783. *Some Aminophosphines.*

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The preparations and properties of certain bisdialkylaminophenylphosphines, $Ph{\cdot}P(NR_2)_2$ and $Ph{\cdot}P(NR'_2){\cdot}NR_2$, and of diethylaminodiphenylphosphine, Ph_2PNEt_2, are described. 1 : 1 Compounds with methyl iodide are formed. The location of the methyl group in the adduct with $Ph{\cdot}P(NEt_2)_2$ has been established by nuclear magnetic resonance studies. Complex formation with mercuric iodide is reported.

COMPOUNDS in which tervalent phosphorus is directly bound to nitrogen have been little investigated so far, although they are clearly of interest both as potential ligands and as precursors of possible polymeric material. The first investigation of these aminophosphines, by Michaelis,[1] led to the preparation of compounds in the series $Cl_2P{\cdot}NR_2$, $Cl_2P{\cdot}NHR$ and $R{\cdot}P(NR'_2)_2$. Recently, further examples of these compounds have been reported, notably $(CF_3)_2P{\cdot}NHMe$,[3] $Me_2P{\cdot}NMe_2$,[4] $Et_2P{\cdot}NEt_2$,[5] and $Ph_2P{\cdot}NPh_2$.[6] The phosphorus–nitrogen bond can be readily formed by the elimination of hydrogen halide between a halogenophosphine and a primary or secondary amine in benzene or ether at room temperature or below. Replacement of the second chlorine atom of dichlorophosphines is slower than that of the first, and it is possible to isolate the intermediate monochloro-compound. In general, the reactions proceed smoothly, the bulk of the amine hydrochloride being precipitated at once. However, further small quantities of hydrochloride invariably separate after removal of the bulk of the precipitated hydrochloride, particularly during isolation and purification of the product. A similar observation has been made by other workers studying the reaction of phosphonitrilic chloride with amines.[7] The apparent solubility of the amine hydrochlorides in benzene and ether may well be due to interaction between the phosphine and amine, giving an intermediate, possibly of the form $[(R_2N)_2Ph{\cdot}P{\leftarrow}NHR_2]HCl$, which breaks down completely only when heated. It proved impossible to eliminate this feature of the preparation. Even in the most favourable cases, where considerable care was taken to avoid the ingress of moisture or oxygen in the preparation, isolation, and subsequent purification, the samples of aminophosphines, although clear when freshly distilled, became cloudy on storage. Only by repeated distillation was it possible to obtain a sample which was free from this contamination. The compounds shown in Table 1 have been isolated; all are liquids, readily soluble in benzene, toluene, light petroleum, ether, methanol and ethanol, but insoluble in water. They show no obvious tendency to aerial oxidation, hydrolysis, or polymerisation. The phosphorus–nitrogen bond is readily cleaved by the action of anhydrous hydrogen chloride, as has already been demonstrated by Burg and Slota.[4] Thus, bisdiethylaminophenylphosphine gave a quantitative yield of diethylamine hydrochloride

TABLE 1.

B. p. of $Ph{\cdot}P(NR_2){\cdot}NR'_2$.

R	Me	Me	Et	Et	Pr^n
R′........................	Me	Et	Et	Pr^n	Pr^n
B. p./mm.	61°/0·1	72·5°/0·1—0·2	91·5°/0·1	100°/0·05	122°/0·1

