389. *Synthesis and Chemistry of Phospholes*

By I. G. M. Campbell, R. C. Cookson, M. B. Hocking, and A. N. Hughes

The preparation and properties of some phospholes (phosphacylopentadienes) are described. The product of the reaction of 1,2,5-triphenylphosphole with diazomethane is shown to be a cyclopropane derivative (XVI; R = H), but the reaction of the phosphole with methyl diazoacetate yields a compound for which the ring-expanded structure (XVIII; R = CO_2Me) cannot be rigorously excluded. Nuclear magnetic resonance spectra were important in determining these structures, and some interesting long-range couplings with phosphorus have been encountered.

In spite of the interesting question of the degree of aromaticity in the phosphole ring, there are few references [1-5] to the phosphorus analogue of pyrrole and its derivatives. However, several phosphacyclopentanes have been obtained [6] since the early synthesis

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[1] R. E. Donadio, Ph.D. Dissertation, Temple University, U.S.A., 1958.

[2] (*a*) F. C. Leavitt, T. A. Manuel, and F. Johnson, *J. Amer. Chem. Soc.*, 1959, **81**, 3163; (*b*) F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas, and D. S. Lehman, *ibid.*, 1960, **82**, 5099.

[3] E. H. Braye and W. Hübel, *Chem. and Ind.*, 1959, 250.

[4] E. H. Braye, W. Hübel, and I. Caplier, *J. Amer. Chem. Soc.*, 1961, **83**, 4406.

[5] I. G. M. Campbell and J. K. Way, *J.*, 1961, 2133.

[6] A. Furst and R. J. Horvat, *Science*, 1951, **114**, 330; B. Helferich and E. Aufderhaar, *Annalen*, 1962, **658**, 100.

of 1-phenyl-1-phosphacyclopentane,[7] and an easy preparation of the phosphacylcopent-3-enes has been patented by McCormack.[8] We were therefore tempted to try dehydrogenation of this type of compound as a route to the phosphole ring system. A Note [9] described our preliminary results, and we now report details and further work.

Dehydrogenation of the five-membered ring in the decahydrophosphafluorene oxide (II; R = H), prepared by the hydrolysis of the Diels–Alder-like adduct obtained from (I; R = H) and phenyldichlorophosphine by McCormack's method, was first attempted by bromination and dehydrobromination. Although sufficient bromine was absorbed to account for the production of a dibromide from which hydrogen bromide was eliminated as collidine hydrobromide, the product, a yellow viscous oil, was patently a mixture. Palladium on charcoal was equally ineffective, with or without a hydrogen acceptor, but heating of the phosphafluorenes (II; R = H or Me) with selenium dispersed in potassium dihydrogen phosphate (2 : 1) at 270—370° dehydrogenated them completely, and simultaneously replaced oxygen by selenium, to give the selenides (III; R = H and Me) in 25 and 30% yield, respectively. Pure selenium was much less effective, giving only 4% of (III; R = H) and none of (III; R = Me). The structure of (III; R = H) was proved by conversion to the oxide (VI; R = H) for comparison with an authentic sample. Conversion of a phosphine selenide to the oxide is said to occur on warming with hydrogen peroxide,[10] but the method failed in this case, and the methylation process used by Hantzsch and Hibbert [11] to convert trimethylphosphine sulphide to the oxide had to be used. The primary products of this reaction proved to be trimethylselenonium iodide and the phosphine di-iodide (IV; R = H), although further methylation of the latter gave a small amount of the phosphonium tri-iodide (V; R = H) (a quaternary tri-iodide has been obtained by methylation of triphenylphosphine di-iodide [12]). Dilute sodium hydroxide converted the crude di-iodide (IV; R = H) into the oxide (VI; R = H), thus proving that dehydrogenation was complete.

In order to study a simple phosphacyclopentadiene lacking fused rings, we intended to dehydrogenate the phosphacylopentene oxide expected from the adduct (VII) from 1,4-diphenyl-1,3-butadiene and phenylphosphonous dichloride. However, at 100° no adduct formed, and at higher temperatures hydrogen chloride was evolved (in the first experiment almost explosively). Control of the temperature at 214—217° for ten hours gave 1,2,5-triphenylphosphole (VIII), m. p. 187°, in 50—66% yield. 1,2,3,4-Tetraphenylbutadiene behaved similarly, and gave a 50% yield of the pentaphenylphosphole obtained previously by the interaction of phenylphosphonous dichloride and 1,4-dilithio-1,2,3,4-tetraphenylbutadiene.[2b] There is some indication that the reaction follows a Diels–Alder mechanism [*via* (VII)], because phenylphosphonic dichloride, which cannot form the initial adduct, failed to react.

Attempts were made to extend the scope of the synthesis by pyrolysis (under nitrogen) of the adduct obtained from butadiene and phenylphosphonous dichloride,[8] and by treatment of the adduct with sodium hydride in dry toluene, but only tars were produced. We also tried to form the phosphole ring by interaction of phenylphosphine with 1,4-diketones, but without success.

1,2,5-Triphenylphosphole is bright yellow and shows a strong blue fluorescence in solution; 1,2,3,4,5-pentaphenylphosphole shows a similar fluorescence [4] and the corresponding oxides do so to a lesser extent. 1,2,5-Triphenylphosphole absorbs in the ultraviolet region at a much longer wavelength than does 1,2,5-triphenylpyrrole [13] (see the Table), which suggests that the phosphole has less aromatic character. Apparently it is

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[7] G. Grüttner and E. Krause, *Ber.*, 1916, **49**, 437.

[8] W. B. McCormack, U.S.P. 2,663,737 (1953) (*Chem. Abs.*, 1955, **49**, 7601).

[9] I. G. M. Campbell, R. C. Cookson, and M. B. Hocking, *Chem. and Ind.*, 1962, 359.

[10] G. M. Kosolapoff, " Organophosphorus Compounds," Chapman and Hall, London, 1950, p. 100.

[11] A. Hantzsch and H. Hibbert, *Ber.*, 1907, **40**, 1508.

