.*, 1968, 182.
[6] For similar rearrangements see N. E. Waite, J. C. Tebby, R. S. Ward, and D. H. Williams, *J. Chem. Soc.* (*C*), 1969, 1100.

and by a general lack of crystallinity. A 19 : 1 mixture of the isomers of 2,2,3-trimethyl-1-phenylphosphetan (26) gave, with ethyl propiolate in wet ether, a mixture of the product (27) of CH_2 migration together with the product of CMe_2 migration. These were separated by chromatography but could not be differentiated on the basis of their spectra. The same mixture of isomeric phosphetans with dimethyl acetylenedicarboxylate gave a crystalline 1 : 2 adduct which, in the light of its n.m.r. spectrum, is probably the stable ylide (24; R = H) formed with migration of the CMe_2 group. The preferential migration of CMe_2 both in this case and in the corresponding reaction with the 2,2,3,3-tetramethylphosphetan may indicate that the flow of electrons is as in (25) and that the migrating centre acquires a positive charge in the transition state. Alkaline hydrolysis of the iodomethyl salt formed from the same phosphetan gave a noncrystalline mixture of phospholan oxides which could not be separated.



Alkaline Hydrolysis of 1-*Phenylphosphetan Oxides*.—Both isomers of the pentamethylphosphetan oxide (5) are stable in 10N-sodium hydroxide at 100° but the corresponding 2,2,3-trimethyl (28; R = H) and 2,2,3,3-tetramethyl (28; R = Me) oxides are readily hydrolysed in refluxing 2N-sodium hydroxide to give the phosphinic acids (29; R = H or Me). The alkaline hydrolysis of acyclic phosphine oxides normally requires fusion with sodium hydroxide [7] and involves expulsion from the phosphorus of the group which is most stable as the anion. The ready hydrolysis with ring fission of the oxides (28) is again a consequence of the preference of the four-membered ring for the apical-equatorial position in the intermediate trigonal bipyramids, and of the



relief of ring strain both in forming such intermediates and in their ring opening. The phosphinic acids (29) show in their mass spectra peaks corresponding to dimeric species. This behaviour of phosphinic acids has previously been noted by Dimroth.[8]

* *cis* and *trans* refer to the relative dispositions of the 1-phenyl and the 3-methyl groups.

[7] L. Horner, H. Hoffmann, and H. G. Wippell, *Chem. Ber.*, 1958, **91**, 64.

EXPERIMENTAL

Experiments involving trivalent phosphorus compounds were carried out under oxygen-free nitrogen. Except where stated ^1H n.m.r. spectra were recorded for solutions in deuteriochloroform with a Varian A-60 spectrometer. Mass spectra were determined with an A.E.I. MS9 instrument; in each case the molecular ion is given first followed by peaks of structural significance. Light petroleum had b.p. 40—60°.

1,2,2,3,4,4-*Hexamethyl*-cis-1-*phenylphosphetanium Iodide*.*—Trichlorosilane (6·4 g, 0·047 mol) in chloroform (20 ml) was added dropwise to a solution of 2,2,3,4,4-pentamethyl-*cis*-1-phenylphosphetan oxide (11·0 g, 0·047 mol) in chloroform (100 ml) with the temperature maintained at 0°. After 4 h stirring at 0°, excess of iodomethane was added and the solution was stirred for a further 24 h. Water (75 ml) was added and the resultant silica was filtered off. The organic layer was dried and evaporated to give the *phosphetanium salt* (15·6 g, 92%), m.p. 279—280° (from chloroform–ethyl acetate), $\nu_{max.}$ 1435, 1300, 1110, 914, 895, and 786 cm^{-1}, $\tau(CF_3{\cdot}CO_2H)$ 1·85—2·26 (5H), 6·97 (1H, quintet), 7·65 (3H, d, J_{PH} 13 Hz), 8·34 (6H, d, J_{PH} 20 Hz), 8·49 (6H, d, J_{PH} 20 Hz), and 8·79 (3H, dd, J 7, J_{PH} 1·5 Hz) (Found: C, 49·6; H, 6·6; P, 8·4. $C_{15}H_{24}IP$ requires C, 49·75; H, 6·7; P, 8·55%).

