CLXIV.—*Tertiary Phosphines containing the Higher Alkyl Radicals.*

By Walter Cule Davies, Percy Leonard Pearse, and William Jacob Jones.

Cahours (*Jahresber.*, 1873, 518) stated that zinc propyl on interaction with phosphorus trichloride gave tripropylphosphine. Attempts by Collie (J., 1888, **53**, 715) to prepare tripropylphosphine, by heating phosphonium iodide with propyl alcohol in sealed tubes, were unsuccessful. However, by distilling propyltriethylphosphonium chloride he obtained propyldiethylphosphine hydrochloride, and similarly, from *iso*amyltriethylphosphonium chloride, *iso*amyldiethylphosphine hydrochloride. Hofmann (*Ber.*, 1873, **6**, 292) obtained small quantities of tri*iso*propyl-, tri*iso*butyl-, and tri*iso*amyl-phosphine, in an impure state, by digesting the secondary phosphine with the corresponding iodide and treating the product with alkali. In a similar manner he prepared the hydriodide of ethyl*iso*propyl*iso*butylphosphine by heating *iso*propyl*iso*butylphosphine with ethyl iodide. Hofmann failed to obtain tertiary bases by heating phosphonium iodide with *iso*butyl and *iso*amyl alcohol, respectively. Moreover, Hofmann (*Phil. Trans.*, 1860, **150**,

412) made unsuccessful attempts to prepare tri*iso*amyl- and triallylphosphine by heating the corresponding iodide with phosphorus and zinc.

None of the preceding methods affords a satisfactory means of preparing tertiary phosphines containing higher alkyl radicals in good yield and in pure condition. For this purpose the use of Grignard reagents is much to be preferred and has already proved to be successful in the case of phosphines containing the *n*-butyl radical (Davies and Jones, this vol., p. 33). This method, however, is restricted, because with the higher alkyl halides the yield of organomagnesium derivative is often poor, and, where Grignard reagents derived from secondary and tertiary alkyl halides are caused to interact with phosphorus halides, side reactions seriously interfere with the yield of tertiary phosphine. In the course of the present investigation tertiary phosphines containing the following alkyl groups have been prepared: *n*-propyl, *iso*butyl, *n*-amyl, β-methylbutyl, γ-methylbutyl (*iso*amyl), and δ-methylamyl (*iso*hexyl).

In the air the trialkylphosphines are directly converted into their oxides, the *n*-series being less readily oxidised than the *iso*-series, whereas phosphines containing aryl groups are unaffected. On analysis by combustion with copper oxide the phosphines give low results for carbon and for hydrogen, particularly if they are not previously thoroughly mixed with powdered copper oxide. No satisfactory results were obtained in estimations of phosphorus, although repeated attempts were made by the following methods: heating the phosphine with fuming nitric acid in a sealed tube, with sodium carbonate in a current of oxygen (compare Bay, *Compt. rend.*, 1908, **146**, 814), with a mixture of concentrated nitric and sulphuric acids, with potassium persulphate and concentrated sulphuric acid (Poggi and Polverini, *Atti R. Accad. Lincei*, 1926, **4**, 315), and with "perhydrol" and concentrated sulphuric acid. Trialkylphosphines combine directly with carbon disulphide to give stable red crystalline compounds, but in the case of the alkylarylphosphines the red compounds formed immediately dissociate completely on being isolated. All the phosphines here described combine with methyl iodide, but difficulty is experienced in obtaining phosphonium halides by combination with the higher alkyl halides.

The method of preparing phosphines adopted in the present investigation is similar to that which has been already described (Davies and Jones, *loc. cit.*), but the proportions of the Grignard reagent and of the phosphorus chloride have been varied according to the yield of organomagnesium halide obtained and to the chlorine-content of the particular phosphorus chloride used.

Experimental.

