569. *Triethylenediphosphine* (1 : 4-*Diphospha*bicyclo[2 : 2 : 2]-*octane*).

By Roy C. Hinton and Frederick G. Mann.

Triethylenediphosphine has been synthesised by combining tribenzylphosphine and ethylene dibromide to give the salt

$$[(PhCH_2)_3P{\cdot}C_2H_4{\cdot}P(CH_2Ph)_3]Br_2,$$

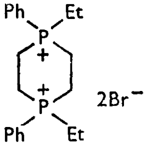
which on treatment with lithium aluminium hydride gives the diphosphine, $(PhCH_2)_2P{\cdot}C_2H_4{\cdot}P(CH_2Ph)_2$. Successive reaction with ethylene dibromide and the hydride give in turn the diphosphine $PhCH_2{\cdot}P<[CH_2{\cdot}CH_2]_2>P{\cdot}CH_2Ph$ and then the triethylenediphosphine.

Triethylenediphosphine, like triethylenediamine, is a highly crystalline, readily volatile substance. The phosphine and certain derivatives show a strong tendency to retain traces of solvent even after sublimation at low pressures.

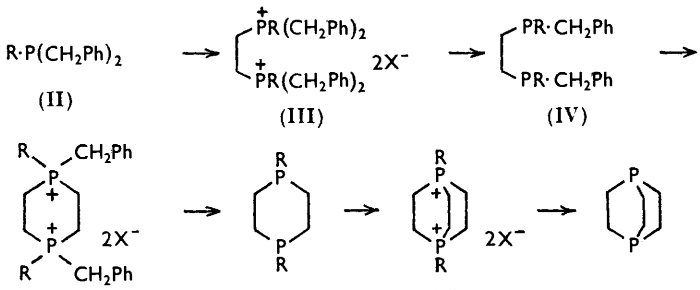
The action of the lithium aluminium hydride in the last stage of the synthesis also causes a cleavage of the triethylenediphosphine system with the production of a polythene $Me{\cdot}[CH_2]_n{\cdot}Me$, where n = *ca.* 34.

Two syntheses of 1 : 4-diethyl-1 : 4-diphenyldiethylenediphosphonium dibromide (I), systematically named 1 : 4-diethyl-1 : 4-diphenyl-1 : 4-diphosphonia*cyclo*hexane dibromide, have been recorded by Hitchcock and Mann.[1] The corresponding ditertiary phosphine (VI; R = Ph), which was required for further cyclic diquaternisation with ethylene dibromide, could not be obtained from the salt (I) by thermal decomposition, which caused fission of the ring with formation of *sym*-ethylenebis(ethylphenylphosphine).

Bailey and Buckler[2] have shown, however, that quaternary phosphonium halides having a benzyl group as part of the phosphonium cation lose this group on treatment with lithium aluminium hydride, with liberation of the corresponding tertiary phosphine. We have therefore investigated the application of this reaction to our diphosphonium derivatives, with the ultimate object of isolating triethylenediphosphine (VIII), systematically named 1 : 4-diphospha*bicyclo*[2 : 2 : 2]octane.



(I)



(II) (III) (IV) (V) (VI) (VII) (VIII)

In preliminary experiments, dibenzylphenylphosphine[3] (II; R = Ph) was quaternised with ethylene dibromide to form *sym*-ethylenebis(dibenzylphenylphosphonium) dibromide (III; R = Ph, X = Br). This salt, when heated, decomposed with the formation of dibenzylphenylphosphine hydrobromide. When, however, the salt (III; R = Ph; X = Br) in tetrahydrofuran was treated with lithium aluminium hydride, smooth conversion into *sym*-ethylenebis(benzylphenylphosphine) (IV; R = Ph) in 95% yield occurred.

[1] Hitchcock and Mann, *J.*, 1958, 2081.
[2] Bailey and Buckler, *J. Amer. Chem. Soc.*, 1957, **79**, 3567.
[3] Mann, Millar, and Stewart, *J.*, 1954, 2832.

This diphosphine was characterised by formation of its dimethiodide and its chelated palladobromide derivative (IX; R = Ph).

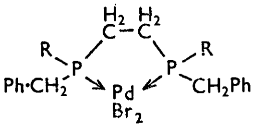
In an attempted alternative synthesis of the diphosphine, a solution of phenylphosphine in liquid ammonia was treated in turn with one equivalent of sodium, benzyl bromide, and sodium again, and finally with half an equivalent of ethylene dibromide (cf. ref. 1). The major product was, however, dibenzylphenylphosphine, with a lower-boiling fraction which was probably benzylphenylphosphine; the diphosphine was not detected.

The diphosphine (IV; R = Ph) reacted vigorously with ethylene dibromide to form the cyclic diphosphonium dibromide (V; R = Ph, X = Br), which on treatment with the hydride as before afforded 1 : 4-diphenyldiethylenediphosphine (VI; R = Ph). The identity of this diphosphine, *i.e.*, the fact that it was not the corresponding derivative having the tetraethylenetetraphosphine ring system, was confirmed by the determination of the molecular weight of its dioxide.

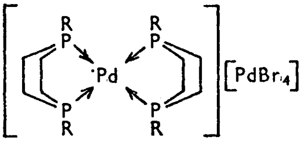
This diphosphine also reacted vigorously with ethylene dibromide to form the bicyclodiphosphonium dibromide (VII; R = Ph, X = Br), but this salt and the corresponding dipicrate were difficult to purify.