The phosphetanium iodide (2 g, 5·5 mmol) was stirred at room temperature with N-sodium hydroxide (20 ml) for 15 h. Ether extraction then gave a mixture of *phosphine oxides* (1·35 g, 97%). The n.m.r. spectrum ($CDCl_3$) due to the major isomer (>90%) (I) was identical with that described.[1] That of the minor isomer had peaks at τ 8·44 (d, J_{PH} 12·5 Hz, P–*Me*), 8·62, 8·78, 8·83, 8·92, 8·99, and 9·10; the other peaks were obscured by those of the major isomer. Recrystallization from ether–light petroleum (b.p. 40—60°) gave the pure major phosphine oxide (I) (1·23 g, 88%), m.p. 155—162° (freshly sublimed sample), n.m.r. and i.r. spectra identical with those described.[1]

2,2,3,4,4-*Pentamethyl*-trans-1-*phenylphosphetan Oxide*.—2,4,4-Trimethylpent-2-ene (28 g, 0·25 mol) was added slowly to a solution of aluminium chloride (33·3 g, 0·25 mol) and dichloro(phenyl)phosphine (45 g, 0·25 mol) in methylene chloride (150 ml); the temperature was maintained below 10°. After stirring for 2 h the solution was added slowly to ice–water (2 kg). The organic layer was washed with water, aqueous sodium hydroxide, and water, dried, and evaporated. The residue was chromatographed on basic alumina (750 g). Elution with ether–light petroleum (1 : 1) (500 ml) gave 2,2,3,4,4-pentamethyl-*cis*-1-phenylphosphetan oxide (2·5 g), m.p. and mixed m.p. 126—127°, n.m.r. spectrum identical with that of an authentic sample. Elution with ether–methanol (100 : 1; 3·5 l) gave pure 2,2,3,4,4-pentamethyl-*trans*-1-phenylphosphetan oxide (12·2 g, 21%), m.p. and mixed m.p.[2] 117—118°, n.m.r. spectrum identical with that of an authentic sample.

1,2,2,3,4,4-*Hexamethyl*-trans-1-*phenylphosphetanium Iodide*.—A solution of 2,2,3,4,4-pentamethyl-*trans*-1-phenylphosphetan oxide (5·9 g, 0·025 mol) in chloroform was reduced with trichlorosilane (3·4 g, 0·025 mol) as before, and then quarternised with iodomethane to give the *phosphetanium iodide* (8·2 g, 90%), m.p. 296—297°, $\nu_{max.}$ 1435, 1300, 1112, 908, 898, and 784 cm^{-1}, $\tau(CF_3{\cdot}CO_2H)$

[8] K. Dimroth, K. Vogel, W. Mach, and U. Schoeler, *Angew. Chem. Internat. Edn.*, 1968, **7**, 371.

1·95—2·50 (5H), 7·0 (1H, dq, *J* 7, J_{PH} 2 Hz), 7·60 (3H, d, J_{PH} 13·5 Hz), 8·36 (12H, d, J_{PH} 20 Hz), and 8·80 (3H, dd, *J* 7·0, J_{PH} 1·5 Hz) (Found: C, 49·7; H, 6·7; P, 8·3. $C_{15}H_{24}IP$ requires C, 49·75; H, 6·7; P, 8·55%).

The phosphetanium iodide (2 g, 5·5 mmol) was stirred at room temperature with N-sodium hydroxide (20 ml) for 15 h. Ether extraction then gave a mixture of phosphine oxides (1·34 g, 96%) whose n.m.r. spectrum ($CDCl_3$) was identical with that of the phosphine oxides obtained from hydrolysis of the *cis*-phosphetanium iodide. The pure major isomer (>90%) was obtained on recrystallization from ether–light petroleum (b.p. 40–60°) (1·21 g, 87%), m.p. and mixed m.p. 156—162° (freshly sublimed samples).