Tri-n-*propylphosphine* is prepared by the addition of 12 c.c. of phosphorus trichloride in 50 c.c. of ether to a Grignard solution made from 56 c.c. of *n*-propyl bromide, 15 g. of magnesium and 300 c.c. of ether. Yield of purified phosphine, 10 g. B. p. 103·5°/50 mm., 187·5°/760 mm.; $d_{4^\circ}^{25^\circ}$ 0·807 (Found: C, 66·9; H, 13·3; *M*, 161. $C_9H_{21}P$ requires C, 67·4; H, 13·2%; *M*, 160). The *carbon disulphide compound*, $C_9H_{21}P,CS_2$, m. p. 108° (Found: S, 26·9. $C_{10}H_{21}S_2P$ requires S, 27·1%), is prepared by mixing alcoholic solutions of its components, and recrystallised from alcohol. *Tri*-n-*propylphosphine mercurichloride*, m. p. 137°, is obtained by mixing alcoholic solutions of the constituents and repeatedly crystallising the product from glacial acetic acid, the crystals being washed with alcohol and dried. The chlorine-content was determined by heating the compound with sodium carbonate in a combustion tube, dissolving the product in dilute nitric acid, and precipitating silver chloride by addition of silver nitrate (Found: Cl, 16·7. $C_9H_{21}P,HgCl_2$ requires Cl, 16·4%). *Methyltri*-n-*propylphosphonium iodide* (Found: I, 41·5. $C_{10}H_{24}IP$ requires I, 42·0%), m. p. 212·5°, and *tetra*-n-*propylphosphonium bromide* (Found: Br, 28·0. $C_{12}H_{28}BrP$ requires Br, 28·2%), decomposing at 200°, are best recrystallised from alcohol, and their halide content can be determined by solution in water and precipitation with silver nitrate.

Phenyldi-n-*propylphosphine* is prepared by introducing an ethereal solution of 19 c.c. of phenyldichlorophosphine to magnesium *n*-propyl bromide obtained from 36 c.c. of *n*-propyl bromide and 10 g. of magnesium. Yield, 17 g. B. p. 159°/50 mm.; $d_{4^\circ}^{25^\circ}$ 0·925 (Found: C, 73·9; H, 10·0; *M*, 193. $C_{12}H_{19}P$ requires C, 74·2; H, 9·9%; *M*, 194). The *mercuric chloride compound*, m. p. 192·5°, separates as needles from alcohol (Found: Cl, 15·3. $C_{12}H_{19}P,HgCl_2$ requires Cl, 15·2%). *Phenylmethyldi*-n-*propylphosphonium iodide* melts at 137° (Found: I, 37·6. $C_{13}H_{22}IP$ requires I, 37·8%) and can be recrystallised from water. *Phenyltri*-n-*propylphosphonium bromide* has m. p. 131·5° (Found: Br, 24·9. $C_{15}H_{26}BrP$ requires Br, 25·2%).

p-*Tolyldi*-n-*propylphosphine* is obtained by adding 20 c.c. of *p*-tolyldichlorophosphine to magnesium *n*-propyl bromide prepared in ethereal solution from 36 c.c. of *n*-propyl bromide. Yield, 14 g. B. p. 174°/50 mm.; $d_{4^\circ}^{25^\circ}$ 0·921 (Found: C, 74·7; H, 10·3; *M*, 203. $C_{13}H_{21}P$ requires C, 75·0; H, 10·2%; *M*, 208). p-*Tolyldi*-n-*propylphosphine mercurichloride* melts at 129·5°, and is obtained as prisms from glacial acetic acid (Found: Cl, 14·9. $C_{13}H_{21}P,HgCl_2$ requires Cl, 14·8%). p-*Tolylmethyldi*-n-*propylphosphonium iodide*, m. p. 81·5° (Found: I, 36·1. $C_{14}H_{24}IP$ requires I, 36·2%), can be recrystallised from alcohol. p-*Tolyltri*-n-*propylphosphonium bromide*, m. p. 125·5° (Found : Br, 24·0. $C_{16}H_{28}BrP$ requires Br, 24·1%), is formed with difficulty, and is obtained by refluxing the components in ethereal solution; well-developed, hygroscopic needles crystallise on cooling.

*Tri*iso*butylphosphine* (yield, 12 g.), obtained by the addition of 14 c.c. of phosphorus trichloride to magnesium *iso*butyl bromide prepared from 94 c.c. of *iso*butyl bromide and 20 g. of magnesium, has b. p. 126°/50 mm. (Found : C, 69·7; H, 13·3; *M*, 191. $C_{12}H_{27}P$ requires C, 71·2; H, 13·5%; *M*, 202). The phosphine combines with carbon disulphide, giving highly unstable red crystals. *Tri*iso*butylphosphine mercurichloride*, m. p. 191·5°, is obtained as plates from alcohol (Found: Cl, 14·8. $C_{12}H_{27}P,HgCl_2$ requires Cl, 15·0%). Methyltri*iso*butylphosphonium iodide has already been prepared by Hofmann (*Ber.*, 1873, **6**, 300), m. p. 287° (Found : I, 36·8. Calc. for $C_{13}H_{30}IP$: I, 36·8%). It readily crystallises from water, being very soluble in hot water and only slightly in cold.