[12] H. Hoffmann, R. Grünewald, and L. Horner, *Chem. Ber.*, 1960, **93**, 861.

[13] S. M. King, C. R. Bauer, and R. E. Lutz, *J. Amer. Chem. Soc.*, 1951, **73**, 2253.

Details of the ultraviolet spectra of 1,2,5-triphenylphosphole and its derivatives, and of 1,2,5-triphenylpyrrole

Compound	$\lambda_{\text{max.}}$ (mμ) (log ε)
1,2,5-Triphenylpyrrole [13]	301(4·29)
(VIII)	222(4·38), 369(4·25)
Oxide of (VIII)	221(4·32), 243(4·22), 394(4·16)
Selenide of (VIII)	222(4·41), 380(4·14)
Methiodide of (VIII)	222(4·56), 405(4·10)
(X)	223(4·49), 239(4·29), 385(4·17)
(XVI; R = H)	215(4·44), 273(4·06), 373(2·24)
(XVI; R = CO_2H)	217(4·49), 273(4·10)
(XX)	215(4·20), 260(3·84), 325(2·48), 365(1·88)
NN-dihydro-(XX)	221(4·45), 255(3·69), 333(2·08)
$Ph_3P{=}O$	223(4·38), 254(2·99), 259(3·15), 265(3·28), 271(3·21), 295(1·00)
$Ph_3P{=}S$	220(4·12), 249(3·56)
$Ph_3P{=}Se$	220(4·54), 266(3·73)

not a characteristic diene, for it fails to react with either maleic anhydride or acrylonitrile in benzene at 80°, conditions under which its oxide forms normal adducts. However, at 150—200°, both the phosphole and its oxide undergo Diels–Alder reactions with dimethyl acetylenedicarboxylate, and with maleic anhydride, with elimination of the PPh bridge and, in the case of maleic anhydride, aromatisation to 3,6-diphenylphathalic anhydride. It is, therefore, difficult to estimate the aromaticity of the phosphole in this way, particularly as some furans,[14] pyrroles,[15] and at least one thiophen [16] undergo Diels–Alder reactions. Ready complex-formation has been demonstrated for the phosphole with tungsten, chromium, and molybdenum hexacarbonyls and with two iron carbonyls.[17] Similar results were obtained for pentaphenylphosphole.

As expected, 1,2,5-triphenylphosphole formed an oxide, sulphide, and selenide under standard conditions, although the sulphide appeared to dimerise. With bromine, only the *P*-dibromide was formed, without substitution of the ring, and *p*-nitrophenyldiazonium fluoborate left the phosphole untouched. Quaternisation occurred smoothly to give the methiodide, but proceeded more slowly with ethyl α-bromoacetate to give the phosphonium salt (IX), from which the phosphorane (X) was obtained in good yield in aqueous sodium hydroxide. The stability of this phosphorane was shown by its failure to undergo the Wittig reaction on prolonged boiling with cyclohexanone in benzene. At the time this work was carried out, no Wittig reagents involving phosphorus as a ring member had been isolated, but Märkl has recently obtained two 1,1-diphenyl-1-phosphanaphthalenes [18] and 1,1-diphenylphosphabenzene [19] in which the ylide link is internal to the ring, not external, as in the present case, which is an analogue of fulvene.

On one occasion, treatment of the quaternary salt (IX) with concentrated aqueous alkali gave no phosphorane, but produced instead the phosphole oxide and a compound, $C_{23}H_{21}OP$, which contained one double bond (catalytic hydrogenation), a P=O group, and no ester carbonyl group (infrared spectrum). This evidence suggested that hydrolysis, decarboxylation, and oxidation had produced compound (XI) or (XII) by ring-expansion or fission of the $P{-}CH_2$ bond in an unstable 3-membered-ring intermediate (XIII). The nuclear magnetic resonance (n.m.r.) spectrum (in $CDCl_3$) is consistent only with structure (XII) since it shows (aromatic and olefinic) : benzyl : methyl protons in the ratio 17 : 1 : 3. The methyl absorption at 9·27 τ and the benzylic absorption at 5·62 τ both occur as doublets (the latter broadened by slight coupling with the olefinic protons) with J = 12 and 19·5 c./sec., respectively, because of coupling with phosphorus. The larger H–P coupling

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[14] J. A. Norton, *Chem. Rev.*, 1942, **31**, 319; C. E. Griffin and J. T. Brown, *J. Org. Chem.*, 1961, **26**, 853.

[15] R. M. Acheson, A. R. Hands, and J. M. Vernon, *Proc. Chem. Soc.*, 1961, 164.

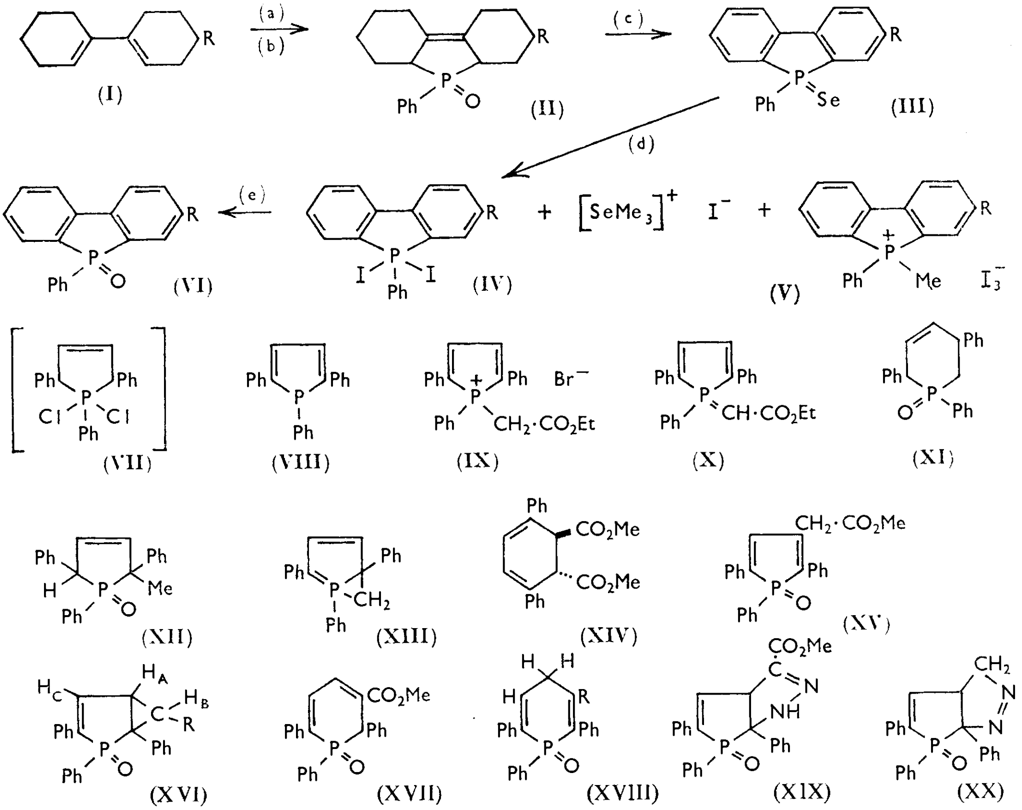
[16] D. B. Clapp, *J. Amer. Chem. Soc.*, 1939, **61**, 2733.

