766. *The Preparation and Properties of* 10-*Phenylphenoxphosphine.*

By Frederick G. Mann and Ian T. Millar.

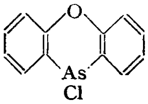
The preparation and properties of the above phosphine, which contains a novel heterocyclic system, are described. The significance of the absorption spectra of the phosphine and its methiodide is briefly discussed.

Arsenic trichloride and phosphorus trichloride show a striking dissimilarity in their behaviour towards a hot mixture of diphenyl ether and aluminium chloride, for the former readily gives 10-chlorophenoxarsine (I) (Turner, D.Sc. Dissertation, Univ. London, 1920; Lewis, Lowry, and Bergeim, *J. Amer. Chem. Soc.*, 1921, **43**, 891), whereas phosphorus trichloride apparently furnishes solely *p*-phenoxyphenyldichlorophosphine, $Ph{\cdot}O{\cdot}C_6H_4{\cdot}PCl_2$ (Davies and Morris, *J.*, 1932, 2880). Although there is no decisive evidence for the cause of this difference, it is probable that the first action of the arsenic trichloride is similarly to give *p*-phenoxyphenyldichloroarsine with smaller quantities of the *ortho*-isomer. Under the influence of the aluminium chloride and the temperature, both these compounds tend to form equilibria $Ph{\cdot}O{\cdot}C_6H_4{\cdot}AsCl_2 + HCl \rightleftharpoons Ph{\cdot}O{\cdot}Ph + AsCl_3$. The *ortho*-compound however also undergoes cyclisation to give the phenoxarsine (I), and since this is an irreversible reaction under these conditions, it ultimately becomes the dominant reaction. In the phosphorus reaction, Davies and Morris (*loc. cit.*) were unable to detect the formation of any *o*-phenoxyphenyldichlorophosphine, and, apart from this factor, dismutations of the above type occur much less readily in phosphines than in arsines.

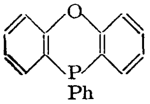
Some evidence which supports this mechanism has been provided by Aeschlimann (*J.*, 1927, 413), who showed that phenyldichloroarsine reacts with diphenyl ether and aluminium chloride also to form the chloro-arsine (I). It is probable that here the most rapid reaction is again the dismutation, $2PhAsCl_2 \rightleftharpoons Ph_2AsCl + AsCl_3$, with the trichloride then fulfilling its above rôle. The preparation of 10-alkyl- or 10-aryl-phenoxarsines is therefore best performed by the action of the appropriate Grignard reagent on the chloroarsine (I) (Aeschlimann, *loc. cit.*; Roberts and Turner, *J.*, 1926, 1207).

To prepare compounds having the novel phenoxphosphine ring system, we have therefore had recourse to 2 : 2′-dibromodiphenyl ether. This compound reacts very sluggishly with magnesium, but readily forms a dilithio-derivative, which when treated with phenyldichlorophosphine furnishes 10-phenylphenoxphosphine (II) as colourless crystals, m. p. 94·5—95°, in 63% yield.

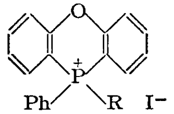
The heterocyclic system present in (II) is of particular interest, because there is considerable stereochemical evidence that the molecules of other analogous tricyclic compounds are folded about an axis passing through the two heterocyclic atoms: for example, the phenoxarsines (Lesslie and Turner, *J.*, 1934, 1170; 1935, 1051, 1268; 1936, 730; Lesslie, *J.*, 1949, 1183), the phenoxstibines (Campbell, *J.*, 1947, 4), and the dihydroarsanthrens (Chatt and Mann, *J.*, 1940, 1184). The intervalency angle of oxygen in diphenyl ether has been determined by Leonard and Sutton (*J. Amer. Chem. Soc.*, 1948, **70**, 1564), using dipole measurements, as 116° ± 4°, and that in 4 : 4′-di-iododiphenyl ether by Plieth (*Z. Naturforsch.*, 1947, **2***a*, 409), using *X*-ray crystal analysis, as 123° ± 2°; that of tervalent phosphorus in tertiary phosphines is, however, *ca.* 100° (Springall and Brockway, *J. Amer. Chem. Soc.*, 1938, **60**, 996), and consequently the phenoxphosphine molecule (II) might also be folded about the O–P axis. If this folded structure were stable the 10-phenyl derivative (II) might exist in two geometrically isomeric forms, in one of which the phenyl group would be projecting within the angle subtended by the two *o*-phenylene groups, and the second in which this group would project behind this angle. No evidence of such isomerism has been detected; this may be due either to one of the above forms having a markedly greater stability than the other, or to ready oscillation of the phenyl group about the O–P axis, thereby rendering the molecule effectively planar.



