

## 782. The Synthesis and Properties of 4-Methyl-*o*-phenylenebis-(diethylphosphine).

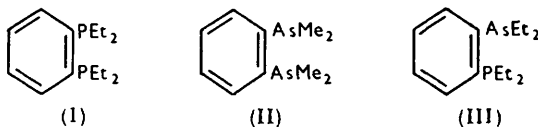
By F. A. HART and F. G. MANN.

It is shown that 3-bromo-4-iodotoluene reacts with magnesium to give a practicable yield of the corresponding di-Grignard reagent, since the product when treated with chlorodiethylphosphine affords 4-methyl-*o*-phenylenebis-(diethylphosphine), and with diethyliodoarsine gives the corresponding diarsine.

The diphosphine acts as a powerful chelating molecule in co-ordinating with metallic ions. It also unites vigorously with ethylene dibromide by diquaternisation, producing the first known compound having a ring system consisting solely of carbon atoms and two phosphorus atoms.

An investigation of the "stepwise" reaction of the halogen atoms in 3-bromo-4-iodotoluene with magnesium has revealed 2:6-dimethyldiphenylene as one of the products.

A COMPOUND such as *o*-phenylenebis(diethylphosphine) (I) would be of great value for two distinct purposes. It would almost certainly co-ordinate with metals to form a chelated ring system of high stability, and it would also undergo diquaternisation with ethylene dibromide to form a cyclic system containing two phosphorus atoms. Both types of reaction are shown by *o*-phenylenebis(dimethylarsine) (II)<sup>1,2,3</sup> and by *o*-diethylphosphinophenyldiethylarsine (III)<sup>4,5</sup> but the synthesis of compounds of type (II) or (III)



involves in each case one or more stages which cannot be applied to that of a diphosphine of type (I). It was clear, therefore, that the synthesis of the diphosphine (I) would probably involve the *o*-dimetallation (stepwise or in one stage) of the benzene ring: on the other hand, the work of Heaney, Mann, and Millar on the action of magnesium and lithium on *o*-di-iodobenzene<sup>6</sup> and *o*-bromiodobenzene<sup>7</sup> showed that the direct production of, for example, *o*-phenylenebis(magnesium halide) occurs in only low yield.

We have, therefore, investigated the action of magnesium (one equivalent) on 3-bromo-4-iodotoluene (IV), to determine in particular whether the highly active iodine would now ensure the formation of the Grignard compound (V) without the concurrent and major formation of diphenyl derivatives experienced by Heaney, Mann, and Millar.<sup>6,7</sup> If so, the compound (V), treated with chlorodiethylphosphine,  $\text{Et}_2\text{PCl}$ , would give the bromo-phosphine (VI), which then, on the basis of Jones and Mann's synthesis of the phosphine-arsine (III), might be converted into the lithio-derivative (VII) and thence into the required diphosphine (VIII). It was found, however, that the action of one equivalent of magnesium on the dihalide (IV) must have given the required Grignard compound (V), together with an appreciable proportion of the alternative compound (IX), for treatment with chlorodiethylphosphine gave a fraction which contained both the bromo-phosphine (VI) and the iodo-phosphine (X), for derivatives of each phosphine could be isolated. Moreover, this fraction contained some other component, possibly unchanged dihalide (IV), for treatment

<sup>1</sup> Chatt and Mann, *J.*, 1939, 1622.

<sup>2</sup> Glauert and Mann, *J.*, 1950, 682.

<sup>3</sup> Mann and Baker, *J.*, 1952, 4142.

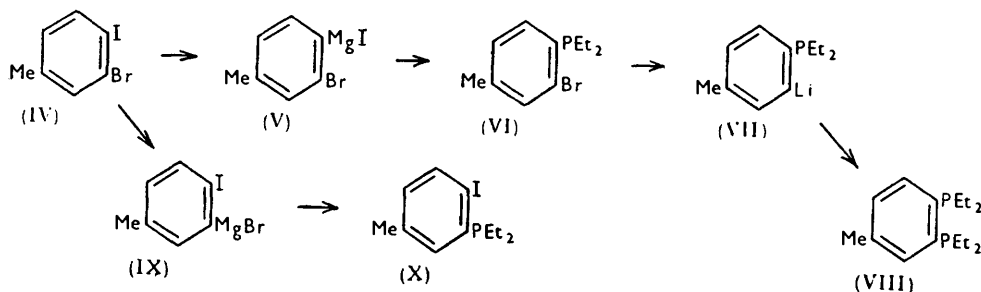
<sup>4</sup> Emrys R. H. Jones and Mann, *J.*, 1955, 4472.

