

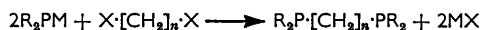
283. The Preparation of Di- and Tri-tertiary Phosphines.

By W. HEWERTSON and H. R. WATSON.

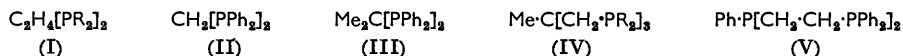
Convenient preparative routes to sodium diphenylphosphide and lithium diethylphosphide are described. Reaction of these phosphides with aliphatic polychloro-compounds allows ready preparation of bi- and tri-dentate tertiary phosphines.

DITERTIARY phosphines are of interest because they form very stable complexes with transition metals, and we have investigated routes to polyphosphines which allow more convenient preparation of known compounds and give new bi- and tri-dentate tertiary phosphines.

Most of the reported preparations of bidentate tertiary phosphines are based on the reaction:



where R = alkyl or aryl, M = alkali metal, X = halogen, and $n = 1-5$. The metal organophosphides have been made by (a) metallation of a secondary phosphine,^{1,2,3} (b) cleavage of triphenylphosphine,⁴ or (c) reaction of chlorodiphenylphosphine with the metal. The present work is based on convenient methods for preparing *in situ* sodium diphenylphosphide or lithium diethylphosphide, from which we have prepared the di- and tri-tertiary phosphines (I-V; R = Et or Ph).



Cleavage of Triphenylphosphine.—Alkali metals cleave triphenylphosphine to give the metal diphenylphosphide and the metal phenyl. Lithium in cold tetrahydrofuran,⁵ and sodium or potassium in hot dioxan,⁶ effect cleavage. Reference is made^{5,6} to the corresponding use of alkali metals in liquid ammonia by Muller and Rudorff,⁷ but details are not available to us.

Triphenylphosphine reacts immediately with sodium in liquid ammonia, and the resulting solution gives a good yield of the diphosphine (I; R = Ph) after treatment with 1,2-dichloroethane (1 mol.). With dichloromethane the yield of diphosphine (II) is only 10%. The following reactions probably occur:



The formation of diphenylmethane is unexpected because the equilibrium $PhNa + NH_3(lq.) \rightleftharpoons PhH + NaNH_2$ lies to the right.⁸ The mechanism is supported, however, by the following observations: (a) Small quantities of bibenzyl or diphenylmethane were

¹ Wymore and Bailar, *J. Inorg. Nuclear Chem.*, 1960, **14**, 42.

² Hitchcock and Mann, *J.*, 1958, 2081.

³ Issleib and Muller, *Chem. Ber.*, 1959, **92**, 3175.

⁴ Chatt and Hart, *J.*, 1960, 1378.

⁵ Wittenberg and Gilman, *J. Org. Chem.*, 1958, **23**, 1063.

⁶ Issleib and Frohlich, *Z. Naturforsch.*, 1959, **14b**, 349.

⁷ Muller and Rudorff, Dissertation, W. Muller, Tübingen, 1957, quoted in refs. 5 and 6.

⁸ Wooster and Mitchell, *J. Amer. Chem. Soc.*, 1930, **52**, 688.

isolated during the preparations of diphosphines (I; R = Ph) and (II). (b) A deep red colour, characteristic of sodium diphenylmethide, develops when the dichloromethane is added. (c) When diphenylmethane (0.5 mol.) is added to sodium diphenylphosphide solution, prepared from sodium and diphenylphosphine, a deep red colour develops, and the yield of diphosphine (I; R = Ph) after addition of dihalide is reduced to 40%.

An ammonium halide (1 mol.), when added to the cleaved triphenylphosphine solution, preferentially destroys phenylsodium and sodamide. From the solution the diphosphine (II) was obtained in 72% yield.

The diphosphine (III) (from 2,2-dichloropropane) is a colourless crystalline solid which is more sensitive to atmospheric oxidation than the corresponding compound (II). Its dioxide is of interest as a ligand.

Reaction between the trihalide $\text{Me}\cdot\text{C}[\text{CH}_2\text{Cl}]_3$ and sodium diphenylphosphide appears to be slow in liquid ammonia and was completed in boiling tetrahydrofuran. The product (IV; R = Ph), obtained in good yield, is a colourless crystalline solid which is slowly oxidised in air.

Sodium diphenylphosphide and the dibromide $\text{Ph}\cdot\text{P}[\text{CH}_2\cdot\text{CH}_2\text{Br}]_2$ give the triphosphine (V) in 16% yield. The free dibromide undergoes self-quaternisation; after isolation, it must be used quickly.