This preparation of the dibromide (VII; R = Ph, X = Br) revealed the synthetic route to the dicyclic diphosphine (VIII). For this purpose, tribenzylphosphine (II; R = CH_2Ph) was quaternised with ethylene dibromide to the diphosphonium dibromide (III; R = CH_2Ph, X = Br), which was reduced to the diphosphine (IV; R = CH_2Ph). This diphosphine also readily gave a chelated palladium derivative (IX; R = CH_2Ph).

The diphosphine (IV; R = CH_2Ph) in turn gave the cyclic diphosphonium dibromide (V; R = CH_2Ph, X = Br), which on reduction afforded the cyclic diphosphine (VI; R = CH_2Ph). It is noteworthy that cold benzyl bromide reconverted this diphosphine into the cyclic dibromide (V; R = CH_2Ph, X = Br), but boiling benzyl bromide caused ring fission and formation of the original dibromide (III; R = CH_2Ph, X = Br). The diphosphine reacted readily with ethylene dibromide to give 1 : 4-dibenzyltriethylenediphosphonium dibromide (VII; R = CH_2Ph, X = Br).



(IX)



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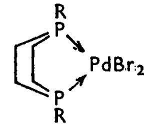

(XI)

The formation of the triethylenediphosphonium salts (VII; R = Ph and CH_2Ph, X = Br) by the action of ethylene dibromide on the monocyclic diphosphines (VI; R = Ph and CH_2Ph) shows clearly that the ring system in the latter compounds must be capable of existing in the " boat " conformation. This is confirmed by the reaction of potassium palladobromide with warm ethanolic 1 : 4-dibenzyldiethylenediphosphine (VI; R = CH_2Ph) to give the salt (X; R = CH_2Ph), a buff-coloured microcrystalline powder, insoluble in all the usual hot solvents, and the deep orange-brown 1 : 4-dibenzyldiethylenediphosphinedibromopalladium (XI; R = CH_2Ph), which is readily soluble in various solvents and shows a normal molecular weight in boiling chloroform. It is noteworthy that the salt (X; R = CH_2Ph) decomposed without melting between 200° and 300°, whereas the compound (XI; R = CH_2Ph) had m. p. 145—152°. The diphenyldiphosphine (VI; R = Ph) gave an analogous salt (X; R = Ph), having properties almost identical with those of its benzyl homologue: it also gave a soluble orange-brown compound, undoubtedly of type (XI), but insufficient material precluded complete purification.

This behaviour recalls that of *o*-phenylenebisdimethylarsine,[4] $C_6H_4(AsMe_2)_2$, and

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[4] Chatt and Mann, *J.*, 1939, 1622.

o-dimethylaminophenyldiethylphosphine,[5] $NMe_2{\cdot}C_6H_4{\cdot}PEt_2$, each of which reacts readily with potassium palladochloride to give stable insoluble salts of type (X), which on prolonged digestion with boiling ethanolic hydrochloric acid and ethanol respectively undergo conversion into the covalent dichlorides of type (XI).

The 1 : 4-dibenzyldiethylenediphosphinedibromo-palladium (XI; R = CH_2Ph) is identical in type with, and closely similar in appearance to, 1 : 4-dimethylpiperazine-dibromopalladium, in which the piperazine ring has also adopted the "boat" conformation.[6]

The reduction of the 1 : 4-dibenzyltriethylenediphosphonium dibromide (VII; R = CH_2Ph, X = Br) in tetrahydrofuran was carried out as usual with lithium aluminium hydride, the solvent being then removed, and the cold residue treated with ether and aqueous sodium potassium tartrate. Investigation of the ethereal layer showed, however, that the hydride had not only reduced the dibromide to the required triethylenediphosphine (VIII), but had caused considerable rupture of the ring system with the production of (*a*) a polythene $Me{\cdot}[CH_2]_n{\cdot}Me$, where $n = ca.$ 34, formed by polymerisation of the liberated ${\cdot}CH_2{\cdot}CH_2{\cdot}$ units, and (*b*) a second phosphine which has not yet been identified.

The ether was removed from the extract, and the distillation apparatus then fitted with an ice-cooled receiver, and heated on a steam-bath whilst nitrogen was passed through the apparatus. The diphosphine (VIII) separated as needle-shaped crystals in the trap.

The pure diphosphine had m. p. 252° under nitrogen in a sealed tube, and showed a normal molecular weight in boiling chloroform solution. It was characterised as its crystalline dimethiodide (XII; X = I), dimethopicrate (XII; $X = O{\cdot}C_6H_2O_6N_3$), and its bis(aurous chloride) derivative (XIII). It sublimes very readily at low pressures, and in this respect resembles triethylenediamine [7] and quinuclidine.[8]

(XII) $Me{\cdot}{}^{+}P{<}[CH_2{\cdot}CH_2]_3{>}P^{+}Me,2X^{-}$ $ClAu{\leftarrow}P{<}[CH_2{\cdot}CH_2]_3{>}P{\rightarrow}AuCl$ (XIII)

(XIV) $OP{<}[CH_2{\cdot}CH_2]_3{>}PO$ $[C_6H_{12}P^{+}]X^{-}$ (XV)

The diphosphine (VIII) and certain derivatives have a remarkable capacity for tenaciously retaining traces of solvent. Distillation of a benzene solution of the diphosphine under nitrogen at 15 mm. gave a crystalline residue, which when sublimed at 100°/0·2 mm. gave crystals of composition $C_6H_{12}P_2,\frac{1}{6}C_6H_6$, and repeated sublimation was necessary to obtain the pure diphosphine. Similarly a very crude sample of the aurous chloride derivative (XIII), prepared directly from the initial ethereal extract, when heated at 300°/0·2 mm., gave a sublimate of composition $C_6H_{12}P_2,\frac{1}{4}H_2O$ in two independent experiments, and this sublimate had the chemical properties of the pure diphosphine. Since it is highly unlikely that the diphosphine and the solvent molecules remained associated in the vapour phase during sublimation, the proportion of solvent in these sublimates is probably fortuitous. These sublimations were carried out in tubes which, being sealed at one end, would never become entirely free from solvent molecules during the sublimation. The passage of a very fine stream of nitrogen through the sublimation tube would probably have accelerated the complete removal of solvent, but would also have caused considerable loss of the volatile diphosphine.