(I)

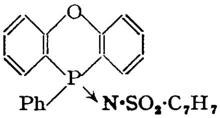


(II)

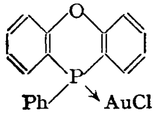


(III)

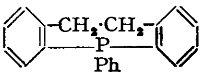
When the phosphorus atom in (II) becomes tetrahedral, the increase in the intervalency angle at this atom would almost certainly make the three rings virtually coplanar. We find that the methiodide (III; R = Me), the phosphine oxide, the phosphinimine (IV), the aurous chloride derivative (V), and the corresponding auric trichloride derivative are highly crystalline compounds showing no evidence of isomerism.



(IV)



(V)

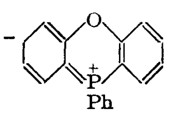


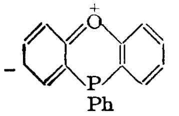
(VI)

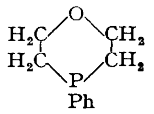
Although some trialkylphosphines are sufficiently basic to form crystalline salts with acids (cf. Beeby and Mann, *J.*, 1951, 411), the phenoxphosphine (II) is only very weakly basic, as would be expected for a triarylphosphine: it will dissolve readily in hot concentrated hydrochloric acid but the solution on cooling deposits the free phosphine.

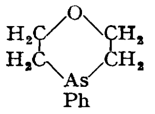
The high stability of the heterocyclic ring in the phosphine (II) is shown by the following results: (*a*) the phosphine is unaffected when its solution in concentrated hydrochloric, hydrobromic, or hydriodic acid is boiled, or heated in sealed tubes, for considerable periods; (*b*) when a mixture of the phosphine, bromobenzene, and aluminium chloride is heated at 210° for 2 hr., the product, when suitably treated with potassium iodide, yields 10 : 10-diphenylphenoxphosphonium iodide (III; R = Ph). These are the conditions under which Chatt and Mann (*J.*, 1940, 1192) prepared tetraphenylphosphonium iodide, and their rather rigorous nature had apparently no disruptive effect on the phenoxphosphine system.

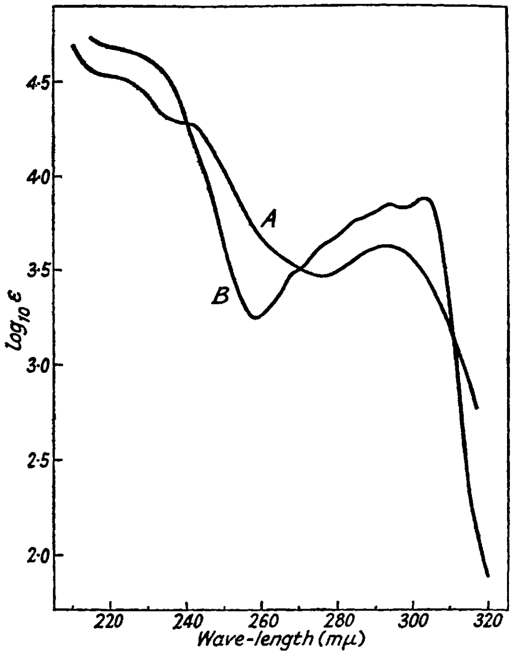
In the annexed Figure, the absorption spectra of the phenoxphosphine (II) and its methiodide (III; R = Me) are shown. The former has $\lambda_{\text{max.}}$ 294 mμ (ε 4300); $\lambda_{\text{min.}}$ 275 mμ (ε 3000), and the latter $\lambda_{\text{max.}}$ 303 and 294 mμ (ε 7700, 7100) and $\lambda_{\text{min.}}$ 297 and 258 mμ (ε 6980, 1800). It is noteworthy that the spectrum of the phosphine bears a strong general resemblance to those of triphenylphosphine and of 1-phenyl-1-phospha-2 : 3-6 : 7-dibenzo-*cyclo*hepta-2 : 6-diene (VI), and that of the methiodide bears a similar resemblance to those of the corresponding salts of the last two phosphines, the chief difference being that the principal band of the phosphine (II) and its methiodide shows a marked displacement to higher wave-lengths compared with those of triphenylphosphine, the phosphine (VI), and their respective methiodides. The significance of the spectra of triphenylphosphine and of (VI) and their quaternary salts has been briefly discussed by Mann and Millar (*J.*, 1953, 1130). It will be seen that if the phenoxphosphine possessed three independently absorbing benzene rings, in accordance with the formal structure (II), several absorption bands, with the main absorption at about 255 mμ, would be expected. The structure of the phosphine (II) however may involve resonance with numerous polar forms of type (II*A*), precisely as triphenylphosphine and the phosphine (VI) may, but in addition it may show further resonance with similar forms of type (II*B*). This markedly increased resonance may be responsible not only for the absence of benzenoid bands, but also for the general shift to higher wave-lengths. In the methiodide of the phosphine (II) the polar forms of type (II*A*) are necessarily suppressed, but those of type (II*B*) may of course still operate: possibly it is this factor which allows the emergence of two bands at 294 and 303 mμ (which may represent the normal absorption of the benzene rings considerably displaced) but which are merged into one broad band in the more highly resonating parent phosphine.


