

**429.** *The Synthesis of Derivatives of 1 : 4-Diphenyldiethylene-diphosphine.*

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Two syntheses of the diethobromide of 1 : 4-diphenyldiethylenediphosphine are described. This dibromide, when heated under a variety of conditions, underwent rupture of the ring system with the formation of *s*-ethylenebis(ethylphenylphosphine), and the parent 1 : 4-diphenyldiethylenediphosphine could not be thus obtained. Other attempts to prepare the cyclic ditertiary phosphine without a thermal decomposition stage have been investigated without success.

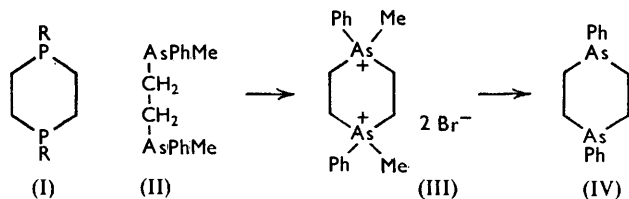
WE have investigated many routes which could possibly lead to the isolation of 1 : 4-disubstituted diethylenediphosphines (systematically 1 : 4-disubstituted 1 : 4-diphosphacyclohexanes) of type (I). Comparable arsenic compounds were prepared by Jones and Mann,<sup>1</sup> who condensed *s*-ethylenebis(methylphenylarsine) (II) with ethylene dibromide to give 1 : 4-dimethyl-1 : 4-diphenyldiethylenediarsonium dibromide (III) in 21% yield and considerable amorphous material presumably formed by extensive linear condensation: heating the dibromide (III) then gave the diarsine (IV) in 29% yield.

In view of these results, we have converted phenylphosphine (V), by the action of sodium in liquid ammonia, into phenylmonosodiophosphine, which readily reacted with ethyl bromide to form ethylphenylphosphine (VI), a method precisely parallel to that by which Mann and Smith prepared a series of alkylphenylarsines.<sup>2</sup> The phosphine (VI) was then converted *in situ* into the sodio-derivative, which reacted with ethylene dibromide to form *s*-ethylenebis(ethylphenylphosphine) (VII) in 35% overall

<sup>1</sup> Emrys R. H. Jones and Mann, *J.*, 1955, 401.

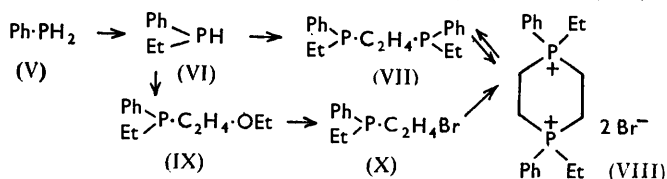
<sup>2</sup> Mann and Smith, *J.*, 1952, 4544.

yield from the phosphine (I). It is noteworthy that these groups cannot be introduced in the reverse order into the phosphine molecule. Phenylmonosodiophosphine in ammonia, when treated in turn with one equivalent of ethylene dibromide, sodium, and ethyl bromide, did not furnish the diphosphine (VII), and our experience indicates that ethylene dibromide possibly reacts only with the sodio-derivatives of secondary phosphines.



The diphosphine (VII) when heated with ethylene dibromide gave 1 : 4-diethyl-1 : 4-diphenyldiethylenediphosphonium dibromide (VIII), but only in moderate yield.

In an alternative and more efficient synthesis, ethylphenylphosphine (VI) was converted in liquid ammonia into the monosodio-derivative, which with 2-ethoxyethyl iodide formed 2-ethoxyethyl-ethylphenylphosphine (IX) in 63% yield. Hydrogen

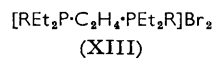
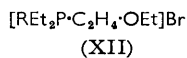
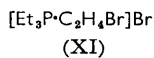


bromide converted this phosphine in boiling acetic acid into the liquid 2-bromoethyl-ethylphenylphosphine (X), which underwent self-quaternisation, spontaneously at room temperature and readily in boiling toluene, to form the diphosphonium dibromide (VIII).

The dibromide (VIII) and the corresponding dichloride and dicitrate are highly crystalline and, like the diarsonium dibromide (III), showed no sign of *cis-trans*-isomerism: the two series thus differ from similar piperazine diquaternary salts, which Hanby and Rydon<sup>3</sup> have obtained as geometric isomers.

