

CCXCVII.—*Tertiary Arylalkylphosphines. Part I.*

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THE present communication contains an account of the preparation and properties of alkylphosphines derived from *p*-ethyl- and from *p*-methoxy-phenyldichlorophosphine. These chlorophosphines have already been described by Michaelis (*Annalen*, 1896, **293**, 314, 249), who also prepared *p*-ethylphenyl- and *p*-methoxyphenyldiethylphosphines (*ibid.*, pp. 324, 256).

The method of preparing *p*-methoxyphenyldichlorophosphine adopted in the present work differed somewhat from that of Michaelis, since in our hands his procedure, *viz.*, only 4–6 hours' heating, yielded no chlorophosphine. However, the pure chlorophosphine was obtained in the following way. A mixture of 150 c.c. of dry anisole, 125 c.c. of phosphorus trichloride, and 30 g. of commercial aluminium chloride was refluxed for 36 hours. The product was distilled under 20 mm. until all the liquid had passed over. The distillate was then fractionally redistilled under low pressure, whereby the dichlorophosphine (30 g.), b. p. 150°/18 mm., was obtained. A sample of this, on being tested with water, gave hydrochloric acid and an immediate separation of needles of anisylphosphinous acid, which, after recrystallisation from water, melted at 113° (Michaelis gave 112°). According to Kunz (*Ber.*, 1894, **27**, 2559), when pure aluminium chloride is used in the preparation, the product is phenoxydichlorophosphine, which, on treatment with water, yields phenol and phosphorous and hydrochloric acids.

For the preparation of *p*-ethylphenyldichlorophosphine, 170 c.c. of ethylbenzene, 125 c.c. of phosphorus trichloride, and 30 g. of aluminium chloride were used. The b. p. of the chlorophosphine was 127°/12 mm.

The values given by Michaelis for the boiling point and density of *p*-methoxyphenyldichlorophosphine, *viz.*, *ca.* 130°/12–15 mm., and 1.0764 at 15°, respectively, are seriously in error; we found b. p. 150°/18 mm. and d_4^{25} 1.331. The present value for the density of *p*-ethylphenyldichlorophosphine, *viz.*, d_4^{25} 1.225, however, agrees well with the value recorded by Michaelis, *viz.*, 1.227 at 17°.

In the preparation of the phosphines, a solution of an equivalent of the *n*-alkyl bromide in 150 c.c. of absolute ether, together with a trace of iodine, was added with continuous stirring in the course of 2 hours to 12.1 g. of magnesium turnings and 150 c.c. of ether in an apparatus through which a stream of hydrogen was passed. The amounts of alkyl bromide used were as follows: propyl, 45.5 c.c.;

butyl, 53.5 c.c.; amyl, 62 c.c. The proportions here given ensured excess of Grignard reagent over chlorophosphine; this was found to favour yield of phosphine. The Grignard solution was now cooled to 0°, and to it was added, drop by drop, a solution of 21 c.c. of *p*-ethylphenyldichlorophosphine, or of 20 c.c. of *p*-methoxyphenyldichlorophosphine, in 50 c.c. of ether. The resulting mixture was warmed for $\frac{1}{2}$ hour on a steam-bath, then cooled below 0°, and a solution of 50 g. of ammonium chloride in 250 c.c. of water was slowly added with stirring until the solids dissolved. The ethereal solution was separated and dried, and the ether was distilled off. The liquid then remaining was fractionally distilled under reduced pressure, the phosphine obtained being purified by redistillation. All temperatures and weights were corrected.

The phosphines here described possess the usual phosphinic odour, and give the characteristic red coloration with carbon disulphide. They are insoluble in water, but dissolve freely in ether, alcohol, or benzene.

On deducting the refractivities of the alkyl, ethylphenyl, and anisyl groups present (Eisenlohr, *Z. physikal. Chem.*, 1910, **75**, 585) from the given molecular refractivities, values for the atomic refractivity (for the D line) of phosphorus in these phosphines are obtained, *viz.*, 10.15 and 10.65 in the ethylphenyl compounds, and 10.31, 10.21, and 10.63 in the methoxyphenyl compounds. Comparison with the value given by Zecchini (*Gazzetta*, 1893, **23**, 97) for phosphorus in triethylphosphine, *viz.*, 9.47, shows clearly the great optically exaltative effect of the linking of the phenyl group to phosphorus. The similar effect with nitrogen and the phenyl group has been much studied, and has been attributed to the establishment of a virtual conjugation involving the nitrogen atom and the endocyclic double bonds (Brühl, *Ber.*, 1907, **40**, 900, 1155; Eisenlohr, *Ber.*, 1911, **44**, 3188; *Z. physikal. Chem.*, 1912, **79**, 129).