In benzene solution the diphosphine is remarkably protected from oxidation, and it is unaffected when the cold solution is subjected to the passage of a fine stream of oxygen for several hours, or when the hot solution is similarly treated with air, or when the warm solution is treated with acetone–hydrogen peroxide. In cold ethanolic solution, however, the diphosphine is rapidly converted into the crystalline dioxide (XIV), which even after being heated at 150°/1 mm. for five hours had the composition $C_6H_{12}O_2P_2,\frac{1}{3}C_2H_5{\cdot}OH$; heating at 220°/1 mm. for 4 hours was necessary to obtain the solvent-free dioxide.

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[5] Mann and Watson, *J.*, 1957, 3950.
[6] *Idem*, *J.*, 1958, 2772.
[7] Mann and Baker, *J.*, 1957, 1881.
[8] Meisenheimer, *Annalen*, 1920, **420**, 194.

Similarly the diphosphine in boiling benzene solution reacted readily with sulphur to give the insoluble disulphide, which however after 4 hr. at 125°/1 mm. had, in two independent experiments, the composition $C_6H_{12}S_2P_2,\frac{1}{8}C_6H_6$. The dibenzyl dibromide (VII; $R = CH_2Ph$, $X = Br$) formed a stable hemihydrate, and the corresponding dipicrate a diethanolate.

The non-volatile residue from the initial volatilisation of the diphosphine was extracted with boiling ethanol, leaving an insoluble gum. The ethanol extract deposited white crystalline flakes having a greasy consistency: purification by recrystallisation and then sublimation afforded a hydrocarbon of analytical composition $[CH_2]_n$, and having the molecular weight of 520 in boiling chloroform, and 510 in chloroform at 30°, the latter being determined by the extra-sensitive Thermistor technique.[9] The infrared spectrum of this hydrocarbon was identical with that of a pure sample of the hydrocarbon $Me{\cdot}[CH_2]_{98}{\cdot}Me$,[10] kindly supplied by Dr. N. Sheppard, except that the band at 1378 cm.$^{-1}$ due to the methyl groups was about three times as strong in the spectrum of our hydrocarbon as that in the standard compound. It is clear therefore that our hydrocarbon is a polythene of formula $Me{\cdot}[CH_2]_n{\cdot}Me$, where n is *ca.* 34.

In an attempt to identify the third constituent of the reduction product, the crude ethereal solvent was added to ethereal methyl iodide, giving an immediate precipitate, which contained traces of aluminium and could not be purified: this iodide was clearly different from the dimethiodide (XII; $X = I$). The corresponding methobromide and methotoluene-*p*-sulphonate were also prepared. These impure salts all gave the same picrate, of composition (XV; $X = C_6H_2O_7N_3$), which was then converted into the bromide (XV; $X = Br$) and iodide. The small quantity available of these salts precluded identification, and in the absence of molecular-weight determinations their complexity is unknown. The fact that the quaternised cation contains an even number of carbon atoms may indicate that the salts have been formed from a secondary phosphine which has undergone rapid methylation to the tertiary phosphine before quaternisation.

The infrared spectra of certain of our cyclic diphosphine compounds have been recorded. The spectrum of the diphosphine (VIII) is very simple, in accordance with its symmetrical structure, but shows two sharp bands at 643 and 700 cm.$^{-1}$ associated with the C–P stretching frequency in a tertiary phosphine. The spectrum of the dioxide (XIV) shows the expected strong rather broad band at 1165 cm.$^{-1}$ of the $\geqslant$P=O group. 1 : 4-Dibenzyldiethylenediphosphine monoxide shows bands associated with all these units, namely, the C–P (tertiary phosphine) band at 637, the strong $\geqslant$P=O band at 1165, and the strong sharp C–P=O band at 743 cm.$^{-1}$ Tribenzylphosphine oxide shows the $\geqslant$P=O band at 1188, and the C–P=O band as probably one of two twin bands at 762 and 768 cm.$^{-1}$ respectively, the other being associated with the benzene rings. For comparison, in trimethylphosphine the C–P stretching frequencies appear as two bands at 653 and 708,[11] and in trimethylphosphine oxide the C–P=O frequency gives a strong band at 756, and the $\geqslant$P=O frequency a band at 1170 cm.$^{-1}$.[12]

EXPERIMENTAL

All compounds were colourless unless otherwise stated. To obtain consistent m. p.s, certain compounds were heated in evacuated tubes (noted as E.T.), with the immersion temperature noted as I.T.

Dibenzylphenylphosphine (II; $R = Ph$) was prepared from dichlorophenylphosphine by the method of Mann, Millar, and Stewart.[3]

sym-*Ethylenebis(dibenzylphenylphosphonium) Dibromide* (III; $R = Ph$, $X = Br$).—A mixture of the phosphine (II; $R = Ph$) (102 g.) and ethylene dibromide (44 g., 0·75 mol.) was heated in nitrogen under reflux on a steam-bath. After *ca.* 1 hr. a vigorous reaction occurred,

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[9] Iyengar, *Rec. Trav. chim.*, 1954, **73**, 789.

[10] G. Ställberg, S. Ställberg-Stenhagen, and E. Stenhagen, *Acta Chem. Scand.*, 1952, **6**, 313.