The thermal decomposition of the dibromide (VIII) was investigated, in the hope that it would entail loss of ethylene and hydrogen bromide, and the formation of 1 : 4-diphenyldiethylenediphosphine (I; R = Ph). In spite of a wide variety of conditions employed, however, this decomposition always caused rupture of the cyclic system, with regeneration of the ethylenebis(ethylphenylphosphine) (VII).

It appears highly improbable, therefore, that 1 : 4-disubstituted diethylenediphosphines (I) can be thus prepared from their diphosphonium dihalides. The thermal decomposition of phosphonium bromides fails signally also for the preparation of various intermediate compounds. For example, 2-bromoethyltriethylphosphonium bromide (XI) on being heated underwent general charring, and the formation of a tertiary phosphine could not be detected: 2-ethoxyethyltriethylphosphonium bromide (XII; R = Et) and

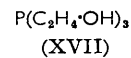
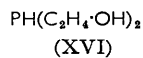
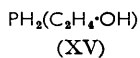
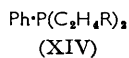


its phenyl analogue (XII; R = Ph) gave similar unsatisfactory results. *s*-Ethylenebis-(triethylphosphonium) dibromide (XIII; R = Et) and the phenyl analogue (XIII; R = Ph) underwent smooth thermal decomposition with the formation of triethyl- and diethylphenyl-phosphine respectively, but ditertiary phosphines of type (VII) cannot apparently be prepared in this way. The trimethylene homologue of (XIII; R = Et) also similarly gave triethylphosphine.

To avoid thermal decompositions, therefore, phenylphosphine in liquid ammonia was

<sup>3</sup> Hanby and Rydon, *J.*, 1945, 833.

treated in turn with one equivalent of sodium and of 2-ethoxyethyl iodide, and the process then repeated, to form the liquid di-(2-ethoxyethyl)phenylphosphine (XIV; R = OEt). This phosphine, treated in boiling acetic acid with hydrogen bromide, gave ultimately a viscous syrup, presumably the 2-bromoethyl derivative (XIV; R = Br); it was treated



without delay with phenylphosphinebis(magnesium bromide),  $\text{Ph}\cdot\text{P}(\text{MgBr})_2$ , in the hope of obtaining the 1 : 4-diphenyl compound (I; R = Ph), but no decisive product could be isolated. This result is in marked contrast to the ready reaction of di-(2-bromoethyl)-aniline with this reagent<sup>4</sup> and with the arsenic analogue,  $\text{Ph}\cdot\text{As}(\text{MgBr})_2$ ,<sup>5</sup> to form the highly crystalline hexahydro-1 : 4-diphenyl-1 : 4-azaphosphine and -arsarsine respectively. The present failure may have been due to impurities in the phosphine (XIV; R = Br).

It has been claimed<sup>6</sup> that phosphine reacts with ethylene oxide to give the 2-hydroxyethylphosphines (XV), (XVI), and (XVII) in low yield, but we find that phenylphosphine, when heated with ethylene oxide in sealed tubes, formed solely polymeric material: the desired di-(2-hydroxyethyl)phenylphosphine (XIV; R = OH), moreover, could not be obtained by the action of ethylene oxide on the magnesium derivative,  $\text{Ph}\cdot\text{P}(\text{MgBr})_2$ .

Phenylphosphine in the presence of potassium carbonate underwent no reaction when heated in nitrogen under reflux with ethylene dibromide, bromohydrin, or chlorohydrin.

Other methods for the preparation of cyclic ditertiary diphosphines of type (I) are now being investigated.

It is noteworthy that the basic strength of triethylphosphine enables it to form a picrate which can be recrystallised unchanged from hot ethanol: this is apparently the first recorded example of a tertiary phosphine picrate having a stability of this order.

The therapeutic properties of the diphosphonium dichloride (as VIII) have been investigated by Imperial Chemical Industries Limited, Pharmaceuticals Division, who find that it is ineffective against a *Trypanosoma congolense* infection in mice and against *Streptococcus haemolyticus in vitro*. It showed feeble activity against a mouse nematode infection, but much less than that exhibited by some of the phosphoric esters in current use.

#### EXPERIMENTAL

Compounds were colourless unless otherwise stated.

