74. *The Stereochemistry of Organic Derivatives of Phosphorus. Part I. The Synthesis of Acidic and Basic Dissymmetric Tertiary Phosphines. The Optical Resolution of Phenyl-*p*-(carboxymethoxy)phenyl-*n*-butylphosphine Sulphide.*

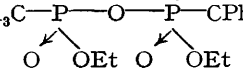
By W. Cule Davies and Frederick G. Mann.

An account is given of the new methods developed for the synthesis of tertiary phosphines in which the phosphorus atom is linked to three unlike alkyl or aryl groups, one of which also carries an acidic or basic group for subsequent salt formation. The oxides, sulphides, and selenides * of such compounds, of the type abcP→S, should be susceptible to optical resolution. The resolution of one such compound, phenyl-*p*-(carboxymethoxy)phenyl-*n*-butylphosphine sulphide (XV), is described. The *d*- and the *l*-form of this acid, having $[M]_D$ +9·6° and −9·7°, have been isolated by the fractional crystallisation of the *l*- and *d*-α-phenylethylamine salts, respectively.

Although there is now considerable physical evidence for the configuration of derivatives of 3- and 4-covalent phosphorus, there is a remarkable paucity of independent chemical evidence for such configurations. Chemical investigations have been directed almost exclusively to the attempted optical resolution of suitable derivatives of 4-covalent phosphorus. Such resolution, if successful, would have shown that the phosphorus atom and the four attached groups could not be uniplanar, and therefore that the phosphorus atom probably (but not necessarily) had a tetrahedal configuration. These derivatives fall mainly into three distinct classes.

(A) *Phosphoric and Phosphonic Acids.*—Early attempts to resolve substituted phosphoric acids, of type (NHR)(NHR')(OH)P→O and (OR)(OR')(OH)P→O (Caven, J., 1902, **81**, 1362; Luff and Kipping, J., 1909, **95**, 1993), and phosphonic acids, of type RR'(OH)P→O (Pope and Gibson, J., 1912, **101**, 740), are now known to have been fore-doomed to failure, as resonance in the phosphorus anion makes the phosphorus atom symmetric. The *d*-hydrindamide of phenyl-*p*-tolylphosphoric acid, (OPh)(OTol)(C_9H_9NH)P→O,

* Interatomic distances indicate that in these oxides and sulphides (and presumably therefore in the selenides also), the bond joining the phosphorus to the Group 6 element is a resonance hybrid between a double bond and a co-ordinate link. Since there is no symbol for such a bond, the → symbol is used conventionally throughout this paper. The precise nature of this covalent link does not, of course, affect the stereochemical considerations underlying our work.

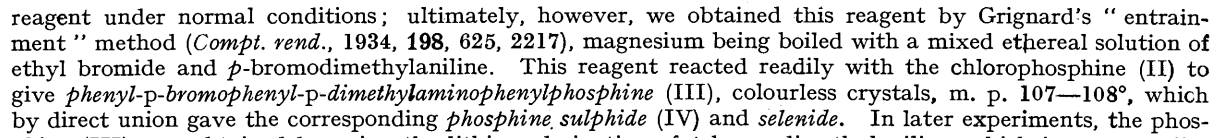
was separated into diastereoisomerides (Luff and Kipping, *loc. cit.*) but an optically active acid could clearly not be obtained by removing the hydrindamine residue (see also Kipping and Challenger, J., 1911, **99**, 626). It is noteworthy that Hatt (J., 1933. 776) separated ethyl triphenylmethylpyrophosphonate,  , into two forms, m. p. 222—223° and 228—231°, one of which must have been the racemic and the other the *meso*-form : both forms on hydrolysis necessarily gave the same acid, in which of course ionisation and resonance caused each phosphorus atom to become symmetric.

(B) *Phosphonium Salts.*—It is a striking fact that no phosphonium salt of type [abcdP]X, where a, b, c, d are different alkyl or aryl groups and X is a univalent acid radical, has yet been resolved (cf. Michaelis, *Annalen*, 1901, **315**, 54; Pope and Gibson, *loc. cit.*, p. 735; Wedekind, *Ber.*, 1912, **45**, 2933; Radcliffe and Brindley, *Chem. and Ind.*, 1923, **42**, 64; Meisenheimer *et al.*, *Annalen*, 1926, **449**, 224; Kamai, *J. Gen. Chem. Russ.*, 1932, **2**, 526). This failure is due partly to the great experimental difficulties in synthesising and isolating suitable crystalline compounds, but possibly also to some more fundamental and still unknown factor. All phosphonium salts investigated have had at least one alkyl group, and may therefore have given a " dissociation-equilibrium," [abcdP]X $\rightleftarrows$ abcP + dX, in solution, a process known to occur with quaternary ammonium and arsonium salts (cf. Burrows and Turner, J., 1921, **119**, 426; Davies and Cox, J., 1937, 614; Holliman and Mann, J., 1943, 550) and which would cause rapid racemisation : Wedekind (*loc. cit.*) has, however, adduced some evidence that phosphonium salts do not so dissociate in solution. The critical test would be the attempted resolution of a phosphonium salt in which a, b, c, d were unlike aryl radicals, and in which this dissociation could not occur. The synthesis of such a salt, now possible by Chatt and Mann's reaction (J., 1940, 1192), will be undertaken directly conditions permit.

(C) *Tertiary Phosphine Oxides, Sulphides, and Selenides.*—The only complete resolution of a 4-covalent phosphorus compound was achieved by Meisenheimer *et al.* (Ber., 1911, **44**, 356; *loc. cit.*), who resolved compounds of type abcP→O through their camphor- and bromocamphor-sulphonates. Meisenheimer's method has two disadvantages : (i) experimental difficulties (due mainly to retarded crystallisation) entailed over 15 years' work to obtain a satisfactory resolution, (ii) the polar P→O linkage was utilised for combination with the optically active sulphonic acids, and the method cannot therefore be applied to the corresponding sulphides and selenides.

We wished to prepare and resolve three similar compounds, abcP→O, abcP→S, abcP→Se, and then to compare their rotatory dispersions. For this purpose, therefore, one of the radicals, a, b, or c had to carry an acidic or basic group for subsequent salt formation. The object of this paper is primarily to describe the new synthetic methods developed for preparing such compounds, and to record the initial resolution of one compound, *phenyl*-p-(*carboxymethoxy*)*phenyl*-n-*butylphosphine sulphide* (XV).

In our first experiments, *p*-bromophenyldichlorophosphine (I) was converted by diphenylmercury into *phenyl*-p-*bromophenylchlorophosphine* (II), a liquid which was characterised by its ready conversion into *phenyl*-p-*bromophenylphosphonic acid*, $Ph(C_6H_4Br)(OH)P{\rightarrow}O$. *p*-Bromodimethylaniline will not form a Grignard



reagent under normal conditions; ultimately, however, we obtained this reagent by Grignard's " entrainment " method (*Compt. rend.*, 1934, **198**, 625, 2217), magnesium being boiled with a mixed ethereal solution of ethyl bromide and *p*-bromodimethylaniline. This reagent reacted readily with the chlorophosphine (II) to give *phenyl*-p-*bromophenyl*-p-*dimethylaminophenylphosphine* (III), colourless crystals, m. p. 107—108°, which by direct union gave the corresponding *phosphine sulphide* (IV) and *selenide*. In later experiments, the phosphine (III) was obtained by using the lithium derivative of *p*-bromodimethylaniline, which is more readily prepared and even more reactive than the corresponding Grignard reagent.