[11] Daasch and Smith, *J. Chem. Phys.*, 1951, **19**, 22.

[12] Rosenbaum, Rubin, and Sandberg, *ibid.*, 1940, **8**, 366.

and was moderated by cooling: the heating was then continued for 2 hr. more. The cool product, on thorough stirring with ether, formed a white solid (119 g., 89%), which when collected, washed with ether, and dried was sufficiently pure for the next stage. The pure *dibromide*, isolated by ethereal precipitation from cold methanolic solution, had m. p. 300—304° (decomp.) (Found: C, 65·1; H, 5·8. $C_{42}H_{42}Br_2P_2$ requires C, 65·6; H, 5·5%). The *dipicrate* (III; R = Ph, X = $C_6H_2O_7N_3$), precipitated from a methanolic solution of the dibromide by sodium picrate, formed yellow crystals, m. p. 209—217° (decomp.), from acetone (Found: C, 61·1; H, 4·2; N, 8·0. $C_{54}H_{46}O_{14}N_6P_2$ requires C, 60·9; H, 4·35; N, 7·9%).

Thermal Decomposition.—The dibromide, when heated in a sublimation tube to *ca* 270°/0·1 mm., deposited crystals of *dibenzylphenylphosphine hydrobromide*, m. p. 164—166° after resublimation (Found: C, 64·6; H, 5·3. $C_{20}H_{19}P,HBr$ requires C, 64·7; H, 5·4%). A warm ethanolic solution of the hydrobromide, when treated with aqueous-ethanolic potassium palladobromide, deposited the bis(dibenzylphenylphosphine)dibromopalladium, pale yellow crystals (from dioxan), m. p. 244° (decomp.) [lit.,[3] 240—242° (decomp.)] (Found: C, 56·3; H, 4·15. Calc. for $C_{40}H_{38}Br_2P_2Pd$: C, 56·7; H, 4·5%).

sym-*Ethylenebis*(*benzylphenylphosphine*) (IV; R = Ph).—Lithium aluminium hydride (2 g.) was added under nitrogen to a suspension of the dibromide (III; R = Ph, X = Br) (20 g.) in pure tetrahydrofuran (100 c.c.), which was boiled under reflux for 6 hr., concentrated to *ca.* 15 c.c., and cooled. Undried ether (150 c.c.) was cautiously added, and the hydrolysis completed by slow addition of 20% aqueous sodium potassium tartrate. The ethereal layer was syphoned off under nitrogen pressure, dried (Na_2SO_4), filtered, and distilled, leaving the crude crystalline *diphosphine* (IV; R = Ph) (10·5 g., 95%): a sample, when sublimed at 200°/0·0005 mm., had m. p. 85—98° (E.T.) (Found: C, 78·8; H, 6·95. $C_{28}H_{28}P_2$ requires C, 78·8; H, 6·6%). The crystalline *dimethiodide*, readily formed in hot methyl iodide, had m. p. 300—303° (E.T., I.T. 290°) after crystallisation from methanol (Found: C, 51·1; H, 4·9. $C_{30}H_{34}I_2P_2$ requires C, 50·75; H, 4·8%).

Potassium palladobromide, dissolved in a minimum of water and then diluted with ethanol, was added dropwise to a hot ethanolic solution of the diphosphine until the liquid just became brown. The solution, when boiled, filtered, and cooled, deposited sym-*ethylenebis*(*benzylphenylphosphine*)*dibromopalladium* (IX; R = Ph), yellow crystals which, immersed at 200°, slowly became black and melted sharply at 222° (E.T.) (Found: C, 48·8; H, 3·9. $C_{28}H_{28}Br_2P_2Pd$ requires C, 48·5; H, 4·1%).

For the detailed experimental conditions employed in the following preparation, see ref. 1. Sodium (6·4 g., 0·9 equiv.) was added in small pieces to a solution of phenylphosphine (34 g.) in liquid ammonia (300 c.c.). After 15 min., benzyl bromide (44·2 g., 1 mol.) was added dropwise, and then sodium (7·1 g.) as before. The solution was stirred for 1 hr., and then ethylene dibromide (29·1 g., 0·5 mol.) added dropwise with stirring. Finally ether (300 c.c.) was added, followed, after evaporation of the ammonia, by cold freshly boiled water (100 c.c.). The ethereal layer, when syphoned off under nitrogen pressure, dried (Na_2SO_4), and distilled, finally at 0·5 mm., gave fractions: (*a*) b. p. 108—110°, 4·7 g.; (*b*) 110—195°, 1·8 g.; (*c*) b. p. 195—214°, 10·3 g. Fraction (*a*), a foul-smelling, readily oxidised liquid, was probably benzylphenylphosphine. Fraction (*c*) was dibenzylphenylphosphine (12%) (Found: C, 82·8; H, 6·1. Calc. for $C_{20}H_{19}P$: C, 82·7; H, 6·6%). For further characterisation, a portion was converted by hot ethereal benzyl bromide into tribenzylphenylphosphonium bromide, which tended to dissociate on recrystallisation from ethanol and was therefore converted in turn into the yellow *picrate*, m. p. 164·5—166·5° (from ethanolic acetone) (Found: C, 65·0; H, 4·5; N, 6·9. $C_{33}H_{28}O_7N_3P$ requires C, 65·0; H, 4·6; N, 6·9%). A second portion was converted into the pale yellow bis(dibenzylphenylphosphine)dibromopalladium, m. p. 240° (decomp.), 246—247° (decomp.) (E.T.) (from dioxan) (Found: C, 56·6; H, 4·8%).