*Reactions in Liquid Ammonia.*—The following general directions apply to all such experiments recorded below. Phenylphosphine (V) (5–40 g.) was pipetted directly from an ampoule into liquid ammonia (25–250 c.c.) in a flask through which nitrogen was passing, immersed in acetone–solid carbon dioxide. Ether (5–40 c.c.), used to wash the ampoule, was added. Small pieces of sodium (1 equiv.) were dropped into the stirred solution, each piece dissolving exothermically forming a local characteristic blue colour which was rapidly replaced by the orange colour of the sodiophosphine. When a permanent blue-black colour indicated a slight excess of sodium, the solution was stirred for 15 min., and the first alkyl halide (1 mol.) in ether (3–20 c.c.) added during 10 min., giving first the orange colour and ultimately an almost colourless suspension of a white precipitate. Sodium (*ca.* 1 equiv.) was added as before (the reaction being now slower) until the blue-black coloration became permanent, and the mixture was then stirred for at least 1 hr. The second alkyl halide (*ca.* 1 mol.) in ether (3–20 c.c.) was added dropwise until the orange colour faded to white. The bath was removed, ether added, and the ammonia allowed to boil away. Cold boiled water (20–100 c.c.) was cautiously added, and the ethereal phosphine solution separated under nitrogen, dried, and distilled.

*s-Ethylenebis(ethylphenylphosphine)* (VII).—This was prepared from phenylphosphine (V) (24.8 g.) in liquid ammonia (250 c.c.), sodium (5.2 g., 1 equiv.), ethyl bromide (24.6 g., 1 mol.), sodium as before, and ethylene dibromide (21.1 g., 0.5 mol.). Distillation gave the fractions: (a) b. p. 55–60°/0.4 mm., 9.0 g., probably diethylphenylphosphine, (b) b. p. 148–165°/0.4 mm.,

<sup>4</sup> Mann and Millar, *J.*, 1952, 3039.

<sup>5</sup> Beeby and Mann, *J.*, 1951, 886.

<sup>6</sup> Knunyants and Sterlin, *Compt. rend. Acad. Sci. U.R.S.S.*, 1947, 56, 49; *Chem. Abs.*, 1948, 42, 519.

12.2 g. (36%), the *diphosphine* (VII), which solidified, and had m. p. 69—70° after crystallisation from ethanol (Found: C, 71.4; H, 8.1.  $C_{18}H_{24}P_2$  requires C, 71.5; H, 8.0%). An ethereal solution of the diphosphine, when treated with methyl iodide, deposited the crystalline *dimethiodide*, m. p. 199—200° (from methanol) (Found: C, 41.1; H, 5.3.  $C_{20}H_{30}I_2P_2$  requires C, 41.0; H, 5.2%). A boiling ethanolic solution, treated with ethyl bromide, gave the *diethobromide*, m. p. 255—257° (from ethanol) (Found: C, 50.6; H, 6.9.  $C_{22}H_{34}Br_2P_2$  requires C, 50.8; H, 6.6%).

The m. p. of the pure diphosphine was unaffected when the crystals were exposed to the air at room temperature for 24 hr.

When in a similar experiment to the above the order of addition of the ethyl bromide and ethylene dibromide was reversed, distillation gave diethylphenylphosphine, b. p. 200—218° (61% calc. on the ethyl bromide), identified as triethylphenylphosphonium bromide, m. p. 184—186° (lit.,<sup>7</sup> 187—188°) (Found: C, 52.6; H, 7.4. Calc. for  $C_{12}H_{20}BrP$ : C, 52.4; H, 7.3%), and as *di-bromobis(diethylphenylphosphine)palladium*, orange crystals, m. p. 132—133° (from ethanol) (Found: C, 40.2; H, 5.1.  $C_{20}H_{30}Br_2P_2Pd$  requires C, 40.1; H, 5.1%).

In another experiment, phenylphosphine in liquid ammonia was treated with sodium (1 equiv.) and ethylene dibromide (0.5 mol.), and the addition of these reagents then repeated. The resulting crude yellow viscous product did not crystallise or give any crystalline derivative, and almost certainly was not the diphosphine (I; R = Ph).

I : 4-Diethyl-1 : 4-diphenyldiethylenediphosphonium Dibromide (VIII).—A solution of the diphosphine (VII) (0.5 g.) and ethylene dibromide (0.6 g., 2 mols.) in ethanol (10 c.c.) was boiled under reflux in nitrogen for 2 hr., and evaporated. The gummy residue, when washed with ether and recrystallised from ethanol, gave the *dibromide* (VIII), which decomposed at ca. 370° without melting (Found: C, 48.9; H, 5.7%; M, apparent, cryoscopic in 0.57% aqueous solution, 165, in 1.1% solution, 167.  $C_{20}H_{28}Br_2P_2$  requires C, 49.0; H, 5.8%; M, 490). The total ionisation of a uni-bivalent salt, indicated by the molecular-weight determinations, was confirmed by the molecular conductivity,  $\Lambda_M$ , 215 mho/cm.<sup>2</sup>, of an aqueous solution, dilution 1480 l., at 20°.

