665. *The Preparation of* o-*Phenylenedi(tertiary phosphines) and a Tri(tertiary phosphine).*

By F. A. Hart.

o-Phenylenebisdiethylphosphine (IV) has been prepared by two new methods, and a tri(tertiary phosphine) (VII) has been synthesised. New *o*-phenylenedi(tertiary phosphines) are also described.

Compounds of type (I), where R is an alkyl or aryl group and E, E′ are Group Vb elements, are of interest in two respects: they are chelate ligands which often form very stable complexes with transition metals,[1,2] the diarsine especially having been much used to stabilise unusual valency states and co-ordination numbers,[3] and they are intermediates from which heterocyclic compounds can often be made, by diquaternisation with ethylene dihalide followed by pyrolysis.[4]

(I) $o\text{-}R_2E{\cdot}C_6H_4{\cdot}E'R_2$ $\quad$ $o\text{-}X{\cdot}C_6H_4{\cdot}PR_2$ (II)

There are good methods for the preparation of some such compounds,[5,6] but the two *o*-phenylenedi(tertiary phosphines), 4-methyl-*o*-phenylene-[2] and *o*-phenylene-bisdiethylphosphine (IV),[7] were obtained in a pure state only in a small quantity. This is particularly regrettable since there is evidence [8] that the di(tertiary phosphine) may be the most effective chelate ligand of type (I).

The 4-methyl-bisphosphine was prepared [2] by treating 3-bromo-4-iodotoluene with two equivalents of magnesium and two equivalents of chlorodiethylphosphine. This reaction cannot be applied to prepare the bisphosphine (IV), which has however been made [7] by allowing *o*-chlorophenyl-lithium to decompose to benzyne at about —70° in the presence of tetraethyldiphosphine, $Et_2P{\cdot}PEt_2$. Since tetraethyldiphosphine was also formed during the preparation of the 4-methyl-bisphosphine, it is possible that the latter was the addition product of $Et_2P{\cdot}PEt_2$ and methylbenzyne produced by the elimination of magnesium bromide iodide from 4-methyl-2-bromophenylmagnesium iodide.

Two reasonably convenient syntheses of *o*-phenylenebisdiethylphosphine (IV) are now reported.

The limitations of the one-stage *o*-phenylenebisphosphine syntheses led to a re-consideration of a two-stage method with a compound of type (II; $X =$ halogen) as an

---

[1] Stewart, *Chem. and Ind.*, 1958, 264; Chatt and Mann, *J.*, 1939, 1622.
[2] Hart and Mann, *J.*, 1957, 3939.
[3] Nyholm, *J.*, 1950, 851 *et seq.*
[4] Mann and Baker, *J.*, 1952, 4142.
[5] Fischer, *Ber.*, 1892, **25**, 2838; Chatt and Mann, *J.*, 1939, 610; Eberley and Smith, *J. Org. Chem.*, 1957, **22**, 1710; Mann and Watson, *J.*, 1957, 3945; Mann and Stewart, *J.*, 1955, 1269.
[6] Jones and Mann, *J.*, 1955, 4472.
[7] Chatt, Fielding, and Hart, U.S.P. 2,922,819.
[8] Chatt and Hart, *J.*, 1960, 1378.

intermediate. This would be analogous to previous arsine syntheses,[6] but with the difficulty that the Bart reaction cannot be used.

Two intermediates of type (II) were found which could each be converted into the required bisphosphine. *o*-Bromochlorobenzene in ether, entrained with ethyl bromide, gave a mono-Grignard reagent which with chlorodiethylphosphine gave *o*-chlorophenyldiethylphosphine (III) in 50% yield. This was metallated by lithium in tetrahydrofuran (but not in ether), and the lithio-compound on treatment with chlorodiethylphosphine gave *o*-phenylenebisdiethylphosphine (IV) in 27% yield.

$$o\text{-}C_6H_4BrCl \longrightarrow \underset{(III)}{o\text{-}Cl\cdot C_6H_4\cdot PEt_2} \longrightarrow \underset{(IV)}{o\text{-}C_6H_4(PEt_2)_2}$$

The *o*-chlorophenylphosphines (II; X = Cl, R = Me and Ph) are readily obtained in a similar way, but are converted into the bisphosphines (I; E = E′ = P) in only 11% and 2% yield respectively. It is likely that the lithium splits a phosphorus–carbon bond[9] instead of replacing the chlorine atom.