[17] D. K. Jenkins, Ph.D. Thesis, Southampton, 1963.

[18] G. Märkl, *Angew. Chem.* (*Internat. Edn.*), 1963, **2**, 153.

[19] G. Märkl, *Angew. Chem.* (*Internat. Edn.*), 1963, **2**, 479.

for β than α protons recently observed by Hendrickson *et al.*[20] (*e.g.*, Et_3PO: $J_{H(\alpha)-P} = 11{\cdot}9$; $J_{H(\beta)-P} = 16{\cdot}3$ c./sec.) seems therefore not to be general.



Reagents: (a) $PhPCl_2$, (b) H_2O, (c) Se, KH_2PO_4, (d) excess of MeI, (e) NaOH aq.

1,2,5-Triphenylphosphole and its oxide reacted with methyl diazoacetate and with diazomethane, and gave a variety of products depending on the conditions. In refluxing dioxan with copper powder, the phosphole and diazoacetic ester produced a colourless compound, $C_{22}H_{20}O_4$, with a pronounced blue fluorescence in solution. Infrared and ultraviolet spectra and catalytic hydrogenation indicated dimethyl 3,6-diphenylcyclohexa-3,5-diene-1,2-dicarboxylate (XIV). This could result from a Diels–Alder reaction of dimethyl fumarate (formed by decomposition of methyl diazoacetate) on the phosphole ring with loss of the P–Ph bridge, and the possibility was to some extent confirmed when the same compound was obtained by heating the phosphole oxide with dimethyl fumarate at 220°, though the phosphole itself failed to react. Hydrogenation of (XIV) gave a cyclohexanedicarboxylic ester, m. p. 105—106°, which was not identical with the "all *cis*" isomer, m. p. 104—105°[21] (prepared for comparison) and was probably dimethyl *cis,cis*-3,6-diphenylcyclohexane-*cis,trans*-dicarboxylate.

A mixture of the phosphole (VIII) and methyl diazoacetate, heated in boiling dioxan *without* copper powder, gave a very small quantity of a colourless compound, $C_{25}H_{21}O_3P$, and when the phosphole oxide was used, a much larger but still poor yield of the same compound was obtained. The infrared spectrum of this product showed bands characteristic of P=O, P–Ph, and ester groups; four structures, (XV), (XVI; R = CO_2Me), (XVII),

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[20] J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, 1964, **20**, 449.
[21] K. Alder and M. Schumacher, *Annalen*, 1950, **571**, 87.

and (XVIII; R = CO_2Me), are possible. Structure (XV) is ruled out by the ultraviolet spectrum which does not remotely resemble that of the parent phosphole oxide. The n.m.r. spectrum (in $CDCl_3$) showed a ratio of 16 aromatic and olefinic protons to 5 others, and occurred as a doublet (J = 12 c./sec.) of doublets (J = 3·5 c./sec.) at 6·98 τ and a doublet (J = 12 c./sec.) of triplets (J = 3·5 c./sec.) at 6·66 τ partly obscured by a singlet from the methoxyl protons at 6·56 τ. This rules out structure (XVII), and allows (XVI) or (XVIII; R = CO_2Me). Structure (XVII) is also unlikely on chemical grounds, because the compound failed to react as a diene with dimethyl acetylenedicarboxylate, and some evidence against (XVI) was provided by the compound's stability to acid and base. Sodium methoxide simply hydrolysed the ester to the acid.

The absence of the methoxyl group signal, which had partly overlain the peaks from one of the aliphatic protons, resulted in a clearer n.m.r. spectrum from the acid, thus establishing the structure (XVI; R = CO_2H) or (XVIII; R = CO_2H). In trifluoroacetic acid, H_A appeared as a doublet of doublets at 6·71 τ, H_B as a doublet of triplets at 6·31 τ, and H_C as a widely spaced doublet of doublets at 2·29 τ, with $J_{AB} = 12$, $J_{AC} = 0$, $J_{AP} = 3$, $J_{BC} = 3$, $J_{BP} = 3$, and $J_{CP} = 42$ c./sec. The assignment of coupling was confirmed by double irradiation.

In contrast to the unsubstituted cyclopropane (XVI; R = H), this acid shows no long-wavelength band in its ultraviolet spectrum (see Table), and the coupling constant J_{AB} (12) appears to be larger than usual for cyclopropanes, where J normally lies between 6 and 10.[22] Structure (XVIII) cannot therefore be rigorously excluded.