(II*A*)


(II*B*)


(VII)


(VIII)



Absorption spectra in ethanolic solution of:
(*A*) 10-*phenylphenoxphosphine.*
(*B*) 10-*methyl*-10-*phenylphenoxphosphonium iodide.*

The only other recorded compound, in which the heterocyclic ring contains oxygen and the C–P–C linkage, is tetrahydro-4-phenyl-1 : 4-oxaphosphine (VII), which Lecoq (*Bull. Soc. chim. Belge*, 1933, **42**, 119) claims to have prepared by the action of phenylphosphine-bis(magnesium bromide) on 2 : 2′-di-iododiethyl ether, a method analogous to that by which Beeby and Mann (*J.*, 1951, 886) subsequently prepared the arsenic analogue (VIII).

It is noteworthy however that Lecoq states that the phosphine (VII) has m. p. 135—137°, whereas in contrast 4-phenylmorpholine has m. p. 53° (Knorr, *Ber.*, 1889, **22**, 2094) and the arsine (VIII) is a mobile liquid, b. p. 149—151°/18 mm., which shows no signs of crystallisation. Moreover Lecoq isolated his phosphine by allowing an ethereal solution to evaporate spontaneously in the air, conditions under which a dialkyl-aryl-phosphine would normally undergo very ready oxidation. It is probable therefore that Lecoq's crystalline material (in spite of the analytical evidence) was the phosphine oxide.

We have failed to repeat Lecoq's work. We find that phenylphosphinebis(magnesium bromide) reacts with both the di-iododiethyl ether and its bromo-analogue to give a pale amber resin, which could be distilled under nitrogen at *ca.* 300°/0·5 mm. but the distillate rapidly re-formed the resin. All attempts to crystallise the resin, or to obtain crystalline derivatives, failed. No evidence of the formation of a more volatile product could be obtained. It is probable that this resin is a stable linear condensation product of type $[\cdot(CH_2)_2\cdot O\cdot(CH_2)_2\cdot PPh\cdot]_n$ similar to that which is always formed during the preparation of both the arsine (VIII) (Beeby and Mann, *loc. cit.*) and its thio-analogue (Job, Reich, and Vergnaud, *Bull. Soc. chim.*, 1924, **35**, 1404).

EXPERIMENTAL

2-*Amino-2'-bromodiphenyl Ether.*—Iron "pin dust" (51 g.) was added to a boiling agitated solution of 2'-bromo-2-nitrodiphenyl ether (59 g.) (cf. Henley, *J.*, 1930, 1222) in ethanol (70 c.c.) containing water (10 c.c.). Concentrated hydrochloric acid (10 c.c.) was then added dropwise, and the vigorously stirred mixture was boiled under reflux for 6 hr., after which an aqueous solution of potassium hydroxide (7 g.) was added. The hot mixture was filtered and the residue washed with an equal volume of hot ethanol. The combined filtrate, when cooled, deposited the amino-ether, m. p. 55—56° (35 g., 66%), sufficiently pure for the next stage. This amine was prepared on a very small scale by McCombie, Macmillan, and Scarborough (*J.*, 1930, 1202), who record m. p. 60°.