The alternative preparation of compound (IV) utilises the low-temperature halogen–lithium exchange between *o*-dibromobenzene and n-butyl-lithium.[10] *o*-Dibromobenzene at −130° was treated first with n-butyl-lithium and then with chlorodiethylphosphine, giving *o*-bromophenyldiethylphosphine (V) in 26% yield. Unchanged *o*-dibromobenzene (66%) was recovered and butyldiethylphosphine (32%) was also isolated. The intermediate (V) readily underwent lithium–halogen exchange with n-butyl-lithium at room temperature, and treatment with chlorodiethylphosphine gave *o*-phenylenebisdiethylphosphine (IV) in 56% yield.

$$o\text{-}C_6H_4Br_2 \longrightarrow \underset{(V)}{o\text{-}Br\cdot C_6H_4\cdot PEt_2} \longrightarrow (IV)$$

However, only traces of *o*-bromophenyldiphenylphosphine (II; X = Br, R = Ph), an intermediate in the possible preparation of *o*-phenylenebisdiphenylphosphine (I; R = Ph, E = E′ = P), were obtained when chlorodiphenylphosphine reacted with *o*-dibromobenzene and n-butyl-lithium at −130°. 84% of the *o*-dibromobenzene was recovered, and butyldiphenylphosphine was obtained in 77% yield, indicating that the chlorodiphenylphosphine had reacted preferentially with n-butyl-lithium, in this way progressively displacing what is apparently an equilibrium:

$$o\text{-}C_6H_4Br_2 + Bu^nLi \rightleftharpoons o\text{-}C_6H_4BrLi + Bu^nBr$$

On the other hand, chlorodiphenylphosphine reacted normally with diethyl-*o*-lithiophenylphosphine at room temperature, to give *o*-diethylphosphinophenyldiphenylphosphine (VI) in 58% yield.

The *o*-bromo-phosphine (V) may be used to prepare the new tri(tertiary phosphine) (VII), which has the correct stereochemistry to occupy three vicinal octahedral co-ordination positions in a metal complex. *o*-Bromophenyldiethylphosphine (V) with n-butyl-lithium gave the *o*-lithio-derivative, which with dichlorophenylphosphine gave the trisphosphine (VII), but in only 6·4% yield, as colourless crystals, stable in air when pure. Its complexes are under investigation.

$$\text{(VI)}\quad o\text{-}Ph_2P\cdot C_6H_4\cdot PEt_2 \qquad o\text{-}Li\cdot C_6H_4\cdot PEt_2 \longrightarrow Ph\cdot P(C_6H_4\cdot PEt_2\text{-}o)_2\quad \text{(VII)}$$

EXPERIMENTAL

Microanalyses were carried out by the Microanalytical Department of these laboratories. Light petroleum had b. p. 40—60°. Operations, except recrystallisations, were carried out under nitrogen.

o-*Chlorophenyldiethylphosphine*.—Magnesium (12·35 g., 1·08 mol.) was treated in a Grignard-type apparatus with ethyl bromide (4 g., 0·08 mol.) in ether (50 c.c.) and a 50 c.c. portion of a

---

[9] Wittenberg and Gilman, *J. Org. Chem.*, 1958, **23**, 1063.

[10] Gilman and Gorsich, *J. Amer. Chem. Soc.*, 1956, **78**, 2217.

solution of *o*-chlorobromobenzene (90 g., 1 mol.) in ether (600 c.c.). When the reaction started, the flask was cooled in ice-water and the rest of the chlorobromobenzene solution added during 35 min. with stirring, which was continued for 90 min. more. Chlorodiethylphosphine (58·9 g., 1 mol.) in ether (100 c.c.) was next added during 20 min., with stirring and cooling in ice-water. The mixture was boiled for 15 min., cooled to 0°, and hydrolysed with concentrated aqueous ammonium chloride. The aqueous layer was washed with ether, and the ether was removed at 12 mm. from the combined ethereal layers. The residue was distilled at 0·4 mm., giving the *phosphine* (46·8 g., 50%), b. p. 83—85° (Found: C, 59·7; H, 7·1. $C_{10}H_{14}ClP$ requires C, 59·8; H, 7·0%). Treatment with hot alcoholic ethyl iodide gave the *ethiodide*, m. p. 178—179° (from ethyl methyl ketone) (Found: C, 40·6; H, 5·4. $C_{12}H_{19}ClIP$ requires C, 40·4; H, 5·4%).