1 : 4-*Dibenzyl*-1 : 4-*diphenyldiethylenediphosphonium Dibromide* (V; R = Ph, X = Br).—A mixture of the diphosphine (IV; R = Ph) (4 g.) and ethylene dibromide (2·2 g., 1·25 mols.) was heated under nitrogen in a sealed tube at 100° for 6 hr. The product, when thoroughly stirred with ether, collected, and washed with ethanol, afforded the pure *dibromide* (5 g.), m. p. 375° (effervescence, with darkening at 370°) (E.T., I.T. 360°) (Found: C, 58·2; H, 5·7. $C_{30}H_{32}Br_2P_2$ requires C, 58·6; H, 5·25%). The dibromide when treated with sodium picrate, each in aqueous solution, deposited the yellow *dipicrate*, which was too insoluble for recrystallisation and decomposed slowly when heated below 100° (Found: C, 55·6; H, 4·2; N, 9·5. $C_{42}H_{36}O_{14}N_6P_2$ requires C, 55·4; H, 4·0; N, 9·2%).

For the preparation of this dibromide on a larger scale, the isolation of the pure diphosphine (IV; R = Ph) is unnecessary. A suspension of the dibromide (III; R = Ph, X = Br) (120 g.) in tetrahydrofuran (500 c.c.) was treated with lithium aluminium hydride (12 g.) as above, and the ether removed from the dried ethereal extract. Ethylene dibromide (26·4 g.) was added under nitrogen to the crude residual diphosphine, which was then heated on the steam-bath. A vigorous reaction occurred after *ca.* 1 hr., and more dibromide (12 g.) was subsequently added and the heating continued for 1 hr. more. The cold residue when thoroughly triturated with ethanol afforded the pure dibromide (V; R = Ph, X = Br) (32·8 g., 32% overall yield from the dichlorophenylphosphine initially employed).

1 : 4-*Diphenyldiethylenediphosphine* (VI; R = Ph).—The dibromide (V; R = Ph, X = Br) (32·8 g.) in tetrahydrofuran (250 c.c.) was treated as above with the hydride (4·5 g.). Evaporation of the ethereal extract gave the crude *diphosphine* (VI; R = Ph) (7 g.): a sample, twice sublimed at 140°/0·001 mm. and then washed with methanol to remove a liquid impurity (possibly a hydrocarbon), had m. p. 92—95° (E.T.) (Found: C, 70·7; H, 6·7. $C_{16}H_{18}P_2$ requires C, 70·6; H, 6·7%).

When air was passed through a cold ethereal solution of the diphosphine for 4 hr., the *dioxide* separated as a sticky solid, which when digested with boiling acetone formed a fine powder, m. p. 250° (E.T.), 267° (effervescence, E.T., I.T. 220°), in each case with earlier darkening (Found: C, 63·5; H, 5·8%; *M*, in boiling 0·403% chloroform solution, 295. $C_{16}H_{18}O_2P_2$ requires C, 63·2; H, 6·0%; *M*, 304). It is insoluble in most of the usual liquids.

1 : 4-*Diphenyltriethylenediphosphonium Dipicrate* (VII; R = Ph, X = $C_6H_2O_7N_3$).—A mixture of the diphosphine (VI; R = Ph) (1·3 g.) and ethylene dibromide (0·7 g., 1 mol.), when heated in nitrogen under reflux on a water-bath, rapidly underwent a vigorous reaction. After 15 min. the product, when cooled and stirred with ether, became crystalline, but when collected and exposed to air readily became very sticky. Its solution in methanol was therefore treated with methanolic sodium picrate, the orange dipicrate (VII; R = Ph, X = $C_6H_2O_2N_3$), m. p. 240° (effervescence, preliminary darkening) (E.T.), being precipitated (Found: C, 48·2; H, 4·2. Calc. for $C_{30}H_{26}O_{14}N_6P_2$: C, 47·6; H, 3·5%). The dipicrate when warmed with solvents readily gave an almost insoluble gum, and recrystallisation was not achieved.

Bis-(1 : 4-*diphenyldiethylenediphosphine*)*palladium Palladobromide* (X; R = Ph).—This was prepared by the interaction of the diphosphine (0·0469 g.) and potassium palladobromide (0·0790 g.) (0·91 mol.), precisely as the 1 : 4-dibenzyl analogue described below, and obtained as an insoluble dark buff-coloured powder, which after drying at 65°/0·1 mm. for 4 hr. blackened between 290° and 340° with formation of a white sublimate (E.T.) (Found: C, 35·3; H, 3·2. $C_{32}H_{36}Br_4P_4Pd_2$ requires C, 35·7; H, 3·4%).

Tribenzylphosphine (II; R = CH_2Ph).—This phosphine was prepared by a modification of the method of Bailey and Buckler,[2] who however converted the phosphine without isolation into its methobromide. A solution of benzylmagnesium chloride was prepared by the addition of benzyl chloride (200 g.) to a stirred suspension of magnesium (40 g., 1·05 equiv.) in ether (1 l.) at a rate sufficient to maintain gentle boiling under reflux. The mixture was then boiled for 1 hr., cooled, stirred, and treated in turn with benzene (250 c.c.) and dropwise with phosphorus trichloride (65 g.) in benzene (100 c.c.) under nitrogen. The mixture, containing a white deposit, was boiled under reflux for 30 min. and then cooled in ice-water whilst cautiously treated with saturated aqueous ammonium chloride solution (500 c.c.). The ethereal layer was syphoned off under nitrogen pressure and dried (Na_2SO_4), and the solvent removed, leaving the *phosphine* (II; R = CH_2Ph) (122 g., 85%) sufficiently pure for the next stage. It had b. p. 203—210°/0·5 mm., and when twice sublimed at 140°/0·001 mm., had m. p. 92—95° (E.T.) (Found: C, 82·3; H, 7·3. $C_{21}H_{21}P$ requires C, 82·8; H, 7·0%).