The phosphine sulphide (IV) was too weakly basic for stable salt formation : it also reacted only very sluggishly with methyl iodide, but finally, by working in nitromethane solution, the crystalline *methiodide* (V) was isolated. This iodide in turn gave the crystalline *metho*-d-*camphorsulphonate* and *metho*-d-α-*bromocamphorsulphonate*, but these salts after repeated crystallisation gave no evidence of resolution, each with calcium bromide giving the inactive *methobromide*. The metho-*d*-camphornitronate was also prepared, but only as a glassy substance that could not be obtained crystalline.

In view of these results, it was decided to introduce the 2-pyridyl group into the phosphine for salt formation. By again utilising the entrainment method, 2-pyridylmagnesium bromide was prepared (Overhoff and Proost, *Rec. Trav. chim.*, 1938, **57**, 179), although the corresponding lithium derivative could not be obtained. This Grignard reagent reacted with the chlorophosphine (II), giving *phenyl*-p-*bromophenyl*-2-*pyridylphosphine* (VI), m. p. 90—91°, which then gave the *sulphide* (VII). The 2-pyridyl group in (VII) proved, however, so weakly basic that the sulphide crystallised unchanged from an alcoholic solution of *d*-camphorsulphonic acid and from an aqueous-acetone solution of *d*-bromocamphorsulphonic acid. The sulphide was also unaffected by boiling in methyl iodide for 2 hours, but when heated with excess of methyl iodide at 100° it underwent complete disruption, forming tetramethylphosphonium iodide in almost theoretical yield; prolonged exposure

to methyl iodide in warm nitromethane solution gave, however, the *methiodide* (VIII) of the phosphine sulphide, but only in very low yield. In view of these difficulties, work on derivatives of (VIII) was discontinued.

Since it appeared probable that the weakly basic properties of the 2-pyridyl group in the sulphide (VII) were due to the close proximity of the nitrogen and the phosphorus atom, the distance between these atoms was increased by preparing the isomeric 3-pyridyl derivative. A Grignard reagent was obtained with difficulty from 3-bromopyridine, and when treated with the chlorophosphine (II) it furnished phenyl-*p*-bromophenyl-3-pyridylphosphine, which was characterised as its crystalline *picrate*. This phosphine readily gave the *phosphine sulphide*, but the nitrogen atom in this compound was even more feebly basic than that in the 2-pyridyl isomeride, and the sulphide would not combine with camphorsulphonic or bromocamphorsulphonic acid, nor could a methiodide be prepared. It is noteworthy that whereas picrates were readily formed by both the 2-pyridylphosphine (VI) and its 3-pyridyl isomeride, such salts could not be obtained from the corresponding phosphine sulphides. This deactivation of the tertiary nitrogen atom accompanying increased covalency of the phosphorus atom is being separately studied.

The synthesis of dissymmetric tertiary phosphine sulphides containing an acidic group was now investigated. The general method visualised was the preparation of a tertiary phosphine containing a *p*-anisyl radical, its demethylation to the *p*-hydroxyphenylphosphine, and the condensation of the sodium salt of the latter with ethyl bromoacetate to give finally the *p*-(carboxymethoxy)phenylphosphine :

$$(C_6H_4\cdot OMe)R^1R^2P \longrightarrow (C_6H_4\cdot OH)R^1R^2P \longrightarrow (C_6H_4\cdot O\cdot CH_2\cdot CO_2H)R^1R^2P$$

No tertiary phosphine containing a hydroxyphenyl radical had previously been prepared, however; furthermore, in the arsine series Michaelis and Weitz (*Ber.*, 1887, **20**, 48) had shown that warm hydriodic acid decomposed tri-*p*-anisylarsine into anisole and the dianisyliodoarsine, and more vigorous treatment decomposed it into anisole and arsenic tri-iodide. To test our proposed synthesis, therefore, *p*-anisyldichlorophosphine (IX) was converted into *p*-anisyldiethylphosphine, which under suitable treatment with hydriodic acid underwent smooth conversion into p-*hydroxyphenyldiethylphosphine*, the first phosphine of this type to be isolated : this phosphine gave a highly crystalline *methiodide*.

In view of this encouraging result, the dichlorophosphine (IX) was converted by diphenylmercury into *phenyl*-p-*anisylchlorophosphine* (X) and the latter by a Grignard reagent into *phenyl*-p-*anisyl*-n-*butylphosphine* (XI). This phosphine was demethylated with hydriodic acid. The crude, viscous product was apparently the hydriodide $Ph(C_6H_4\cdot OH)BuP,HI$, which with sodium carbonate gave a compound whose properties indicated zwitterion formation, $Ph(C_6H_4\cdot \overset{-}{O})Bu\overset{+}{P}H$; the reaction product was therefore benzoylated in caustic alkaline suspension to furnish the crystalline p-*benzoyloxyphenylphosphine* (XII). The latter united readily with sulphur to form the *phosphine sulphide* (XIII), which on alkaline hydrolysis gave the highly crystalline *phenyl*-p-*hydroxy*-

$$\underset{\text{(IX.)}}{(C_6H_4\cdot OMe)Cl_2P} \longrightarrow \underset{\text{(X.)}}{Ph(C_6H_4\cdot OMe)ClP} \longrightarrow \underset{\text{(XI.)}}{Ph(C_6H_4\cdot OMe)BuP} \longrightarrow \underset{\text{(XII.)}}{Ph(C_6H_4\cdot OBz)BuP}$$

$$\longrightarrow \underset{\text{(XIII.)}}{Ph(C_6H_4\cdot OBz)BuP\rightarrow S} \longrightarrow \underset{\text{(XIV.)}}{Ph(C_6H_4\cdot OH)BuP\rightarrow S} \longrightarrow \underset{\text{(XV.)}}{Ph(C_6H_4\cdot O\cdot CH_2\cdot CO_2H)BuP\rightarrow S}$$

phenyl-n-*butylphosphine sulphide* (XIV). An alcoholic solution of the sodium derivative of this hydroxy-compound (XIV) condensed readily with ethyl bromoacetate, and the product on alkaline hydrolysis yielded the crude sodium salt of the carboxymethoxy-phosphine sulphide (XV). This salt without purification was treated in alcoholic solution with *d*-α-phenylethylamine hydrochloride, and the highly crystalline d-α-*phenylethylamine* salt of *phenyl*-p-(*carboxymethoxy*)*phenyl*-n-*butylphosphine sulphide* (XV) separated. This salt had originally m. p. 195—201°, but fractional crystallisation from alcohol caused a steady rise in m. p. and ultimately gave the optically pure *d*-amine *l*-acid, m. p. 209—210°. The latter salt, when decomposed by dilute sulphuric acid, furnished the *l*-phenyl-*p*-carboxymethoxyphenyl-*n*-butylphosphine sulphide, having $[M]_D$ −9·7° in benzene solution. Further crystallisation of the amine-salt did not change its m. p. or increase the rotation of the liberated phosphine sulphide-acid. The *l*-acid gave a l-*ammonium* salt which was freely soluble in water, but its complete rotatory dispersion has not yet been measured owing to temporary lack of facilities. The following values in the visible spectrum, for a 4·770% aqueous solution of the ammonium salt, show clearly, however, that it possesses complex anomalous rotatory dispersion, which is not unexpected in view of its structure :

Wave-length of light, A.	6708	6104	5893	5780	5461	5086	4358
$[M]$	−9·6°	−10·5°	−10·7°	−11·9°	−11·5°	−8·2°	−0·6°

The acid recovered from the earlier mother-liquors of the above fractional crystallisations was now converted into the l-α-*phenylethylamine* salt of the d-*acid*, which had at first m. p. 193—200°, raised by fractional crystallisation to 209—210°. From this salt, the free *d*-phosphine sulphide acid (XV) was obtained, having $[M]_D$ +9·6° in benzene solution; this in turn furnished the d-*ammonium* salt, a 3·142% aqueous solution of which had $[M]_{5893}$ +11·3°, $[M]_{5461}$ +12·2°. The rotation of the ammonium salt is therefore dependent on the concentration of the solution.