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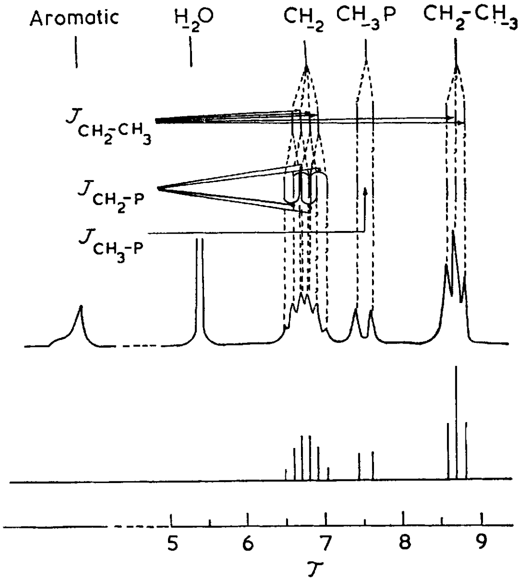
[1] Michaelis, *Annalen*, 1903, **326**, 129.
[2] Michaelis, *Ber.*, 1898, **31**, 1041.
[3] Harris, *J.*, 1958, 512.
[4] Burg and Slota, *J. Amer. Chem. Soc.*, 1958, **80**, 1107.
[5] Issleib and Seidel, *Chem. Ber.*, 1959, **92**, 2681.
[6] Sisler and Smith, *J. Org. Chem.*, 1961, **26**, 611.
[7] John, Moeller, and Audrieth, *J. Amer. Chem. Soc.*, 1961, **83**, 2608.

when treated with an excess of dry hydrogen chloride. Aqueous hydrochloric acid hydrolysed the phosphorus–nitrogen bond, all the compounds being soluble, particularly on warming. No obvious reaction occurred with dilute aqueous sodium hydroxide, the liquids remaining immiscible, even on warming.

TABLE 2.

Compound	State	Compound	State
$Ph\cdot P(NMe_2)_2,MeI$	Solid	$PhP(NEt_2)\cdot NPr^n{}_2,MeI$	Waxy solid
$Ph\cdot P(NMe_2)\cdot NEt_2,MeI$	Hygroscopic oil	$PhP(NPr^n{}_2)_2,MeI$	Solid
$PhP(NEt_2)_2,MeI$	Oil		

Of particular interest is the presence in these compounds of three potentially basic atoms. Methyl iodide adducts listed in Table 2, are readily formed, but do not appear to deviate from a 1 : 1 formulation. Three of the compounds are typical quaternary salts, being solids; two are definitely crystalline; the other two, however, have been obtained as liquids, which have not crystallised, despite considerable efforts to induce this. All are soluble in water. $PhP(NEt_2)_2,MeI$ in methyl cyanide is a 1 : 1 electrolyte, in which free iodide ion is present; the molecular weight in aqueous solution is roughly half the formula weight. Despite the physical state of the bisdiethylamino- and diethylaminodimethylamino-adducts their behaviour is entirely in accord with their being quaternary salts; it is, of course, possible that these two represent some quinquecovalent form of the phosphorus, which readily breaks down to ionic forms in suitable solvent media. The liquid adducts have solubilities similar to those of the solids, all being insoluble in ether and benzene and soluble in nitrobenzene. Burg and Slota,[4] in considering the 1 : 1 methyl iodide adduct formed by dimethyldimethylaminophosphine, conclude that the methyl group is attached directly to the phosphorus. An examination of the proton magnetic resonance spectrum of an aqueous solution of the corresponding bisdiethylaminophenylphosphine adduct shows that this is also true in the compounds in which two nitrogen atoms are present in addition to the phosphorus. The spectrum (Figure) is, as we show below, only interpreted satisfactorily in terms of the presence of a



Proton magnetic resonance spectrum of the 1 : 1 methyl iodide adduct formed by bisdiethylaminophenylphosphine, observed at 60 Mc./sec. The magnetic field increases from left to right. τ values were obtained by measuring the chemical shifts relative to $(CH_3)_3C\cdot OH$ (τ 8·74), used as an internal standard.

CH_3–P group. In addition, it has been shown that the action of the methanolic hydrogen chloride on compound $Ph_2P{\cdot}NEt_2,MeI$ yields diethylamine hydrochloride, but no diethylmethylamine hydrochloride. If scission of the P–N bond occurs without rearrangement before decomposition, this is an additional indication of the absence of the methyl group from the nitrogen.