Cleavage of Triphenylarsine and Triphenylstibine.—Although triphenylarsine or -stibine react slowly with lithium in tetrahydrofuran, they are cleaved immediately by sodium in liquid ammonia. Addition of 1,2-dichloroethane to the cleaved triphenylarsine solution gave 1,2-bis(diphenylarsino)ethane in good yield, but the dihalide and cleaved triphenylstibine gave tetraphenyldistibine, Sb_2Ph_4 , and none of the expected 1,2-bis(diphenylstibino)ethane. Issleib and Muller³ have described the corresponding formation of diphosphines P_2R_4 , where R = alkyl.

Reaction of Chlorodialkylphosphines with Lithium.—When chlorodiphenylphosphine is heated with sodium in dioxan, tetraphenyldiphosphine is formed and it is subsequently cleaved by the sodium to give sodium diphenylphosphide.⁹ Chlorodialkylphosphines react with sodium under the same conditions,¹⁰ giving tetra-alkyldiphosphines. Under vigorous conditions tetraethylidiphosphine reacts with sodium in dioxan, to give sodium diethylphosphide.¹¹

We find that lithium flakes and chlorodiethylphosphine undergo a rapid exothermic reaction in cold tetrahydrofuran, giving tetraethylidiphosphine and lithium chloride. This diphosphine is cleaved by lithium in boiling tetrahydrofuran, and a yellow solution of lithium diethylphosphide results. The phosphide solution is conveniently prepared in one stage from chlorodiethylphosphine and an excess of lithium. It yields diethylphosphine when treated with water, and with di- or tri-chloro-hydrocarbons it gives the corresponding tertiary phosphines.

The diphosphine (I; R = Et)^{1,4} is conveniently prepared in 94% yield from 1,2-dichloroethane and lithium diethylphosphide in tetrahydrofuran. The corresponding reaction in ether gives only ethylene and tetraethylidiphosphine.³ (Lithium diethylphosphide gives a colourless solution in ether or dioxan, whereas a yellow solution, previously ascribed to decomposition of the phosphide by solvent,¹² is obtained in tetrahydrofuran. The present work suggests that chemical reaction with tetrahydrofuran does not occur, but that the solvent causes sufficient ionisation of the Li-P bond to alter the course of reaction with the dihalide.)

The triphosphine (IV; R = Et) was obtained in 41% yield from the trichloride $\text{Me}\cdot\text{C}[\text{CH}_2\text{Cl}]_3$ and lithium diethylphosphide in tetrahydrofuran. It is a colourless oil which can ignite spontaneously.

⁹ Kuchen and Buchwald, *Angew. Chem.*, 1957, **69**, 307.

¹⁰ Issleib and Seidel, *Chem. Ber.*, 1959, **92**, 2681.

¹¹ Issleib and Tzschach, *Chem. Ber.*, 1960, **93**, 1852.

¹² Issleib and Tzschach, *Chem. Ber.*, 1959, **92**, 1118.

Molecular models show that the triphosphines (IV; R = Et and Ph) are excellently disposed to co-ordinate to the three positions on the face of an octahedron. The triphosphine (V) can occupy three positions, either on the face or on the edge of an octahedron.

EXPERIMENTAL

Microanalyses were carried out by the Microanalytical Department of these laboratories. Molecular weights were determined ebullioscopically in benzene. M. p.s are corrected; those of phosphines were determined in evacuated tubes. Triphenylphosphine, from Messrs. Albright and Wilson, was dried before use. Chlorodiethylphosphine was prepared in *ca.* 750 g. batches, by Beeby and Mann's method.¹³ Tetrahydrofuran was distilled from sodium diphenylketyl. Quaternary iodides were prepared by heating the phosphine with an excess of alkyl iodide for several hours in the corresponding alcohol. Picrates were precipitated when an aqueous solution of the quaternary iodide was added to an excess of saturated aqueous sodium picrate solution. All operations, except purification of derivatives, were performed under dry nitrogen with air-free solvents.

Preparations using Sodium Diphenylphosphide in Liquid Ammonia.—*Bis(diphenylphosphino)methane* (II). Triphenylphosphine (131 g.) was added during 10 min. to a stirred solution of sodium (23.0 g., 2 mol.) in liquid ammonia (1500 c.c.) at -75° . An immediate reaction took place and the solution became deep orange. Ammonium bromide (49 g., 1 mol.) was added, whereupon an exothermic reaction occurred, the solution remaining orange. After 1 hr., dichloromethane (21.2 g., 0.5 mol.) in ether (20 c.c.) was added, and the solution progressively paled.