It is noteworthy that when a mixture of the diphosphine (VII) and ethylene dibromide (1 or 5 mols.) in methanol or ethanol was heated in nitrogen either under reflux or in a sealed tube at 100°, the final gummy residue could not be obtained crystalline: only the above use of the dibromide (2 mols.) proved successful.

The dibromide (VIII) in aqueous solution gave a yellow *dipicrate*, m. p. 240—245° (decomp.) after crystallisation from much water (Found: C, 48.7; H, 4.3; N, 10.9.  $C_{32}H_{32}O_{14}N_6P_2$  requires C, 48.9; H, 4.1; N, 10.7%). The aqueous solution of the dibromide, when shaken with an excess of silver chloride for 10 hr., filtered, and evaporated, gave the *dichloride*, which, after recrystallisation from ethanol and drying at 100°/0.1 mm., decomposed at ca. 350° without melting (Found: C, 59.8; H, 7.2.  $C_{20}H_{28}Cl_2P_2$  requires C, 59.8; H, 7.0%).

The diphosphine (VII) did not react with ethylene dichloride: it reacted readily with trimethylene or *o*-xylylene dibromide, but in each case the viscous syrupy product could not be purified or converted into a satisfactory derivative.

2-Ethoxyethyl-ethylphenylphosphine (IX).—Phenylphosphine (V) (22.5 g.) in ammonia (150 c.c.), when treated with sodium (4.7 g., 1 equiv.), ethyl bromide (22.3 g., 1 mol.), sodium as before, and 2-ethoxyethyl iodide (41.0 g., 1 mol.), gave the *phosphine* (IX) (27.0 g., 63%), b. p. 141—149°/18 mm. (Found, for a refractionated sample, b. p. 146.5°/18 mm.: C, 68.7; H, 9.1.  $C_{12}H_{19}OP$  requires C, 68.5; H, 9.1%).

A solution of the phosphine (IX) (30.5 g.) in acetic acid (400 c.c.) was boiled under reflux in nitrogen whilst hydrogen bromide was passed through it for 8 hr., and the solvent was then evaporated under reduced pressure. The residual crude hydrobromide of 2-bromoethyl-ethylphenylphosphine (X) was shaken in nitrogen with a mixture of chloroform and air-free aqueous sodium hydrogen carbonate. Evaporation of the dried chloroform extract gave the liquid phosphine (X) (ca. 70%), which in toluene solution, after 2 hours' boiling, gave the dibromide (VIII), decomposing at ca. 370° (Found: C, 49.3; H, 6.1%); this gave the dipicrate, m. p. and mixed m. p. 240—245° (decomp.) (Found: C, 48.6; H, 4.5; N, 11.0%). Samples of the free phosphine, when set aside under nitrogen, underwent spontaneous but erratic self-quaternisation: a sample heated to ca. 110° underwent such vigorous exothermic quaternisation that partial decomposition reduced the yield of the dibromide (VIII) to 30%.

<sup>7</sup> Davies and Lewis, *J.*, 1934, 1599.

*Thermal Decomposition of the Dibromide* (VIII).—A mixture of the dibromide and anhydrous potassium carbonate was placed in a small distillation flask, the side-arm of which was fitted directly into a similar flask to permit subsequent direct refractionation of the initial crude distillate. The mixture was then heated in nitrogen at 360–370°/10 mm. for 2 hr. The clear limpid distillate, when refractionated, gave the diphosphine (VII), b. p. 160–175°/1 mm., m. p. and mixed m. p. 67–70°, after crystallisation from ethanol (Found: C, 71.7; H, 8.4%); it gave the dimethiodide, m. p. and mixed m. p. 199–200°, after crystallisation from methanol.

Alternatively, the pure dibromide (VIII), when heated in a tube in nitrogen at 360–370°/10 mm., gave a hard yellow sublimate, undoubtedly of the dihydrobromide of the diphosphine (VII). The powdered sublimate was shaken with benzene and aqueous sodium hydrogen carbonate, and the benzene extract, when dried and distilled, gave the diphosphine (VII), b. p. 162–163°/0.5 mm., m. p. and mixed m. p. 70–71° after crystallisation from ethanol.