It is noteworthy that the crystalline *ethyl* homologue of the acid (XV), *i.e.*, $Ph(C_6H_4\cdot O\cdot CH_2\cdot CO_2H)EtPS$, in the preparation of which we were kindly assisted by Mr. J. Harley-Mason, gave well characterised *salts* with

l-α-phenylethylamine, *d-sec.*-butylamine, and *d*-α-aminocamphor, but none of these salts after repeated crystallisation furnished any evidence of optical resolution.

Certain other points arising in this investigation deserve brief mention. We have utilised some of the above phosphines to prepare *phenyl*-p-*anisylmethylethylphosphonium* and *phenyl*-p-*anisylethyl*-n-*propylphosphonium iodides*, and *phenyl*-p-*anisyl*-p-*tolyl*-p-*chlorophenacylphosphonium bromide*. From none of these salts, however, could we isolate a crystalline *d*-camphorsulphonate or *d*-α-bromocamphorsulphonate.

We have also utilised two of our dissymmetric tertiary phosphines to prepare *dichlorobis*(*phenyl*-p-*bromophenyl*-p-*dimethylaminophenylphosphine*)*palladium* (XVI) and *dichlorobis*(*phenyl*-p-*bromophenylethylphosphine*)-*palladium* (XVII). Both these compounds would undoubtedly have only the *trans*-configuration. Each,

(XVI.) $[\{Ph(C_6H_4Br)(C_6H_4\cdot NMe_2)P\}_2PdCl_2]$ $[\{Ph(C_6H_4Br)EtP\}_2PdCl_2]$ (XVII.)

however, contains two similar asymmetric 4-covalent phosphorus atoms and therefore could exist in two forms, *meso* and racemic, similar to the two forms of ethylene-αβ-bis(phenylbutylarsine)dichloropalladium, isolated by Chatt and Mann (J., 1939, 1625). The compound (XVI) was too slightly soluble for effective fractional crystallisation but (XVII) was crystallised repeatedly; it appeared, however, to be homogeneous, and no indication of two forms was detected.

The reagent, 2-pyridylmagnesium bromide, used in the synthesis of the phosphine (VI), has also been used to prepare the crystalline *tri*-2-*pyridylphosphine* and *tri*-2-*pyridylarsine*. A detailed investigation of the chemical and therapeutic properties of these novel types of tertiary phosphine and arsine is now in progress.

Experimental.

The names of solvents used for recrystallisation are given in parenthesis immediately after the names of the compounds concerned. All rotations were determined in a 4-dcm. tube at 16° ± 1°, sodium-*D* light ($\lambda = 5893$) being used unless otherwise stated.

p-*Bromophenyldichlorophosphine* (I).—A mixture of bromobenzene (400 c.c.), phosphorus trichloride (500 c.c., 1·5 mols.), and aluminium chloride (120 g., 0·24 mol.) was refluxed for 48 hours. The cold product was extracted with petrol (b. p. 60—80°; 650 c.c.), and the petrol and excess trichloride then removed, and the residue fractionally distilled at reduced pressure. The phosphine (I) was collected, b. p. 136—142°/13 mm. (69 g.), and then refractionated: b. p. 139°/13 mm., 147—148°/21 mm. (cf. Michaelis, *Annalen*, 1896, **293**, 237).

Phenyl-p-*bromophenylchlorophosphine* (II).—A mixture of the phosphine (I; 98 g.) and powdered diphenylmercury (85 g.; 0·63 mol.) was heated at 210° for 1½ hours in a nitrogen atmosphere. The cold product was vigorously shaken with petrol (b. p. 60—80°; 200 c.c.), filtered at the pump, and the undissolved residue thoroughly washed on the filter with more petrol. The united extract and washings were distilled, the solvent at normal pressure and the residue under reduced pressure; a fraction of crude unchanged dichlorophosphine (b. p. 120—190°/11 mm.) was collected, and then the crude chlorophosphine, b. p. 195—215°/11 mm.; the latter, on redistillation, gave the pure *phosphine* (II), b. p. 203—204°/11 mm., 35—40 g. (Found: C, 47·9; H, 3·2; Cl + Br, 38·4. $C_{12}H_9ClBrP$ requires C, 48·1; H, 3·0; Cl + Br, 38·5%).

The early fraction, b. p. 120—190°/11 mm., on refractionation gave a large quantity of unchanged (I), b. p. 135—143°/11 mm., and a small quantity of crude (II), b. p. 195—215°/11 mm.

When chlorine was passed over a shallow agitated layer of the phosphine (II), the yellow solid trichloride, $Ph(C_6H_4Br)Cl_3P$, was rapidly formed. This was decomposed with cold water, which was subsequently boiled; the solid residue gave *phenyl*-p-*bromophenylphosphonic acid*, colourless crystals (alcohol), m. p. 174·5° (Found: C, 48·8; H, 3·5. $C_{12}H_{10}O_2BrP$ requires C, 48·5; H, 3·4%). The acid is soluble in most organic liquids, but only slightly soluble in boiling water.

Phenyl-p-*bromophenylethylphosphine* was prepared directly for recognition, as it must necessarily arise as a by-product in the preparation of the phosphine (III) when the "entrainment" Grignard reagent is employed. A solution of the chlorophosphine (II; 14 g.) in ether (50 c.c.) was added to a chilled, agitated Grignard reagent prepared from ethyl bromide (10·2 g., 2 mols.), magnesium (3 g.), and ether (150 c.c.). The mixture was refluxed for 30 minutes, cooled, hydrolysed with aqueous ammonium chloride and, after the usual treatment, the *ethylphosphine* was isolated as a colourless liquid, b. p. 136—138°/0·05 mm. (Found: C, 57·9; H, 5·0. $C_{14}H_{14}BrP$ requires C, 57·4; H, 4·8%).

Phenyl-p-*bromophenyl*-p-*dimethylaminophenylphosphine* (III).—(A) *By the Grignard method.* Ethyl bromide (0·8 c.c.) in ether (40 c.c.) was poured on magnesium (11 g.) containing an iodine crystal. When the vigorous reaction ensued, a solution of *p*-bromodimethylaniline (40 g.) and ethyl bromide (6·2 c.c.) in ether (150 c.c.) was added with stirring during 45 minutes, the mixture boiling spontaneously meanwhile. The mixture was refluxed for 2 hours, set aside for 1—2 hours, and finally a solution of the chlorophosphine (II, 20 g.) in benzene (50 c.c.) was added dropwise during 30 minutes to the stirred Grignard reagent, which was kept at 15—20° whilst the moderate interaction occurred. The ether was then distilled off, benzene (200 c.c.) added, and the mixture boiled for 1·5—2 hours and finally cooled in ice, whilst a solution of ammonium chloride (50 g.) in cold water (200 c.c.) was slowly added with vigorous stirring. The benzene layer was separated from the filtered product, the benzene distilled off, and the residue distilled in steam to remove dimethylaniline and *p*-bromodimethylaniline (6—8 g.). The viscous oily residue was dissolved in warm ether, dried, and after removal of the solvent gave the following fractions on distillation at 0·05 mm.: (i) *p*-bromodimethylaniline (trace); (ii) b. p. 100—180°, 4·5 c.c., mainly the above ethyl-phosphine; (iii) b. p. 180—206°, 1 c.c.; (iv) b. p. 206—240° (mainly 218—220°), 11 c.c.; (v) b. p. 240—260°, 0·5 c.c. A solution of the yellow viscous fraction (iv) in a minimum of hot alcohol, when vigorously stirred during spontaneous cooling, deposited the crude *phosphine* (III), 9 g. (37%), which after recrystallisation from alcohol was obtained as colourless crystals, m. p. 107—108° (Found: C, 62·4; H, 4·9; N, 3·8; Br, 20·8. $C_{20}H_{19}NBrP$ requires C, 62·5; H, 5·0; N, 3·7; Br, 20·8%). Fractions (iii) and (v), when mixed with alcohol, slowly deposited more crude phosphine (0·5 g.).