Reaction of Sodamide with 1,2,2,3,4,4-*Hexamethyl*-cis-1-*phenylphosphetanium Iodide*.—The phosphetanium iodide (2·5 g, 7·0 mmol) was dissolved with stirring in a solution of sodamide (280 mg, 7·0 mmol) in liquid ammonia (50 ml; freshly distilled from sodium). After 1 h under reflux the ammonia was evaporated off and dry benzene (50 ml) was added. The benzene solution was refluxed for ½ h, filtered, and added with stirring to 66% hydriodic acid (20 ml). The organic layer was separated, dried, and evaporated. The resulting viscous oil (630 mg) was dissolved in dry methanol (15 ml) and treated with an excess of diazomethane. The residue, after evaporation of the methanol, was chromatographed on basic alumina (75 g). Elution with ether–ethyl acetate (1 : 1) afforded *methyl methyl*-(1,1,2,3,3-*pentamethyl*-3-*phenylpropyl*)*phosphinate* (167 mg, 21%), m.p. 58—59° (from ether–light petroleum), $\nu_{max.}$ 1210, 1190, 1045, 885, 760, and 710 cm^{-1}, *m/e* 283, 282, 173, 164, 163, 119, 94, and 93, τ($CDCl_3$) 2·44—2·90 (5H), 6·36 (3H, d, J_{PH} 10 Hz), 7·15 (1H, sextet), 8·54 (3H, s), 8·68 (3H, d, *J* 7 Hz), 8·70 (3H, d, J_{PH} 12·5 Hz), 8·82 (3H, d, J_{PH} 17 Hz), 8·83 (3H, s), and 9·39 (3H, d, J_{PH} 19 Hz) (Found: C, 67·95; H, 9·7; P, 10·9. $C_{16}H_{27}O_2P$ requires C, 68·1; H, 9·6; P, 11·0%). Elution with ether–ethyl acetate (1 : 3) afforded the other *isomer* (175 mg, 23%), m.p. 66—67° (from ether–light petroleum), i.r. and mass spectra as just described, m.p. 58—59°, τ ($CDCl_3$) 2·47—3·05 (5H, m), 6·28 (3H, d, J_{PH} 10·0 Hz), 7·17 (1H, sextet), 8·54 (3H, s), 8·68 (3H, d, J_{PH} 12·5 Hz), 8·70 (3H, d, *J* 7 Hz), 8·80 (3H, d, J_{PH} 18 Hz), 8·82 (3H, s), and 9·36 (3H, d, J_{PH} 18·5 Hz) (Found: C, 68·0; H, 9·6; P, 10·8%). Elution with ethyl acetate afforded *methyl*-(1,1,2,3,3-*pentamethyl*-3-*phenylpropyl*)*phosphine oxide* (275 mg, 40%), m.p. 127—131° (from ether–light petroleum), $\nu_{max.}$ 2290, 1185, 1158, 760, and 710 cm^{-1}, *m/e* 252, 134, 133, 119, and 91, τ ($CDCl_3$) 2·4—3·0 (5H, m), −0·10 and 7·61 (1H, d, J_{PH} 468 Hz), 7·13 (1H, dq, *J* 7, J_{PH} 6 Hz), 8·53 (3H, s), 8·55 (3H, d, J_{PH} 11·5 Hz), 8·73 (3H, d, *J* 6·5 Hz), 8·75 (3H, s), 8·81 (3H, d, J_{PH} 20 Hz), and 9·36 (3H, d, J_{PH} 20·5 Hz) (Found: C, 71·3; H, 9·8; P, 12·2. $C_{15}H_{25}OP$ requires C, 71·4; H, 10·0; P, 12·3%).

Reaction of Butyl-lithium with 1,2,2,3,4,4-*Hexamethyl*-cis-1-*phenylphosphetanium Iodide*.—The phosphetanium iodide (500 mg, 1·38 mmol) was stirred with 1·8N-butyl-lithium (0·8 ml) in dry tetrahydrofuran (15 ml) at room temperature for 0·25 h. Excess of iodomethane was then added and the solution was stirred for a further 0·5 h. The solvent was removed and the residue, in chloroform (30 ml), was washed, dried, and evaporated. Successive recrystallizations of the residue gave *butyldimethyl*-(1,1,2,3,3-*pentamethyl*-3-*phenylpropyl*)*phosphonium iodide* (370 mg, 61%), m.p. 119—121°, $\nu_{max.}$ (KBr) 1095, 770, and 710 cm^{-1}, τ ($CDCl_3$) 2·1—3·0 (5H, m), 6·64—*ca.* 8·4 (7H, m, $[CH_2]_3$ and $PhCMe_2{\cdot}CH$), 7·96 (6H, d, J_{PH} 13 Hz), 8·47 (3H, d, *J* 6 Hz), 8·53 (3H, s), 8·74 (3H, s), 8·90 (3H, d, J_{PH} 20 Hz), 9·23 (3H, d, J_{PH} 20 Hz); the $Me[CH_2]_3$ signal was hidden under that from the other methyl protons (Found: C, 55·5; H, 8·3; P, 7·05. $C_{20}H_{36}IP$ requires C, 55·3; H, 8·35; P, 7·1%).