When air was passed through an ethereal solution, the *oxide* readily separated as a crystalline powder, m. p. 209—212° (E.T.) (from acetone) (Found: C, 78·5; H, 6·7. $C_{21}H_{21}OP$ requires C, 78·7; H, 6·6%). The *methiodide*, prepared in the normal way, formed crystals, m. p. 170—171° (E.T.), from ethanol (Found: C, 59·0; H, 5·2. $C_{22}H_{24}IP$ requires C, 59·2; H, 5·4%).

sym-*Ethylenebis*(*tribenzylphosphonium*) *Dibromide* (III; R = CH_2Ph, X = Br).—A mixture of the phosphine (II; R = CH_2Ph) (122 g.) and ethylene dibromide (44 g., 1·2 mols.) was heated in a 250 c.c. flask under reflux on a steam-bath. A vigorous reaction occurred after *ca.* 1 hr.; more ethylene dibromide (22 g.) was added and heating continued for 2 hr. more. The product when thoroughly washed with ether afforded the crude *dibromide* (160 g., 97%) suitable for the next stage: a sample, recrystallised from methanol, had m. p. 275—279° (E.T.)

(Found: C, 65·9; H, 5·8. $C_{44}H_{46}Br_2P_2$ requires C, 66·3; H, 5·8%). In methanolic solution, it readily deposited the yellow *dipicrate*, m. p. 220—222° (effervescence, previous darkening, E.T) (from ethyl methyl ketone) (Found: C, 61·4; H, 4·8; N, 7·75. $C_{56}H_{50}O_{14}N_6P_2$ requires C, 61·5; H, 4·6; N, 7·7%).

sym-*Ethylenebis*(*dibenzylphosphine*) (IV; R = CH_2Ph).—This was prepared precisely as the diphosphine (IV; R = Ph), evaporation of the ethereal extract giving the crude product in 76% yield. A sample after sublimation at 180°/0·01 mm. still contained a trace of impurity (Found: C, 80·4; H, 7·1. $C_{30}H_{32}P_2$ requires C, 79·3; H, 7·1%). It gave the *diphosphine-dibromopalladium* (IX; R = CH_2Ph), as fine pale brown crystals, m. p. 215—217° (considerable preliminary darkening) (from ethanol) (Found: C, 49·9; H, 4·3. $C_{30}H_{32}Br_2P_2Pd$ requires C, 50·0; H, 4·5%).

1 : 1 : 4 : 4-*Tetrabenzyldiethylenediphosphonium Dibromide* (V; R = CH_2Ph, X = Br).—This salt was prepared in the usual way from the diphosphine (IV; R = CH_2Ph) (25 g.) and two additions of ethylene dibromide (13·2 g., 1 + 0·3 mols.). The crude product on recrystallisation from ethanol gave the *dibromide* (15 g., 37% yield from phosphorus trichloride), m. p. 287—292° (effervescence, E.T.) (Found: C, 59·8; H, 5·8. $C_{32}H_{36}Br_2P_2$ requires C, 59·8; H, 5·6%). It gave a yellow *dipicrate*, m. p. 214° (decomp., E.T.) (Found: N, 8·6. $C_{44}H_{40}O_{14}N_6P_2$ requires N, 8·95%).

1 : 4-*Dibenzyldiethylenediphosphine* (VI; R = CH_2Ph).—The crude *diphosphine* was obtained in 76% yield by the usual reduction: a portion, when recrystallised from ethanol, sublimed at 200°/0·5 mm., washed with ethanol and resublimed, had m. p. 128—130° (under nitrogen in sealed tube) (Found: C, 72·3; H, 7·85. $C_{18}H_{22}P_2$ requires C, 72·0; H, 7·4%).

Benzyl bromide was added to a cold ethanolic solution of the diphosphine, which on agitation deposited the dibromide (V; R = CH_2Ph, X = Br), m. p. and mixed m. p. 288—292° (effervescence, E.T.) after crystallisation from ethanol. A portion of the diphosphine was heated with an excess of benzyl bromide at 100° for $\frac{1}{2}$ hr. Addition of ether precipitated a white gum which was separated and dissolved in hot ethanol: on cooling, the solution deposited the dibromide (III; R = CH_2Ph, X = Br), which was now insoluble in ethanol, but after crystallisation from methanol had m. p. 275—280°, mixed with the authentic salt (III; R = CH_2Ph, X = Br) 278—280°, mixed with the salt (V; R = CH_2Ph, X = Br) 260—263° (all E.T.).

When air was passed through an ethereal solution of the diphosphine, the *monoxide* separated as a gum which was converted into a powder by the addition of acetone and the evaporation of the ether by the air-stream, and when then recrystallised from propan-1-ol had m. p. 302—305° (I.T. 290°) (Found: C, 68·6; H, 7·4%; *M*, in 0·384% boiling chloroform, 293. $C_{18}H_{22}OP_2$ requires C, 68·4; H, 7·0%; *M*, 316). An acetone solution of the monoxide, when treated with hydrogen peroxide, deposited a powder, undoubtedly the dioxide, insoluble in all the normal liquids.