The proportion of reagents used above (chloro-phosphine, 1 mol.; bromo-amine, 3 mols., total ethyl bromide, 1·35 mols., magnesium, 6·75 atoms) ensures an excess of magnesium over the two bromo-compounds, and of the total Grignard reagents over the chloro-phosphine. A blank preparation of the above mixed Grignard reagent showed on analysis (by hydrolysis followed by estimation of dimethylaniline formed) that 60% of the *p*-bromodimethylaniline used had formed a Grignard reagent. The distribution of the chloro-phosphine between the two Grignard reagents will depend on the relative quantities and reactivities of these reagents. It is possible that the reagent from *p*-bromodimethylaniline is more reactive than that from ethyl bromide, for Gilman, St. John, St. John, and Lichtenwalter (*Rec. Trav. chim.*, 1936, **55**, 577, 588) have shown that the Grignard reagent from *p*-bromotoluene is more reactive than that from bromo-

benzene, which in turn is more reactive than that from ethyl bromide. The proportions used above probably approach the optimum.

(B) *By the lithium method.* A piece of clean, ether-washed lithium (0·8 g., 2·9 atoms) was rapidly cut into minute shavings and immediately immersed in dry ether (15 c.c.) contained in the usual reaction vessel fitted with stirrer, reflux condenser, dropping-funnel, and nitrogen inlet tube. A solution of *p*-bromodimethylaniline (10 g., 1·25 mols.) in ether (15 c.c.) was slowly added (20 minutes), the mixture being at first gently warmed to start the reaction, which then continued spontaneously, causing gentle boiling of the solvent. The complete mixture was refluxed for 1 hour, and was then thoroughly chilled, diluted with ether (30 c.c.), and vigorously stirred whilst a solution of the chloro-phosphine (12 g.) in ether (40 c.c.) was added during 1 hour. The mixture, which had become brown and deposited some solid, was set aside for 1 hour, then cooled to 0°, and water (200 c.c.) slowly added. Throughout the whole preparation until this stage, a nitrogen atmosphere was maintained in the apparatus. The ethereal layer was collected, dried (sodium sulphate), the solvent removed, and the yellow oily residue distilled at 0·1 mm. pressure. Two fractions were obtained: (i) b. p. rising to 200° (2 c.c.), mainly dimethylaniline; (ii) b. p. 210—240° (mostly at 230—232°), a pale yellow viscous oil which on dilution with alcohol gave the crystalline phosphine, 7 g. (45%).

Phenyl-p-*bromophenyl*-p-*dimethylaminophenylphosphine Sulphide* (IV).—When solutions of the phosphine (3 g.) and rhombic sulphur (0·25 g., 1 atom), each in carbon disulphide (10 c.c.), were mixed, heat was evolved. The mixture was refluxed for 30 minutes, the solvent evaporated, and the solid residue furnished the colourless *sulphide* (methyl alcohol), m. p. 126° (1·9 g.) (Found: C, 57·8; H, 4·6; N, 3·5. $C_{20}H_{19}NBrSP$ requires C, 57·7; H, 4·6; N, 3·4%). The *methiodide* (V) of this base was best obtained by keeping a mixed solution of the sulphide (6 g.) and methyl iodide (10 c.c.) in nitromethane (25 c.c.) at 40—50° for 3 days; the solid (3·9 g.) which had separated was collected, a second crop (0·8 g.) being obtained by dilution of the filtrate with ether; colourless crystals (methyl alcohol), m. p. 158—159° (Found: C, 45·5; H, 3·9. $C_{21}H_{22}NBrISP$ requires C, 45·2; H, 4·0%). The methiodide is also formed when a solution of the sulphide in methyl iodide is set aside at room temperature for 2—3 days; in ethereal solution, however, little union occurs even after refluxing for 3 days.

The metho-d-*camphorsulphonate*. The filtrate from mixed hot aqueous methyl-alcoholic solutions of the iodide and of silver camphorsulphonate (1 mol.) was evaporated in a vacuum; the residual oil, dissolved in a minimum of warm acetone, deposited colourless crystals of the *metho-sulphonate*. These, repeatedly recrystallised from methyl alcohol–ether, or acetone–ether, were always obtained as long homogeneous needles of unchanged m. p. (224—226°, decomp.) and rotation (Found: C, 56·1; H, 5·4. $C_{21}H_{22}NBrSP,C_{10}H_{15}O_4S$ requires C, 56·2; H, 5·6%). The lack of resolution was confirmed by mixing cold concentrated methyl-alcoholic solutions of the sulphonate and of calcium bromide; the crystalline *methobromide methyl alcoholate*, m. p. 145°, was collected and thoroughly washed with cold methyl alcohol (Found: C, 48·7; H, 5·3; Br, 29·1. $C_{21}H_{22}NBr_2SP,CH_4O$ requires C, 48·6; H, 4·8; Br 29·4%). It was only slightly soluble in most cold solvents; in diacetone alcohol, in which it was more soluble, it was optically inactive.

The *metho*-d-*α-bromocamphorsulphonate* was similarly obtained as a residual viscous oil which readily crystallised when mixed with ether; colourless crystals, unaffected in rotation by repeated recrystallisation from acetone or methyl alcohol–ether; m. p. 198—199° (Found: C, 49·4; H, 4·6; Br, 21·5. $C_{21}H_{22}NBrSP,C_{10}H_{14}O_4BrS$ requires C, 50·2; H, 4·9; Br, 21·6%). The final crop was also converted into an inactive methobromide as before.

Phenyl-p-*bromophenyl*-p'-*dimethylaminophenylphosphine Selenide*.—A solution of the phosphine (III; 2 g.) in carbon disulphide was boiled with powdered selenium (0·45 g.) for 1 hour. The solvent was removed from the filtered solution, and the residue gave the colourless *selenide* (methyl alcohol), m. p. 135·5—136·5° (Found: C, 51·8; H, 4·45. $C_{20}H_{19}NBrSeP$ requires C, 51·9; H, 4·1%).

Phenyl-p-*bromophenyl*-2-*pyridylphosphine* (VI) was prepared by the dropwise addition of a solution of the phosphine (II; 13 g.) in benzene (100 c.c.) to a Grignard reagent prepared by the entrainment method from ethyl bromide (4 c.c. in all), 2-bromopyridine (9·6 c.c.), magnesium (5 g.), and ether (120 c.c.), the method being essentially as for (III) (p. 279). After the removal of the solvent, the residue, on distillation at 0·01 mm. pressure, gave two fractions: (1) b. p. 90—150° (1·5 g.), mainly 2 : 2'-dipyridyl, rapidly solidifying in the receiver, and having m. p. 69—70° after recrystallisation (petrol); (ii) b. p. 160—230°, a viscous liquid. Fraction (ii), on redistillation at 0·01 mm., gave: (iii) b. p. 140—160°, a mobile, pale yellow liquid, mainly the monoethylphosphine; (iv) b. p. 180—230°, a thick viscous liquid. A solution of fraction (iv) in an equal volume of methyl alcohol, set aside at 5°, deposited the crystalline *phosphine* (VI; 2 g.), colourless crystals (methyl alcohol or petrol), m. p. 90—91° (Found: N, 4·35. $C_{17}H_{13}NBrP$ requires N, 4·1%).