The bisaminophosphines are good ligands. In this paper complexes with mercury(II) are reported; compounds with copper(I), nickel(II), and cobalt(II) will be reported later. The mercury(II) complexes were readily formed by mixing alcoholic solutions of mercury(II) iodide and the appropriate phosphine. The compounds isolated (Table 3) are colourless and crystalline, sparingly soluble in water but soluble in warm alcohol. In each case a 2 : 1 complex has been prepared and these might be expected to be of the form $[R\text{-}Hg\text{-}R]^{2+}(I^-)_2$ or an appropriate tetrahedral covalent form. The high solubility of these complexes in benzene and low solubility in hydroxylic solvents, together with their monomeric nature in benzene, are more in accord with the idea of tetrahedral complexes. The 1 : 1 complexes appear to be different. The methyl and ethyl analogues are not readily soluble in organic solvents other than alcohols. It was possible to obtain the molecular weight of only the ethyl derivative, in tetrahydrothiophen 1,1-dioxide (dielectric constant 44 at 30°). The value obtained, 1080, is considerably in excess of that required for the monomer [$Ph{\cdot}P(NEt_2)_2HgI_2$ requires *M*, 706]. The n-propyl derivative in benzene was sufficiently soluble for the molecular weight to be determined cryoscopically: again the value, 1370 ± 50 is considerably in excess of that required for the monomer [$PhP{\cdot}(NPr_2)_2HgI_2$ requires *M*, 762]. Mann and his co-workers[8] have shown that the dimeric nature of the simple 1 : 1 phosphine–mercury(II) halide complexes arises from a *trans*-bridged structure. The molecular-weights for these aminophosphine complexes are relatively close to the dimer values and suggest that similar dimeric species are present. The deviation from the exact value for the dimer is indicative of dissociation, which may be ionic in tetrahydrothiophen dioxide and non-ionic in benzene. The nature of the mercury(II) complexes in general supports the monodentate function of these aminophosphines, and the similarity with the simple phosphines suggests that the ligand atom is phosphorus.

TABLE 3.

1 : 1 Compounds $[Ph{\cdot}P(NR_2)_2]HgI_2$.

R	Me	Et	Pr^n
M. p.	192—196°	176—178°	134—136°

2 : 1 Compounds $[Ph{\cdot}P(NR_2){\cdot}NR'_2]_2HgI_2$.

R	Me	Me	Et	Et	Pr^n
R′	Me	Et	Et	Pr^n	Pr^n
M. p.	86—88°	159—161°	142—143°	102—108°	126—127°

The mercuric iodide adducts of the methiodides were readily formed in alcoholic solution as pale green crystalline solids. The compounds isolated are shown in Table 4; all except one are of the form $R^+HgI_3^-$. The exception $[PhP(NEt_2)_2,MeI]_2HgI_2$ may well be formulated as $(R^+)_2HgI_4^{2-}$. In this case, despite several attempts, the 1 : 1 compound

TABLE 4.

Compound	M. p.	Compound	M. p.
$Ph{\cdot}P(NMe_2)_2,MeI,HgI_2$	132—134°	$Ph{\cdot}P(NEt_2){\cdot}NPr^n_2,MeI,HgI_2$	82—84°
$Ph{\cdot}P(NMe_2)(NEt_2),MeI,HgI_2$	90—92	$Ph{\cdot}P(NPr^n_2)_2,MeI,HgI_2$	59—61
$[Ph{\cdot}P(NEt_2)_2,MeI]_2HgI_2$	79—81		

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[8] Evans, Mann, Peiser, and Purdie, *J.*, 1940, 209.

has not been prepared. Support for the formulation of this 2 : 1 compound was forthcoming from cryoscopic molecular-weight measurements in tetrahydrothiophen dioxide, which gave a value about one-third of the calculated value, in keeping with the idea of three ions' being present.

Although compounds of the P–N system have been investigated previously, in our other investigations it was necessary to prepare certain derivatives of monodiethylaminodiphenylphosphine; these are shown in Table 5. The copper(I) complex of formula RCuI is a tetramer in benzene solution, in keeping with the behaviour of simpler phosphines.

TABLE 5.