1 : 4-*Dibenzyltriethylenediphosphonium Dibromide* (VII; R = CH_2Ph, X = Br).—A mixture of the diphosphine (VI; R = CH_2Ph) (6·5 g.) and ethylene dibromide (5·5 g., 1·4 mols.), when heated on a steam-bath, underwent a violent reaction. More ethylene dibromide (2 g.) was added and the mixture heated for 30 min., cooled, and washed with cold ethanol. The crude *dibromide* (7 g., 66%) became sticky on exposure to air: a fresh sample, when washed with ethanol, methanol, and ether, and dried at 110°/0·1 mm. for 7 hr., was apparently still a *hemihydrate*, m. p. 340—344° (effervescence, preliminary darkening) (E.T.) (Found: C, 48·6; H, 5·8. $C_{20}H_{26}Br_2P_2,\frac{1}{2}H_2O$ requires C, 48·3; H, 5·5%). It was extremely hygroscopic. A very dilute hot aqueous solution, when treated with aqueous sodium picrate, deposited the yellow *dipicrate*, which when collected and washed with ethanol became orange in colour, apparently with conversion into a *diethanolate*; this was heated at 50°/0·1 mm. for 3 hr. (Found, in independent preparations: C, 49·1, 49·5; H, 5·1, 4·5; N, 9·65, 9·6. $C_{32}H_{30}O_{14}N_6P_2,2C_2H_6O$ requires C, 49·3; H, 4·8; N, 9·6%): on heating (E.T.), the colour became paler from 140°, a yellow sublimate formed from 195° and the black residue melted at 243°.

Palladium Bromide Derivatives of the Diphosphine (VI; R = CH_2Ph).—A solution of potassium palladobromide (0·4704 g., 0·89 mol.) in a minimum of warm water was diluted with hot ethanol (10 c.c.) and then slowly added to a stirred boiling solution of the diphosphine (0·3136 g., 1 mol.) in ethanol (80 c.c.). The colour of the palladobromide was rapidly discharged and a yellow almost amorphous product began to separate, but the final solution was red. The insoluble *bis*-(1 : 4-*dibenzyldiethylenediphosphine*)*palladium palladobromide* (X; R = CH_2Ph), when collected from the boiling mixture, washed in turn with hot ethanol, water, cold ethanol, and ether, and dried at 60°/0·1 mm. for 8 hr., formed a dark buff-coloured powder, which blackened slowly between 200° and 300° with the formation of a white sublimate (E.T.) (Found: C, 38·0; H, 3·8. $C_{36}H_{44}Br_4P_4Pd_2$ requires C, 38·15; H, 3·9%).

The initial filtrate was allowed to evaporate to *ca.* 40 c.c., filtered to remove a small crop of the palladobromide, and then evaporated in a desiccator to dryness. The orange residue was washed with water, dried, and extracted with boiling acetone. The filtered extract on evaporation afforded 1 : 4-*dibenzyldiethylenediphosphine dibromopalladium* (XI; R = CH_2Ph)1 an orange crystalline powder, m. p. 145—152° (preliminary softening) after drying at 55°/0·d mm. for 5 hr. (Found: C, 38·1; H, 3·8%; *M*, in 0·286% chloroform, 524. $C_{18}H_{22}Br_2P_2P$, requires C, 38·15; H, 3·9%; *M*, 567). It is readily soluble in cold ethanol.

Reduction of 1 : 4-*Dibenzyltriethylenediphosphonium Dibromide* (VII; R = CH_2Ph, X = Br).—Lithium aluminium hydride (2 g.) was added under nitrogen to a suspension of the dibromide (4 g.) in tetrahydrofuran (100 c.c.) which was boiled under reflux for 6 hr. The solvent, after being distilled off, did not contain any tertiary phosphine. The cold residue was treated with ether, and then hydrolysed as before. The ether extract was collected under nitrogen, dried, and pumped slowly into a small distilling-flask so that the rates of addition and distillation were almost equal. The distilled ether was also free from tertiary phosphine. The receiver was then replaced by a narrow cylindrical trap in which the entry tube reached almost to the bottom. The trap was immersed in ice-water whilst the residue was heated on the steam-bath, with the nitrogen passing through the apparatus throughout the whole operation. Deposition of the crystalline diphosphine (VIII) in the trap was complete after *ca.* 6 hours' heating. The diphosphine was then dissolved out of the trap with benzene, which was distilled off at 15 mm. The crystalline residue was sublimed in nitrogen at 100°/0·2 mm., giving the impure diphosphine (Found: C, 53·1; H, 8·3. Calc. for $C_6H_{12}P_2,\frac{1}{6}C_6H_6$: C, 52·8; H, 8·2%). Repeated resublimation ultimately gave the pure *diphosphine* (VIII), which when heated in a sealed tube under nitrogen on a Kofler stage had m. p. 252° with partial sublimation (Found: C, 49·4; H, 8·2%; *M*, in 0·260% freezing benzene, 136. $C_6H_{12}P_2$ requires C, 49·3; H, 8·3%; *M*, 146). The true yield of the diphosphine in this preparation is difficult to assess, chiefly because of losses during sublimation, but the pure solvent-free diphosphine isolated weighed 30 mg. The diphosphine is freely soluble in cold methanol, ethanol, ether, and benzene.

When the crude ethereal extract was added to ethereal chloroauric acid ($HAuCl_4,4H_2O$), the latter was reduced, with the precipitation of an impure dark yellow chloroaurous derivative. This product, when collected, washed, dried, and heated at 300°/0·2 mm., gave a crystalline sublimate of the diphosphine (VIII) still associated with water (Found, in independent experiments: C, 48·0, 48·1; H, 8·7, 8·9. Calc. for $C_6H_{12}P_2,\frac{1}{4}H_2O$: C, 47·85; H, 8·4%). This sublimate, when treated cautiously with chloroauric acid, each in ethereal solution, deposited the pure yellow *triethylenediphosphinedichlorodigold* (XIII), which decomposed within 24 hr. at room temperature (Found: C, 11·7; H, 2·3. $C_6H_{12}Cl_2P_2Au_2$ requires C, 11·8; H, 2·0%). The yield of the sublimed diphosphine (VIII) by this method is, however, very small and uncertain.