o-*Chlorophenyldimethylphosphine*.—To a Grignard reagent prepared from *o*-bromochlorobenzene (71·7 g., 1 mol.), ethyl bromide (3·0 g., 0·07 mol.), and magnesium (9·7 g., 1·07 mol.) in ether (350 c.c.), chlorodimethylphosphine (36·1 g., 1 mol.) in ether (200 c.c.) was added during 15 min., with cooling in ice and stirring. After being stirred for another 90 min. at 15°, the mixture was hydrolysed and the product isolated as before. Distillation at 0·25 mm. gave 28·3 g. of the *phosphine*, b. p. 44—45°; it was redistilled, giving 24·0 g. (37%) of material, b. p. 43°/0·25 mm. (Found: C, 55·6; H, 6·0. $C_8H_{10}ClP$ requires C, 55·7; H, 5·8%). Treatment with methanolic methyl iodide gave the *methiodide*, m. p. 303—305° (from aqueous methanol) (Found: C, 34·5; H, 4·3. $C_9H_{13}ClIP$ requires C, 34·4; H, 4·2%).

o-*Chlorophenyldiphenylphosphine*.—To a Grignard reagent from *o*-bromochlorobenzene (150 g., 1·15 mol.), ethyl bromide (9·1 g., 0·12 mol.), and magnesium (21·0 g., 1·27 mol.) in ether (600 c.c.), chlorodiphenylphosphine (150 g., 1 mol.) in ether (400 c.c.) was added during 15 min. at 0° with stirring. After a further hour's stirring, the mixture was hydrolysed with aqueous ammonium chloride, and the white crystalline product isolated as before. Recrystallised thrice from ethanol, the *phosphine* had m. p. 107—108° (105 g., 52%) (Found: C, 72·9; H, 5·2. $C_{18}H_{14}ClP$ requires C, 72·9; H, 4·75%).

o-*Bromophenyldiethylphosphine*.—Solutions of *o*-dibromobenzene (100 g., 1 mol.) in ether (400 c.c.) and light petroleum (400 c.c.), and of n-butyl-lithium (1 mol.) in light petroleum (456 c.c.) and ether (400 c.c.) were separately contained in two round-bottomed flasks fitted with pentane thermometers. The vigorously stirred solutions were cooled to −130° in liquid nitrogen (contained in two Polythene bowls placed upon and surrounded by cotton wool). The butyl-lithium solution was next poured into the dibromobenzene solution through a ball-and-socket-jointed tube, and the mixture was stirred at −130° for 20 min. A solution of chlorodiethylphosphine (52·6 g., 1 mol.) in light petroleum (160 c.c.) and ether (160 c.c.), similarly cooled to −130°, was added in the same way. The mixture was stirred at the same temperature for 2 hr. and then allowed to warm to room temperature. The solution was extracted with water (100 c.c.), and the organic layer was separated and evaporated; the residue on distillation at 0·15 mm. gave (*a*) butyldiethylphosphine (20·0 g., 32%), identified as its *ethopicrate*, m. p. 82—83° (from aqueous ethanol) (Found: C, 47·7; H, 6·6. $C_{16}H_{26}O_7N_3P$ requires C, 47·6; H, 6·5%), (*b*) *o*-dibromobenzene (65·6 g.; 66% recovery), b. p. 48°, and (*c*) o-*bromophenyldiethylphosphine* (27·1 g., 26%), b. p. 90—91° (Found: C, 50·0; H, 6·4; Br, 31·75. $C_{10}H_{14}BrP$ requires C, 49·0; H, 5·8; Br, 32·6%). The analytical figures from fraction (*c*) were not improved by refractionation. With warm ethanolic methyl iodide fraction (*c*) gave the *methiodide*, m. p. 123—124° (from ethyl acetate–ethanol) (Found: C, 34·1; H, 4·5. $C_{11}H_{17}BrIP$ requires C, 34·1; H, 4·4%), which was converted into the *methopicrate*, m. p. 116—117·5° (from aqueous methanol) (Found: C, 41·8; H, 4·1; N, 8·8. $C_{17}H_{19}O_7N_3BrP$ requires C, 41·8; H, 3·9; N, 8·6%).