$Ph_2P{\cdot}NEt_2$	B. p. 126°/0·1 mm.	$Ph_2P{\cdot}NEt_2,HgI_2$	M. p. 188—190°
$Ph_2P{\cdot}NEt_2,MeI$	M. p. 112—115°	$(Ph_2P{\cdot}NEt_2CuI)_4$	M. p. 225—227
$Ph_2P{\cdot}NEt_2,MeI,HgI_2$	M. p. 116—118		

The Proton Magnetic Resonance Spectrum of an Aqueous Solution of the 1 : 1 *Methyl Iodide Adduct Formed by Bisdiethylaminophenylphosphine.*—The spectrum was recorded on an A.E.I. R.S.2 spectrometer, operating at 60 Mc./sec., from a M-solution of the adduct in water, and it is shown in the Figure. In addition to the peaks arising from the aromatic protons and the solvent, the spectrum consists of a multiplet of six peaks, a doublet, and a triplet. The multiplet arises from the methylene protons. It consists of two superimposed quartets which result from the coupling of the methylene proton spins with those of the neighbouring methyl-group protons and the phosphorus nucleus. The methylene-protons are all chemically equivalent. The triplet arises from coupling of the methyl group protons with those on the neighbouring methylene group. The doublet arises from the remaining methyl group. The line spectrum of the Figure is calculated, by using first-order splitting rules, from the τ values and coupling constants listed in Table 6, and when it is compared with the observed spectrum it immediately follows that the methyl group is attached to the phosphorus atom and not to a nitrogen atom. The adduct is $\{Ph{\cdot}P(Me)[NEt_2]_2\}^+I^-$.

TABLE 6.

Group	Aromatic	$-CH_2-$	CH_3-P	$-CH_2-CH_3$
τ	~2·0	6·73	7·56	8·84

Coupling constants: $J(CH_2-CH_3) = 6{\cdot}7$; $J(CH_2-P) = 11{\cdot}3$; $J(CH_3-P) = 12{\cdot}6$ cycles/sec.

Both the chemical and the nuclear magnetic resonance investigations show that a very significant feature of the N·P·N system, as with the P·N system, is the apparent complete lack of basic character on the part of the nitrogen. Basic character depends on the π-electron density on the nitrogen atom and it follows from our results that the $p\pi$–$d\pi$ bonding between the filled p-orbital of the nitrogen and the vacant d-orbitals of the phosphorus removes all donor characteristics from the nitrogen and reinforces those of the phosphorus. The full effect of this transfer of π-electron density to the phosphorus, $P \leftarrow N$, should emerge from studies of the wide range of complexes formed by these compounds.

The main contribution to coupling constants arises from nuclear and electron-spin interactions within σ-electronic frameworks and, because of this, coupling constants are normally rapidly attentuated as bonds are interposed between the nuclei concerned. However, $J(CH_2-P)$ and $J(CH_3-P)$ are of the same order of magnitude, and so coupling must be enhanced through the P–N–C–H σ-framework. The coupling between the phosphorus nucleus and a methylene proton depends on the s-electron density of the two nuclei and on the interactions between these s-electrons and the other electrons in the σ-framework. The value of $J(CH_2-P)$ indicates that polarisation of the electrons in the σ-framework is in the sense $P \rightarrow N \leftarrow C$, so that the interactions between these electrons are enhanced, and hence also the coupling of the phosphorus nuclear spin to the spins of the methylene protons. The polarisation of the electron density in the P–N bond in the adduct is opposite in sense to that between the same two atoms in the phosphine.

EXPERIMENTAL

Dichlorophenylphosphine and chlorodiphenylphosphine were obtained commercially and were used without purification. Where necessary, amines were dried over potassium hydroxide. The detailed preparations of bisdimethylaminophenylphosphine and its derivatives are quoted as examples of the methods employed.

Considerable difficulty was experienced in obtaining concordant and acceptable analytical figures for carbon and hydrogen. Confirmation of the compounds listed has in some cases to depend on the satisfactory analysis of derivatives rather than the original material. Extensive use of infrared spectra showed the purity of the material employed at all stages of the preparations. In particular, the absence of a frequency which could be assigned to P=O was of significance in assessing the possible presence of phosphine oxides as impurities.

