438. p-*Phenoxyphenyldichlorophosphine.*

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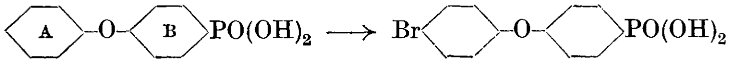
No phosphorus-containing derivatives of diphenyl ether have hitherto been obtained, but p-*phenoxyphenyldichlorophosphine* has now been prepared by the condensation of phosphorus trichloride with diphenyl ether in the presence of aluminium chloride.

The orientation of the product was established by two methods. (1) *Tri*-p-*phenoxyphenylphosphine* was prepared from phosphorus trichloride and *p*-phenoxyphenylmagnesium bromide and converted into *tri*-p-*phenoxyphenylmethylphosphonium iodide* : this was identical with the methiodide of the tertiary phosphine obtained from the phenoxyphenyldichlorophosphine and *p*-phenoxyphenylmagnesium bromide.

(2) A modification of Michaelis's bromination method (*Annalen*, 1896, **293**, 224) was employed to determine the position of the $PO(OH)_2$ group in the *phosphonic acid* derived from the dichlorophosphine. Bromine attacked the *p*-position of the nucleus A more readily than it eliminated the phosphorus-containing group from the *p'*-position of the nucleus B, giving p-*bromo*-p'-*phosphonodiphenyl ether*, which by treatment with bromine and water at 160° was converted into *pp'*-dibromodiphenyl ether. With this method of orientation there is a possibility of the phosphonic acid group being eliminated by heat (cf. Michaelis, *loc. cit.*, p. 207), with production of diphenyl ether, which would on bromination yield *pp'*-dibromodiphenyl ether.



The absence of *o*- and *m*-phenoxyphenyldichlorophosphines in the product of the condensation of phosphorus trichloride with diphenyl ether is shown by the homogeneity of the resulting compound and of its derivatives. Moreover, there does not appear to be any tendency for PCl_2 groups to enter both nuclei simultaneously. The exclusive *p*-direction of the entering group by phenoxyl is in full accord with the theories of aromatic substitution described by Lea and Robinson (J., 1926, 411) and Lapworth and Robinson (*Mem. Manchester Phil. Soc.*, 1927, **72**, 43).

EXPERIMENTAL.

The methods of Davies and Davies (J., 1931, 1207) for the estimation of P have been used throughout.

All thermometer readings are corrected.

p-*Phenoxyphenyldichlorophosphine.*—A mixture of 170 g. of Ph_2O, 137 g. of PCl_3, and 20 g. of $AlCl_3$ was refluxed for 36 hr., and the product distilled up to

207°/12 mm. Fractional redistillation under reduced press. gave PCl_3, Ph_2O, and the dichlorophosphine, which was redistilled (yield, 37 g.). p-*Phenoxyphenyldichlorophosphine* is a colourless oily liquid which fumes slightly in the air and has a characteristic odour; b. p. 200°/12 mm.; $d_4^{20°}$ 1·3122 (*vac.*) (Found: C, 52·8; H, 3·1; P, 11·5. $C_{12}H_9OCl_2P$ requires C, 53·1; H, 3·3; P, 11·4%). It is miscible with Et_2O, but is decomposed by H_2O and EtOH. At 270° in an inert atmosphere, HCl is slowly evolved, leaving a thick gum. Boiling pyridine also removes HCl.

p-Phenoxyphenyldichlorophosphine dichloride was obtained in quant. yield as a yellow, extremely hygroscopic, cryst. solid by passing a slow current of dry Cl over a thin layer of the well-cooled dichlorophosphine. On account of the difficulty of purification it was not analysed. Its composition follows from its mode of prepn. and from the product which it yields with H_2O.

When the solid dichloride was added gradually to H_2O, an oil separated. The mixture was boiled and allowed to cool; the oil then solidified to a cryst. mass of p-*phenoxyphenylphosphonic acid monohydrate*, which was recrystallised from AcOH, forming lustrous plates, m. p. 185°, almost insol. in H_2O, C_6H_6, light petroleum, and CCl_4, but sol. in EtOH (Found: C, 53·7; H, 4·7; P, 11·4; H_2O, 7·2; equiv., 134·6. $C_{12}H_{13}O_5P$ requires C, 53·7; H, 4·9; P, 11·6; H_2O, 6·7%; *M*, 268). The H_2O content was determined by heating the acid in vac. for 4 hr. at 169°. At a higher temp., *e.g.*, at 180°, a more profound change took place, about 1½ mol. of water were lost, and when cold the product was a glassy solid. The equiv. of the acid was obtained by dissolving a weighed quantity in NaOH aq. and titrating the excess of alkali with succinic acid and phenolphthalein.