Reaction of Potassium Cyanide with 1,2,2,3,4,4-*Hexamethyl*-1-*phenylphosphetanium Iodide*.—The phosphetanium salt (4·7 g, 13·0 mmol; 3 : 2 isomer ratio) and potassium cyanide (850 mg, 13·0 mmol) in ethanol (100 ml) were refluxed for 60 h. The solvent was removed and a solution of the residue in chloroform was washed, dried, and evaporated. The residue was chromatographed on basic alumina (300 g). Elution with ether–methanol (100 : 1) gave one isomer of (3-*hydroxy*-1,1,2,3,3-*pentamethylpropyl*)*methyl*-(*phenyl*)*phosphine oxide* (1·94 g, 55%), m.p. 141—142° (from ether–light petroleum), $\nu_{max.}$ 3280, 1440, 1292, 1173, 1143, 1105, 1078, 882, 755, and 705 cm^{-1}, *m/e* (no molecular ion) 250, 182, 181, 140, 125, and 58, τ ($CDCl_3$) 2·03—2·63 (5H, m), 3·38br (1H, s), 8·07 (3H, d, J_{PH} 12 Hz), 8·67 (3H, s), 8·72 (3H, d, *J* 7 Hz), 8·82 (3H, d, J_{PH} 19 Hz), 8·89 (3H, d, J_{PH} 19 Hz), and 9·10 (3H, s); the $HO{\cdot}CMe_2{\cdot}CH$ signal was hidden under that from the lower-field methyl protons (Found: C, 67·3; H, 9·5. $C_{15}H_{25}PO_2$ requires C, 67·15; H, 9·4%). Elution with ether–methanol (100 : 2) afforded the other *isomer* (925 mg, 27%), m.p. 140—141° (from ether–light petroleum), $\nu_{max.}$ 3320, 1435, 1152, 1104, 1078, 868, 745, and 700 cm^{-1}, mass spectrum, identical with that just described, τ ($CDCl_3$) 2·08—2·95 (5H, m), 3·76br (1H, s), 8·13 (3H, d, J_{PH} 12 Hz), 8·68 (3H, d, J_{PH} 20 Hz), 8·75 (3H, s), 8·75 (3H, d, *J* 5 Hz), 8·84 (3H, d, J_{PH} 17 Hz), and 9·12 (3H, s); the $HO{\cdot}CMe_2{\cdot}CH$ signal was hidden under that of the lower-field methyl protons (Found: C, 67·0; H, 9·2; P, 11·55%). Elution with ether–methanol (100 : 3) gave the phosphine oxide (2) (160 mg, 5%), i.r. and n.m.r. spectra identical with those of an authentic sample.

A solution of the above alcohol (m.p. 141—142°) (500 mg, 1·87 mmol) and toluene-*p*-sulphonic acid monohydrate (199 mg, 1·0 mmol) in benzene (150 ml) was boiled under reflux for 6 h, with azeotropic separation of water (Dean–Stark). The solution was cooled and washed with a 5% aqueous solution of sodium hydrogen carbonate and with water. The dried benzene extract was evaporated to give (*methyl*)*phenyl*-(1,1,2,3-*tetramethylbut*-3-*enyl*)*phosphine oxide* (335 mg, 72%), m.p. 99—101° (from light petroleum), $\nu_{max.}$ 1630, 1435, 1298, 1160, 895, and 878 cm^{-1}, mass spectrum identical with that of the alcohol, τ($CDCl_3$) 2·1—2·65 (5H, m), 5·17br (2H, s), 7·17 (1H, dq, *J* 7, J_{PH} 1·5 Hz), 8·15 (3H, d, *J* 0·5 Hz), 8·23 (3H, d, *J* 12 Hz), 8·84 (3H, d, *J* 7 Hz), 8·90 (3H, d, *J* 15·5 Hz), and 8·94 (3H, d, *J* 17 Hz) (Found: C, 71·9; H, 9·3. $C_{15}H_{23}OP$ requires C, 72·0; H, 9·5%).

cis-1,2,2,3,4,4-*Hexamethylphosphetan Oxide*.*—Ethereal methylmagnesium iodide (2·0N; 25 ml) was added dropwise to a solution of 1-chloro-2,2,3,4,4-pentamethylphosphetan oxide (9·7 g, 0·05 mol) in ether (50 ml) with the temperature maintained at 0°. The solution was refluxed for 0·5 h, cooled to room temperature, and poured on a slurry of sulphuric acid (2·0N; 25 ml) and crushed ice (200 g). The organic layer was washed successively with water, dilute aqueous sodium hydrogen carbonate, and water, dried, and evaporated. The residue gave *cis*-1,2,2,3,4,4-hexamethylphosphetan oxide (7·1 g, 82%), m.p. 171—172° (from light petroleum), τ ($CDCl_3$) 8·44 (3H, d, J_{PH} 11·5 Hz), 8·73 (6H, d, J_{PH} 16 Hz), 8·83 (6H, d, *J* 18·5 Hz), and 9·08

* *cis* Refers to the relative dispositions of the 1- and 3-methyl groups.

(3H, dd, J, 7, J_{PH} 1 Hz); the signal from the ring proton was hidden under that from the lower-field methyl protons.