Bisdimethylaminophenylphosphine.—Dimethylamine (58 g., 1·3 moles) in dry benzene (100 ml.) was added dropwise, with stirring, to the phenyldichlorophosphine (40 g., 0·22 mole) in benzene (300 ml.) at 0°. Entry of air to the mixture was prevented by the use of a nitrogen stream. The mixture was stirred for about a day to ensure an easily filterable precipitate. The hydrochloride was separated by filtration under nitrogen and washed with dry benzene and the washings were combined with the filtrate. The benzene was removed by distillation, giving a product (39·6 g., 90·4%) that was distilled through a 14″ Fenske column. A fraction (26·2 g.), b. p. 59·0—59·5°/0·2 mm. (Found: N, 13·8%), was purified by redissolving it in benzene, washing it with several portions of cold water to remove traces of the amine hydrochloride complex, drying (CaH_2) and distillation; this *product* had b. p. 61·0°/~1 mm. (Found: N, 14·3. $C_{10}H_{17}N_2P$ requires N, 14·3%).

Bisdimethylaminophenylphosphine Methiodide.—Bisdimethylaminophenylphosphine (0·439 g.) was treated in ether with an excess of methyl iodide. Evaporation under a vacuum gave a white solid (0·743 g., 98·2%) (Found: N, 8·3. $C_{11}H_{20}IN_2P$ requires N, 8·3%). The *methiodide* was water-soluble, giving an immediate precipitate with aqueous silver nitrate solution.

Mercuric Iodide Complexes of Bisdimethylaminophenylphosphine.—(*a*) 1 : 1 *Complex.* Bisdimethylaminophenylphosphine (0·502 g., 2·56 mmoles) in methanol was added to mercuric iodide (1·140 g., 2·52 mmoles) in methanol. The fine white *complex* (1·506 g.) which separated was filtered off and washed with ether. Recrystallisation from acetone gave pale yellow crystals, m. p. 192—196° (Found: I, 39·2. $C_{10}H_{17}HgI_2N_2P$ requires I, 39·1%).

(*b*) 2 : 1 *Complex.* Bisdimethylaminophenylphosphine (0·305 g.) in a few ml. of methanol was mixed with a solution of mercuric iodide in methanol. A white crystalline precipitate appeared at once. This *complex* recrystallised from ethanol as needles, m. p. 86—88° (0·610 g., 92%) (Found: C, 27·2; H, 4·1; I, 29·35; N, 6·0. $C_{20}H_{34}HgI_2N_4P_2$ requires C, 28·4; H, 4·0; I, 29·9; N, 6·6%).

Mercuric Iodide Complex of Bisdimethylaminophenylphosphine Methiodide.—Direct addition of a methanolic solution of the methiodide to an excess of mercuric iodide, dissolved in methanol, gave greenish crystals of the *adduct*, m. p. 132—134° (Found: C, 16·7; H, 2·2; Hg, 24·9; N, 4·3. $C_{11}H_{20}HgI_3N_2P$ requires C, 16·7; H, 2·5; Hg, 25·2; N, 3·5%). Alternatively the methanolic solution of mercuric iodide is added to an ethereal solution of the phosphine and methyl iodide.

Bisdiethylaminophenylphosphine.—Reaction of diethylamine (174 g., 2·38 moles) and dichlorophenylphosphine (103 g., 0·57 mole) was carried out as described for dimethylamine, except that ether was employed as solvent. 100 G. (70%) of a fraction, b. p. 80°/0·025 mm., were obtained (Found: N, 10·6%). This was washed with water as described above, giving a liquid *phosphine*, b. p. 91·5°/0·1 mm. [Found: C, 66·3; H, 9·9; N, 11·1%; *M*, 257 (cryoscopic in benzene), 245 (ebullioscopic in benzene). $C_{14}H_{25}N_2P$ requires C, 66·6; H, 10·0; N, 11·1%; *M*, 252].