*2-Bromoethyltriethylphosphonium Bromide* (XI).—A mixture of triethylphosphine (5.1 g.), ethylene dibromide (40.5 g., 5 mols.), and ethanol (4 c.c.) was set aside under nitrogen for 2 days and then boiled under reflux for 1 hr. After removal of the solvent, the residue was washed with ether and recrystallised from ethanol, affording the deliquescent bromide (5.5 g., 42%), m. p. ca. 235° (decomp.) (lit.,<sup>8</sup> 235°) (Found: C, 30.9; H, 6.5. Calc. for C<sub>8</sub>H<sub>19</sub>Br<sub>2</sub>P: C, 31.4; H, 6.3%).

The bromide (4 g.), when heated at 325°/20 mm. in nitrogen for 2 hr., gave no distillate, although hydrogen bromide (0.6 mol.) collected in a liquid-nitrogen trap. The charred residue (2.5 g.) could not be purified or converted into a satisfactory derivative.

A mixture of triethylphosphine (5 g.), 2-ethoxyethyl bromide (7.1 g., 1.1 mols.), and ethanol (5 c.c.) was boiled under reflux in nitrogen for 2 hr., and the solvent removed. The residual bromide (XII; R = Et) was too deliquescent for recrystallisation: heating it in nitrogen at 0.1 mm. gave no distillate at 250°, and increasing the temperature to 400° caused only slow charring. The bromide (XII; R = Ph), a highly deliquescent salt prepared in the same way, behaved similarly on being heated.

*s-Ethylenebis(triethylphosphonium) Dibromide* (XIII; R = Et).—Triethylphosphine (5.0 g.), ethylene dibromide (3.2 g., 0.4 mol.), and ethanol were heated under nitrogen in a sealed tube at 100° for 15 hr. The hygroscopic dibromide (6.6 g., 92%) precipitated with ether and recrystallised from ethanol had m. p. 260° (decomp.) (Found: C, 38.8; H, 8.2. Calc. for C<sub>14</sub>H<sub>34</sub>Br<sub>2</sub>P<sub>2</sub>: C, 39.6; H, 8.1%); it gave a yellow *dipicrate*, m. p. 208–210° (from much ethanol) (Found: C, 43.7; H, 5.3; N, 11.5. C<sub>26</sub>H<sub>38</sub>O<sub>14</sub>N<sub>6</sub>P<sub>2</sub> requires C, 43.3; H, 5.3; N, 11.7%).

The dibromide, when heated in nitrogen at 0.1 mm. with a brush flame, or at 350°/15 mm., gave triethylphosphine (ca. 40%) as its hydrobromide. The free phosphine was identified (a) by precipitation from ethanolic solution of its yellow *picrate*, m. p. 106–107° (decomp.) (from ethanol) (Found: C, 41.0; H, 5.3; N, 12.3. C<sub>6</sub>H<sub>15</sub>P, C<sub>6</sub>H<sub>3</sub>O<sub>7</sub>N<sub>3</sub> requires C, 41.5; H, 5.2; N, 12.1%), (b) as its ethiodide, m. p. 293–297° (decomp.) (Found: C, 35.1; H, 7.7. Calc. for C<sub>8</sub>H<sub>20</sub>IP: C, 35.0; H, 7.4%), (c) as the yellow dichlorodiphosphinepalladium, m. p. 137–138° (lit.,<sup>9</sup> 139°) (Found: C, 35.0; H, 7.0. Calc. for C<sub>12</sub>H<sub>30</sub>Cl<sub>2</sub>P<sub>2</sub>Pd: C, 34.8; H, 7.3%), and (d) as the pale orange *dibromodiphosphinepalladium*, m. p. 131–132° (from ethanol) (Found: C, 28.7; H, 5.4. C<sub>12</sub>H<sub>30</sub>Br<sub>2</sub>P<sub>2</sub>Pd requires C, 28.7; H, 6.0%). These derivatives, when mixed with authentic samples, underwent no change in m. p.

Hofmann<sup>8</sup> showed that the dihydroxide corresponding to the dibromide (XIII; R = Et) when heated yielded triethylphosphine, its oxide, and ethylene.