To obtain large quantities of (VI), the crude product from a number of such preparations should be united for redistillation: it is inadvisable to increase the above quantities in any one preparation. In our initial preparations, the crystalline phosphine could not be isolated from fraction (iv). The latter in alcoholic solution was therefore treated with methyl-alcoholic picric acid: the precipitated sticky *picrate* solidified on vigorous stirring and ultimately gave yellow leaflets (ethyl alcohol), m. p. 132° (Found: N, 9·8; Br, 14·05. $C_{17}H_{13}NBrP,C_6H_3O_7N_3$ requires N, 9·8; Br, 14·0%). The picrate was decomposed with 10% aqueous sodium hydroxide, and the phosphine, after extraction with ether, was readily recrystallised from methyl alcohol: it was used to seed subsequent solutions of fractions (iv).

The *phosphine sulphide* (VII) was readily obtained from the phosphine (VI; 6 g.) and sulphur (0·6 g.) in carbon disulphide (30 c.c.); colourless crystals (ethyl alcohol), m. p. 109°, 6 g. (Found: C, 54·5; H, 3·55. $C_{17}H_{13}NBrSP$ requires C, 54·6; H, 3·5%). Its *methiodide* (VIII) was best prepared by warming a solution of the sulphide (VII; 2 g.) in methyl iodide (10 c.c.) and nitromethane (20 c.c.) at 50° for 48 hours. The deep red solution was evaporated in a vacuum, and the residual oil scratched to induce crystallisation; washing with ether and 3 recrystallisations from alcohol gave a small yield of the yellow methiodide, m. p. 132—134° (decomp.) (Found: N, 2·6; ionic I, 24·8. $C_{18}H_{16}NBrISP$ requires N, 2·7; I, 24·6%).

The sulphide (VII; 0·3 g.) was unchanged after 2 hours' refluxing with methyl iodide (6 c.c.). Another mixture (VII, 0·5 g.; iodide, 4 c.c.) was heated in a sealed tube at 100° for 4 hours. On cooling, the crystalline product furnished tetramethylphosphonium iodide, colourless crystals (ethyl alcohol), dissociating at 210° (Found: ionic I, 58·2. Calc. for $C_4H_{12}IP$: I, 58·3%).

Methylation with methyl sulphate proved unsatisfactory. The sulphide (VII) was unaffected by heating with excess ethyl iodide at 100° even for 24 hours.

Phenyl-p-*bromophenyl*-3-*pyridylphosphine*.—This was prepared similarly to (VI), a solution of (II; 39 g., 25 c.c.) in benzene (100 c.c.) being added to a Grignard reagent obtained from ethyl bromide (11·5 c.c. in all), 3-bromopyridine (48 g.), magnesium (15 g.), and ether (240 c.c.). The crude residual oil on distillation gave a main fraction, b. p. 190—240°/0·2 mm., which on redistillation gave a small fraction, b. p. 150—195°/0·05 mm., and a larger fraction, b. p. 202—210°/0·15 mm. The latter, clearly the required phosphine, was a viscous, colourless oil which would not solidify. A portion for identification was converted in methyl-alcoholic solution into the *phosphine picrate*, yellow crystals (ethyl alcohol), m. p. 143—144° (decomp.) (Found: C, 47·8; H, 3·27; N, 10·2. $C_{17}H_{13}NBrP,C_6H_3O_7N_3$ requires C, 48·2; H, 3·0; N, 9·8%). The reminder was converted directly into the *phosphine sulphide*, colourless crystals (ethyl alcohol), m. p. 115—116° (Found: C, 54·6; H, 3·5; N, 3·7; Br, 22·0. $C_{17}H_{13}NBrSP$ requires C, 54·5; H, 3·55; N, 3·7; Br, 21·4%).

This sulphide, like the isomeric (VII), was recovered unchanged from alcoholic and acetone solutions of camphor- and bromocamphor-sulphonic acids. Attempts to prepare a methiodide under various conditions gave intractable gums.

p-*Anisyldichlorophosphine* (IX).—The following preparation differs in detail from those of Michaelis (*Annalen*, 1896, **293**, 249) and Jackson, Davies, and Jones (J., 1930, 2298). A mixture of anisole (600 g., 530 c.c.), phosphorus trichloride (760 g., 476 c.c.; 1 mol.), and aluminium chloride (120 g., 0·16 mol.) was refluxed for 36 hours. The cold product was extracted thrice with petrol (b. p. 60—80°), the solvent expelled from the extract, and the residue twice fractionated at reduced pressure; the phosphine (IX) was obtained, b. p. 150°/13 mm., 100 g.

p-*Anisyldiethylphosphine*.—This was originally prepared by Michaelis (*loc. cit.*) by the action of diethylzinc on (IX). We prepared it by adding a solution of (IX; 26 g.) in ether (50 c.c.) dropwise to a chilled, agitated Grignard reagent prepared from ethyl bromide (55 g.), magnesium (12 g.), and ether (300 c.c.). The mixture was refluxed for 30 minutes, and then worked up as usual, the diethylphosphine being obtained as a colourless liquid, b. p. 166—171°/40 mm. (19 g.). The phosphine readily reacts with methyl iodide, giving *p*-anisylmethyldiethylphosphonium iodide (alcohol–ether), m. p. 132—133° (Found : I, 37·5. Calc. for $C_{12}H_{20}OIP$: I, 37·5%) : Michaelis (*loc. cit.*) in error gives m. p. 91°.

p-*Hydroxyphenyldiethylphosphine*.—The above phosphine (10 g.) and hydriodic acid of constant b. p. (70 c.c.) were heated together at 135° for 2 hours in a carbon dioxide atmosphere in a Zeisel apparatus. The residual liquid was neutralised with sodium carbonate and extracted with ether; the solvent was removed from the dried, filtered extract, and distillation then gave the crude *phosphine* as a viscous oil, b. p. 168—176°/19 mm. (Found : C, 64·8; H, 9·4. $C_{10}H_{15}OP$ requires C, 65·9; H, 8·3%). As crystallisation of the phosphine was difficult, the latter was united directly with methyl iodide to give p-*hydroxyphenylmethyldiethylphosphonium iodide*, colourless crystals (ethyl alcohol), m. p. 168—169° (Found : C, 40·7; H, 5·8; I, 39·0. $C_{11}H_{18}OIP$ requires C, 40·8; H, 5·6; I, 39·1%). The phosphine also united vigorously with sulphur in carbon disulphide solution, but the phosphine sulphide could not be crystallised.

Phenyl-p-*anisylchlorophosphine* (X).—A mixture of the phosphine (IX; 130 g.) and thoroughly dried diphenylmercury (130 g., 0·6 mol.) was heated rapidly in an oil bath to 175—180°, and kept at this temperature for 1·5 hours. The cold product was repeatedly triturated with petrol (b. p. 60—80°). The united extracts were set aside overnight, separated from a small heavy oily layer, and the petrol removed. The residue, distilled at low pressure, gave first a fraction of crude unchanged (IX), b. p. rising to 120°/0·05 mm., and then the phosphine (X), b. p. 130—140°/0·03 mm., 47 g.; the latter was carefully refractionated, and the pure *phosphine* obtained as a colourless liquid, b. p. 137°/0·03 mm., 149—152°/0·15 mm. (35 g.) (Found : Cl, 14·3. $C_{13}H_{12}OClP$ requires Cl, 14·15%). Distillation of the crude phosphine at water-pump pressures often caused vigorous decomposition.