Bisdiethylaminophenylphosphine Methiodide.—This reaction was carried out as described in the case of the dimethylamino-compound; the product was, however, a viscous liquid (yield 100% for a 1 : 1 *complex*) (Found: I, 31·6; N, 6·9. $C_{15}H_{28}IN_2P$ requires I, 32·2; N, 7·1%). The liquid methiodide was stable up to 250°; above this temperature decomposition occurred.

The liquid was water-soluble, the solution being acid and containing free iodide ions. The molecular weight (cryoscopic in water) was 206 (*M* calc., 394). The conductance Λ_m in dry acetonitrile was 112·1 ohm.$^{-1}$ cm.^{2} mole^{-1}.

Mercuric Iodide Complexes of Bisdiethylaminophenylphosphine.—(*a*) 1 : 1 *Complex.* The phosphine (1·29 g.) was treated in methanol with an excess of a saturated solution of mercuric iodide in methanol. The white *complex* (2·70 g.) that separated, recrystallised from ethanol, then having m. p. 176—178° (75%). It was sparingly soluble in benzene but readily soluble in tetrahydrothiophen dioxide [Found: C, 24·4; H, 3·7; N, 4·6%; *M* (cryoscopic in $C_4H_8O_2S$), 1080. $C_{14}H_{25}HgI_2N_2P$ requires C, 23·8; H, 3·4; N, 4·0%; *M*, 706].

(*b*) 2 : 1 *Complex.* An excess of a methanol solution of the phosphine was added to a solution of mercuric iodide in methanol. A white crystalline *complex*, m. p. 142—143°, was obtained [Found: C, 35·4; H, 5·2; I, 26·5; N, 6·0%; *M* (cryoscopic in benzene), 970. $C_{28}H_{50}HgI_2N_4P_2$ requires C, 35·1; H, 5·2; I, 26·5; N, 5·9%; *M*, 958].

Mercuric Iodide Complex of Bisdiethylaminophenylphosphine Methiodide.—The methiodide (1·970 g.) yielded a greenish crystalline *complex* (2·043 g.) when mixed with an alcoholic solution of mercuric iodide and left overnight; this had m. p. 79—81° [Found: C, 29·0; H, 4·4; N, 4·6%; *M* (cryoscopic in $C_4H_4O_2S$), 406. $C_{30}H_{56}HgI_4N_4P_2$ requires C, 29·0; H, 4·4; N, 4·5%; *M*, 1244].

Bisdipropylaminophenylphosphine.—Dichlorophenylphosphine (40 g., 0·22 mole) was treated with di-n-propylamine (100 g., 1 mole). A *product* (54%), b. p. 140°/0·2 mm., was obtained (N, 9·4%) that was washed with water as described above, to give a liquid, b. p. 122°/0·1 mm. (Found: N, 9·1. $C_{16}H_{29}N_2P$ requires N, 9·1%).

With an excess of methyl iodide this gave a *methiodide*, m. p. 111—114° (Found: N, 6·15. $C_{17}H_{32}IN_2P$ requires N, 6·2%).

Mercuric Iodide Complexes of Bisdipropylaminophenylphosphine.—(*a*) 1 : 1 *Complex.* The aminophosphine (0·498 g., 1·61 mmoles) in methanol was added to a methanolic solution of mercuric iodide (0·720 g., 1·59 mmoles); the *complex* (0·858 g.) had m. p. 134—136° [Found: I, 33·7%; *M* (cryoscopic in benzene), 1370 ± 50. $C_{18}H_{33}HgI_2N_2P$ requires I, 33·3%; *M*, 762].

(*b*) 1 : 2 *Complex.* The aminophosphine (2·2 g., 7·15 mmoles) reacted with mercuric iodide (1·5 g., 3·3 mmoles) to give a white solid *complex*, m. p. 126—127° (Found: I, 23·8; N, 4·9. $C_{32}H_{58}HgI_2N_4P_2$ requires I, 23·8; N, 5·2%).