Both the phosphole and its oxide reacted with methyl diazoacetate in dioxan at room temperature when set aside for prolonged periods (*ca.* 40 days). The product was the pyrazoline (XIX). This structure, rather than the azo-form, was assumed, since the NH link was indicated by a fairly strong infrared band at 3130 cm.$^{-1}$. Furthermore, the P=O group should facilitate the normal nucleophilic attack at position 3 by the methine carbon atom of the diazo-ester.[23] The pyrazoline (XIX) readily lost nitrogen on heating with a trace of copper in solvents boiling above 140°, and gave the nitrogen-free compound (XVI; R = CO_2Me) or (XVIII; R = CO_2Me). No identifiable products could be obtained on treating the phosphole or its oxide with methyl diazoacetate or diazomethane in dioxan containing cuprous bromide, although Müller *et al.*[24] have found this catalyst to be very suitable for reactions with furan and thiophen. Irradiation with ultraviolet light also does not catalyse the addition; a pale yellow dimer was isolated from irradiation of the phosphole oxide in dioxan–ether, either alone or mixed with the diazoacetic ester.

The phosphole oxide reacted very slowly with diazomethane at $-20°$, but after 6 days a quantitative yield of the corresponding pyrazoline was obtained. This apparently had structure (XX) since there was no NH absorption in the infrared region, and a weak band at 365 mμ (ε 75) indicated an azo-group. The latter disappeared when the pyrazoline was reduced with sodium borohydride, whereas the other ultraviolet bands remained at almost the same wavelength, though they were somewhat altered in intensity; the expected NH band appeared in the infrared spectrum. Nitrogen was eliminated much more readily from the pyrazoline (XX) than from the ester (XIX) [another indication that (XX) had the azo structure], and led to the cyclopropane (XVI; R = H). The cyclopropane structure was the only one possible, in that catalytic hydrogenation indicated the presence of one double bond and the n.m.r. spectrum (in trifluoroacetic acid) showed a ratio of sixteen aromatic and olefinic protons to one methine proton (centred on τ = 7) and two methylene protons (centred on τ = 8). These last two bands were split into seven and eleven maxima, respectively, showing extensive long-range coupling with phosphorus. The

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[22] D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1963, **85**, 3218; T. Shono, T. Marikawa, A. Oka, and R. Oda, *Tetrahedron Letters*, 1964, 791, and references cited therein.

[23] "Heterocyclic Compounds," ed. R. C. Elderfield, Chapman and Hall, London, 1957, vol. 5, p. 83; R. Huisgen, *Angew. Chem.* (*Internat. Edn.*), 1963, **2**, 567.

[24] E. Müller, H. Kessler, H. Fricke, and H. Suhr, *Tetrahedron Letters*, 1963, 1047.

cyclopropane, also formed by the photochemical reaction between diazomethane and the phosphole oxide, proved particularly stable. It was unaffected by bromine in boiling chloroform, by boiling fuming hydrobromic acid, or even by warm concentrated sulphuric acid.

The details of the ultraviolet spectra of the phosphole and its derivatives, collected in the Table appear to be more consistent with a diene system than with a benzenoid type of ring. An interesting feature is the weak long-wavelength band observed in the cyclopropane (XVI; R = H), in the pyrazoline (XX), and in its reduction product, absorption which may arise from $n \longrightarrow \pi^*$ transitions of the P=O link. Of the three triphenylphosphine derivatives containing the P=X link, only the oxide shows a weak band at 295 mμ, and this may be a vibrational band.

Both from physical and from chemical evidence, it appears that the heterocyclic ring in 1,2,5-triphenylphosphole has little or no aromatic character. Only the n.m.r. spectrum might be construed as indicating aromaticity. Here all the protons resonate as a complex multiplet between 2·35 and 2·9 τ, but in the oxide, in which the phosphorus lone-pair is not available to the ring, this multiplet is broadened and one peak of the doublet expected from the two hetero-ring protons is separated from the main band and appears at τ 3·15. Obviously, these data are not conclusive and do not provide a clear decision on the aromaticity of the phosphole ring, but the evidence is in general agreement with theoretical predictions [25] and with estimates of the resonance energy of similar systems.[26]

EXPERIMENTAL

Except where otherwise stated, all n.m.r. spectra were measured on a Varian A.60 specrtometer, with tetramethylsilane as internal reference. Ultraviolet (in 95% ethanol) and infrared measurements (Nujol mull) were made on the Unicam S.P. 700 and S.P. 100 instruments, respectively.

9-Phenyldecahydro-9-phosphafluorene 9-Oxide (II; R = H).—1,1′-Dihydroxy-1,1′-bicyclohexyl, m. p. 125—128° (150 g.) was dehydrated by heating at 140—160° with anhydrous potassium alum (15 g.) and gave 1,1′-bicyclohexenyl, b. p. 244—256°, in 79% yield (lit.,[27] b. p. 245—251°, m. p. 28°). A mixture of this diene (26·15 g.) and phenylphosphonous dichloride (28·8 g.) was heated on a boiling water bath for 7 days, taking care to exclude all moisture. The orange liquid was cooled, washed with warm light petroleum to remove starting materials, and the residue was poured on to ice. The mixture was extracted with chloroform (150 ml.) and the chloroform solution was washed with saturated aqueous sodium hydrogen carbonate solution, dried ($CaCl_2$), and evaporated. 9-Phenyldecahydro-9-phosphafluorene 9-oxide was obtained crude as a viscous yellow oil (33·2 g.; 73%). Neither distillation, b. p. 200—220°/0·14 mm. (lit.,[8] b. p. 210—220°/0·5 mm.), nor chromatography in benzene on silica gel produced a crystalline product (Found: C, 75·0; H, 8·1. Calc. for $C_{18}H_{23}OP$: C, 75·5; H, 8·1%) $\nu_{max.}$ (thin film) 1450, 1442 (*P*-Phenyl), and 1200 and 1175 cm.$^{-1}$ (P=O).