The rate of oxidation of *p*-ethylphenyl- and of *p*-methoxyphenylphosphines is comparatively slow, so that special precautions to prevent ingress of air during manipulation (Dyke, Davies, and Jones, this vol., p. 463), although adopted in the present work, are not absolutely necessary. These phosphines immediately combine with the halogens, and, compared with stibines, their avidity for methyl and other alkyl iodides is considerable. The low degree of crystallisability of their derivatives, however, is particularly marked in the case of the ethylphenylphosphines. The methylphosphonium hydroxides derived from these phosphines react alkaline, absorb carbon dioxide from the air, and precipitate the hydroxides of lead, copper, tin, ferric iron, aluminium, and zinc from solutions of their respective salts.

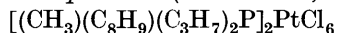
p-Ethylphenyl-di-*n*-propylphosphine (Found: C, 75.7; H, 10.4. $C_{14}H_{23}P$ requires C, 75.6; H, 10.4%) has b. p. $157^{\circ}/21$ mm.; d_4^{25} 0.9147; n_D^{25} 1.5370; $[R_L]_F$ 75.86; n_D^{25} 1.5255; $[R_L]_D$ 74.50; n_C^{25} 1.5208; $[R_L]_C$ 73.94. Yield of purified phosphine, 13 g. When an equivalent of bromine in ether is added to a similar solution of the phosphine, an oily precipitate of *p*-ethylphenyl-di-*n*-propylphosphine dibromide (Found: Br, 42.1. $C_{14}H_{23}Br_2P$ requires Br, 41.8%) is immediately obtained.

p-Ethylphenyl-di-*n*-butylphosphine (Found: C, 76.6; H, 11.0. $C_{16}H_{27}P$ requires C, 76.7; H, 10.8%) boils at $176^{\circ}/15$ mm.; d_4^{25} 0.9042; n_D^{25} 1.5319; $[R_L]_F$ 85.74; n_D^{25} 1.5208; $[R_L]_D$ 84.24; n_C^{25} 1.5162; $[R_L]_C$ 83.61. Yield, 12 g. The dibromide (Found: Br, 38.2. $C_{16}H_{27}Br_2P$ requires Br, 39.0%) forms a thick liquid.

p-Ethylphenyl-di-*n*-amylphosphine (Found: C, 78.0; H, 10.9. $C_{18}H_{31}P$ requires C, 77.6; H, 11.2%) boils at $201^{\circ}/18$ mm. and has d_4^{25} 0.9022. Yield, 13 g.

With the exception of *p*-ethylphenyl-di-*n*-amylphosphine mercurichloride (Found: Cl, 13.1. $C_{18}H_{31}P, HgCl_2$ requires Cl, 12.9%), which, after recrystallisation from glacial acetic acid, formed elongated prisms, m. p. 95° , the mercurichlorides and methiodides of these *p*-ethylphenyldialkylphosphines remained non-crystalline even after being preserved for 6 months.

p-Ethylphenylmethyl-di-*n*-propylphosphonium hydroxide is left as an oil when an alcoholic solution of the phosphonium iodide is shaken with well-washed, freshly precipitated silver oxide, the silver iodide filtered off, and the alcohol expelled in a vacuum. The solution of the hydroxide reacts alkaline and precipitates the difficultly soluble metallic hydroxides from solutions of their salts. The corresponding chloroplatinate (Found: Pt, 22.3.



requires Pt, 22.1%) is precipitated in yellow needles, m. p. 195° (after recrystallisation from alcohol), when aqueous chloroplatinic acid is added to a boiling alcoholic solution of the phosphonium hydroxide acidified with hydrochloric acid.