Action of Bromine on p-*Phenoxyphenylphosphonic Acid Monohydrate.*—The acid (2·68 g.), suspended in 10 c.c. of CCl_4, was heated with 1·6 g. of Br for 1 hr., the solvent expelled, and the residue extracted with hot AcOH, from which p-*bromo*-p′-*phosphonodiphenyl ether* crystallised in colourless lustrous plates (1·8 g.), m. p. 209°, almost insol. in H_2O, Et_2O, C_6H_6, and CCl_4, but sol. in EtOH (Found: P, 9·6; equiv., 161. $C_{12}H_{10}O_4BrP$ requires P, 9·4%; *M*, 329).

1·16 G. of the bromo-acid, 0·54 g. of Br, and 1 g. of H_2O were heated in a sealed tube at 160° for 8 hr. CCl_4 then extracted 1·5 c.c. of a liquid, which was fractionally distilled under reduced press. A middle fraction (1 c.c.), which slowly solidified, was crystallised repeatedly from EtOH; it then had m. p. 58°, and 58·5° in admixture with *pp*′-dibromodiphenyl ether.

pp′-*Diphenoxydiphenyl.*—In preps. involving the use of *p*-phenoxyphenylmagnesium bromide, there was obtained, as a product of the synthetic action of the Mg on *p*-bromodiphenyl ether, pp′-*diphenoxydiphenyl*, which was prepared in quantity as follows: The Grignard solution prepared from 83 g. of *p*-bromodiphenyl ether (and a little EtBr), 8 g. of Mg, and 100 c.c. of Et_2O was rapidly added to a well-stirred suspension of 63 g. (equiv. quantity) of dry AgBr in a mixture of 100 c.c. of Et_2O and 100 c.c. of C_6H_6, and the whole refluxed for 3 hr. The Et_2O and C_6H_6 were expelled, the residue was treated with 500 c.c. of *N*-HCl, and the liquid filtered. The residue on the filter was extracted with boiling EtOH, which removed 18 g. of *pp*′-diphenoxydiphenyl; light colourless needles, m. p. 150°, after recrystn. from boiling EtOH or light petroleum (Found: C, 84·9; H, 5·4. $C_{24}H_{18}O_2$ requires C, 85·2; H, 5·4%), sol. in cold C_6H_6 or $CHCl_3$, slightly sol. in cold EtOH, CCl_4, CS_2 and light petroleum, but sol. in the hot solvents.

Mercury Bis-p-*diphenyl Ether*.—34 G. of $HgCl_2$ were added in small portions to a *filtered* Grignard solution (83 g. of *p*-bromodiphenyl ether, 8 g. of Mg, and 250 c.c. of Et_2O), the mixture was boiled for 4 hr., and after 12 hr. the Et_2O was expelled and the residue treated with 300 c.c. of 2*N*-HCl. The liquid was decanted, and the solid repeatedly extracted with boiling C_6H_6. The extract on cooling gave 16 g. of *mercury bis*-p-*diphenyl ether*, colourless minute crystals, m. p. 192° after two crystns.; sol. in hot $CHCl_3$ and hot C_6H_6, insol. in H_2O, Et_2O, and EtOH (Found: Hg, 37·6. $C_{24}H_{18}O_2Hg$ requires Hg, 37·2%). *pp'*-Diphenoxydiphenyl, which is also formed, remains in the C_6H_6 solution.

p-*Phenoxyphenyldimethylphosphine*.—A solution of 35·5 g. of MeI in 100 c.c. of absolute Et_2O, together with a trace of I, was stirred during 2 hr. into 6 g. of Mg and 100 c.c. of Et_2O in an apparatus through which a current of H was passing. A solution of 17 g. of *p*-phenoxyphenyldichlorophosphine in 50 c.c. of Et_2O was added drop by drop to the well-cooled Grignard reagent, the mixture warmed for ½ hr., again cooled, and treated with NH_4Cl aq. The ethereal solution was dried over anhyd. Na_2SO_4, the Et_2O removed, the residue fractionally distilled under reduced press., and the phosphine fraction redistilled. p-*Phenoxyphenyldimethylphosphine* (7·5 g.) had b. p. 183°/13 mm. and $d_{4°}^{20°}$ 1·1037 (vac.) (Found: C, 72·4; H, 6·7; *M*, 222·1. $C_{14}H_{15}OP$ requires C, 73·0; H, 6·6%; *M*, 230·1). It has a limited miscibility with EtOH at 15°.

p-*Phenoxyphenyltrimethylphosphonium iodide*, prepared from the phosphine and MeI in Et_2O and recryst. from EtOH, formed colourless rods, m. p. 242° (Found: I, 34·0. $C_{15}H_{18}OIP$ requires I, 34·1%). A solution of the hydroxide, prepared from an aq. solution of the methiodide and Ag_2O, had an alkaline reaction and pptd. the difficulty sol. metallic hydroxides from solutions of their salts.