<sup>5</sup> Cochran, Hart, and Mann, *J.*, 1957, 2816.

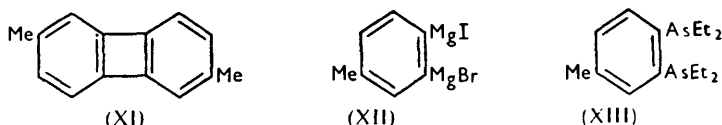
<sup>6</sup> Heaney, Mann, and Millar, *J.*, 1956, 1.

<sup>7</sup> *Idem*, *J.*, 1957, preceding paper.

with *n*-butyl-lithium followed by further treatment with chlorodiethylphosphine afforded on distillation 2:6-dimethyldiphenylene (XI) (cf. p. 3941) and no phosphine. The absence of a tertiary phosphine in the distillate was presumably due to its quaternisation by *n*-butyl iodide liberated by the action of the *n*-butyl-lithium: in analogous earlier



experiments in which *n*-butyl bromide has been liberated, quaternisation had been negligible.<sup>1,4,8</sup> In view of these difficulties, this "step-wise" synthetic route was abandoned.

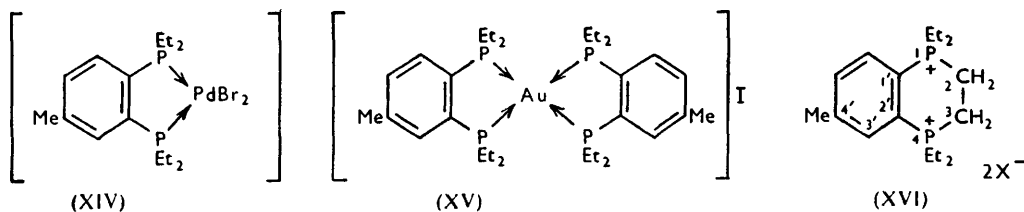


The ethereal 3-bromo-4-iodotoluene (IV) was therefore treated directly with three equivalents of magnesium, and the reaction product then treated, in a model experiment, with diethyldiarsine,  $\text{Et}_2\text{AsI}$ . The isolation of 4-methyl-*o*-phenylenebis(diethylarsine) (XIII) in 23% yield showed that the required di-Grignard reagent (XII) had been formed in useful quantity.

The product from the reaction with three equivalents of magnesium was therefore treated with chlorodiethylphosphine (two equivalents), and after hydrolysis furnished two main fractions. The first was tetraethyldiphosphine,  $\text{Et}_2\text{P}\cdot\text{PEt}_2$ , which was spontaneously inflammable but was identified by its reaction with ethyl iodide to form tetraethylphosphonium iodide and with aqueous hydrogen peroxide to form diethylphosphinic acid,  $\text{Et}_2\text{PO}\cdot\text{OH}$ , which gave a highly crystalline ammonium salt.

The second fraction was the required 4-methyl-*o*-phenylenebis(diethylphosphine) (VIII), which after refractionation was obtained as a clear colourless malodorous liquid.

This diphosphine showed the expected properties. An ethanolic solution, when added to aqueous-ethanolic potassium palladobromide (one equivalent) deposited a sticky



precipitate: vigorous shaking ultimately gave a clear orange-yellow solution, from which the crystalline cream-coloured dibromo-4-methyl-*o*-phenylenebis(diethylphosphine)-palladium (XIV) was isolated. Similarly, the ethanolic diphosphine when added in slight excess to ethanolic chloroauric acid gave a colourless solution, which on treatment with

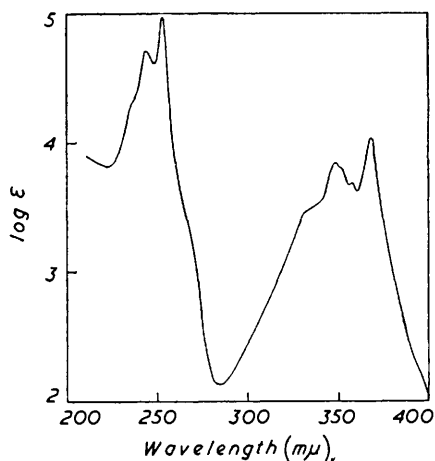
<sup>8</sup> Mann and Millar, *J.*, 1953, 3746.