2-Methyl-9-phenyldecahydro-9-phosphafluorene 9-Oxide (II; R = Me).—1-Chlorocyclohexene, b. p. 101—104°/107 mm., was prepared and lithiated by the method of Braude and Coles.[28] Interaction of the resulting cyclohexenyl-lithium with 4-methylcyclohexanone in dry ether, followed by hydrolysis, gave *1-cyclohexene-1-yl-4′-methylcyclohexan-1′-ol*, m. p. 105—106·5°, in very low yield (8—9%) (Found: C, 80·6; H, 11·3. $C_{13}H_{22}O$ requires C, 80·3; H, 11·4%). Dehydration with a catalytic amount of alumina at 200—260° (Wood's metal bath) for 1·5 hr. gave 4-methyl-1,1′-bicyclohexenyl, b. p. 152°/44 mm., in 92% yield. The diene (5·7 g.) and phenylphosphonous dichloride (10·1 g.) were heated together on a water-bath for 9 days, with exclusion of moisture. Isolation of the product by the method used in the previous experiment gave 2-methyl-9-phenyldecahydro-9-phosphafluorene 9-oxide (2·65 g., 27%), b. p. 196—206°/0·01 mm., as a yellow viscous oil which formed a *cadmium iodide complex* m. p. 217° (Found: C, 47·1; H, 4·9. $(C_{19}H_{25}OP)_2CdI_2$ requires C, 47·2; H, 5·2%).

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[25] D. A. Brown, *J.*, 1962, 929.
[26] A. F. Bedford, D. M. Heinekey, I. T. Millar, and C. T. Mortimer, *J.*, 1962, 2932.
[27] E. de B. Barnett and C. A. Lawrence, *J.*, 1935, 1104.
[28] E. A. Braude and J. A. Coles, *J.*, 1950, 2014.

Dehydrogenation of 9-*Phenyldecahydro*-9-*phosphafluorene* 9-*Oxides*.—Attempts to dehydrogenate (II; R = H) by bromination and dehydrobromination, or by using chloranil, sulphur, or palladium in charcoal (10% or 30%), were unsuccessful. The decahydro-derivative (5·8 g.) was heated with a mixture of selenium and potassium dihydrogen phosphate 2 : 1 (10·9 g.) in a metal-bath at 270—370° for 5·5 hr. The evolution of hydrogen selenide was followed by the progression of a red band in a tower of calcium hypochlorite. The residue was extracted with boiling benzene, and evaporation of the extract gave a brown gum (4·6 g.) which was chromatographed in benzene on silica gel. Elution with benzene (140 ml.) gave an oil (1·2 g.) which was not further investigated. The main product (2·37 g.) came off in the next fraction (600 ml.), and recrystallisation from benzene gave 9-*phenyl*-9-*phosphafluorene* 9-*selenide* (III; R = H) (1·69 g., 25%), m. p. 162—164° (Found: C, 63·6; H, 3·8; P, 9·1. $C_{18}H_{13}PSe$ requires C, 63·7; H, 3·9; P, 9·1%).

The 2-methyl derivative (II; R = Me) (1·23 g.) was similarly treated with the selenium reagent (1·67 g.) at 200—330° for 8 hr., and the extract was chromatographed on alumina in benzene–light petroleum (b. p. 60—80°). The main fraction, cream needles, m. p. 162·5—164°, proved to be 2-*methyl*-9-*phenyl*-9-*phosphafluorene* 9-*selenide* (III; R = Me) (0·45 g., 31%) (Found: C, 64·8; H, 4·4. $C_{19}H_{15}PSe$ requires C, 64·6; H, 4·3%).

Conversion of the Selenide (III; R = H) *to the Oxide*.—The selenide (0·276 g.) was heated for 3 hr. at the b. p. with methyl iodide (7·5 ml.). Colourless crystals (77 mg.) separated and proved to be trimethylselenonium iodide, m. p. 150—152° (sublimation) (Found: C, 14·8; H, 3·3. Calc. for C_3H_9ISe: C, 14·4; H, 3·6%). On evaporating the mother-liquor to half its original volume, red crystals (22 mg.) separated. Recrystallisation from ethanol gave a compound, m. p. 105—108°, which was tentatively identified as the *methotri-iodide* of 9-phenyl-9-phosphafluorene (V; R = H) (Found: C, 35·3; H, 2·5; I, 55·3. $C_{19}H_{16}I_3P$ requires C, 34·8; H, 2·5; I, 58·0%). The tri-iodide (49 mg.), in ethyl acetate, was shaken with aqueous sodium thiosulphate solution, and gave colourless prisms (32 mg.), m. p. 229—230° (decomp.), of the corresponding phosphonium *tetrathionate* (Found: C, 59·2; H, 4·0; P, 7·8; S, 16·3. $(C_{19}H_{16}P)_2S_4O_6$ requires C, 58·9; H, 4·2; P, 8·0; S, 16·6%). The dark residue, obtained on complete evaporation of the remaining methyl iodide, was treated with dilute sodium hydroxide solution which removed the colour and formed a precipitate which, on crystallisation from ethanol, proved to be 9-phenyl-9-phosphafluorene 9-oxide (VI; R = H) (110 mg.), m. p. and mixed m. p. 166—168°, infrared spectrum identical with that of an authentic sample (Found: C, 78·2; H, 4·7; P, 11·0. Calc. for $C_{18}H_{13}OP$: C, 78·3; H, 4·8; P, 11·2%).

1,2,5-*Triphenyl*-1-*phosphacyclopentadiene* [1,2,5-*Triphenylphosphole* (VIII)].—A mixture of 1,4-diphenylbuta-1,3-diene (15·6 g.) and phenylphosphonous dichloride (20·2 g.) was heated slowly to 214—217° in a slow stream of nitrogen. Hydrogen chloride evolution started almost immediately and was essentially complete after 10 hr. (93% of calculated). Temperature-control appeared to be critical, since below 200° the reaction time was considerably lengthened with no improvement in yield, and above 225° decomposition occurred. The cooled mixture was extracted with light petroleum, to remove starting materials, and the residue was dissolved in chloroform (500 ml.). The solution, after washing with hydrogen carbonate and water, was dried and evaporated to 200 ml., when 1,2,5-*triphenylphosphole* separated as yellow needles (66%), m. p. 187—189° (Found: C, 84·9; H, 5·4; P, 9·6. $C_{22}H_{17}P$ requires C, 84·6; H, 5·5; P, 9·9%). The phosphole, in solution, showed a strong blue fluorescence which was at a maximum with an incident radiation of wavelength 300 mμ, when a concentration of 0·5 mg./l. (ethanol) was equivalent to 1 mg./l. of fluorescein.[29]

The *oxide*, yellow prisms, obtained by the action of hydrogen peroxide on the phosphole in ethyl acetate–ethanol, had m. p. 237—239° (Found: C, 80·6; H, 5·2; P, 9·4. $C_{22}H_{17}OP$ requires C, 80·4; H, 5·2; P, 9·4%).