o-*Bromophenyldiphenylphosphine*.—To a stirred solution of *o*-dibromobenzene (60 g., 1 mol.) in light petroleum (220 c.c.) and ether (220 c.c.) at −130°, was added dropwise a solution of n-butyl-lithium (1 mol.) in light petroleum (420 c.c.) and ether (400 c.c.). After 10 min., chlorodiphenylphosphine (56·0 g., 1 mol.) in light petroleum (200 c.c.) and ether (200 c.c.) was added during 25 min. After 1 hr., the mixture was allowed to warm to room temperature and extracted with water. The organic layer was separated, and the solvents were removed. Distillation at 0·3 mm. gave (*a*) *o*-dibromobenzene (50·5 g., 84%), b. p. 34—36°, and (*b*) butyldiphenylphosphine (47·55 g., 77%), b. p. 117—120°, identified as its *butyloiodide*, m. p. 154—155° (from ethyl methyl ketone–ethyl acetate) (Found: C, 56·6; H, 6·7. $C_{20}H_{30}PI$ requires C, 56·35; H, 6·6%), and (*c*) a residual syrup, which on chromatography on alumina with 1 : 1

benzene–light petroleum as eluant and recrystallisation from alcohol, gave o-*bromophenyldiphenylphosphine* (0·4 g.), m. p. 115° (Found: C, 63·3; H, 4·4; Br, 23·4. $C_{18}H_{14}BrP$ requires C, 63·4; H, 4·1; Br, 23·4%).

o-*Phenylenebisdiethylphosphine.*—(*A*) *o*-Chlorophenyldiethylphosphine (165 g., 1 mol.) in tetrahydrofuran (1 l.) contained in a Grignard-type assembly was cooled to −45° (carbon dioxide and acetone) and lithium foil (11·45 g., 2 atom-equiv.) was added. After 2 hours' stirring nearly all the lithium had dissolved. Chlorodiethylphosphine (102·5 g., 1 mol.) in tetrahydrofuran (150 c.c.) was added with stirring during 20 min. at about −35°. The mixture, after warming to room temperature, was heated at 45° for 20 min., then cooled and stirred with water (500 c.c.) and benzene (200 c.c.). The lower layer was extracted with benzene (50 c.c.). The solvent was removed from the combined organic portions, and the residue gave on distillation at 0·2 mm. (*a*) diethylphenylphosphine (50·7 g., 37%), b. p. 44—48° (ethiodide, m. p. 137—138·5°), and (*b*) *o*-phenylenebisdiethylphosphine (56·9 g., 27%), b. p. 100—103°, containing traces of impurity which were removed on refractionation (Found: C, 65·8; H, 9·5. Calc. for $C_{14}H_{24}P_2$: C, 66·1; H, 9·5%). The bisphosphine was further characterised, by treatment with hot ethanolic ethylene dibromide, followed by aqueous sodium picrate, as the 1,1,4,4-tetraethylethylene-*o*-phenylenediphosphonium dipicrate, m. p. 230—232° (from ethanol–dimethylformamide) (Found: C, 45·7; H, 4·75; N, 11·4. Calc. for $C_{20}H_{16}O_7N_3P_2$: C, 45·5; H, 4·4; N, 11·35%).

Use of 40% excess of chlorodiethylphosphine in this experiment did not increase the yield of diphosphine.

(*B*) n-Butyl-lithium in light petroleum (0·765N; 340 c.c., 1·1 mol.) was added at 10° to a stirred solution of *o*-bromophenyldiethylphosphine (58·1 g., 1 mol.) in light petroleum (100 c.c) and ether (100 c.c.). After 15 min., chlorodiethylphosphine (37 g., 1·25 mol.) in light petroleum (100 c.c.) was added during 10 min. Heat is evolved during these two additions, and the temperature of the solution was kept below 10°. After 100 min., the mixture was stirred with water (100 c.c.). The aqueous layer was made just alkaline with aqueous sodium hydroxide and twice extracted with light petroleum (2 × 100 c.c.). The solvents were removed from the combined organic portions and distillation at 0·04 mm. gave a fraction, b. p. 97—106°. Refractionation gave the pure diphosphine (33·5 g., 56%) (Found: C, 66·15; H, 9·7%).