Similarly prepared, *p*-ethylphenylmethyl-di-*n*-amylphosphonium chloroplatinate (Found: Pt, 19.2. $[(CH_3)(C_8H_9)(C_5H_{11})_2P]_2PtCl_6$ requires Pt, 19.6%) forms yellow crystals (m. p. not sharp).

p-Methoxyphenyl-di-*n*-propylphosphine (Found: C, 69.1; H, 9.0. $C_{13}H_{21}OP$ requires C, 69.6; H, 9.4%) boils at $165^{\circ}/17$ mm., and has d_4^{25} 0.9738; n_D^{25} 1.5477; $[R_L]_F$ 73.08; n_D^{25} 1.5352; $[R_L]_D$ 71.69; n_C^{25} 1.5301; $[R_L]_C$ 71.12. Yield, 13 g. Treated in ethereal solution with bromine, the phosphine gives the dibromide (Found: Br, 42.5. $C_{13}H_{21}OBr_2P$ requires Br, 41.6%), a thick liquid.

p-Methoxyphenyl-di-*n*-propylphosphine mercurichloride is precipit-

ated as a gummy solid when alcoholic solutions of its components are mixed. On being preserved, the gum is gradually transformed to a crystalline mass, the saturated solution of which in glacial acetic acid deposits prismatic crystals, m. p. 134° (Found: Cl, 14.9. $C_{13}H_{21}OP, HgCl_2$ requires Cl, 14.3%), on being allowed to evaporate. *p-Methoxyphenylmethyldi-n-propylphosphonium iodide* is precipitated as an oil when ethereal solutions of the phosphine and of methyl iodide are mixed. On standing in a vacuum desiccator, the oil gradually crystallises. Before analysis, the crystals [Found: I, 34.7. $(CH_3)(C_7H_7O)(C_3H_7)_2PI$ requires I, 34.7%], m. p. 60°, were washed with ether. Attempts to effect recrystallisation from water, alcohol, or alcohol-light petroleum all resulted in precipitation of the methiodide as an oil, which, however, on being separated from solvent and preserved, re-solidified.

p-Methoxyphenyldi-n-butylphosphine (Found: C, 71.0; H, 9.9. $C_{15}H_{25}OP$ requires C, 71.4; H, 10.0%) boils at 190°/16 mm.; d_4^{25} 0.9600; n_D^{25} 1.5389; $[R_L]_F$ 82.28; n_D^{25} 1.5274; $[R_L]_D$ 80.82; n_C^{25} 1.5226; $[R_L]_C$ 80.20. Yield, 12 g. The *methiodide* is obtained similarly to that of the propyl phosphine. It melts at 86° (Found: C, 48.4; H, 7.4; I, 32.0. $C_{16}H_{28}OIP$ requires C, 48.7; H, 7.2; I, 32.2%). The phosphonium hydroxide forms an oil, which on treatment with chloroplatinic acid yields *p-methoxyphenylmethyldi-n-butylphosphonium chloroplatinate* (Found: Pt, 20.5.



requires Pt, 20.7%), which forms fine yellow needles, and, after recrystallisation from alcohol, melts at 196°.

p-Methoxyphenyldi-n-amylphosphine (Found: C, 72.8; H, 10.1. $C_{17}H_{29}OP$ requires C, 72.8; H, 10.4%) has b. p. 202°/18 mm.; d_4^{25} 0.9382; n_D^{25} 1.5289; $[R_L]_F$ 92.10; n_D^{25} 1.5178; $[R_L]_D$ 90.48; n_C^{25} 1.5132; $[R_L]_C$ 89.80. Yield, 12 g. The *dibromide* (Found: Br, 37.2. $C_{17}H_{29}OBr_2P$ requires Br, 36.3%) melts ca. 85°. Recrystallised from acetic acid, the *mercurichloride* (Found: Cl, 13.2. $C_{17}H_{29}OP, HgCl_2$ requires Cl, 12.9%) forms elongated plates, m. p. 114°. Even after long preservation, the *methiodide* remained as an oil (Found: I, 29.5, 29.5. $C_{18}H_{32}OIP$ requires I, 30.1%). *p-Methoxyphenylmethyldi-n-amylphosphonium chloroplatinate* [Found: Pt, 19.7. $(C_{18}H_{32}OP)_2PtCl_6$ requires Pt, 19.6%], recrystallised from alcohol, forms yellowish-brown hexagonal plates, m. p. 153°.