The *selenide* was obtained as yellow needles (94%), m. p. 205·5—206·5°, by heating the phosphole with selenium in benzene for 2—3 hr. (Found: C, 67·4; H, 4·2. $C_{22}H_{17}PSe$ requires C, 67·5; H, 4·4%).

The yellow *sulphide*, m. p. 215—216·5°, was obtained by heating the phosphole with sulphur in xylene at the b. p. and crystallising from methyl ethyl ketone (Found: C, 76·8; H, 4·8. $C_{22}H_{17}PS$ requires C, 76·7; H, 5·0%). An insoluble residue proved to be a polymeric sulphide, m. p. 350—351°, which crystallised as colourless needles from dimethylformamide (Found: C, 76·9; H, 4·9%).

[29] J. E. Stanfield, Unicam Instruments Ltd., personal communication.

The *methiodide* was obtained as a yellow monohydrate, m. p. 218·5—222° (decomp.), on heating the phosphole with excess of methyl iodide for 2 hr., followed by crystallisation from methanol–light petroleum (Found: C, 58·0; H, 4·7; P, 6·3; I, 26·8. $C_{23}H_{20}PI,H_2O$ requires C, 58·9; H, 4·7; P, 6·5; I, 26·9%).

Addition of bromine to the phosphole in carbon tetrachloride gave a red dibromide which fumed on exposure to air and was rapidly converted into the oxide (84%), m. p. 237—238·5°. Attempts to brominate the oxide under a variety of conditions were unsuccessful.

1,2,3,4,5-*Pentaphenylphosphole*.—A mixture of 1,2,3,4-tetraphenylbuta-1,3-diene (1·57 g.) and phenylphosphonous dichloride (1·2 ml.) was heated at 210—230° for 10 hr. The yellow crystalline mass was washed with warm light petroleum, and the residue was dissolved in chloroform, washed with sodium hydrogen carbonate and water, dried, and evaporated to low bulk. On cooling, 1,2,3,4,5-pentaphenylphosphole, m. p. 254·5—255·5° (lit.,[2b] m. p. 256—257°), separated as yellow needles (0·812 g., 40%) (Found: C, 87·8; H, 5·1; P, 6·9. Calc. for $C_{34}H_{25}P$: C, 87·9; H, 5·5; P, 6·7%). The phosphole was oxidised in benzene with hydrogen peroxide to the oxide, m. p. 284—285° (Found: C, 85·4; H, 5·2; P, 6·5. Calc. for $C_{34}H_{25}OP$: C, 85·0; H, 5·25; P, 6·5%).

Hydrogenation of 1,2,5-*Triphenylphosphole Oxide*.—The phosphole oxide (307 mg.), in ethyl acetate–glacial acetic acid, with hydrated platinum oxide (100 mg.), absorbed the calculated volume of hydrogen (equivalent to 2 double bonds) in 70 min. The initially green solution became colourless, and removal of the catalyst and solvents left a solid which, on crystallisation from carbon tetrachloride, gave 1,2,5-*triphenylphosphacyclopentane* as colourless needles, m. p. 205—207° (Found: C, 79·6; H, 5·5; P, 9·4. $C_{22}H_{21}OP$ requires C, 79·5; H, 6·3; P, 9·3%). The phosphole could not be hydrogenated, presumably because the tervalent phosphorus poisoned the catalyst.

Elimination of the Phosphorus Fragment.—(a) The phosphole (215 mg.) was heated with maleic anhydride (1 g.) at 120—130° for 3 min. From the black residue, 3,6-diphenylphthalic anhydride, m. p. and mixed m. p. 227—228° (lit., m. p. 224°), was obtained. The yield represents only 11% of the reactants.

(b) The phosphole (278 mg.) was heated at 180° with dimethyl acetylenedicarboxylate (157 mg.) for 1 min., and from the cooled tar, dimethyl 3,6-diphenylphthalate (137 mg., 40%), m. p. 189—191°, was obtained after crystallisation from methanol.

(c) From the phosphole oxide (1·75 g.), with dimethyl acetylenedicarboxylate (1·14 g.) at 156° for 2 min., the phthalate (1·30 g., 71%) was obtained by crystallisation, sublimation, and chromatography of the dark residues.

(d) When the phosphole oxide (541 mg.) and dimethyl fumarate (700 mg.) were heated together at 160—230° for 15 min., a vigorous reaction took place above 210°. Unreacted dimethyl fumarate (366 mg.) was sublimed from the mixture at 90°/15 mm., and fractional crystallisation of the residue from ethyl acetate gave *dimethyl* 3,6-*diphenylcyclohexa*-3,5-*diene*-trans-1,2-*dicarboxylate* as pale yellow needles (411 mg., 73%), m. p. 169—171° (Found: C, 75·8; H, 5·5. $C_{22}H_{20}O_4$ requires C, 75·8; H, 5·8%).

Dimethyl 3,6-*Diphenylcyclohexane*-1,2-*dicarboxylate* (*all* cis-).—Dimethyl *cis,cis*-3,6-diphenylcyclohexa-1,4-diene-1,2-dicarboxylate (1·02 g.), m. p. 95—98° (lit.,[21] m. p. 96°), prepared from 1,4-diphenylbutadiene and dimethylacetylene dicarboxylate, was dissolved in methanol (125 ml.) and added to previously reduced platinum oxide (102 mg.) in methanol (25 ml.). The mixture was shaken in a hydrogen atmosphere for 3·5 hr. The mixture was filtered, concentrated, and allowed to crystallise. The product (822 mg.) was recrystallised from methanol to give dimethyl 3,6-diphenylcyclohexane-1,2-dicarboxylate (all *cis*-), m. p. 96—99° (lit.,[21] m. p. 104—105°).