It gives a *hydrobromide*, colourless crystals (from hydrobromic acid), m. p. 174—176° (Found: C, 41·9; H, 3·4; N, 4·2. $C_{12}H_{10}ONBr,HBr$ requires C, 41·7; H, 3·2; N, 4·0%).

2 : 2'-*Dibromodiphenyl Ether.*—Sodium nitrite (10·5 g.) in water (25 c.c.) was slowly added to a vigorously stirred solution of the amine (40 g.) in concentrated (48%) hydrobromic acid (100 c.c.) which had been cooled to *ca.* 5°. After 30 minutes' further stirring, the diazotised solution was slowly added to a boiling solution of cuprous bromide (20 g.) in concentrated hydrobromic acid (20 c.c.). The oily lower layer was separated, the aqueous layer extracted with chloroform, and the united oil and extract washed in turn with aqueous sodium hydroxide and water, dried, and distilled. Fractionation gave the pure *ether* as a colourless liquid, b. p. 134—136°/0·5 mm. (14 g., 28%) (Found: C, 44·3; H, 2·7. $C_{12}H_8OBr_2$ requires C, 43·95; H, 2·5%).

10-*Phenylphenoxphosphine* (II).—This preparation was performed in a flask fitted with a sealed stirrer, reflux condenser, and a dropping funnel, and through which nitrogen was passed throughout the experiment. A 1·5N-solution (73·5 c.c.) of *n*-butyl-lithium (2·2 mols.) in light petroleum (b. p. 40—45°) was added to a solution of the dibromo-ether (16·4 g.) in a mixture of benzene (100 c.c.) and the light petroleum (100 c.c.). The complete mixture was then boiled under reflux with stirring for 4 hr., cooled whilst a solution of phenyldichlorophosphine (8·95 g.) in benzene (100 c.c.) was added during 30 min., boiled again for 3 hr., and finally cooled in ice-water and hydrolysed with air-free water (200 c.c.). The aqueous layer was siphoned off under nitrogen, the clear orange-red organic layer dried (Na_2SO_4), and the solvent removed. The syrupy residue, which partly solidified, was however distilled and the fraction of b. p. 191—193°/0·5 mm. solidified completely; when then recrystallised from ethanol it gave the *phosphine* (II), colourless crystals, m. p. 94·5—95° (8·75 g., 63%) (Found: C, 78·3; H, 4·45. $C_{18}H_{13}OP$ requires C, 78·4; H, 4·75%). A resinous solid, which could not be crystallised, remained in the distillation flask.

The phosphine readily gave a *methiodide* (III; R = Me) (systematically 10-*methyl*-10-*phenylphenoxphosphonium iodide*), colourless crystals (from ethanol), m. p. 236—237° (Found: C, 54·75; H, 3·9. $C_{19}H_{16}OIP$ requires C, 54·6; H, 3·9%); its ethanolic solution gave no precipitate with sodium picrate solution.

A mixture of the phosphine (1·4 g.), bromobenzene (1·6 g., 2 mols.), and aluminium chloride (1·35 g., 2 mols.) was heated at 205—210° for 2 hr. under nitrogen. The mixture was then poured into water (100 c.c.) and boiled, unchanged phosphine (0·4 g.) separating on cooling. The cold filtered solution, when treated with potassium iodide (5 g.), deposited a semi-solid gum, which was dissolved in hot water (50 c.c.), treated with sodium sulphite (0·5 g.), boiled, cooled, and finally filtered into a solution of potassium iodide (5 g.) in water (150 c.c.). The precipitated crystalline 10 : 10-*diphenylphenoxphosphonium iodide* (III; R = Ph), when collected and recrystallised from water, furnished the colourless crystalline *monohydrate*, m. p. 195—197° (Found: C, 57·9; H, 3·7. $C_{24}H_{18}OIP,H_2O$ requires C, 57·85; H, 4·05%).

This iodide, when treated in aqueous solution with sodium picrate, gave the *picrate*, yellow crystals (from ethanol), m. p. 190—192° (decomp.) (Found: C, 61·8; H, 3·5; N, 7·2. $C_{30}H_{20}O_8N_3P$ requires C, 61·95; H, 3·5; N, 7·2%).