p-*Phenoxyphenyltrimethylphosphonium chloroplatinate* [Found: Cl, 23·2. $(PhO{\cdot}C_6H_4{\cdot}PMe_3)_2PtCl_6$ requires Cl, 23·7%] was pptd. as orange crystals, m. p. 226° (recryst. from much H_2O or EtOH), when H_2PtCl_6 aq. was added to a boiling HCl solution of the phosphonium hydroxide.

p-*Phenoxyphenyldiethylphosphine* (8·6 g.) was prepared by adding 17 g. of *p*-phenoxyphenyldichlorophosphine to EtMgBr, obtained from 27·6 g. of EtBr and 6 g. of Mg; b. p. 208°/13 mm., $d_{4°}^{20°}$ 1·0711 (vac.) (Found: C, 74·0; H, 7·4; P, 11·9; *M*, 244. $C_{16}H_{19}OP$ requires C, 74·4; H, 7·4; P, 12·0%; *M*, 258·2). p-*Phenoxyphenylmethyldiethylphosphonium iodide*, m. p. 163°, crystallises as flat rectangular plates from a hot conc. solution in EtOH (Found: I, 31·7. $C_{17}H_{22}OIP$ requires I, 31·7%). The *phosphonium chloroplatinate*, m. p. 222° (Found: Cl, 21·7. $C_{34}H_{44}O_2Cl_6P_2Pt$ requires Cl, 22·3%), was almost insol. in H_2O and EtOH.

p-*Phenoxyphenyldi*-n-*propylphosphine* had b. p. 218°/13 mm.; $d_{4°}^{20°}$ 1·0562 (vac.) (Found: C, 75·1; H, 8·4; *M*, 291·6. $C_{18}H_{23}OP$ requires C, 75·5; H, 8·1%; *M*, 286·2). The *methiodide* formed octahedral crystals, m. p. 126° (Found: I, 29·7. $C_{19}H_{26}OIP$ requires I, 29·6%), from a hot conc. solution in EtOH. p-*Phenoxyphenylmethyldi*-n-*propylphosphonium chloroplatinate*, m. p. 221—222° (Found: Cl, 20·1. $C_{38}H_{52}O_2Cl_6P_2Pt$ requires Cl, 21·1%), was a buff-coloured ppt. insol. in H_2O and in EtOH.

p-*Phenoxyphenyldi*-n-*butylphosphine* was prepared by adding 17 g. of *p*-phenoxyphenyldichlorophosphine to the Grignard solution obtained from 34·3 g. of BuBr and 6 g. of Mg (yield, 7 g.); b. p. 235°/13 mm.; $d_{4°}^{20°}$ 1·0310 (vac.) (Found: C, 76·0; H, 8·7; *M*, 293·7. $C_{20}H_{27}OP$ requires C, 76·4; H, 8·7%; *M*, 314·2). When ethereal solutions of its generators were mixed, p-*phenoxyphenylmethyldi*-n-*butylphosphonium iodide* separated as an oil which rapidly crystallised. Recryst. from EtOH, it formed colourless rods, m. p. 227° (Found: I, 28·1. $C_{21}H_{30}OIP$ requires I, 27·8%). The corresponding *chloroplatinate* was an insol. buff-coloured ppt., m. p. 225° (Found: Cl, 19·4. $C_{42}H_{60}O_2Cl_6P_2Pt$ requires Cl, 19·9%).

Tri-p-*phenoxyphenylphosphine.*—(A) This was obtained, together with some *pp'*-diphenoxydiphenyl, as an oil when 17 g. of *p*-phenoxyphenyldichlorophosphine were added to *p*-phenoxyphenylmagnesium bromide prepared from 83 g. of *p*-bromodiphenyl ether and 8 g. of Mg. The oil was obtained solid by pressing the semi-solid substance, obtained by pptn. of the C_6H_6 solution of the oil with hot EtOH, on a porous plate; recryst. from C_6H_6–EtOH, it formed shining plates, m. p. 111° (Found: C, 79·7; H, 5·1; P, 6·1. $C_{36}H_{27}O_3P$ requires C, 80·3; H, 5·1; P, 5·8%). *Tri*-p-*phenoxyphenylmethylphosphonium iodide* separated as a solid, m. p. 115° to a cloudy liquid (Found: I, 18·7. $C_{37}H_{30}OIP$ requires I, 18·7%), when dil. ethereal solutions of its generators were mixed. Attempts to recrystallise it were unsuccessful.

(B) The semi-solid mass obtained when 13·8 g. of PCl_3 were added to a Grignard solution prepared from 124·5 g. of *p*-bromodiphenyl ether and 12 g. of Mg could not be purified, but yielded a solid methiodide (Found: I, 18·7%), m. p. and mixed m. p. with (A), 115° to a cloudy liquid.

Attempted Synthesis of Arylphosphonic Acids.—Attempts to prepare such acids from diazo-solutions and phosphorous acid were unsuccessful.

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