1,1,2,2,3,4,4-*Heptamethylphosphetanium Iodide*.—A solution of the aforementioned hexamethylphosphetan oxide (4·22 g, 0·03 mol) in chloroform was reduced with trichlorosilane (3·04 g, 0·03 mol) as described before and quaternised with iodomethane to give the *heptamethylphosphetanium iodide* (6·4 g, 88%), m.p. >335° (from water), $\nu_{max.}$ 1290, 965, 945, 910, 870, 770, and 735 cm^{-1}, τ (CF_3·CO_2H) 7·22 (1H, dq, J 7·5, J_{PH} 1·5 Hz), 7·84 (3H, d, J_{PH} 14 Hz), 7·90 (3H, d, J_{PH} 14 Hz), 8·50 (6H, d, J_{PH} 20 Hz), 8·57 (6H, d, J_{PH} 20 Hz), and 8·92 (3H, dd, J_{PH} 1·5 J 7·5 Hz) (Found: C, 40·0; H, 7·5; P, 10·2. $C_{10}H_{22}IP$ requires C, 40·0; H 7·4; P, 10·3%).

The heptamethylphosphetanium iodide (3·0 g, 0·01 mol) was stirred at room temperature with 2N-sodium hydroxide (20 ml) for 15 h. Ether extraction then gave dimethyl-(1,1,2,3-tetramethylbutyl)phosphine oxide (1·6 g, 84%), b.p. *ca.* 35° at 2 mmHg, $\nu_{max.}$ 1303, 1290, 1145, 930, 857, and 734 cm^{-1}, *m/e* 190, 147, 120, 77, and 43, τ ($CDCl_3$) 7·47—8·70 (2H, m), 8·57 (6H, d, J_{PH} 12·5 Hz), 8·85 (3H, d, J_{PH} 18 Hz), 8·92 (3H, d, J_{PH} 18 Hz), 8·97 (3H, s), 9·06 (3H, d, J 7 Hz), 9·12 (3H, s), and 9·14 (3H, d, J 7 Hz) (Found: C, 62·9; H, 12·1; P, 16·1. $C_{10}H_{23}OP$ requires C, 63·1; H, 12·1; P, 16·3%).

2,2,3,3-*Tetramethyl*-1-*phenylphosphetan*.— 2,2,3,3-Tetramethyl-1-phenylphosphetan oxide [9] (5·55 g, 0·025 mol) and silicon fluid (Hopkin and Williams MS1107; 5 g) were stirred at 140° for 4 h giving a bulky polymeric mass. Distillation yielded 2,2,3,3-tetramethyl-1-phenylphosphetan (3·64 g, 71%), b.p. 78° at 0·35 mmHg, n.m.r. spectrum as described by Chorvat and Cremer.[9]

1-*Iodomethyl*-2,2,3,3-*tetramethyl*-1-*phenylphosphetanium Iodide*.—Quaternisation of the aforementioned phosphetan with di-iodomethane in boiling benzene afforded the *iodomethylphosphetanium iodide* (72%), m.p. 214—215° (decomp.) (from methanol), $\nu_{max.}$ 1435 cm^{-1}, τ (CF_3·CO_2H) 1·75—2·30 (5H), 6·00 (2H, d, J_{PH} 6 Hz), 6·84 (2H, d, J_{PH} 14 Hz), 8·18 (3H, d, J_{PH} 22 Hz), 8·56 (3H, d, J_{PH} 24 Hz); 8·58 (3H, s), and 8·73 (3H, s) (Found: C, 35·25; H, 4·5; P, 6·8. $C_{14}H_{21}I_2P$ requires C, 35·5; H, 4·5; P, 6·5%).

1,2,2,3,3-*Pentamethyl*-1-*phenylphosphetanium Iodide*.—Quaternisation of the phosphetan with iodomethane in benzene at 40° yielded the *methylphosphetanium iodide* (85%), m.p. 193—194° [from acetone–dichloromethane (7 : 3)], $\nu_{max.}$ (KBr) 1440 cm^{-1}, τ ($CDCl_3$) 1·50—2·45 (5H), 6·35—6·90 (2H), 7·25 (3H, d, J_{PH} 14 Hz), 8·21 (3H, d, J_{PH} 21 Hz), 8·67 (3H, s), 8·73 (3H, d, J_{PH} 20 Hz), and 8·83 (3H, s) (Found: C, 48·5; H, 6·3; P, 8·5. $C_{14}H_{22}IP$ requires C, 48·3; H, 6·4; P, 8·9%).