Retention of the Phosphorus Fragment.—The phosphole oxide reacted with maleic anhydride on refluxing in benzene (4 hr.) to give the normal *adduct*, m. p. 229—231°, in 78% yield (Found: C, 73·2; H, 4·6; P, 7·2. $C_{26}H_{19}O_4P$ requires: C, 73·2; H, 4·45; P, 7·3%).

Under similar conditions, the phosphole oxide formed the normal *adduct* (40% yield) with acrylonitrile, m. p. 180° (Found: C, 78·0; H, 5·5; N, 3·5; P, 8·2. $C_{25}H_{20}NP$ requires C, 78·7; H, 5·2; N, 3·7; P, 8·1%).

Phosphorane Formation.—A solution of the phosphole (3·86 g.) and ethyl bromoacetate (3·87 g.) in benzene (50 ml.) was heated under reflux for 47 hr. Orange crystals (4·55 g.), m. p. 170—171° (decomp.), were filtered off, and evaporation of the mother-liquor gave a further crop (0·76 g.). Recrystallisation from acetone gave the *phosphonium salt* (IX), m. p. 184·5—

185° (decomp.) (Found: C, 65·2; H, 5·2; P, 6·6. $C_{26}H_{24}BrO_2P$ requires C, 65·1; H, 5·0; P, 6·5%).

The phosphonium salt (1·14 g.) in water (250 ml.) was treated with 4N-sodium hydroxide solution until the solution became just alkaline to phenolphthalein. The orange precipitate was washed with water, dried, and crystallised from ethyl acetate to give the phosphole oxide (337 mg.) and a second fraction [light yellow crystals (245 mg.)] which, on recrystallisation from light petroleum–ethyl acetate, gave 2-*methyl*-1,2,5-*triphenyl*-1-*phosphacyclopent*-3-*ene* 1-*oxide* (XII) as small colourless needles, m. p. 175·5—176·5° (Found: C, 79·9; H, 5·9; P, 8·9. $C_{23}H_{21}OP$ requires C, 80·2; H, 6·1; P, 9·0%). Catalytic hydrogenation established the presence of one double bond, and gave the *dihydro-derivative* (Found: C, 79·8; H, 6·2; P, 9·6. $C_{23}H_{23}OP$ requires C, 79·7; H, 6·7; P, 8·9%).

The crude phosphonium salt (5·148 g.) in water (1·6 l.) was treated with 3 ml. of 4N-sodium hydroxide solution. The orange precipitate was collected, washed, dried, and recrystallised twice from dry ethyl acetate to give the *phosphorane* (X), m. p. 161—163°, although considerable decomposition to the phosphole oxide also took place (Found: C, 79·3; H, 5·6; P, 8·2. $C_{26}H_{23}O_2P$ requires C, 78·4; H, 5·8; P, 7·8%). This compound does not undergo a Wittig reaction with cyclohexanone.

Reactions of the Phosphole and its Oxide with Methyl Diazoacetate.—(a) *In hot dioxan with catalyst.* 1,2,5-Triphenylphosphole (0·471 g.) was dissolved in peroxide-free dioxan (25 ml.) and heated to boiling. Methyl diazoacetate (1 ml.) in dioxan (6 ml.) was added during 15 min. and, 2 hr. later, copper powder (0·5 g.) was added. After a further 75 min., the mixture was filtered and the solvent was removed. Dimethyl fumarate (38 mg.) was sublimed from the residual gum, and the residue was chromatographed on alumina in benzene. The phosphole oxide (40 mg.) was eluted, followed by a colourless compound which, on crystallisation from ethyl acetate, gave dimethyl 3,6-diphenylcyclohexa-3,5-diene-*trans*-1,2-dicarboxylate, identical with the compound prepared by the interaction of dimethyl fumarate and the phosphole oxide.

(b) *In refluxing dioxan without catalyst.* Methyl diazoacetate (3·1 ml.) in dioxan (7 ml.) was added to 1,2,5-triphenylphosphole (1·61 g.) in the same solvent (40 ml.), and the solution was heated under reflux for 22·5 hr. Removal of the solvent, followed by chromatography of the residue on alumina in benzene, gave, first, 1,2,5-triphenylphosphole oxide (356 mg.), and then a light-yellow glass (189 mg.). Recrystallisation of this glass from ethyl acetate–light petroleum gave colourless needles of the *cyclopropane* (XVI; R = CO_2Me) or the *phosphacyclohexadiene* (XVIII; R = CO_2Me), m. p. 217—218° (Found: C, 75·0; H, 5·0; P, 7·5. $C_{25}H_{21}O_3P$ requires C, 75·0; H, 5·3; P, 7·7%). The structure of this compound was deduced from infrared, ultraviolet, and n.m.r. data together with hydrogenation (see Discussion section). Under similar conditions, the phosphole oxide (12 g.) and methyl diazoacetate (42 ml.) gave the same ester (3·95 g., 27%).

The corresponding acid was prepared by refluxing the ester (3·95 g.) in methanol (300 ml.) containing sodium methoxide (10 g. sodium) for 3 hr. The mixture was neutralised with 4N-sulphuric acid and extracted with methylene chloride. Evaporation of the extract, followed by recrystallisation from ethanol–ethyl acetate, gave the *acid* (XVI; R = CO_2H or XVIII; R = CO_2H) (3·3 g.), m. p. 285—287° (decomp.) (Found: C, 74·4; H, 4·8; P, 8·1. $C_{24}H_{19}O_3P$ requires C, 74·6; H, 4·9; P, 8·0%). Re-esterification of the acid with diazomethane in ether–dioxan at 0° gave the original ester in 92% yield.