*Phenyldi*iso*butylphosphine* is prepared by adding 11 c.c. of phenyldichlorophosphine to the Grignard reagent obtained from 47 c.c. of *iso*butyl bromide and 10 g. of magnesium. Yield, 10 g. B. p. 168°/50 mm.; $d_{4°}^{25°}$ 0·910 (Found: C, 75·4; H, 10·6; *M*, 218. $C_{14}H_{23}P$ requires C, 75·6; H, 10·4%; *M*, 222). The *mercuric chloride compound*, after several recrystallisations from alcohol, from which it forms as needles, melts to a cloudy liquid at 158·5° (Found : Cl, 14·3. $C_{14}H_{23}P,HgCl_2$ requires Cl, 14·4%). *Phenylmethyldi*iso*butylphosphonium iodide*, m. p. 166·5°, crystallises as pearly leaflets from water (Found : I, 34·7. $C_{15}H_{26}IP$ requires I, 34·8%).

p-*Tolyldi*iso*butylphosphine*, obtained from 15 c.c. of *p*-tolyldichlorophosphine and the Grignard solution prepared from 47 c.c. of *iso*butyl bromide (yield, 6 g.), has b. p. 182·5—184·5°/50 mm. and $d_{4°}^{25°}$ 0·915 (Found: C, 75·0; H, 10·7; *M*, 233. $C_{15}H_{25}P$ requires C, 76·1; H, 10·7%; *M*, 236.) *p*-Tolyldi*iso*butylphosphine mercurichloride is precipitated when alcoholic solutions of its generators are mixed, and on recrystallisation from alcohol forms cubic crystals in poor yield and impure. p-*Tolylmethyldi*iso*butylphosphonium iodide* separates as an oil which on long preservation crystallises (Found : I, 32·4. $C_{16}H_{28}IP$ requires I, 33·6%).

Tri-n-*amylphosphine* has b. p. 185·5°/50 mm. and $d_{4°}^{25°}$ 0·820 (Found: C, 73·0; H, 13·7; *M*, 236. $C_{15}H_{33}P$ requires C, 73·7; H, 13·6%; *M*, 244), and is prepared by the interaction between 10·5 c.c. of phosphorus trichloride and magnesium *n*-amyl bromide made from 78 c.c. of the bromide and 15 g. of magnesium. Yield, 9 g. *Tri*-n-*amylphosphine carbon disulphide* is prepared in quantitative yield on mixing the constituents in alcoholic solution; m. p. 55°

(Found : C, 60·1; H, 10·4. $C_{16}H_{33}S_2P$ requires C, 59·9; H, 10·4%). The mercurichloride and the methiodide of the phosphine could not be obtained crystalline.

The preparation of *phenyldi*-n-*amylphosphine* is effected by adding 11·5 c.c. of phenyldichlorophosphine to the Grignard solution obtained from 42 c.c. of *n*-amyl bromide and 8 g. of magnesium (yield, 10 g.); b. p. 210°/50 mm., $d_{4^\circ}^{25^\circ}$ 0·902 (Found : C, 76·2; H, 10·9; *M*, 247. $C_{16}H_{27}P$ requires C, 76·8; H, 10·9%; *M*, 250). This phosphine is only partially miscible with absolute ethyl alcohol at 15°. It forms a *compound* with mercuric chloride, m. p. 108°, which crystallises well from alcohol (Found : Cl, 13·4. $C_{16}H_{27}P,HgCl_2$ requires Cl, 13·6%). *Phenylmethyldi*-n-*amylphosphonium iodide* forms leaflets from water, m. p. 90·5° (Found : I, 32·2. $C_{17}H_{30}IP$ requires I, 32·4%).

p-*Tolyldi*-n-*amylphosphine* has b. p. 220°/50 mm. and $d_{4^\circ}^{25^\circ}$ 0·898 (Found : C, 76·6; H, 11·4; *M*, 260. $C_{17}H_{29}P$ requires C, 77·2; H, 11·1%; *M*, 264). It is prepared by the addition of 11 c.c. of *p*-tolyldichlorophosphine to magnesium *n*-amyl bromide obtained from 51 c.c. of the bromide and 10 g. of magnesium. Yield, 11 g. This *p*-tolylphosphine is still less completely miscible with absolute ethyl alcohol than the corresponding phenylphosphine. The *compound* with mercuric chloride separates as an oil, which crystallises well from glacial acetic acid. It melts at 112° (Found : Cl, 13·3. $C_{17}H_{29}P,HgCl_2$ requires Cl, 13·2%). p-*Tolylmethyldi*-n-*amylphosphonium iodide* separates as an oil which on long preservation crystallises (Found : I, 30·6. $C_{18}H_{32}IP$ requires I, 31·2%).