Ammonia was allowed to boil from the colourless mixture, and the residual solid, having been washed with water (1200 c.c.) and methanol (4×50 c.c.), was collected and recrystallised from propan-1-ol as colourless needles (74 g., 77%). Further recrystallisation gave the pure compound, m. p. $120.5-121.5^{\circ}$ (Issleib and Muller³ give m. p. 122°) (Found: C, 78.2; H, 5.9. Calc. for $C_{25}H_{22}P_2$: C, 78.1; H, 5.8%). The *dimethiodide*, from methanol, had m. p. 322° (Found: C, 48.4; H, 4.25. $C_{27}H_{28}I_2P_2$ requires C, 48.5; H, 4.2%).

1,2-Bis(diphenylphosphino)ethane (I; R = Ph).—This was prepared similarly (75%) by use of 1,2-dichloroethane in place of dichloromethane. A good yield (82%) is also obtained if no ammonium halide is added to the cleaved triphenylphosphine solution, and one mol. of the dihalide is used. The compound, identical with that obtained previously by one of us,⁴ has m. p. $143-144^{\circ}$. Issleib and Muller³ give m. p. $159-161^{\circ}$.

2,2-Bis(diphenylphosphino)propane (III).—This was prepared as above (28%) with 2,2-dichloropropane¹⁴ replacing dichloromethane. The *diphosphine* recrystallised from propan-1-ol as air-sensitive needles, m. p. $123-123.5^{\circ}$ (Found: C, 78.2; H, 6.35. $C_{27}H_{28}P_2$ requires C, 78.6; H, 6.35%). The *dimethiodide* has m. p. $287-287.5^{\circ}$ (from ethanol) (Found: C, 50.2; H, 4.8. $C_{29}H_{32}I_2P_2$ requires C, 50.0; H, 4.6%). Admixture of equimolar quantities of potassium bromopalladate and the diphosphine in ethanol afforded a buff precipitate which, dissolved in warm dimethylformamide, gave the *dibromopalladium derivative*, pale yellow crystals, m. p. 365° (after decomp.) (from dimethylformamide-ethanol) (Found: C, 48.1; H, 3.9. $C_{27}H_{26}Br_2P_2Pd$ requires C, 47.8; H, 3.9%).

2,2-Bis(diphenylphosphino)propane Dioxide.—A solution of bromine (11.44 g., 1 mol.) in chloroform (400 c.c.) reacted immediately when added dropwise to a cooled solution of the diphosphine (III) (46.0 g.) in chloroform (400 c.c.). The resulting mixture was hydrolysed with an excess of sodium hydrogen carbonate solution, and the chloroform layer, having been separated and washed with water, afforded the *dioxide* (47 g., 95%) after removal of solvent. Recrystallisation from benzene gave lozenges, m. p. $270-271^{\circ}$ (Found: C, 73.1; H, 6.0. $C_{27}H_{26}O_2P_2$ requires C, 73.0; H, 5.9%).

1,1,1-Tris(diphenylphosphinomethyl)ethane (IV; R = Ph).—The trichloride $Me-C[CH_2Cl]_3$ was prepared from the corresponding triol.¹⁵ Sodium diphenylphosphide was prepared from diphenylphosphine (56.86 g.) and sodium (7.03 g., 1 mol.) in liquid ammonia (400 c.c.) at -75° . The trichloride (17.88 g., 0.33 mol.) in an equal volume of ether was added during 30 min. The solution paled and solid was deposited. The ammonia was allowed to evaporate and the orange solid residue was heated under reflux with tetrahydrofuran (250 c.c.) for 8 hr. The

¹³ Beeby and Mann, *J.*, 1951, 411.

¹⁴ Henne and Renoll, *J. Amer. Chem. Soc.*, 1937, **59**, 2434.

¹⁵ Urry and Eiszner, *J. Amer. Chem. Soc.*, 1952, **74**, 5822.

solution was admixed with water (250 c.c.) and ether (100 c.c.). The organic layer, having been separated and washed with water, was distilled at atmospheric pressure to remove the mixed solvents and then at 0.01 mm. to remove diphenylphosphine (*ca.* 3 g., b. p. 95–100°). The residual colourless gum was crystallised from hot ethanol, and then twice from light petroleum (b. p. 80–100°), to give the *triphosphine* (46.2 g., 73%), m. p. 100–101° (Found: C, 79.1; H, 6.4%; *M*, 620.5. $C_{41}H_{39}P_3$ requires C, 78.8; H, 6.3%; *M*, 625). In air the dry compound is slowly oxidised. The *trimethiodide* had m. p. 310–311° (from nitromethane) (Found: C, 50.5; H, 4.8. $C_{44}H_{48}I_3P_3$ requires C, 50.3; H, 4.6%).