Mercuric Iodide Complex of Bisdipropylaminophenylphosphine Methiodide.—This aminophosphine (1·45 g., 4·71 mmoles) was converted into the methiodide which was treated in methanolic solution with mercuric iodide (2·15 g., 4·74 mmoles) in methanol. A crystalline *complex* separated slowly and after a week 1·7 g. were available; it had m. p. 59—61° (Found: C, 24·3; H, 4·2; Hg, 21·7; N, 2·9. $C_{17}H_{32}HgI_3N_2P$ requires C, 25·2; H, 4·0; Hg, 22·1; N, 3·1%).

Chlorodiethylaminophenylphosphine.—To dichlorophenylphosphine (100 g., 0·56 mole) in benzene (800 ml.) was added diethylamine (87 g., 1·19 moles) in benzene (100 ml.). The product $PhP(NEt_2)Cl$ (57 g., 48%), had b. p. 82—84°/0·05 mm.

Diethylaminodimethylaminophenylphosphine.—The preceding compound (19·0 g., 0·088 mole) and an excess of dimethylamine yielded a fraction, b. p. 61—62°/0·05 mm., that was washed with water as described above, giving a *product*, b. p. 72·5°/0·1 mm. (Found: N, 12·4. $C_{12}H_{21}N_2P$ requires N, 12·5%).

With an excess of methyl iodide this afforded a waxy hygroscopic methiodide whose analysis was not possible. The weight increase (0·663 g. from 0·390 g.) is close to that required for a 1 : 1 adduct.

Mercuric Iodide Complex of Diethylaminodimethylaminophenylphosphine.—This phosphine (1·032 g., 4·60 mmoles) with mercuric iodide (1·300 g., 2·80 mmoles) gave a white crystalline *complex* (1·91 g.), m. p. 159—161° (Found: I, 28·1; N, 5·7. $C_{24}H_{12}HgI_2N_4P_2$ requires I, 28·2; N, 6·2%).

Mercuric Iodide Complex of Diethylaminodimethylaminophenylphosphine Methiodide.—The phosphine (0·660 g., 2·95 mmoles) was converted into the methiodide and then treated with mercuric iodide, slowly yielding a greenish *complex* (0·20 g.), m. p. 90—92° (Found: C, 18·9; H, 2·85; N, 3·8. $C_{13}H_{24}HgI_3N_2P$ requires C, 19·0; H, 2·9; N, 3·4%).

Diethylaminodipropylaminophenylphosphine.—The compound $PhClP{\cdot}NEt_2$ (5·08 g., 0·0236 mole) with n-propylamine (10·0 g., 0·1 mole) gave a *product* (3·1 g., 47%), b. p. 110—114°/0·05 mm. (Found: C, 68·0; H, 10·2; N, 9·95. $C_{16}H_{29}N_2P$ requires C, 68·5; H, 10·4; N, 10·0%).

Diethylaminodipropylaminophenylphosphine Methiodide.—The phosphine (0·181 g., 0·645 mmole) gave an oily *methiodide* (0·275 g.) which solidified slowly and then had m. p. 107° (Found: N, 6·6. $C_{17}H_{32}IN_2P$ requires N, 6·6%).

Mercuric Iodide Complex of Diethylaminodipropylaminophenylphosphine.—The phosphine (0·404 g., 1·44 mmoles) with mercuric iodide gave, with some difficulty, a *complex* (0·289 g., 40%), m. p. 102—108° (Found: C, 37·8; H, 5·8; N, 5·3. $C_{32}H_{58}N_4P_2HgI_2$ requires C, 37·8; H, 5·7; N, 5·5%).

Mercuric Iodide Complex of Diethylaminodipropylaminophenylphosphine Methiodide.—The methiodide of this phosphine (0·623 g., 2·6 mmoles) with mercuric iodide in methanol gave, on addition of ether and storage in a refrigerator for some days, a greenish *complex*, m. p. 82—84° (Found: C, 22·9; H, 3·9; N, 3·1. $C_{17}H_{32}HgI_3N_2P$ requires C, 23·3; H, 3·7; N, 3·2%).