aqueous sodium iodide gave the highly crystalline colourless di-[4-methyl-*o*-phenylenebis(diethylphosphine)]gold iodide (XV), identical in type with the diarsine compounds prepared by Nyholm<sup>9</sup> and the phosphine-arsine compounds prepared by Cochran, Hart, and Mann.<sup>5</sup>

The diphosphine (VIII), when warmed with ethylene dibromide (one equivalent), reacted vigorously giving a solid product, which on recrystallisation furnished 1 : 1 : 4 : 4-tetraethylethylene-4'-methyl-*o*-phenylenediphosphonium dibromide (XVI; X = Br), the structure of which was confirmed by ready conversion by sodium picrate in cold aqueous ethanol into the corresponding dipicrate [XVI; X = O·C<sub>6</sub>H<sub>2</sub>(NO<sub>2</sub>)<sub>3</sub>]. The salt (XVI; X = Br) is the first known compound having a ring system consisting of two phosphorus atoms linked solely by carbon atoms.

Although the original fraction of the diphosphine (VIII) was thus pure enough for the ready preparation of derivatives, a sample of high purity could not be obtained by the further fractionation of the limited quantity available. The pure diphosphine was ultimately obtained by gently heating a mixture of the iodide (XV) and copper powder

Ultraviolet absorption spectrum of 2 : 6-dimethyldiphenylene (XI) in light petroleum.



at 200°/0.5 mm., the iodide undergoing smooth decomposition, with liberation of the diphosphine.

The formation of tetraethyldiphosphine Et<sub>2</sub>P·PEt<sub>2</sub> in the preparation of the required diphosphine (VIII) must result from the direct action of magnesium on the chlorodiethylphosphine. Experiments in which the proportion of the chlorophosphine was reduced always furnished, however, a smaller yield of the diphosphine (VIII).

The identification of the colourless crystalline 2 : 6-dimethyldiphenylene (XI), m. p. 139—141°, is based on the following evidence. (a) Analysis and molecular-weight determinations. (b) The compound could be only the 2 : 6- or the 2 : 7-dimethyldiphenylene, and the latter has been described by Lothrop<sup>10</sup> as pale yellow crystals, m. p. 112°. (c) The ultraviolet absorption, determined in solution in purified light petroleum, b. p. 80—100° (see Fig.), is closely similar in general type to that of diphenylene.<sup>7,11,12</sup> Moreover, the formation of diphenylene by the action of magnesium on *o*-bromoiodobenzene<sup>7</sup> makes that of dimethyldiphenylene from 3-bromo-4-iodotoluene not unexpected.

The origin of the dimethyldiphenylene (XI) is at present uncertain. It could arise by loss of magnesium halide from either of the Grignard compounds (V) or (IX), or of lithium bromide from (XVII), to form the "tolylene" (XVIII), which could dimerise to

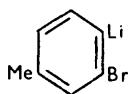
<sup>9</sup> Nyholm, *Nature*, 1951, **168**, 705; Nyholm and Stevenson, *Rec. Trav. chim.*, 1956, **75**, 687.

<sup>10</sup> Lothrop, *J. Amer. Chem. Soc.*, 1941, **63**, 1187.

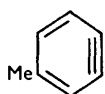
<sup>11</sup> Baker, Boarland, and McOmie, *J.*, 1954, 1476.

<sup>12</sup> Carr, Pickett, and Voris, *J. Amer. Chem. Soc.*, 1941, **63**, 3230.

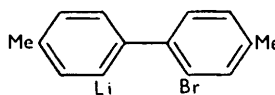
the dimethyldiphenylene (XI).<sup>7,13</sup> This dimerisation might well give a mixture of 2 : 6- and 2 : 7-dimethyldiphenylene. Our distilled material required purification, but with the small amount available it was difficult to determine whether the impurity being eliminated was mainly an isomer, or other products. One reaction route may be dismissed. It is not unlikely that the magnesium when reacting with 3-bromo-4-iodotoluene (IV) could form in small amount some 2 : 2'-dibromo-4 : 4'-dimethyldiphenyl, which in turn



(XVII)



(XVIII)



(XIX)

might give the lithio-derivative (XIX), but loss of lithium bromide would then give solely 2 : 7-dimethyldiphenylene.