Phenyl-p-*anisyl*-n-*butylphosphine* (XI).—This was prepared by the action of a solution of the phosphine (X; 60 g.) in ether (100 c.c.) on a Grignard reagent prepared from pure *n*-butyl bromide (76 c.c., 3 mols.) and magnesium (20·4 g., 3·5 atoms) in ether (250 c.c.). After the usual treatment, the *phosphine* (XI) was collected first as a crude fraction, b. p. 132—140°/0·025 mm. (50 g.), and then on refractionation as the pure liquid, b. p. 139—141°/0·025 mm., 176—179°/0·5 mm. (46 g.) (Found : C, 75·5; H, 8·2. $C_{17}H_{21}OP$ requires C, 75·0; H, 7·8%). Isomerisation of a *n*-alkyl group during the conversion of the alkyl halide into the corresponding Grignard reagent is unknown : there is no doubt, therefore, that (XI) contains the *n*-butyl group.

Phenyl-p-*benzoyloxyphenyl*-n-*butylphosphine* (XII).—A mixture of the phosphine (XI; 18 g.) and constant-b. p. hydriodic acid (90 c.c.) was heated at 125—130° for 2·5 hours in a stream of carbon dioxide. The cold product was made alkaline with 20% aqueous sodium hydroxide and immediately shaken with benzoyl chloride (12 c.c.); the crude *benzoyloxy*-compound (XII) (23·5 g.) was rapidly collected. Recrystallisation (ethyl alcohol) gave the pure compound, m. p. 91° (Found : C, 76·5; H, 6·8. $C_{23}H_{23}O_2P$ requires C, 76·2; H, 6·4%). The following points must be noted : (*a*) the use of larger quantities than the above may give difficulties in the subsequent benzoylation; (*b*) the use of sodium carbonate in place of hydroxide does not liberate the hydroxy-phosphine satisfactorily, presumably owing to stable zwitterion formation, $\bar{O}\cdot C_6H_4(Ph)(Bu)\overset{+}{P}H$; (*c*) the crude (XII) should be collected after 10—15 minutes' shaking. Prolonged shaking on one occasion gave the *benzoyloxyphosphine oxide*, white crystals (aqueous alcohol), m. p. 136° (Found : C, 72·75; H, 6·2. $C_{23}H_{23}O_3P$ requires C, 72·95; H, 6·1%).

Sulphide (XIII). A mixture of the phosphine (XII; 18 g.), rhombic sulphur (1·6 g., 1 atom), and alcohol (170 c.c.) was refluxed for 2 hours, allowed to cool spontaneously, and then chilled at 0°. The *sulphide* (XIII) separated as colourless crystals (ethyl alcohol), m. p. 66—67°, 17 g. (Found : C, 69·8; H, 6·0. $C_{23}H_{23}O_2SP$ requires C, 70·0; H, 5·9%) : a second crop was obtained by evaporation of the filtrate. The sulphide separates from *cyclo*hexane solution in waxy crystals containing 0·5 mol. of solvent; m. p. 36—38° (Found : C, 71·9; H, 6·8. $C_{23}H_{23}O_2SP,\frac{1}{2}C_6H_{12}$ requires C, 71·5; H, 6·7%); crystallisation from alcohol then gives the pure (XIII), m. p. 66—67°.

The hydroxy-phosphine sulphide (XIV). A mixture of the benzoyloxy-sulphide (XIII; 8 g.), 10% aqueous sodium hydroxide (160 c.c.) and alcohol (30 c.c.), was refluxed until clear (*ca.* 8 hours). The clear solution was cooled, diluted with water (250 c.c.), and saturated with carbon dioxide. The *hydroxy-sulphide* (XIV) separated as a colourless, sticky mass which ultimately disintegrated to a white powder; this, when collected, washed thoroughly with water, and dried, was pure; m. p. 97—98°, unchanged by recrystallisation from *cyclo*hexane (Found : C, 66·2; H, 6·9. $C_{16}H_{19}OSP$ requires C, 66·2; H, 6·6%). Yield almost theoretical.

Phenyl-p-(*carboxymethoxy*)*phenyl*-n-*butylphosphine Sulphide* (XV) : *Preparation and Resolution*.—A solution of the sulphide (XIV; 9 g.) in alcohol (60 c.c.) and ethyl bromoacetate (17·5 c.c., 5 mols.) were added in this order to alcoholic sodium ethoxide (sodium, 2·9 g., 4 atoms; alcohol, 60 c.c.). The mixture was refluxed for 30 minutes, diluted with water (60 c.c.), and the alcohol evaporated on the water-bath, the solution being maintained just alkaline with aqueous sodium hydroxide. The cold concentrated solution, which deposited a small quantity of the viscous sodium salt of (XV), was cautiously acidified with dilute sulphuric acid. The precipitated crude viscous acid (XV) rapidly became semi-solid in the chilled mixture; the aqueous layer was decanted, the residual acid washed with water, dried, dissolved in boiling alcohol (50—60 c.c.), neutralised with alcoholic sodium hydroxide, and treated with a solution of *d*-α-phenylethylamine hydrochloride (4·6 g.) in hot alcohol (20 c.c.). Precipitated sodium chloride was rapidly collected, and the filtrate on cooling readily deposited white crystals of the d-α-*phenylethylamine* salt of the acid (XV) : average yield, 5 g.

The *d*-amine salt so obtained, once recrystallised from alcohol, had m. p. 195—201°; eight more recrystallisations from alcohol gave the optically pure d-*amine* l-*carboxy-phosphine sulphide*, m. p. 209—210° (Found : C, 66·6; H, 7·0. $C_{18}H_{21}O_3SP,C_8H_{11}N$ requires C, 66·65; H, 6·9%). This salt was too slightly soluble in cold solvents for reliable rotation measurements to be made. Consequently, 1·5194 g. of it were placed in a small separating-funnel, pure benzene (*ca.* 20 c.c.) added, and the mixture thrice extracted thoroughly with dilute sulphuric acid, great care being taken to avoid any loss of the benzene layer when running off the aqueous layer. The benzene layer was then filtered through a fluted filter-paper, previously moistened with benzene, into a 30 c.c. graduated flask, the funnel being subsequently washed out twice with more benzene which was run through the same filter. The filtrate, when made up to 30 c.c., was now a 3·767% solution of the free *l*-carboxyphosphine sulphide (XV). It had α −0·42°, $[M]$ −9·7°. A portion of the above *d*-amine salt which had been nine times recrystallised was now recrystallised thrice more : its m. p. was unchanged.

1·500 G. of this salt, treated as above, gave a 3·720% solution of the acid (XV), which had α −0·41°, $[M]$ −9·6°. The resolution was therefore complete.

A benzene solution of the *l*-acid (XV) was evaporated in a desiccator to a thick syrup, which would not crystallise; it was therefore vigorously triturated with pure petrol (b. p. 40—60°), whereby it was rapidly converted into a sticky but almost solid white mass. Further confinement in a vacuum removed traces of petrol and gave the pure l-*acid* (XV) (Found: C, 62·3; H, 6·4. $C_{18}H_{21}O_3SP$ requires C, 62·1; H, 6·05%). This acid is freely soluble in most organic solvents except *cyclo*hexane and petrol, but is insoluble in water: all attempts to crystallise it failed, however.