Hydrolysis of 1-*Iodomethyl*-2,2,3,3-*tetramethyl*-1-*phenylphosphetanium Iodide*.—A solution of the salt (2·34 g, 4·95 mmol) in 0·5M-sodium hydroxide solution (40 ml) was boiled under reflux for 4 h. The mixture was extracted with ether, and the combined extracts were washed with water and dried. The solvent was evaporated off and the residue (0·88 g) was chromatographed on alumina (90 g). Elution with ether–methanol (24 : 1) afforded 2,2,3,3-*tetramethyl*-1-*phenylphospholan oxide* (21) (0·65 g, 2·74 mmol), m.p. 121—122° (from light petroleum), $\nu_{max.}$ (KBr) 1435, 1220, 1170, 1155, and 1110 cm^{-1}, *m/e* 236, 221, 194, 193, 180, 168, 140, 126, and 125, τ (CCl_4) 2·15—2·75 (5H), 7·45—8·60 (4H), 8·80 (3H, s), 8·97 (3H, d, J_{PH} *ca.* 14 Hz), 9·09 (3H, s), and 9·43 (3H, d, J_{PH} 16·5 Hz) (Found: C, 71·3; H, 8·8; P, 13·4. $C_{14}H_{21}OP$ requires C, 71·2; H, 8·9; P, 13·1%).

Continued elution gave a mixture of (21) and 3,3,4,4-*tetramethyl*-1-*phenylphospholan oxide* (22) [0·13 g, 0·56 mmol; ratio of (22) to (21) 1 : 2·3 by n.m.r. spectroscopy], which on repeated crystallization from light petroleum yielded pure (22) (0·040 g), m.p. 115—116°, $\nu_{max.}$ (KBr) 1435, 1180, 1150, and 1115 cm^{-1}, *m/e* 236, 221, 180, 179, 168, 165, 154, 140, and 125, τ (CCl_4) 2·00—2·75 (5H), 7·65—8·20 (4H), 8·78 (6H, s), and 8·98 (6H, s) (Found: C, 71·3; H, 9·0; P, 12·7. $C_{14}H_{21}OP$ requires C, 71·2; H, 8·9; P, 13·1%).

Reaction of 2,2,3,3-*Tetramethyl*-1-*phenylphosphetan with Dimethyl Acetylenedicarboxylate*.—The phosphetan (1·21 g, 5·87 mmol) in anhydrous benzene (10 ml) was added during 30 min to a stirred solution of dimethyl acetylenedicarboxylate (2·13 g, 15·0 mmol) in benzene (20 ml) at 0°. After 16 h at room temperature the bulk of the solvent was removed and ether (20 ml) was added to the residue. The precipitate (0·93 g) yielded, from ethanol, the pale yellow *phosphorane* (24; R = Me) (0·84 g, 29%), m.p. 221—222°, $\nu_{max.}$ (KBr) 1758, 1740, 1680, 1660, 1520, 1445, 1435, 1390, 1260, 1250, 1200, 1180, 1105, and 1090 cm^{-1}, *m/e* 491, 476, 460, 459, 432, 392, 359, 333, 320, 315, 155, and 139, τ ($CDCl_3$; 60°) 2·05—2·70 (5H), 6·07 (3H, s), 6·40 (3H, s), 6·55 (3H, s), 7·04 (3H, s), 7·13—7·42 (2H), 8·47 (3H, s), 8·55 (3H, s), 8·72 (3H, d, J_{PH} 2·2 Hz), and 8·87 (3H, s), τ ($CDCl_3$; 0°) similar but resonance at τ 6·55, which becomes increasingly broad as the temperature is lowered, appears as two poorly resolved peaks (Δ 1·5 Hz), τ (C_6H_6) 6·05 (3H, s), 6·46 (3H, s), 6·54br (3H, s), 7·32 (3H, s), 7·50—7·92 (2H), 8·28 (3H, s), 8·76 (3H, s), 8·90 (3H, s), and 9·17 (3H, d, J_{PH} 2·2 Hz), τ (CF_3·CO_2H) 1·65—2·40 (5H), 4·51br (1H, d, J_{PH} 17 Hz), *ca.* 5·7—7·4 (*ca.* 2H), 5·95 (*ca.* 6H, s), 6·03br (*ca.* 3H, s), 6·38br (*ca.* 3H, s), and 8·52br (12H, s with high-field shoulder) (Found: C, 61·2; H, 6·4; P, 6·1. $C_{25}H_{31}O_8P$ requires C, 61·2; H, 6·4; P, 6·3%).