A detailed investigation of the hydrocarbons which may be formed, possibly in very small amount, by the action of magnesium, lithium, or *n*-butyl-lithium on 3-bromo-4-iodotoluene (IV) is now being made.

The stability of the palladium compound (XIV), m. p.  $>350^\circ$ , and the aurous iodide (XV), m. p.  $240-241.5^\circ$ , indicates the strong chelating power of the diphosphine (VIII). This diphosphine, by virtue of the nuclear methyl group, offers greater scope than the diphosphine (I) in the study of co-ordination compounds, for (in particular) the fully co-ordinated derivatives of 4-co-ordinate metals could show optical activity or *cis-trans*-isomerism, if the metal has the tetrahedral or uniplanar configuration respectively. We are now investigating the optical resolution of the aurous iodide (XV), and the chemistry of the co-ordinated compounds which the diphosphine forms with various other metallic salts.

#### EXPERIMENTAL

*Reaction of 3-Bromo-4-iodotoluene (IV) with Magnesium (One Equivalent).*—A solution of the toluene derivative (IV) (60 g.) in ether (200 c.c.) was added during 30 min. to activated magnesium (4.91 g., 1 equiv.), the mixture being continuously stirred under nitrogen in an apparatus fitted with a reflux condenser and cooled in ice-water when the vigorous reaction started. After the complete addition, the mixture was stirred at room temperature for 20 min., and then cooled with ice-water whilst chlorodiethylphosphine (25.2 g., 1 mol.) in benzene (100 c.c.) was added during 20 min. The mixture was stirred for  $1\frac{1}{2}$  hr., and then boiled under reflux for 1 hr., and finally cooled and hydrolysed with saturated aqueous ammonium chloride. The organic layer was separated and dried, and the solvent removed. Distillation at 0.3 mm. in nitrogen gave the fractions: (a) b. p.  $76-79.5^\circ$ , 1 c.c.; (b)  $79.5-88^\circ$ , 14.1 g.; (c) b. p.  $96-115^\circ$ , 8.75 g. A glassy residue (ca. 12 g.) could not be distilled.

Fraction (a) was discarded. Fraction (b) apparently contained unchanged (IV): it gave, in small yield, a methiodide too impure to be purified.

The presence of the bromo-phosphine (VI) in fraction (c) was shown by treating a portion in hot ethanol with aqueous-ethanolic potassium palladobromide, whereby *dibromobis-(2-bromo-4-methylphenyldiethylphosphine)palladium*, orange crystals, m. p.  $224-228^\circ$ , after repeated crystallisation from ethyl methyl ketone, was isolated in low yield (Found: C, 33.0; H, 4.65.  $C_{22}H_{32}Br_4P_2Pd$  requires C, 33.6; H, 4.1%). Potassium palladochloride gave the dichloro-analogue, pale yellow crystals, m. p.  $227-230^\circ$  after similar crystallisation (Found: C, 36.6; H, 4.1. Calc. for  $C_{22}H_{32}Cl_2Br_2P_2Pd$ : C, 37.9; H, 4.6%). There is little doubt that only insufficient material prevented the complete elimination by recrystallisation of the corresponding derivatives of diethyl-2-iodo-5-methylphenylphosphine (X) from each of these palladium compounds.

<sup>13</sup> Cf. Lüttringhaus and Schubert, *Naturwiss.*, 1955, **42**, 17.

The presence of the iodo-phosphine (X) in fraction (c) was shown by treating a second portion with methanolic methyl iodide, whereby the *methiodide* of the phosphine (X) was obtained as needles, m. p. 190—192°, after crystallisation from acetone (Found: C, 31.6; H, 4.1.  $C_{12}H_{13}I_2P$  requires C, 32.2; H, 4.3%).

Since the phosphines (VI) and (X) should both give lithio-derivatives, the remainder of fraction (c) in light petroleum (b. p. 40—60°) was treated at room temperature under nitrogen with *n*-butyl-lithium (1 mol.) in the petroleum solution, and after being stirred for 20 min., with chlorodiethylphosphine (2 mols.) also in petroleum. During hydrolysis of the cooled mixture, much insoluble gum was deposited. The dried organic layer, after removal of the solvent, gave on distillation solely 2 : 6-dimethyldiphenylene (ca. 0.50 g.), b. p. 118—124°/0.8 mm., which readily solidified, and after crystallisation in turn from ethanol and light petroleum (b. p. 80—100°), had m. p. 139—141° (Found: C, 93.2; H, 6.7; *M*, in boiling benzene, 200.  $C_{14}H_{12}$  requires C, 93.3; H, 6.7%; *M*, 180).