Reaction of Gaseous Hydrogen Chloride with Bisdiethylaminophenylphosphine.—Dry hydrogen chloride was caused to react with the phosphine (1·965 g., 7·8 mmoles) in a vacuum-system. This yielded a product (3·124 g.), corresponding to an uptake of 31·2 mmoles of acid. The mixture, on extraction with benzene followed by filtration, yielded diethylamine hydrochloride (1·647 g., 15·0 mmoles). The reaction is thus: $Ph{\cdot}P(NEt_2)_2 + 4HCl \longrightarrow 2Et_2NH_2Cl + Ph{\cdot}PCl_2$.

Reaction of Aqueous Hydrochloric Acid and Sodium Hydroxide with Bisdiethylaminophenylphosphine.—The phosphine reacted with cold 2M-hydrochloric acid with evolution of heat. Phenylphosphonous acid, identified by its infrared spectrum, crystallised from the cloudy solution. The overall hydrolysis can be represented: $Ph{\cdot}P(NEt_2)_2 + 2H_2O \longrightarrow Ph{\cdot}PHO{\cdot}OH + 2Et_2NH_2Cl$. With 4M-sodium hydroxide, no reaction was observed, even on boiling.

Diethylaminodiphenylphosphine. Chlorodiphenylphosphine (8·3 g., 0·038 mole) reacted with diethylamine (7·3 g., 0·1 mole). The fraction, b. p. 126°/0·1 mm. (2 g., 38%), was collected as the required *product* (Found: C, 74·0; H, 7·6; N, 5·7; P, 11·7. $C_{16}H_{20}NP$ requires C, 74·6; H, 7·8; N, 5·5; P, 12·1%).

This material (0·133 g., 0·52 mmole) with an excess of methyl iodide gave exothermally a white *methiodide* (Found: I, 31·9; N, 3·2. $C_{17}H_{23}INP$ requires I, 31·9; N, 3·5%). The yield (0·190 g.) was theoretical for the 1 : 1 compound.

Mercuric Iodide Complex of Diethylaminodiphenylphosphine.—The phosphine with an excess of mercuric iodide gave a yellowish *complex*, m. p. 188—190° (from methanol), insoluble in benzene and nitrobenzene (Found: C, 26·75; H, 2·8; N, 2·3. $C_{16}H_{20}HgI_2NP$ requires C, 27·0; H, 2·8; N, 2·0%).

Mercuric Iodide Complex of Diethylaminodiphenylphosphine Methiodide.—The methiodide from this phosphine (0·473 g., 1·8 mmoles) was treated with an excess of mercuric iodide in methanol. Ether was added and, after cooling for some days, this yielded a greenish crystalline *complex*, m. p. 116—118° (Found: C, 24·0; H, 2·8; N, 1·7. $C_{17}H_{23}HgI_3NP$ requires C, 23·9; H, 2·7; N, 1·6%).

Cuprous Iodide Complex of Diethylaminodiphenylphosphine.—Cuprous iodide (~2 g.) was dissolved in saturated potassium iodide solution (30 ml.). The phosphine (0·474 g.) in alcohol (10 ml.) was added. A *complex* (0·638 g.) was precipitated immediately. This solid, recrystallised from ethanol, had m. p. 225—227° and was freely soluble in benzene {Found: C, 43·2; H, 4·4; N, 2·9%; *M* (cryoscopic in benzene), 1620. $C_{16}H_{20}CuINP$ requires C, 43·0; H, 4·5; N, 3·1%; $[C_{16}H_{20}CuINP]_4$ requires *M*, 1788}.

Mercury was determined by the method of Rauscher.[9] We thank Mr. J. McKechnie for technical assistance with part of this work, and Mr. J. M. Cameron, B.Sc., and his assistants for some of the nitrogen determinations.

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[9] Rauscher, *Ind. Eng. Chem., Analyt.*, 1938, **10**, 331.