Reaction of 2,2,3,3-*Tetramethyl*-1-*phenylphosphetan with Ethyl Propiolate*.—Ethyl propiolate (1·08 g, 11·0 mmol) in moist ether (10 ml) was added during 5 min to the phosphetan (2·06 g, 10·0 mmol) in moist ether (30 ml) stirred at room temperature. After boiling under reflux for 20 h, addition of iodomethane produced no precipitate. Volatile material was removed and the residue was chromatographed on alumina. Repeated chromatography gave 5-*ethoxycarbonylmethyl*-2,2,3,3-*tetramethyl*-1-*phenylphospholan oxide* (<1% isolated), m.p. 75—79° and 86—87° (from ether–light petroleum), $\nu_{max.}$ (KBr) 1730, 1440, 1250, and 1160 cm^{-1}, *m/e* 322, 277, 237, 235, 209, 195, 168, and 125, τ ($CDCl_3$) 1·95—2·65 (5H), 5·93 (2H, q, J 7 Hz), 6·80—8·30 (5H), 8·82 (3H, d, J_{PH} 13 Hz), 8·90 (3H, s, and 3H, t, J 7 Hz), 9·07 (3H, s), and 9·30 (3H, d, J_{PH} 17 Hz), and 2-*ethoxycarbonylmethyl*-3,3,4,4-*tetramethyl*-1-*phenylphospholan oxide* (7·16 mmol, 72%), b.p. 170° (block temp.) at 0·2 mmHg, $\nu_{max.}$ (film) 1735, 1440, 1190, and 1170 cm^{-1}, *m/e* 322, 277, 235, 180, 179, and 125, τ ($CDCl_3$) 1·91—2·65 (5H), 6·07 (2H, q, J 7 Hz), 6·22—7·94 (5H), 8·87 (3H, s), 8·90 (3H, s), 8·92 (3H, s), 8·97 (3H, t, J 7 Hz), and 9·00 (3H, s) (Found: C, 67·0; H, 8·6; P, 9·2. $C_{18}H_{27}O_3P$ requires C, 67·1; H, 8·4; P, 9·6%). Solvated crystals, m.p. 35—37°, were obtained by crystallisation from ether–light petroleum.

Hydrolysis of 1,2,2,3,3-*Pentamethyl*-1-*phenylphosphetanium Iodide*.—The salt (2·09 g, 6·00 mmol) was stirred with 0·5M-sodium hydroxide (50 ml) at 106° for 4 h, and the colourless oil which separated was extracted with ether. The combined extracts were washed with water, dried, and

[9] S. E. Cremer and R. J. Chorvat, *J. Org. Chem.*, 1967, **32**, 4066.

concentrated to an oil which showed no absorption at τ 3·3—5·3 (vinylic H). Chromatography on alumina afforded *(methyl)phenyl-(1,1,2,2-tetramethylpropyl)phosphine oxide* (1·26 g, 88%), m.p. 84—85° (from light petroleum), $\nu_{max.}$ (KBr) 1445, 1225, 1170, and 1160 cm^{-1}, *m/e* 238, 223, 182, 181, 140, 139, and 125, τ ($CDCl_3$) 1·95—2·75 (5H), 8·20 (3H, d, J_{PH} 12 Hz), 8·83 (3H, d, J_{PH} 17 Hz), 8·93 (9H, s), and 8·97 (3H, d, J_{PH} 17 Hz), τ (C_6H_6) 8·60 (3H, d, J_{PH} 12 Hz), 8·90 (9H, s), 9·08 (3H, d, J_{PH} 17 Hz), and 9·17 (3H, d, J_{PH} 17 Hz) (Found: C, 70·8; H, 9·9; P, 12·7. $C_{14}H_{23}OP$ requires C, 70·6; H, 9·7; P, 13·0%).

Reaction of 2,2,3-Trimethyl-1-phenylphosphetan with Ethyl Propiolate.—Ethyl propiolate (0·5 g) in ether (10 ml) was added dropwise to the phosphetan [9] (1 g; 19 : 1 isomer ratio) in moist ether (25 ml) at 0° and the mixture was stirred at room temperature for 3 h. Solvent was then removed and the residue was chromatographed on silica (25 g). Elution with ether gave one isomer of ethoxycarbonylmethyl-trimethyl-1-phenylphospholan oxide (0·15 g), b.p. 140° at 2 mmHg, $\nu_{max.}$ 1732, 1440, 1260—1160, 1115, 1040, and 1035 cm^{-1}, *m/e* 308, 293, 279, 263, 247, 235, 224, 209, 195, and 108 (Found: H, 8·5; P, 9·9. $C_{17}H_{25}O_3P$ requires H, 8·1; P, 10·1%). Elution with ether–methanol (20 : 1) gave a second isomer (0·72 g), b.p. 120° at 2 mmHg, $\nu_{max.}$ 1730, 1437, 1280—1160, 1120, 1040, and 860 cm^{-1}, mass spectrum, as for the first isomer (Found: H, 8·4; P, 9·6%). Neither isomer gave a satisfactory analysis for carbon.