(c) *Reaction at room temperature.* Methyl diazoacetate (16 ml.) and the phosphole (4·09 g.) were dissolved in dioxan (100 ml.) and allowed to stand for 42 days at room temperature with exclusion of moisture. The reaction mixture was filtered from the phosphole (0·267 g.), and the residue, after evaporation of solvent, was extracted with boiling methanol. Some of the phosphole (1·08 g.) remained undissolved, and the extract deposited further phosphole contaminated with oxide (0·467 g.). Two later crops of light-yellow crystals (1·81 g.), after recrystallisation from ethanol, yielded the *pyrazoline* (XIX) (34%), m. p. 233—235° (decomp.) (Found: C, 69·8; H, 4·5; N, 6·9; P, 7·3. $C_{25}H_{21}O_3N_2P$ requires C, 70·1; H, 4·9; N, 6·5; P, 7·2%).

A paste of the phosphole oxide (3 g.) and methyl diazoacetate (6 ml.) was set aside at room temperature for 3 months. The oxide slowly dissolved and the yellow solution deposited large colourless crystals (3·48 g., 89%) of the pyrazoline (XIX), m. p. 232—234° (decomp.).

Thermal Decomposition of the Pyrazoline (XIX).—Copper powder (29 mg.) was added to a solution of the pyrazoline (510 mg.) in bis-(2-methoxyethyl) ether (35 ml.) and the mixture was heated under reflux for 3 hr., cooled, and filtered. Addition of water (65 ml.) to the filtrate precipitated a brown gum which crystallised from benzene–light petroleum giving the ester (XVI; R = CO_2Me or XVIII; R = CO_2Me) (205 mg.), m. p. 217·5—219°, identical with the sample prepared previously.

Irradiation of 1,2,5-*Triphenylphosphole* 1-*Oxide*.—An unsuccessful attempt to prepare the pyrazoline or the corresponding ester by irradiation of a mixture of the phosphole oxide with methyl diazoacetate in dioxan produced a colourless polymer of the phosphole oxide, m. p. >300°. A solution of the oxide (2 g.) in dioxan (200 ml.) and ether (150 ml.) was irradiated for 3 hr. with an 85-w lamp. The solution deposited the same polymer (1·23 g.), m. p. >300° (Found: C, 80·0; H, 4·9; P, 9·4. $(C_{22}H_{17}OP)_n$ requires C, 80·4; H, 5·2; P, 9·4%).

Reaction of 1,2,5-*Triphenylphosphole Oxide with Diazomethane*.—The phosphole oxide (5 g.) in dioxan (250 ml.) was treated with diazomethane (*ca.* 10 g.) in ether (500 ml.). The mixture (in a stoppered flask with a pressure-release valve) was set aside at −15 to −18° for 6 days. After removal of diazomethane by a current of nitrogen, the solution was partially evaporated and allowed to crystallise. Recrystallisation from methanol gave very pale yellow needles (4·98 g.) of the *pyrazoline* (XX) which decomposed slowly above 190° (Found: C, 74·5; H, 5·2; N, 7·8; P, 8·7. $C_{23}H_{19}ON_2P$ requires C, 74·6; H, 5·1; N, 7·6; P, 8·4%). The pyrazoline (1 g.) in ethanol (30 ml.) was rapidly reduced (15 min. at room temperature) by addition of sodium borohydride (1 g.) in ethanol (20 ml.). The solid obtained on pouring the reaction mixture into water was recrystallised from aqueous methanol to give the *dihydro-derivative* (0·56 g.), m. p. 256—259° (decomp.) (Found: C, 73·9; H, 5·7; N, 7·7; P, 8·2. $C_{23}H_{21}ON_2P$ requires C, 74·2; H, 5·7; N, 7·5; P, 8·3%).

Thermal Decomposition of the Pyrazoline (XX).—The pyrazoline (14·6 g.) in diglyme (280 ml.) was heated under reflux with a trace of copper for 2·5 hr. The hot mixture was filtered and allowed to cool. The crystals which separated were removed, and the filtrate was poured into water. The solids collected gave a total yield of 7·76 g. of crude product (m. p. 225°). This was dissolved in ethanol, filtered through alumina, and allowed to crystallise to give the *cyclopropane* (XVI; R = H) as pale yellow needles (5·55 g.), m. p. 234—235° (decomp.) (Found: C, 80·9; H, 5·5; P, 9·4. $C_{23}H_{19}OP$ requires C, 80·7; H, 5·6; P, 9·1%). This compound decomposed at its m. p., and resolidified at a slightly higher temperature. Chromatography of the pyrolysis residue in chloroform on silica gel gave two compounds, a deep yellow powder and maroon crystals. The structures of these two products are unknown, since difficulty in purification prevented reliable analysis.

Catalytic hydrogenation of the cyclopropane gave a *dihydro-derivative*, m. p. 220—222° (Found: C, 80·1; H, 6·7; P, 8·8. $C_{23}H_{21}OP$ requires C, 80·2; H, 6·1; P, 9·0%). Some pyrazolines isomerise to amino-nitriles on heating with platinum black,[30] and an attempt was therefore made to isomerise (XX) in order to establish the orientation of the pyrazoline ring. However, refluxing with freshly prepared platinum black in 2-methoxyethanol (124°) for 24 hr. gave only the cyclopropane (XVI; R = H) in 46% yield.

Photochemical Reaction between 1,2,5-*Triphenylphosphole Oxide and Diazomethane*.—The phosphole oxide (2·4 g.) in dioxan (150 ml.) and ether (200 ml.) was mixed with diazomethane (*ca.* 2·5 g.) in ether (120 ml.), and the mixture was irradiated (85-w lamp) for 2 hr. through Pyrex. After filtration, concentration, crystallisation, and recrystallisation from ethanol, the cyclopropane (0·6 g.), m. p. 235° (decomp.), was obtained.

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[30] A. N. Kost, G. A. Golubeva, A. P. Terent'ev, and I. I. Grandberg, *Proc. Acad. Sci.* (*U.S.S.R.*), 1962, **144**, 431.