The trisphosphine (IV; R = Ph) was also made (*ca.* 50% yield) from sodium diphenylphosphide prepared *in situ* from triphenylphosphine. Prepared in this way, however, the compound is often deposited from solution as a gum, presumably because it contains traces of impurities derived from triphenylphosphine. Preparation of diphenylphosphine is simple, and we prefer the less direct route to the triphosphine. (Triphenylphosphine after cleavage in solution is treated with water, and the residue, after evaporation of the ammonia, is extracted with ether. Distillation of the ethereal solution gives pure diphenylphosphine in 81% yield.)

Bis-(2-diphenylphosphinoethyl)phenylphosphine (V).—The phosphine $Ph \cdot P[C_2H_4 \cdot OEt]_2^2$ (30.0 g.) was dissolved in 60% hydrobromic acid (500 c.c.) and glacial acetic acid (500 c.c.), and pure hydrogen bromide was passed through the mixture at reflux for 7 hr. The solvent was removed at 20 mm., and there remained a pale yellow glass. This was extracted as quickly as possible with an ice-cold mixture of light petroleum (b. p. 80–100°) (75 c.c.), ether (30 c.c.), and saturated aqueous sodium hydrogen carbonate (150 c.c.). The organic layer was separated, washed twice with aqueous sodium hydrogen carbonate, and dried by shaking it with anhydrous sodium sulphate for 30 min. The solution was added to sodium diphenylphosphide in liquid ammonia (600 c.c.) at -75° [prepared from triphenylphosphine (62.5 g.), sodium (10.8 g.), and ammonium chloride (12.65 g.)]. No change was observed. The ammonia having boiled off, the solid residue was extracted with water (500 c.c.) and benzene (200 c.c.). The benzene layer was dried, distilled at 1 atm. to remove solvent, and then at 0.75 mm. to remove diphenylphosphine (b. p. 99.5–101°; 16.5 g.). Trituration of the residue with warm methanol (20 c.c.) caused crystallisation of the *triphosphine* as air-sensitive crystals, m. p. 131–132° (10.02 g., 16%) (from benzene-ethanol) (Found: C, 76.7; H, 6.25%; *M*, 548. $C_{34}H_{33}P_3$ requires C, 76.4; H, 6.2%; *M*, 535). The *trimethiodide* crystallised as the dihydrate, m. p. 162–163°, from methanol-ether (Found: C, 44.8; H, 4.5. $C_{37}H_{46}I_3O_2P_3$ requires C, 44.6; H, 4.65%). The *trimethopicate*, m. p. 193–194°, recrystallised from acetone-water (Found: C, 52.8; H, 4.3; N, 9.7. $C_{55}H_{48}N_6O_{21}P_3$ requires C, 52.3; H, 3.8; N, 10.0%).

Preparations from Triphenyl-arsine and -stibine.—1,2-Bis(diphenylarsino)ethane, $C_8H_4[AsPh_2]_2$. Triphenylarsine (30.6 g.) was added in portions (*ca.* 5 g.) to a solution from sodium (4.6 g., 2 mol.) in liquid ammonia (300 c.c.) at -75° . A deep red solution was formed immediately. Addition of 1,2-dichloroethane (10.0 g., 1 mol.) in an equal volume of ether caused progressive loss of colour and formation of a white precipitate. Water (200 c.c.) was added very cautiously, and ammonia was allowed to boil from the mixture. Separation of the suspended solid, followed by washing with methanol and recrystallisation from ethanol, afforded the diarsine (19.7 g., 81%), m. p. 100–101° (Found: C, 64.2; H, 5.1. Calc. for $C_{26}H_{24}As_2$: C, 64.2; H, 5.0%). Chatt and Mann¹⁶ give m. p. 99–102°.

Tetraphenyldistibine, $Ph_2Sb \cdot SbPh_2$. Repetition of the above experiment with triphenylstibine replacing triphenylarsine gave the distibine (66%), bright yellow air-sensitive needles, m. p. 125° (from chloroform-methanol) (Found: C, 52.3, 52.3; H, 3.8, 3.7. Calc. for $C_{24}H_{24}Sb_2$: C, 52.2; H, 3.65%) (lit.,¹⁷ m. p. 121–122°).