Reaction of 2,2,3-Trimethyl-1-phenylphosphetan with Dimethyl Acetylenedicarboxylate.—Dimethyl acetylenedicarboxylate (1·7 g) in benzene (25 ml) was added slowly to a stirred solution of the phosphetan (0·8 g; 19 : 1 isomer ratio) in benzene at 0°. After a further 1 h solvent was removed. Crystallization of the residue from ether gave the yellow *phosphorane* (24; R = H) (44%), m.p. 215—217°, $\nu_{max.}$ 1745, 1715, 1690, 1660, 1575, 1440, and 1180 cm^{-1}, *m/e* 476, 417, and 109, τ 2·1—2·67 (5H, m), 6·02 (3H, s), 6·35 (3H, s), 6·46 (3H, s), 7·13 (3H, s), 8·45 (3H, s), 8·73 (3H, d, *J* 6 Hz), and 8·98 (3H, s) (Found: C, 60·4; H, 6·1; P, 6·2. $C_{24}H_{29}O_8P$ requires C, 60·5; H, 6·1; P, 6·5%).

Hydrolysis of 1-Iodomethyl-2,2,3-trimethyl-1-phenylphosphetanium Iodide.—Di-iodomethane (4 g) and 2,2,3-trimethyl-1-phenylphosphetan (2 g; 19 : 1 isomer ratio) were refluxed in benzene (30 ml) for 5 h to give the *iodomethyl salt* (60%), m.p. 214—215° (from butanol), $\nu_{max.}$ 1440, 1122, 850, 809, 760, and 695 cm^{-1} (Found: C, 33·8; H, 4·2; I, 54·8; P, 6·8. $C_{13}H_{19}I_2P$ requires C, 33·9; H, 4·1; I, 55·2; P, 6·7%).

The salt (1 g) in 2N-sodium hydroxide solution (30 ml) and ethanol (2 ml) was heated at 100° for 3 h. The mixture was extracted with methylene chloride and the combined extracts were washed with water and dried. The solvent was removed and the residue was chromatographed on alumina (20 g). Elution with ether–methanol (100 : 1) gave a mixture of 2,2,3-trimethyl- and 3,3,4-trimethyl-1-phenylphospholan oxide (73%), b.p. 115° at 1 mmHg, $\nu_{max.}$ 1440, 1185, 1150, 1119, and 1096 cm^{-1}, *m/e* 222, 207, 182, 168, 140, 125, and 108, τ 2·1—2·7 (5H, m) and 7·3—9·67 (14H, m).

Alkaline Hydrolysis of Phosphetan Oxides.—The oxide (1 g) was refluxed in 2N-sodium hydroxide (40 ml) and ethanol (10 ml) and the solution was extracted with methylene chloride to remove unchanged oxide. Acidification of the aqueous layer followed by extraction with methylene chloride gave the phosphinic acid. In this way 2,2,3,3-tetramethyl-1-phenylphosphetan oxide gave, after 48 h under reflux, unchanged oxide (53%) and *1,1,2,2-tetramethylpropylphenylphosphinic acid* (44%), m.p. (from water) 169—171°, $\nu_{max.}$ 2280, 1740, 1468, 1181, 1120, 1070, 973, and 949 cm^{-1}, *m/e* 480, 381, 362, 339, 317, 240, 225, 198, 184, 161, and 142, τ −2·45 (s, 1H), 2·08 — 2·82 (m, 5H), 9·03 (d, 6H, J_{PH} 17 Hz), and 9·05 (s, 9H) (Found: C, 63·8; H, 8·6; P, 13·2. $C_{13}H_{21}O_2P$ requires C, 65·0; H, 8·75; P, 12·9%). After 72 h under reflux 2,2,3-trimethyl-1-phenylphosphetan 1-oxide gave *1,1,2-trimethylpropylphenylphosphinic acid* (88%), m.p. (from water) 91—93°, $\nu_{max.}$ 2280, 1740, 1465, 1220, 1150, 1110, 970, 780, and 761 cm^{-1}, *m/e* 452, 367, 267, 226, 210, 183, and 141, τ −1·95 (s, 1H), 2·15—2·8 (m, 5H), 9·07 (d, 6H, J_{PH} 17 Hz), and 9·16 (d, 6H, *J* 7 Hz) (Found: C, 63·4; H, 8·4; P, 13·45. $C_{12}H_{19}O_2P$ requires C, 63·7; H, 8·4; P, 13·7%).

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