*Reaction with Magnesium (3 Equivalents).*—A solution of 3-bromo-4-iodotoluene (IV) (35.8 g.) in ether (200 c.c.) was added dropwise to activated magnesium (8.8 g., 3 atom-equiv.) in a nitrogen atmosphere as before. When the reaction had well started, the stirred mixture was cooled in ice-water whilst the remainder of the solution was added during 30 min. After a further 45 min., a solution of chlorodiethylphosphine (30 g., 2 mols.) in ether (120 c.c.) was added in 15 min., a very viscous brown oil separating meanwhile. Benzene (50 c.c.) was then added and the mixture boiled for 2½ hr., the oil being replaced by sticky solid particles. The cooled solution was hydrolysed with saturated aqueous ammonium chloride, and the organic layer dried ( $Na_2SO_4$ ) and distilled under nitrogen. After removal of the solvent, the residue at 0.25 mm. gave the fractions: (a) b. p. up to 77°, 6.5 g.; (b) b. p. 85—104°, 1.76 g.; (c) b. p. 104—112°, 2.2 g.; (d) b. p. 142—150°, 4.1 g. Since fractions (b), (c), and (d) gave the same derivative with aurous iodide, they were united and carefully refractionated, giving the fractions: (i) b. p. ca. 60°/0.3 mm., 1 c.c.; (ii) b. p. 107—115°/0.25 mm., 4.4 g. The latter fraction was the diphosphine (VIII) (14% yield), but still impure (Found: C, 66.1; H, 8.8. Calc. for  $C_{15}H_{26}P_2$ : C, 67.1; H, 9.8%). [A repetition of this experiment, in which unchanged magnesium was removed before addition of the chlorophosphine, gave only a negligible yield of the diphosphine (VIII).]

The fractions (a) and (i) were united and distilled up a long column in nitrogen, but gave only one indefinite fraction, b. p. 42—60°/0.5 mm. This fraction, which was perhaps without equal for its combination of suffocating and nauseating qualities, consisted mainly of tetraethylphosphine. A portion (4.4 g.) in benzene (20 c.c.) was treated with iodine (5.64 g., 0.9 mol.) in benzene (50 c.c.) under nitrogen. The colour of the iodine was discharged, and a pale yellow solid, undoubtedly diethyliodophosphine,  $Et_2PI$ , was deposited: it was so rapidly affected by air that it was not further investigated. A second portion of the diphosphine was mixed with an excess of ethyl iodide and boiled for 5 min. Evaporation gave a viscous oil, which after being washed with ether and benzene afforded crystalline tetraethylphosphonium iodide (Found: C, 35.35; H, 7.6. Calc. for  $C_8H_{20}IP$ : C, 35.0; H, 7.4%).

A third portion of this fraction was cautiously added to an excess of aqueous hydrogen peroxide (20-vol.), and the solution taken to dryness in a desiccator. The residual diethylphosphinic acid proved to be deliquescent, and was consequently dissolved in ammonia and the solution again taken to dryness. The residue, when stirred with acetone, gave a white deposit of *ammonium diethylphosphinate*, needles, m. p. 160°, from ethanolic solution on dilution with acetone (Found: C, 34.65; H, 10.1; N, 10.1.  $C_4H_{14}O_2NP$  requires C, 34.5; H, 10.1; N, 10.1%).

*Derivatives of 4-Methyl-*o*-phenylenebis(diethylphosphine) (VIII).*—Fraction (ii) proved sufficiently pure to be an excellent source of the following derivatives. A solution of potassium palladobromide (0.23 g.) in water (1 c.c.) was added with shaking to a solution of the phosphine (0.30 g., 2.4 mols.) in ethanol (5 c.c.), a sticky precipitate being rapidly deposited. The mixture, when shaken for 6 hr., gave a clear orange-yellow solution, which was taken to dryness in a desiccator. The residue, when washed with water and recrystallised from ethanol, gave *dibromo-4-methyl-*o*-phenylenebis(diethylphosphine)palladium* (XIV), hard cream-coloured crystals, unaffected by heating to 300° (Found: C, 33.5; H, 5.1.  $C_{15}H_{26}Br_2P_2Pd$  requires C, 33.7; H, 4.9%).