The following derivatives were prepared from the diphosphine (VIII) obtained by the first method.

The addition of an excess of methyl iodide to a cold methanolic solution of the diphosphine gave no apparent reaction until the mixture was warmed; the *dimethiodide* (XII; X = I), m. p. 375—380° (effervescence) (E.T.), was deposited (Found: C, 22·8; H, 4·3. $C_8H_{18}I_2P_2$ requires C, 22·35; H, 4·2%). It is readily soluble in cold water, but almost insoluble in boiling methanol and ethanol. Its cold aqueous solution, treated with aqueous sodium picrate, deposited the *dimethopicrate* (bright yellow crystals from hot water), m. p. 270° (effervescence, with progressive darkening from 130°) (E.T.), m. p. 278° (effervescence, previous darkening) (E.T., I.T. 240°) (Found: C, 38·0; H, 3·6; N, 13·3. $C_{20}H_{22}O_{14}N_6P_2$ requires C, 38·0; H, 3·5; N, 13·3%). It is very slightly soluble in hot acetone, and insoluble in boiling methanol and ethanol.

A cold ethanolic solution of the diphosphine was exposed to the air for 10 hr. and then evaporated in a desiccator. The residual crystalline *dioxide* (XIV) was heated at 150°/1 mm. for 5 hr. (Found: C, 41·6; H, 7·0. Calc. for $C_6H_{12}O_2P_2,\frac{1}{3}C_2H_6O$: C, 41·4; H, 7·3%), and then at 220°/1 mm. for 4 hr. (Found: C, 40·5; H, 6·6. $C_6H_{12}O_2P_2$ requires C, 40·5; H, 6·8%): on heating (E.T.) it sublimed slowly above 300°. It is freely soluble in cold methanol and ethanol, and very sparingly soluble in other organic solvents.

A benzene solution of the diphosphine, when added to a boiling benzene solution of rhombic sulphur, caused a rapid deposition of the insoluble disulphide, which, however, after being heated at 125°/0·1 mm. for 4 hr., still contained solvent (Found, in independent preparations: C, 36·7, 36·9; H, 5·8, 5·9. Calc. for $C_6H_{12}S_2P_2,\frac{1}{8}C_6H_6$: C, 36·85; H, 5·9%). It decomposed slowly without melting above 400°.

The residue in the flask, after the volatilisation of the diphosphine (VIII) in nitrogen, was extracted with boiling ethanol, which, when filtered to remove an insoluble colourless gum and cooled, deposited white greasy crystals of the hydrocarbon. This was twice recrystallised from ethanol and then sublimed at 300°/0·2 mm. (Found: C, 85·9; H, 14·4%; *M*, in 1·702% chloroform solution at 30°, 510; *M*, in 0·3815% boiling chloroform solution, 520). When heated, it slowly softened and melted below 100°.

A blank experiment, with tetrahydrofuran and the hydride in the absence of the phosphonium bromide, showed that this hydrocarbon did not arise by reductive breakdown of the tetrahydrofuran.

Quaternary salts from the crude ethereal extract. A portion of the undried ethereal extract from the reduction was filtered into an excess of ethereal methyl iodide, giving an immediate precipitate, which when collected, thoroughly washed with hot ethanol, and dried, had m. p. 370° (effervescence, shrinking from 345°) (E.T) (Found: C, 30·25, 29·9, 30·4; H, 4·9, 5·1, 4·7%). It was insoluble in all organic solvents: it dissolved in boiling water but separated on cooling as a thick syrup. The corresponding methobromide was prepared at 0°, and set aside overnight. The mother-liquor was decanted, and the residual gummy deposit, after being hardened by digestion with boiling methanol, had m. p. 400° (effervescence, shrinking from 385°) (E.T.): this methobromide was hygroscopic, and was analysed after exposure to air to constant weight (Found: C, 33·1; H, 5·8%). It was soluble in water, but insoluble in boiling methanol and ethanol.

The methotoluene-*p*-sulphonate was prepared similarly to the iodide, but the ether was evaporated from the reaction mixture, and the residue heated at 100° for 30 min. The sulphonate did not crystallise. The above three salts in aqueous or aqueous-ethanolic solution were added to an excess of aqueous sodium picrate. The precipitated yellow picrates (XV; $X = C_6H_2O_7N_3$) did not recrystallise and, when washed with ethanol and dried, became red on heating and decomposed slowly below 200° (Found, for the picrate obtained from the iodide, bromide, and sulphonate respectively, C, 41·85, 42·6, 42·1; H, 4·1, 4·3, 4·2; N, 12·3, 11·95. Calc. for $C_{12}H_{14}O_7N_3P$: C, 42·0; H, 4·1; N, 12·25%).

The picrate was shaken with hot hydrobromic acid, which was then cooled and repeatedly extracted with ether. The mother-liquor was concentrated in a desiccator, and the bromide, m. p. 380° (effervescence) (E.T.), precipitated by acetone (Found: C, 36·3; H, 6·0; Br, 39·0. Calc. for $C_6H_{12}BrP$: C, 37·0; H, 6·2; Br, 41·0%).

The iodide was precipitated by the addition of saturated aqueous sodium iodide to a cold aqueous solution of the bromide, and, when recrystallised from water, had m. p. 370° (effervescence, preliminary shrinking) (E.T.) (Found: C, 28·5; H, 5·5; I, 49·2. Calc. for $C_6H_{12}IP$: C, 29·8; H, 5·0; I, 52·4. Calc. for $C_6H_{12}IP,H_2O$: C, 27·7; H, 5·4; I, 48·8%).

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