247. *Tertiary Phosphines containing Secondary Alkyl Radicals.*

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Previous attempts to prepare tertiary phosphines containing secondary alkyl radicals have failed. Hofmann (*Ber.*, 1873, **6**, 292) prepared the hydriodides of tri*iso*propyl- and ethyl*iso*propyl*iso*butyl-phosphine, but the phosphines obtained therefrom on treatment with alkali were impure. No phosphine was obtained when phosphorus trichloride or aryldichlorophosphines were added to the magnesium derivatives of *iso*propyl and of *sec.*-butyl bromide (Davies, Pearse, and Jones, J., 1929, 1268). Explanation of this result, based on the adverse effect of excess Grignard reagent (Krause and Grosse, *Ber.*, 1925, **58**, *B*, 1933) and on a different reaction course with the magnesium derivatives of secondary alkyl halides from that with those of primary alkyl halides (Ivanoff and Spassoff, *Bull. Soc. chim.*, 1931, **49**, 375), is not applicable in this case. However, by employing much larger amounts of secondary alkyl bromide and magnesium than in the general method, satisfactory yields of *tri-*iso*propyl-*, -sec.-*butyl-*, and p-*phenoxyphenyldi*iso*propyl-phosphine* have now been obtained.

These large excesses are necessary to compensate for the low yield from *sec.*-alkyl bromides of Grignard reagents, which, in turn, must be in excess owing to a reaction occurring between the phosphorus chlorides and a tertiary phosphine.

Experimental.

Effect of Excess Phosphorus Trichloride on the Production of Tertiary Phosphine.—An ethereal solution of phosphorus trichloride (14·2 g., 0·25 mol.) was slowly added to a well-cooled, filtered, ethereal solution of *iso*propylmagnesium bromide, prepared from 10 g. of magnesium and

50·6 g. of the alkyl bromide (corresponding theoretically to 1 mol., but actually, because of side reactions, to about 0·5—0·6 mol.). When half of the trichloride had been added (excess of Grignard reagent), a test portion of the ethereal solution was removed and treated with carbon disulphide. A red coloration, indicating the presence of tri*iso*propylphosphine, developed. When all the trichloride had been added (*i.e.*, excess), the precipitated substances were bright yellow, and a test portion of the ethereal layer gave no coloration with carbon disulphide. No phosphine was obtained in the subsequent separation and distillation.

Preparation of the Phosphines.—To the well-cooled Grignard reagent, previously filtered through a Jena-glass funnel with sintered glass disc (porosity 4), an ethereal solution of the phosphorus chloride was slowly added in an apparatus through which a current of nitrogen was passing. The following quantities were used in the three preparations : (1) 17·2 g. ($\frac{1}{8}$ mol.) of phosphorus trichloride and 123 g. (1 mol.) of *iso*propyl bromide ; (2) 33·9 g. ($\frac{1}{8}$ mol.) of *p*-phenoxyphenyldichlorophosphine and 123 g. of *iso*propyl bromide ; (3) 13·75 g. ($\frac{1}{10}$ mol.) of trichloride and 137 g. (1 mol.) of *sec.*-butyl bromide ; and in each case 24·3 g. of magnesium and a total of 650 c.c. of ether. The reaction product was kept in the cold for ½ hour, and then cautiously treated with ammonium chloride solution. The ethereal solution was dried (sodium sulphate), the ether removed, the residue fractionally distilled under reduced pressure, and the phosphine fraction redistilled.

Special precautions were necessary to replace air by nitrogen or carbon dioxide in the preparations and subsequent manipulations of tri-*iso*propyl- and -*sec.*-butyl-phosphine, which were much more readily oxidised than the corresponding *n*-alkylphosphines.

*Tri*iso*propylphosphine* (yield, 5 g.), b. p. 81°/22 mm., was miscible with alcohol (Found : C, 67·0; H, 13·4. $C_9H_{21}P$ requires C, 67·4; H, 13·2%). Some improvement in the carbon and hydrogen determinations of this and other difficultly combustible phosphorus compounds was obtained by surrounding the glass weighing tube containing the substance with powdered copper oxide contained in a copper cylinder, the ends of which were perforated. The cylinder was then introduced into the combustion tube.

*Methyltri*iso*propylphosphonium iodide*, prepared from the phosphine and methyl iodide in ether and recrystallised from alcohol–ether, was freely soluble in water and alcohol, insoluble in ether, and had not melted at 360° (Found : I, 42·1. $C_{10}H_{24}IP$ requires I, 42·0%).

The carbon disulphide addition *compound*, $Pr^{\beta}{}_3P,CS_2$, brown rhombic plates, m. p. 111° to a colourless liquid (Found : C, 50·8; H, 9·2. $C_{10}H_{21}S_2P$ requires C, 50·8; H, 9·0%), was prepared by mixing cold alcoholic solutions of the components. The crystals were collected, and washed with ice-cold alcohol–carbon disulphide. The compound dissociated in hot solution and was not very stable in the air.

p-*Phenoxyphenyldi*iso*propylphosphine* (yield, 16 g.) had b. p. 209°/13 mm.; $d_4^{25^\circ}$ 1·0423; $n_D^{25^\circ}$ 1·5826; $n_F^{25^\circ} - n_C^{25^\circ}$ 0·0217 (Found : C, 75·2; H, 8·2. $C_{18}H_{23}OP$ requires C, 75·5; H, 8·1%). Its *methiodide* was almost insoluble in cold, but moderately soluble in hot water, and formed hexagonal plates, m. p. 203—204° (Found : I, 29·0. $C_{19}H_{26}OIP$ requires I, 29·6%). The carbon disulphide addition *compound*, prepared by mixing its generators in alcohol and cooling to $-5°$, formed brown crystals, m. p. 46° to a colourless liquid, and was almost insoluble in cold alcohol. It almost immediately became moist in the air and lost its colour. The high carbon and hydrogen content obtained in the analysis was probably due to loss of carbon disulphide before weighing (Found : C, 64·5; H, 6·9. $C_{19}H_{23}OPS_2$ requires C, 63·0; H, 6·4%).

*Tri-*sec.*-butylphosphine* (yield, 6·5 g.) (Found : C, 71·3; H, 13·8. $C_{12}H_{27}P$ requires C, 71·2; H, 13·5%) had b. p. 108°/11 mm. In the first distillation there were obtained 4 g. of purified γδ-dimethylhexane, b. p. 115—116°/760 mm.; $n_D^{25^\circ}$ 1·4028, resulting from the synthetic action of magnesium on *sec.*-butyl bromide. *Methyltri-*sec.*-butylphosphonium iodide*, m. p. 149° (Found : I, 36·8. $C_{13}H_{30}IP$ requires I, 36·8%), was best recrystallised from water. The *compound* with carbon disulphide, m. p. 66° to a pink liquid (Found : C, 56·2; H, 10·0. $C_{13}H_{27}S_2P$ requires C, 56·1; H, 9·8%), was unstable. In the air it was immediately converted into a colourless liquid, containing the parent phosphine, which was then oxidised with exceptional vigour. Addition of methyl iodide to the compound gave a deep red liquid, but addition to a suspension of the compound in ether afforded a white precipitate of methyltri-*sec.*-butylphosphonium iodide.

All thermometer readings are corrected.

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[*Received, June 27th*, 1933.]