Similar experiments, with *p*-bromotoluene in place of bromobenzene, gave only intractable dark products.

A warm acetone solution of the phosphine (II), when diluted with an equal volume of aqueous hydrogen peroxide and set aside overnight, deposited the *oxide*, which formed colourless crystals, m. p. 173—174°, from aqueous acetone (Found: C, 74·25; H, 4·8. $C_{18}H_{13}O_2P$ requires C, 74·0; H, 4·5%).

Solutions of the phosphine (0·54 g.) and of anhydrous chloramine-T (0·45 g., 1 mol.), each in ethanol (15 c.c.), were mixed, boiled for 1 hr., filtered to remove sodium chloride, and evaporated in a vacuum. The residual syrup readily crystallised when rubbed with ethanol, and when then recrystallised, either from ethanol or from benzene–light petroleum (b. p. 60—80°), afforded colourless 10-*phenylphenoxphosphine* 10-*toluene*-p-*sulphonylimine* (IV), m. p. 164—164·5° (Found: C, 67·5; H, 4·6; N, 3·2. $C_{25}H_{20}O_3NSP$ requires C, 67·4; H, 4·55; N, 3·15%). Several similar phosphinimines, prepared from trialkyl- and triaryl-phosphines, have been recorded (Mann and Chaplin, *J.*, 1937, 527).

Metallic Co-ordination Derivatives.—(*a*) When an ethanolic solution of the phosphine (2·1 mols.) and aqueous-ethanolic potassium palladobromide (1 mol.) were mixed and boiled, the crystalline *dibromobis*-(10-*phenylphenoxphosphine*)*palladium*, $[(C_{18}H_{13}OP)_2PdBr_2]$ was precipitated, and separated from ethanol as yellow crystals, m. p. 298—302° (decomp.) (Found: C, 53·2; H, 3·2. $C_{36}H_{26}O_2Br_2P_2Pd$ requires C, 52·8; H, 3·2%).

Repetition of this experiment, with however equimolecular quantities of the reagents, afforded the bridged *dibromobis*-(10-*phenylphenoxphosphine*)-μ-*dibromopalladium*, $[(C_{18}H_{13}OP)PdBr_2]_2$, which separated as reddish-brown crystals, m. p. 279—281° (decomp.), from ethanolic dioxan (1 : 1) (Found: C, 40·1; H, 2·25. $C_{36}H_{26}O_2Br_4P_2Pd_2$ requires C, 39·85; H, 2·4%).

(*b*) When an ethanolic solution of an excess of the phosphine was added to concentrated aqueous chloroauric acid, a dark orange precipitate was initially formed, but was rapidly replaced by a white product when the mixture was boiled. This product, recrystallised from ethanol, gave hard colourless crystals of *monochloro*-(10-*phenylphenoxphosphine*)*gold* (V), m. p. 200° (Found: C, 42·6; H. 2·7. $C_{18}H_{13}OClPAu$ requires C, 42·5; H, 2·6%).

When a solution of chlorine in carbon tetrachloride was added to a chloroform solution of this compound, orange-red crystals of the *trichloro*-derivative, m. p. 157—158° (decomp.), were deposited (Found: C, 36·9; H, 2·2. $C_{18}H_{13}OCl_3PAu$ requires C, 37·3; H, 2·3%) (cf. Mann and Purdie, *J.*, 1940, 1235).

Action of Acids.—(*a*) The phosphine readily dissolved in boiling hydrochloric acid, but cooling deposited the unchanged phosphine, m. p. 92—94° (alone and mixed).

(*b*) A mixture of the phosphine and an excess of aqueous 48% hydrobromic acid was boiled under reflux below nitrogen for 3 hr., a clear solution being rapidly obtained. Cooling and basification deposited the unchanged phosphine. A similar result was obtained when the phosphine was heated with a 50% solution of hydrogen bromide in acetic acid in a sealed tube at 150—155° for 4 hr., or at 180—200° for 10 hr. In the last experiment, however, a dark syrup was obtained and basification gave only a low recovery of the phosphine, although no derivative could be isolated.

(*c*) The phosphine was recovered unchanged after its solution in an excess of constant-boiling hydriodic acid had been boiled under reflux for 4 hr.

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