

VI.—*Tertiary Phosphines containing the n-Butyl Radical.*

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No such phosphines have hitherto been described, but in the course of an investigation now being carried out by the authors on the action of the chlorides of phosphorus on the organo-magnesium halides, the following have been prepared : *tri-n-butylphosphine*, *phenyldi-n-butylphosphine* and *p-tolyldi-n-butylphosphine*. Triethylphosphine (Hibbert, *Ber.*, 1906, 39, 161), triphenylphosphine (Pfeiffer, *Ber.*, 1904, 37, 4620), phenyldimethylphosphine (Meisenheimer, *Annalen*, 1926, 449, 227; Ingold, Shaw, and Wilson, *J.*, 1928, 1280), and phenyldiethylphosphine (Meisenheimer, *loc. cit.*) have already been prepared by this method.

Preparation of the Phosphines.—A solution of 42 c.c. of *n*-butyl bromide in 100 c.c. of absolute ether, together with a granule of iodine, was added in the course of 3 hours to 10 g. of magnesium turnings and 150 c.c. of ether, contained in an apparatus through which hydrogen was passed throughout the course of the preparation, and which permitted of continuous stirring of the liquid. The resulting Grignard solution was cooled to 0° and a solution of 9 c.c. of phosphorus trichloride or 19 c.c. of phenyldichlorophosphine or 20 c.c. of *p*-tolyldichlorophosphine in 50 c.c. of ether was added drop by drop. The mixture was then warmed for $\frac{1}{2}$ hour on the water-bath, cooled below 0°, and cautiously treated with a solution of 50 g. of ammonium chloride in 250 c.c. of water; the precipitated magnesium salts ultimately all dissolved. The ethereal solution was dried over anhydrous sodium sulphate, and the ether distilled off, in an atmosphere of carbon dioxide. The residue was fractionally distilled, and the phosphine redistilled, under 50 mm. pressure. All thermometer readings given are corrected.

The *n*-butylphosphines are colourless liquids having the characteristic phosphinic odour. They are miscible in all proportions with alcohol, ether, and benzene, but immiscible with water, and their molecular weights in freezing benzene are normal. They are far less easily oxidised than the lower tertiary phosphines. For instance, they do not readily combine with the oxygen of the air, but *tri-n-butylphosphine*, on being boiled in a current of air, is converted into *tri-n-butylphosphine oxide*. *Tri-n-butylphosphine* combines directly with carbon disulphide to give a deep red, crystalline compound, but from phenyl- and *p*-tolyl-di-*n*-butylphosphines, although deep red solutions are obtained in carbon disulphide no

crystalline compounds can be produced. All these phosphines combine with alkyl iodides and with mercuric chloride. The phosphonium iodides are ionised in aqueous and in alcoholic solution, and can be quantitatively estimated by means of silver nitrate. Vigorous reaction also occurs between the phosphines and both chlorine and sulphur.

Tri-n-butylphosphine has b. p. $149.5^{\circ}/50$ mm. and d_{4}^{25} 0.8118 (Found: C, 70.8; H, 13.8; *M*, 210. $C_{12}H_{27}P$ requires C, 71.2; H, 13.5%; *M*, 202). Yield, 11 g. The *carbon disulphide addition compound*, $C_{12}H_{27}P,CS_2$, m. p. 65.5° (Found: C, 56.1; H, 10.1. $C_{13}H_{27}S_2P$ requires C, 56.1; H, 9.8%), owing to the vigour of the combination, is best prepared by mixing cold absolute-alcoholic solutions of the components, from which the compound crystallises. It is completely dissociated in hot ethereal and alcoholic solutions. On mixing alcoholic solutions of the components the mercuric chloride addition compound of tri-*n*-butylphosphine is obtained as a plastic mass which is difficult to purify. *Methyltri-n-butylphosphonium iodide*, owing to the violence of the direct interaction of methyl iodide and the phosphine, is most conveniently obtained by mixing dilute ethereal solutions of the reactants: the white crystalline precipitate, m. p. 133.5° , is purified by washing with ether (Found: I, 36.1. $C_{13}H_{30}IP$ requires I, 36.8%). *Ethyltri-n-butylphosphonium iodide* (Found: I, 34.9. $C_{14}H_{32}IP$ requires I, 35.4%) melts at 153° . *Tri-n-butylphosphine oxide* was prepared by adding 10 c.c. of phosphorus oxychloride in 50 c.c. of ether to the Grignard solution already described. Ammonium chloride solution was added and, when the ethereal layer was fractionally distilled under 760 mm. pressure, the oxide passed over at 300° and solidified in the receiver (Found: C, 63.3; H, 12.6; P, 14.9. $C_{12}H_{27}OP$ requires C, 66.0; H, 12.4; P, 14.2%). It forms colourless needles which are extremely hygroscopic. The oxide was also prepared both by boiling the phosphine in a current of air and by oxidising it with warm 40% nitric acid.

Phenyl-di-n-butylphosphine has b. p. $184.5-185.5^{\circ}/50$ mm. and d_{4}^{25} 0.9115 (Found: C, 75.4; H, 10.5; P, 14.6; *M*, 221. $C_{14}H_{23}P$ requires C, 75.6; H, 10.4; P, 14.0%; *M*, 222). Yield, 16 g. The *mercuric chloride compound*, m. p. 160.5° , is obtained as fine needles when alcoholic solutions of its components are mixed and is purified by recrystallisation from alcohol (Found: Cl, 14.7. $C_{14}H_{23}P, HgCl_2$ requires Cl, 14.4%). *Phenylmethyl-di-n-butylphosphonium iodide* is not so soluble in water as the other iodides, and well-formed rods, m. p. 168° , are obtained on recrystallisation from water (Found: I, 34.3. $C_{15}H_{26}IP$ requires I, 34.8%).

Phenylethyl-di-n-butylphosphonium iodide melts at 147° (Found:

I, 33.9. $C_{16}H_{28}IP$ requires I, 33.6%). It is best recrystallised from alcohol-ether.

p-Tolyldi-n-butylphosphine has b. p. $197^{\circ}/50$ mm. and d_4^{25} 0.9076 (Found : C, 75.5; H, 10.8; *M*, 228. $C_{15}H_{25}P$ requires C, 76.1; H, 10.7%; *M*, 236). Yield, 15 g. The *mercuric chloride addition compound* crystallises from alcohol in prisms, m. p. 112° (Found : Cl, 14.2. $C_{15}H_{25}P, HgCl_2$ requires Cl, 14.0%). *p-Tolymethyldi-n-butylphosphonium iodide* melts at 130.5° (Found : I, 33.5. $C_{16}H_{28}IP$ requires I, 33.6%).

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