When a solution of the acid in aqueous ammonia was evaporated at room temperature in a vacuum, the pure l-*ammonium* salt was obtained as a crisp, brittle glass that could be readily powdered (Found: N, 3·8. $C_{18}H_{21}O_3SP,NH_3$ requires N, 3·8%). A 4·770% aqueous solution of this salt gave the following rotations:

Source of light.	λ, A.	α.	$[M]$.	Source of light.	λ, A.	α.	$[M]$.
Li	6708	−0·50°	− 9·6°	Hg	5461	−0·60°	−11·5°
Li	6104	−0·55	−10·5	Cd	5086	−0·43	− 8·2
Na	5893	−0·56	−10·7	Hg	4358	−0·03 *	− 0·6 *
Hg	5780	−0·62	−11·9				

* High accuracy is not claimed for these values owing to the small rotation and considerable absorption of the light.

The ammonium salt can be recrystallised from a concentrated solution in benzene if the latter is saturated with ammonia to suppress dissociation: the salt is thus obtained in colourless, fibrous crystals which on heating dissociate with slow liquefaction between 40° and 80° (Found: N, 3·85%).

The mother-liquors from the preparation and first five recrystallisations of the above *d*-amine salt were united, evaporated to dryness, and the residue decomposed and extracted with a mixture of benzene and dilute sulphuric acid. The benzene solution of the free phosphine sulphide acid (XV) thus obtained was further extracted twice with the sulphuric acid to ensure total removal of the amine. The benzene was then evaporated, and the residual acid (XV) dissolved in alcohol, neutralised with alcoholic sodium hydroxide, and treated with *l*-α-phenylethylamine hydrochloride. The optically impure l-*amine* d-*acid* which separated, when once recrystallised from alcohol, had m. p. 193—200°; eight more recrystallisations from alcohol gave the optically pure salt, m. p. 209—210° (Found: C, 66·8; H, 7·0; N 3·1. $C_{18}H_{21}O_3SP,C_8H_{11}N$ requires C, 66·65; H, 6·9; N, 3·0).

This salt, decomposed as before, furnished a 3·732% benzene solution of the pure *d*-phosphine sulphide acid (XV), which had α +0·41°, $[M]$ +9·6°. This solution gave the pure d-*acid* as a sticky white solid which could not be crystallised (Found: S, 9·4. $C_{18}H_{21}O_3SP$ requires S, 9·3%). The acid furnished the d-*ammonium* salt as described above (Found: N, 3·75%): a 3·142% aqueous solution of this salt had α_{5893} +0·39°, α_{5461} +0·42°; $[M]_{5893}$ +11·3°, $[M]_{5461}$ +12·2°. It was also recrystallised from benzene saturated with ammonia.

Phenyl-p-*anisylethylphosphine* was obtained by the action of the chloro-phosphine (X; 36 g.) in ether (500 c.c.) on a Grignard reagent prepared from ethyl bromide (34 c.c., 3 mols.), magnesium (13 g.), and ether (200 c.c.). The usual treatment and fractionation ultimately gave the oily ethylphosphine, b. p. 137°/0·1 mm., 210—211°/20 mm. (Found: C, 73·4; H, 7·2. $C_{15}H_{17}OP$ requires C, 73·75; H, 7·0%). This phosphine was characterised by direct union with methyl iodide in ethereal solution, giving *phenyl*-p-*anisylmethylethylphosphonium iodide* (ethyl alcohol–ether), m. p. 114—115° (Found: I, 33·0. $C_{16}H_{20}OIP$ requires I, 32·9%). This salt could not be converted into a crystalline camphor- or bromo-camphor-sulphonate.

Phenyl-p-*hydroxyphenylethylphosphine*.—A mixture of the above tertiary phosphine (27 g.) and constant-b. p. hydriodic acid (120 c.c.) was treated as previously described. The product was diluted with water, basified with sodium hydroxide, and extracted with benzene. The benzene extract, on careful fractional distillation, gave a main fraction of the hydroxy-phosphine, b. p. 160—175°/0·1 mm., 17 g. This phosphine, an exceedingly viscous liquid, was characterised as its *benzoyl* derivative, needles (alcohol), m. p. 79—80° (Found: C, 75·0; H, 5·9. $C_{21}H_{19}O_2P$ requires C, 75·5; H, 5·7%); this readily united with sulphur in benzene solution to give the p-*benzoyloxy-phosphine sulphide*, colourless crystals (alcohol), m. p. 83—84°, depressed to 68—76° by admixture with the previous compound (Found: C, 68·4; H, 5·7. $C_{21}H_{19}O_2SP$ requires C, 68·8; H, 5·2%).

Phenyl-p-(*carboxymethoxy*)*phenylethylphosphine Sulphide* (as XV).—Rhombic sulphur (2·2 g., 1 atom), when added to a solution of the above hydroxy-phosphine (16 g.) in benzene (100 c.c.), slowly dissolved with heat evolution. The solution was then boiled for 10 minutes, and the solvent removed. The residual viscous phosphine sulphide could not be crystallised, and was therefore dissolved in sodium ethoxide solution (sodium, 2 g.; alcohol, 100 c.c.), ethyl bromoacetate (16 g.) added, and the mixture refluxed for 1 hour. Water (100 c.c.) was then added, and the alcohol boiled off, the solution being meanwhile kept just alkaline by addition of 10% aqueous sodium hydroxide. Water (100 c.c.) was again added and, after cooling to 30°, the mixture was rapidly extracted with benzene to remove oily impurities; on further cooling and scratching, the sparingly soluble *sodium* salt of the above carboxymethoxy-sulphide crystallised, a second small crop being obtained by adding brine to the mother-liquor. Recrystallisation from water gave the pure, very hygroscopic sodium salt (10 g.) (Found: C, 55·3; H, 5·0. $C_{16}H_{16}O_3SPNa$ requires C, 56·1; H, 4·7%).

The sodium salt was decomposed with dilute sulphuric acid and the product extracted with benzene; evaporation of the benzene from the washed and dried extract ultimately gave the free acid, which, although analytically pure, remained for many weeks as a viscous syrup. Solidification finally occurred, and the product was then recrystallised by adding benzene to a boiling suspension in *cyclo*hexane until a clear solution was obtained; slow cooling gave colourless crystals of *phenyl*-p-(*carboxymethoxy*)*phenylethylphosphine sulphide*, m. p. 84° (Found: C, 60·4; H, 5·3. $C_{16}H_{17}O_3SP$ requires C, 60·0; H, 5·3%).

The l-*phenylethylamine* salt rapidly crystallised when solutions of the sodium salt (18·3 g.) and the amine hydrochloride (8·5 g.) in water (200 c.c. and 50 c.c.) were mixed at 40° and cooled; m. p. 206—207°, unchanged by four recrystallisations from water or by three from alcohol (Found: C, 65·3; H, 7·0; N, 3·2. $C_{16}H_{17}O_3SP,C_8H_{11}N$ requires C, 65·3; H, 6·4; N, 3·2%). The salt was too slightly soluble in cold solvents for rotation measurements. A portion of the final crop was shaken with dilute sulphuric acid and benzene, the benzene solution of the free phosphine sulphide separated, and twice extracted with dilute acid, but it was optically inactive.

The d-sec.-*butylamine* salt, similarly obtained by using an excess of amine hydrochloride, was recrystallised six times from water; m. p. 189—190° (Found: C, 61·4; H, 7·4; N, 3·5. $C_{16}H_{17}O_3SP,C_4H_{11}N$ requires C, 61·1; H, 7·2; N, 3·6%). A benzene solution of the free acid, obtained as above, was inactive. The salt was also recrystallised three times from ethyl alcohol–acetone; m. p. 190—193°; a 0·718% alcoholic solution had α + 0·38°, M + 52°, but again furnished the inactive acid.