Reaction of Chlorodiethylphosphine with Lithium in Tetrahydrofuran.—*Tetraethyldiphosphine*. To a stirred suspension of lithium flakes (1.47 g., 1.05 mol.) in tetrahydrofuran (100 c.c.) at 0° chlorodiethylphosphine (26.27 g., 1 mol.) in tetrahydrofuran (25 c.c.) was added during 15 min. A rapid exothermic reaction ensued. The lithium developed a bright reflecting surface; after 1 hr. it had all dissolved and lithium chloride had been deposited. Solvent having been removed at atmospheric pressure, the residue was extracted with light petroleum (b. p. 40–60°) (75 c.c.), and the extract distilled at atmospheric pressure. Tetraethyldiphosphine (14.7 g., 78%) distilled at 218–219°. The compound was further characterised as the disulphide, m. p. 75–76° (lit.,¹⁰ m. p. 77°).

¹⁶ Chatt and Mann, *J.*, 1939, 610.

¹⁷ Blicke, Oakdale, and Smith, *J. Amer. Chem. Soc.*, 1931, **53**, 1025.

Diethylphosphine. Tetraethyldiphosphine (17.0 g.) and lithium flakes (2.6 g., 4 mol.) were heated under reflux in tetrahydrofuran (100 c.c.) for 4 hr. The lithium was etched rapidly and the solution became bright yellow. The excess of lithium having been separated, the stirred solution was treated dropwise with water until it just became colourless. The mixture was fractionated (15" helix-packed column) at atmospheric pressure. Diethylphosphine (6.9 g., 40%) distilled at 85°.

1,2-Bis(diethylphosphino)ethane (I; R = Et). Chlorodiethylphosphine (58.3 g.) in tetrahydrofuran (50 c.c.) was added to a cooled suspension of lithium flakes (13.0 g., 4 mol.) in tetrahydrofuran (200 c.c.). Then the mixture was heated under reflux overnight. The solution was filtered from lithium and lithium chloride and cooled in ice, and to it 1,2-dichloroethane (20.9 g., 0.45 mol.) in ether (15 c.c.) was added dropwise. The solution paled from yellow to buff, and lithium chloride was deposited. Solvent having been distilled off at atmospheric pressure, the residue was extracted with water (300 c.c.) and light petroleum (b. p. 30—40°) (100 c.c.). With solvent removed from the dried organic layer, the residue was fractionated at 10 mm. The diphosphine (I; R = Et) (40.8 g., 94%) was collected at 124—126°. It was characterised as the *dimethiodide*, m. p. 280—281.5° (from ethanol) (Found: C, 29.45; H, 6.2. $C_{12}H_{30}I_2P_2$ requires C, 29.4; H, 6.2%), and the *dimethopicrate*, m. p. 238.5—239° (from acetone) (Found: C, 41.7; H, 5.3; N, 12.3. $C_{24}H_{34}N_6O_{14}P_2$ requires C, 41.6; H, 4.95; N, 12.1%).

1,1,1-Tris(diethylphosphinomethyl)ethane (IV; R = Et). A solution (50 c.c.) of lithium diethylphosphide was prepared as above from chlorodiethylphosphine (37.24 g.) and lithium (8.4 g.). The trichloride, Me·C[CH₂Cl]₃ (14.9 g., 0.28 mol.), was added dropwise at 0° during 45 min., and the resulting pale buff mixture was left overnight at room temperature. Solvent was removed at atmospheric pressure, and the fraction of b. p. 100—250°/0.1 mm. was collected. Redistillation through a short column gave the *triposphine* (11.7 g., 41%), b. p. 120°/0.1 mm., as a colourless spontaneously inflammable liquid (Found: *M*, 327. $C_{17}H_{39}P_3$ requires *M*, 336). It was characterised as the *triethiodide*, m. p. 357° (decomp.) (from water) (Found: C, 34.0 H, 6.4. $C_{23}H_{54}I_3P_3$ requires C, 34.35; H, 6.8%), and the *triethopicrate*, m. p. 213—214° (from water) (Found: C, 44.2; H, 5.9; N, 11.2. $C_{41}H_{60}N_9O_{21}P_3$ requires C, 44.45; H, 5.5; N, 11.4%).

IMPERIAL CHEMICAL INDUSTRIES LIMITED, HEAVY ORGANIC CHEMICALS DIVISION,
RESEARCH DEPARTMENT: AKERS GROUP,
THE FRYTHE, WELWYN, HERTS.

[Received, August 31st, 1961.]