*s-Ethylenebis(diethylphenylphosphonium) Dibromide* (XIII; R = Ph).—This salt was prepared (a) in 78% yield by heating a mixture of ethylene dibromide and diethylphenylphosphine (2 mols.) in a sealed tube in nitrogen at 160° for 2 hr., and (b) in 57% yield by boiling this mixture diluted with ethanol under reflux in nitrogen for 5 hr. It had m. p. 257–259° (decomp.) after crystallisation from ethanol (Found: C, 50.5; H, 6.3. C<sub>22</sub>H<sub>34</sub>Br<sub>2</sub>P<sub>2</sub> requires C, 50.8; H, 6.6%) and gave a yellow *dipicrate*, m. p. 188–190° (decomp.) (Found: C, 49.5; H, 5.0; N, 10.5. C<sub>34</sub>H<sub>38</sub>O<sub>14</sub>N<sub>6</sub>P<sub>2</sub> requires C, 50.0; H, 4.7; N, 10.3%). The dibromide was apparently unaffected when heated at 310°/0.1 mm. for even 20 hr. Heating at 350°/0.001 mm. or at 360°/12 mm., caused charring with distillation of a liquid which on cooling formed the waxy solid diethylphenylphosphine hydrobromide. The liberated phosphine was identified as its

<sup>8</sup> Hofmann, *Phil. Trans.*, 1860, **150**, 409; *Annalen*, 1861, *Suppl. I*, **156**, 275.

<sup>9</sup> Mann and Purdie, *J.*, 1935, 1549.

ethobromide, m. p. 184—186° (from ethanol) (lit.,<sup>7</sup> 187—188°), and as the dibromodiphosphine-palladium, m. p. and mixed m. p. 132—133° (from ethanol).

*s*-Trimethylenebis(triethylphosphonium) dibromide was prepared as (XIII; R = Et) in 88% yield as deliquescent crystals, m. p. ca. 260° (decomp.) (Found: C, 40.8; H, 8.7.  $C_{15}H_{36}Br_2P_2$  requires C, 41.1; H, 8.3%). When heated at 345°/15 mm. it gave triethylphosphine (ca. 30%), identified as the above ethiodide and dichloro- and dibromo-diphosphinepalladium.

*Di*-(2-ethoxyethyl)phenylphosphine (XIV; R = OEt).—Phenylphosphine (9.3 g.) in liquid ammonia (150 c.c.) was treated in turn with sodium (1.9 g., 1 equiv.) and 2-ethoxyethyl iodide (16.8 g., 1 mol.), and then again with these reagents in this order. After evaporation of the ammonia, distillation in nitrogen gave the phosphine (13.5 g., 64%), b. p. 118—122°/0.5 mm. (Found: C, 66.4; H, 9.3.  $C_{14}H_{23}O_2P$  requires C, 66.1; H, 9.1%). It readily afforded pale orange dibromobis[*di*-(2-ethoxyethyl)phenylphosphine]palladium, m. p. 111—112° (from ethanol) (Found: C, 43.3; H, 6.2.  $C_{28}H_{46}O_4Br_2P_2Pd$  requires C, 43.4; H, 6.0%).

A mixture of phenylphosphine (5.2 g.) and ethylene oxide (4.6 g., 2.2 mols.) under nitrogen, when heated in a sealed tube at 100° for 5 hr., afforded on distillation an almost quantitative recovery of the phosphine. Heating at 100° for 18 hr. gave a gum; attempted distillation up to 200°/0.2 mm. gave a negligible distillate, and the residue was insoluble in all the usual solvents.

Many attempts were made to hydrogenate acetylenebis(diphenylphosphine),  $Ph_2P \cdot C \equiv C \cdot PPh_2$ ,<sup>10</sup> directly or indirectly, and thus ultimately obtain *s*-ethylenebis(diphenylphosphine) (as VII). All hydrogenating metallic catalysts were, as expected, rapidly poisoned and rendered inert by the diphosphine, which was subsequently recovered. Other reducing agents were either without effect or gave crude products from which no pure compound could be isolated. Similar results were obtained with acetylenebis(diphenylarsine).<sup>11</sup>

We are greatly indebted to Imperial Chemical Industries Limited, Pharmaceuticals Division, for the therapeutic tests, to Dr. F. H. C. Stewart for assistance in the preparation of the dibromide (XIII; R = Ph), and to the Department of Scientific and Industrial Research for a grant (to C. H. S. H.).

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[Received, January 23rd, 1958.]

<sup>10</sup> Hartmann, Beermann, and Czempik, *Z. anorg. Chem.*, 1956, **237**, 261.

<sup>11</sup> *Idem*, *Angew. Chem.*, 1955, **67**, 233.