o-*Diethylphosphinophenyldiphenylphosphine.*—n-Butyl-lithium in light petroleum (0·59N; 81·4 c.c., 1 mol.) was added at 10° to a stirred solution of *o*-bromophenyldiethylphosphine (10·0 g., 0·85 mol.) in ether (25 c.c.). Chlorodiphenylphosphine (10·6 g., 1 mol.) in benzene (30 c.c.) was added dropwise, with ice-cooling, and after 30 min. the solution was boiled for 30 min. more, with stirring. The cooled solution was stirred with water (100 c.c.). The water was separated and the organic solvents were removed, finally at 100°/0·5 mm. The crystalline residual *bisphosphine* (8·25 g., 58%) had m. p. 103·5—105·5° when recrystallised from ethanol (Found: C, 75·2; H, 7·1. $C_{22}H_{24}P_2$ requires C, 75·4; H, 6·9%). When boiled for 90 min. with excess of ethanolic ethyl iodide it gave o-*diphenylphosphinotriethylphosphonium iodide*, m. p. 214° (from aqueous ethanol) (Found: C, 57·3; H, 5·8. $C_{24}H_{29}P_2I$ requires C, 56·9; H, 5·8%).

o-*Phenylenebisdimethylphosphine.*—Lithium foil (2·26 g., 2 atom-equiv.) was added to *o*-chlorophenyldimethylphosphine (28·0 g., 1 mol.) in tetrahydrofuran (200 c.c.) at −45°, and the whole was stirred for 2 hr. at −45° and for 20 min. at 0°, then cooled to −45°. Chlorodimethylphosphine (15·7 g.; 1 mol.) in benzene (50 c.c.) was added dropwise. After 1 hr. at room temperature, the solution was stirred with benzene (50 c.c.) and water (100 c.c.), and the product isolated in the usual way. Distillation (0·3 mm.) gave an unidentified fraction (6·6 g.), b. p. 30—33°, and the *bisphosphine* (3·4 g., 11%), b. p. 98—101° (Found: C, 60·8; H, 7·7. $C_{10}H_{16}P_2$ requires C, 60·6; H, 8·1%).

o-*Phenylenebisdiphenylphosphine.*—Lithium foil (2·80 g., 2 atom-equiv.) was added to *o*-chlorophenyldiphenylphosphine (60 g., 1 mol.) in tetrahydrofuran (650 c.c.) at −45°. The mixture was stirred for 3 hr., then chlorodiphenylphosphine (74·3 g., 1 mol.) in tetrahydrofuran (150 c.c.) was added during 15 min. After reaching room temperature, the mixture was stirred with benzene (200 c.c.) and water (200 c.c.). The oil produced was isolated from the upper layer. It was mainly soluble in alcohol, but long storage in alcohol at 5° gave crystals (1·9 g.), having m. p. 183—187° after recrystallisation from ethyl methyl ketone. This bisphosphine was twice sublimed at 150°/0·05 mm. and four times recrystallised from dimethylformamide, then having m. p. 186·5—187·5° and containing a slight but persistent impurity (Found: C, 79·7; H, 5·7. Calc. for $C_{30}H_{24}P_2$: C, 80·7; H, 5·4%).

Bis-(o-*diethylphosphinophenyl*)*phenylphosphine.*—n-Butyl-lithium (1 mol.) in light petroleum (62·1 c.c.) was added during 5 min., with stirring, to an ice-cooled solution of *o*-bromophenyldiethylphosphine (10·0 g., 1 mol.) in ether (50 c.c.). After 30 min., dichlorophenylphosphine (3·65 g., 0·5 mol.) in ether (15 c.c.) was added dropwise. After being stirred at 0° for another 30 min., the solution was boiled for 30 min., cooled, and stirred with water (100 c.c.) and benzene (50 c.c.). The oil produced was isolated in the usual way, and crystallised (2·25 g.) on trituration with methanol. Purified by chromatography on alumina (1 : 1 light petroleum–benzene) and recrystallisation from ethanol, the *tris-phosphine* (1·15 g.) had m. p. 106—107·5° (Found: C, 71·0; H, 7·7. $C_{26}H_{33}P_3$ requires C, 71·2; H, 7·6%).

I thank Mr. D. T. Rosevear for his help with the experiments.

IMPERIAL CHEMICAL INDUSTRIES LIMITED,
AKERS RESEARCH LABORATORIES, THE FRYTHE,
WELWYN, HERTS.

[*Received, February* 22*nd*, 1960.]