Tri(dl-β-*methylbutyl*)*phosphine* was obtained in poor yield by adding 10·5 c.c. of phosphorus trichloride to the Grignard reagent prepared from 77 c.c. of *dl*-β-methylbutyl bromide and 15 g. of magnesium, and has b. p. 113—117°/10 mm. (Found : C, 69·8; H, 13·5. $C_{15}H_{33}P$ requires C, 73·7; H, 13·6%).

Phenyldi(dl-β-*methylbutyl*)*phosphine* is prepared by adding 14 c.c. of phenyldichlorophosphine to magnesium *dl*-β-methylbutyl bromide from 51 c.c. of the bromide and 10 g. of magnesium. Yield, 8 g. B. p. 198°/50 mm.; $d_{4^\circ}^{25^\circ}$ 0·906 (Found : C, 76·4; H, 11·0; *M*, 249. $C_{16}H_{27}P$ requires C, 76·8; H, 10·9%; *M*, 250). On mixing the components in alcoholic solution the *mercuric chloride compound* is formed; it is isolated by separating the alcoholic layer from the oil and allowing the alcoholic solution to evaporate; m. p. 120° (Found : Cl, 13·3. $C_{16}H_{27}P,HgCl_2$ requires Cl, 13·6%). *Phenylmethyldi*(dl-β-*methylbutyl*)*phosphonium iodide*, m. p. 150°, crystallises as glistening plates from water (Found : I, 32·2. $C_{17}H_{30}IP$ requires I, 32·4%).

The preparation of p-*tolyldi*(dl-β-*methylbutyl*)*phosphine* is carried out by adding 11 c.c. of *p*-tolyldichlorophosphine to the Grignard reagent made from 51 c.c. of the bromide (yield, 7 g.); b. p. 210—211°/50 mm., $d_{4^\circ}^{25^\circ}$ 0·902 (Found: C, 77·1; H, 11·5; *M*, 266. $C_{17}H_{29}P$ requires C, 77·2; H, 11·1%; *M*, 264). The *mercurichloride*, m. p. 99°, was prepared in a similar manner to the corresponding phenyl compound (Found: Cl, 13·2. $C_{17}H_{29}P,HgCl_2$ requires Cl, 13·2%). p-*Tolylmethyldi*(dl-β-*methylbutyl*)*phosphonium iodide* (Found: I, 31·4. $C_{18}H_{32}IP$ requires I, 31·2%), m. p. 131°, crystallises from water in rods.

*Tri*iso*amylphosphine* [*tri*(γ-*methylbutyl*)*phosphine*] has b. p. 131°/11 mm. (Found: C, 73·2; H, 13·6; *M*, 237. $C_{15}H_{33}P$ requires C, 73·7; H, 13·6%; *M*, 244). It was prepared from 10·5 c.c. of phosphorus trichloride, 78 c.c. of *iso*amyl bromide, and 15 g. of magnesium. The final ethereal solution of the phosphine was dried, and the ether distilled off in an atmosphere of carbon dioxide as already described (Davies and Jones, *loc. cit.*), but, in order to prevent oxidation of the phosphine, the residue was fractionally distilled in a vacuum, and all subsequent manipulations with the phosphine were carried out in an enclosure filled with carbon dioxide, without bringing it into contact with the air. Yield, 9 g. The *carbon disulphide compound*, m. p. 79·5° (Found: C, 60·1; H, 10·4. $C_{16}H_{33}S_2P$ requires C, 59·9; H, 10·4%), is obtainable in good yield as red needles. When ethereal solutions of its generators are mixed, *methyltri*iso*amylphosphonium iodide* (Found: I, 33·2. $C_{16}H_{36}IP$ requires I, 32·9%) is precipitated as an oil which solidifies on keeping.

*Phenyldi*iso*amylphosphine*, b. p. 198·5°/50 mm., $d_{4^\circ}^{25^\circ}$ 0·900, is obtained from 14 c.c. of phenyldichlorophosphine, 52 c.c. of *iso*amyl bromide, and 10 g. of magnesium (yield, 12 g.) (Found: C, 76·9; H, 11·2; *M*, 248. $C_{16}H_{27}P$ requires C, 76·8; H, 10·9%; *M*, 250). The *mercuric chloride compound* forms needles and melts at 152° to a cloudy liquid (Found: Cl, 13·3. $C_{16}H_{27}P,HgCl_2$ requires Cl, 13·6%). *Phenylmethyldi*iso*amylphosphonium iodide*, m. p. 181·5°, forms soft, pearly flakes from water (Found: I, 32·5. $C_{17}H_{30}IP$ requires I, 32·4%).