The ethanolic phosphine was added to an ethanolic solution of sodium chloraurate until a faint yellow colour persisted. This was removed by the addition of a trace of the phosphine, and the addition of aqueous potassium iodide then precipitated a gummy solid, which when collected, washed with water, dried, and thrice recrystallised from ethyl methyl ketone furnished

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colourless *bis*-[4-methyl-o-phenylenebis(diethylphosphine)]gold iodide (XV), m. p. 240—241.5° (Found: C, 42.2; H 6.2.  $C_{30}H_{52}IP_4Au$  requires C, 41.85; H, 6.1%).

An equimolecular mixture of the phosphine and ethylene dibromide, when cautiously heated, reacted vigorously and then solidified. The hard product was digested with sufficient boiling ethanol to give a clear solution, which was cooled and diluted with ether. The precipitated 1 : 1 : 4 : 4-tetraethylethylene-4'-methyl-o-phenylenediphosphonium dibromide (XVI; X = Br), when recrystallised from ethanol, formed needles, unmelted by heating to 340° (Found: C, 44.8; H, 6.4.  $C_{17}H_{30}Br_2P_2$  requires C, 44.75; H, 6.6%). This gave a yellow *dipicrate* (XVI; X =  $\cdot O \cdot C_6H_2O_6N_3$ ), m. p. 178—179° (from aqueous ethanol) (Found: C, 46.3; H, 4.5; N, 11.55.  $C_{29}H_{34}O_{14}N_6P_2$  requires C, 46.3; H, 4.6; N, 11.15%).

Preparation of simple quaternary salts such as the ethiodide was not attempted because, although in these circumstances quaternisation at one phosphorus atom would tend to deactivate the other,<sup>3,4</sup> a mixture of isomeric monoethiodides would almost certainly have resulted.

*Isolation of the Pure Diphosphine* (VIII).—A mixture of the pulverised iodide (XV) and an excess of copper powder was placed in the sealed end of a glass tube, the upper end of which was then constricted to form two narrow necks. The tube was evacuated to 0.5 mm. and the closed end inserted horizontally into a metal block, which was electrically heated at 200° for 20 min. The iodide decomposed smoothly, and the liberated pure colourless *diphosphine* (VIII) condensed in the cool portion of the tube between the two necks, which were sealed off after the cold tube had been filled with nitrogen (Found: C, 66.8; H, 9.9%).

A sample of this pure phosphine, when exposed to the air for three weeks, remained a slightly viscous liquid, and had not apparently been oxidised.

4-Methyl-o-phenylenebis(diethylarsine) (XIII).—This diarsine was prepared essentially as the diphosphine (VIII), by the action of 3-bromo-4-iodotoluene (9.1 g.) in ether (50 c.c.) on activated magnesium (2.25 g., 3 atom-equiv.), followed by diethyliodoarsine (16 g., 2 mols.) in ether (30 c.c.). The product, worked up as before, gave on distillation two fractions: (a) b. p. 60—64°/0.4 mm (2 g.), which was almost certainly tetraethyldiarsine,  $Et_2As \cdot AsEt_2$ , because when boiled briefly with methyl iodide it gave diethyldimethylarsonium iodide, m. p. 290° (effervescence) from ethanol (Found: C, 25.2; H, 5.6. Calc. for  $C_8H_{16}IAs$ : C, 24.8; H, 5.5%), and (b) b. p. 100—110°/0.2 mm. (2.2 g., 23%), the diarsine (XIII).

For rapid characterisation without further purification, the diarsine (XIII) (2 mols.) in ethanol was added to a solution of cuprous iodide (1 mol.) in aqueous potassium iodide, which was vigorously shaken. The precipitated material, when collected, washed with water, dried, and thrice recrystallised from ethyl methyl ketone, afforded *di*-[4-methyl-o-phenylenebis(diethylarsine)]copper di-iodocuprite,  $[2Me \cdot C_6H_3(AsEt_2)_2, Cu][CuI_2]$ , colourless crystals, m. p. 229—231° (immersed at 220°) (Found: C, 32.9; H, 4.8.  $C_{30}H_{52}I_2As_4Cu_2$  requires C, 32.95; H, 4.8%). The evidence that compounds of this type are salts, and not covalent compounds formed by the union of the diarsine (1 mol.) with cuprous iodide (1 mol.), has been given by Kabesh and Nyholm<sup>14</sup> and by Cochran, Hart, and Mann.<sup>5</sup>

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<sup>14</sup> Kabesh and Nyholm, *J.*, 1951, 38.