The d-*aminocamphor* salt, similarly obtained from aqueous solution, separated as a viscous syrup which rapidly solidified; after four recrystallisations from alcohol, it had m. p. 166—168° (Found: C, 64·4; H, 7·4. $C_{16}H_{17}O_3SP,C_{10}H_{17}ON$ requires C, 64·1; H, 7·0; N, 2·9%). It also furnished the inactive acid.

Phenyl-p-*anisyl*-n-*propylphosphine*.—This was prepared by addition of the phosphine (X; 39 g.) in benzene (80 c.c.) to a Grignard reagent prepared from *n*-propyl bromide (29 c.c.) and magnesium (8 g.) in ether (175 c.c.). After the usual treatment, distillation of the residue gave the crude phosphine, b. p. 155—165°/0·2 mm. (23 g.), and redistillation gave the pure oily *phosphine*, b. p. 163·5°/0·3 mm. (Found : C, 74·2; H, 8·0. $C_{16}H_{19}OP$ requires C, 74·4; H, 7·4%). The phosphine in ethyl acetate combined readily with methyl iodide, giving *phenyl*-p-*anisylmethyl*-n-*propylphosphonium iodide*, colourless crystals (ethyl acetate or water), m. p. 114° (Found : I, 31·7. $C_{17}H_{22}OIP$ requires I, 31·7%), freely soluble in most organic liquids except ethyl acetate, ether, and *cyclo*hexane. It could not be converted into a crystalline camphor- or bromocamphor-sulphonate.

Phenyl-p-*anisyl*-p-*tolylphosphine*.—Addition of the phosphine (X; 34·7 g.) in ether (50 c.c.) to a Grignard reagent prepared from *p*-bromotoluene (70 g.; 3 mols.) and magnesium (9·5 g., 2·85 atoms) in ether (125 c.c.), followed by the usual procedure and fractional distillation, ultimately gave the pure *phosphine*, b. p. 176—183°/0·03 mm., 197—200°/0·1 mm.; it readily solidified and gave colourless crystals (methyl alcohol), m. p. 116—118° (Found : C, 78·1; H, 6·6. $C_{20}H_{19}OP$ requires C, 78·4; H, 6·25%). It combined readily with sulphur in carbon disulphide solution to give a *sulphide* (ethyl alcohol), m. p. 121—124° (Found : C, 71·6; H, 5·8. $C_{20}H_{19}OSP$ requires C, 71·0; H, 5·6%). It also combined with *p*-chlorophenacyl bromide (1 mol.) in warm benzene, precipitating the heavy oily *phenyl*-p-*anisyl*-p-*tolyl*-p-*chlorophenacylphosphonium bromide*; after evaporation of the solvent the bromide solidified on trituration with petrol. Recrystallisation was difficult : addition of petrol to a warm acetone solution until faintly turbid, followed by slow cooling, gave the crystalline bromide, m. p. 199° (Found : C, 62·5; H, 4·7. $C_{28}H_{25}O_2ClBrP$ requires C, 62·3; H, 4·7%). The corresponding camphor- and bromocamphor-sulphonate could not be obtained crystalline.

Phenyl-p-*bromophenyl*-p-*anisylphosphine*.—This was prepared by addition of the phosphine (II; 31 g.) in ether (100 c.c.) to a Grignard reagent prepared from *p*-bromoanisole (33 c.c.) and magnesium (6·5 g.) in ether (140 c.c.). Repeated fractionation of the final residue gave the *phosphine*, b. p. 204°/0·01 mm., which ultimately solidified; colourless crystals (methyl alcohol), m. p. 71° (Found : Br, 21·4. $C_{19}H_{16}OBrP$ requires Br, 21·5%).

Dichlorobis(*phenyl*-p-*bromophenyl*-p-*dimethylaminophenylphosphine*)*palladium* (XVI).—When cold solutions of the phosphine (III; 1 g.) in alcohol (30 c.c.) and of ammonium palladochloride (0·36 g.) in water (4 c.c.) and alcohol (8 c.c.) were mixed, the *compound* (XVI) (0·8 g.) was rapidly precipitated as a brick-red powder. It was recrystallised from benzene, toluene, diacetone alcohol, and from alcoholic ethylene dibromide : all such samples were identical, orange, microcrystalline powders, which on heating shrank at *ca.* 240°, effervesced with partial melting at 247—249°, and finally formed a semi-solid, bright red mass at 250° (Found : C, 51·7; H, 4·5. $C_{40}H_{38}N_2Cl_2Br_2P_2Pd$ requires C, 50·8; H, 4·1%).

Dichlorobis(*phenyl*-p-*bromophenylethylphosphine*)*palladium* (XVII).—When solutions of the tertiary phosphine (7 g.) in alcohol (10 c.c.) and the palladochloride (3·4 g.) in water (35 c.c.) and alcohol (70 c.c.) were shaken together for 1 hour, the immediate precipitate formed a brown gum, which when collected and triturated with hot alcohol furnished (XVII) (5 g.) as a yellow powder. When this was fractionally crystallised from *n*-propyl alcohol, *n*-butyl alcohol, ethyl carbonate, diacetone alcohol and glycol monomethyl ether, and was also fractionally extracted with boiling acetone, no indication of isomerism could be detected, the *compound* (XVII) being obtained as minute, orange needles, m. p. 172·5—174° (decomp., with shrinking at 170°) (Found : C, 43·3; H, 3·9. $C_{28}H_{28}Cl_2Br_2P_2Pd$ requires C, 43·6; H, 3·7%).

Tri-2-*pyridylphosphine*.—This was prepared similarly to (VI), phosphorus trichloride (5·6 c.c.) in benzene (100 c.c.) being added to an "entrainment" Grignard reagent prepared from ethyl bromide (1 + 10·5 c.c.), 2-bromopyridine (28·8 c.c.), and magnesium (15 g.) in ether (300 c.c.). After the initial reaction, the ether was displaced and more benzene (150 c.c.) added. Distillation of the residue gave two main fractions : (i) b. p. 90—130°/0·15 mm., 2 : 2′-dipyridyl, which rapidly solidified in the receiver; (ii) b. p. 170—230°/0·15 mm. (mainly at *ca.* 210°), a viscous, red liquid. The latter, when dissolved in an equal volume of methyl alcohol and set aside at 5° for 2 days, deposited the crystalline *phosphine* (2·25 g.), a further 0·86 g. being subsequently obtained from the mother-liquor; colourless crystals (methyl alcohol), m. p. 113—114° (Found : N, 15·8. $C_{15}H_{12}N_3P$ requires N, 15·8%). The triethylphosphine formed as a by-product in the above reaction distilled over when the benzene was removed.

Tri-2-*pyridylarsine*.—This was prepared as for the phosphine, but by using arsenic trichloride (11·8 g., 5·4 c.c.). Fraction (ii), which now had b. p. 180—210°/0·1 mm. (mainly *ca.* 200°), was a viscous gum (9 g.) which ultimately solidified. Recrystallisation from *cyclo*hexane gave the colourless *arsine*, m. p. 85° (Found : N, 14·0. $C_{15}H_{12}N_3As$ requires N, 13·6%), very soluble in alcohol and benzene.

We sincerely thank Mr. J. Harley-Mason, B.A., for experimental assistance in the preparation of phenyl-*p*-(carboxymethoxy)phenylethylphosphine sulphide, Mr. F. C. Baker for considerable general assistance, and the Leverhulme Trustees for the award of a Leverhulme Fellowship (W. C. D.).

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, March 23rd,* 1944.]