The preparation of p-*tolyldi*iso*amylphosphine* is effected by adding 11 c.c. of *p*-tolyldichlorophosphine to the Grignard reagent obtained from 52 c.c. of *iso*amyl bromide and 10 g. of magnesium. It has b. p. 210°/50 mm. and $d_{4^\circ}^{25^\circ}$ 0·894 (Found: C, 77·1; H, 11·2; *M*, 258. $C_{17}H_{29}P$ requires C, 77·2; H, 11·1%; *M*, 264). This phosphine is only partially miscible with ethyl alcohol at 15°. p-*Tolyldi*iso*amylphosphine mercurichloride* forms as an oil which can be crystallised from glacial acetic acid. The prisms melt at 107° (Found: Cl, 13·3. $C_{17}H_{29}P,HgCl_2$ requires Cl, 13·2%). p-*Tolylmethyldi*iso*amylphos-*

phonium iodide, m. p. 150° (Found : I, 31·1. $C_{18}H_{32}IP$ requires I, 31·2%), readily crystallises from water as hard prisms.

Phenyldi(δ-*methylamyl*)*phosphine* (*phenyldi*iso*hexylphosphine*) is obtained when a solution of 13 c.c. of phenyldichlorophosphine in 100 c.c. of ether is introduced into the Grignard reagent prepared from 60 c.c. of δ-methylamyl bromide, 10 g. of magnesium and 350 c.c. of ether. Yield, 7 g.; b. p. 219°/50 mm. (Found : C, 77·2; H, 11·4. $C_{18}H_{31}P$ requires C, 77·6; H, 11·2%). The δ-methylamyl alcohol used for the preparation of this phosphine was obtained from γ-methylbutyl chloride (*iso*amyl chloride) by the method of Grignard and Tissier (*Compt. rend.*, 1902, **134**, 107). Both *phenylmethyldi*(δ-*methylamyl*)*phosphonium iodide*, m. p. 146° (Found : I, 30·1. $C_{19}H_{34}IP$ requires I, 30·2%), and *phenylethyldi*(δ-*methylamyl*)*phosphonium iodide*, m. p. 115·5° (Found : I, 29·0. $C_{20}H_{36}IP$ requires I, 29·2%), crystallise as glistening flakes from water.

p-*Tolyldi*(δ-*methylamyl*)*phosphine*, b. p. 234—235°/50 mm., $d_{4^\circ}^{25^\circ}$ 0·888 (Found : C, 77·6; H, 11·5; *M*, 284. $C_{19}H_{33}P$ requires C, 78·0; H, 11·4%; *M*, 292), was prepared by adding a solution of 14 c.c. of *p*-tolyldichlorophosphine in 100 c.c. of ether to the Grignard reagent made as described in the case of the previous phosphine. The *mercurichloride*, m. p. 110·5° (Found : Cl, 12·5. $C_{19}H_{33}P,HgCl_2$ requires Cl, 12·6%), forms prisms from glacial acetic acid. The *methiodide* (Found : I, 29·1. $C_{20}H_{36}IP$ requires I, 29·2%) is difficult to recrystallise.

All the preceding preparations of phosphines have involved the use of the Grignard reagents of bromides derived from primary alcohols. In all cases, however, where organometallic compounds of the secondary bromides, *iso*propyl and *sec.*-butyl bromide, were employed, no yield of tertiary phosphine could be obtained, either when ammonium chloride solution was used as described by Davies and Jones (*loc. cit.*), or when the product was subjected to complete distillation as in the procedure adopted by Hibbert (*Ber.*, 1906, **39**, 161) and by Grüttner and Wiernik (*Ber.*, 1915, **48**, 1477). This failure cannot be attributed to insufficient yield of organomagnesium bromide by these alkyl bromides, and it was equally experienced with phosphorus trichloride, phenyldichlorophosphine and *p*-tolyldichlorophosphine. In all these cases the products obtained were evil-smelling mixtures from which no definite substance was isolated.

THE TATEM LABORATORIES, UNIVERSITY COLLEGE,
CARDIFF.

[*Received, April 25th,* 1929.]