213. *The Abnormal Hydrolysis of Certain β-Diarylphosphinopropionic Esters. Part II.*[1] *Correction and Extension.*

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It is shown that *o*-, *m*-, and *p*-methoxyphenylphenylphosphinic acid, on reduction with lithium aluminium hydride in tetrahydrofuran, give a mixture of the secondary phosphine and the corresponding tertiary diarylmethylphosphine: in each case the two products co-distil over a narrow range of temperature. The corresponding *m*- and *p*-ethoxyphenyl acids on reduction give solely the corresponding secondary phosphines.

The earlier finding that the methyl and ethyl propionates, derived from *m*- and *p*-methoxyphenylphenylphosphine, on alkaline (or acid) hydrolysis give the corresponding tertiary diarylmethylphosphine has therefore been carefully checked; in each case this phosphine has originated in the secondary phosphine used, and the esters, when now rigorously purified, give no evidence of this phosphine on hydrolysis. The pure methyl and ethyl esters of (*m*-methoxyphenylphenylphosphino)acetic acid, and the crystalline acid itself, do however produce the diarylmethylphosphine when boiled with acid, but not with alkali.

o-Methoxyphenylphenylphosphinic acid, the corresponding secondary phosphine oxide, and the secondary phosphine itself, when treated with the hydride in tetrahydrofuran, give the tertiary diarylmethylphosphine. Preliminary experiments to elucidate the mechanism of these changes are recorded.

Part I[1] records the reduction of *m*-methoxyphenylphenylphosphinic acid, $MeO{\cdot}C_6H_4{\cdot}PPh(\dot{:}O){\cdot}OH$, by lithium aluminium hydride in tetrahydrofuran to *m*-methoxyphenylphenylphosphine (I), which combined with methyl and ethyl acrylate to form methyl β-*m*-methoxyphenylphenylphosphinopropionate (II; R = Me) and the ethyl ester (II; R = Et), respectively. These esters were also prepared by the reaction of the phosphine (I) in liquid ammonia with sodium and methyl (or ethyl) β-bromopropionate. The corresponding nitrile (III) was prepared by the union of the phosphine (I) and vinyl cyanide. These two esters (II; R = Me or Et), the nitrile (III), and the methyl and ethyl acetates (IV; R = Me or Et) on alkaline (or acid) hydrolysis were recorded as undergoing an abnormal hydrolysis with the formation of *m*-methoxyphenylmethylphenylphosphine (V). The butyrate (VI), and the *m*-ethoxyphenyl esters (VII; R = Me or Et) and (VIII), however, underwent normal hydrolysis to the carboxylic acid.

$m\text{-}MeO{\cdot}C_6H_4{\cdot}PPhH$ (I)

$m\text{-}MeO{\cdot}C_6H_4{\cdot}PPh{\cdot}[CH_2]_2{\cdot}CO_2R$ (II)

$m\text{-}MeO{\cdot}C_6H_4{\cdot}PPh{\cdot}[CH_2]_2{\cdot}CN$ (III)

$m\text{-}MeO{\cdot}C_6H_4{\cdot}PPh{\cdot}CH_2{\cdot}CO_2R$ (IV)

$m\text{-}MeO{\cdot}C_6H_4{\cdot}PPhMe$ (V)

$m\text{-}MeO{\cdot}C_6H_4{\cdot}PPh{\cdot}[CH_2]_3{\cdot}CO_2Me$ (VI)

$m\text{-}EtO{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}CO_2R$ (VII)

$m\text{-}EtO{\cdot}C_6H_4{\cdot}PPh{\cdot}CH_2{\cdot}CO_2Me$ (VIII)

The phosphine (V) was identified by analysis, by synthesis, and by the formation of the crystalline tribromogold derivative, $C_{14}H_{15}OP{\rightarrow}AuBr_3$, the nuclear magnetic resonance spectrum of which in chloroform solution showed the OMe groups as a sharp peak at τ 6·06 and the PMe groups as a doublet at τ 7·26 * (chemical shifts on the tetramethylsilane scale).

The *para*-methoxy-analogues of the esters (II; R = Me or Et) on hydrolysis gave the phosphine, $p\text{-}MeO{\cdot}C_6H_4{\cdot}PPhMe$, but the ethyl ester of the *p*-ethoxy-compound (as VII; R = Et) underwent normal hydrolysis.

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* In Part I, these values were erroneously given as 5·3 and 6·5, respectively.

[1] Part I, R. C. Hinton, Mann, and Todd, *J.*, 1961, 5454.

The above work, which was mainly exploratory, presented a number of anomalous results, for example, that the direct union of the phosphine (I) and methyl acrylate gave a mixture of the ester (II; R = Me) and the methylphosphine (V), but that the proportion of these two products varied widely in a series of apparently identical experiments. The behaviour of the *m*-methoxy-esters of type (II) and (IV) on hydrolysis, compared with that of the *m*-ethoxy-esters of similar type (VII) and (VIII), was striking.

Repetition of this work under rigidly controlled conditions, and with extension to the analogous *o*-methoxyphenyl compounds, has revealed the surprising fact that reduction of the *o*-, *m*-, or *p*-methoxyphenylphenylphosphinic acids or their ethyl esters by lithium aluminium hydride in tetrahydrofuran affords in each case a mixture of the secondary phosphine (as I) and the tertiary methylphosphine (as V). In each case, the two phosphines have very similar boiling points, and appear to co-distil in the reduction mixture, which therefore boils over a narrow range.

The reduction of the *m*- or *p*-ethoxyphenylphenylphosphinic acids gives in each case solely the corresponding secondary phosphine, and no tertiary alkyldiarylphosphine has been detected, in accordance with Part I.[1]

The physical and chemical evidence for the composition of the volatile reduction products of the methoxyphenylphenylphosphinic acids can be summarised.

(1) *Nuclear Magnetic Resonance Spectra.*—The evidence for the presence of P–H and P–Me groups in the " reduction distillates " is shown in Table 1. The values for the pure secondary and tertiary phosphines are included for comparison.

TABLE 1.

Compound reduced	Distillate, b. p./mm.	Position of peaks		
		τ P–H	τ O–Me	τ P–Me
m-MeO·C_6H_4·PPh(:O)OH *	112—115°/0·2	2·06, 7·50	6·61	8·49, 8·59
,, †	119—121°/0·35	2·06, 7·54	6·63	8·52, 8·62
m-MeO·C_6H_4·PPh(:O)·OEt	128—133°/0·4	2·07, 7·54	6·62	8·51, 8·61
,, †	120—124°/0·35	2·08, 7·54	6·63	8·52, 8·62
p-MeO·C_6H_4·PPh(:O)·OH *	118—121°/0·15	2·04, 7·50	6·61	8·51, 8·61 ‡
o-MeO·C_6H_4·PPh(:O)·OH *	106—113°/0·25	1·87, 7·47	6·60	8·48, 8·59
o-MeO·C_6H_4·PPh(:O)·OEt		1·85, 7·47	6·60	8·48, 8·58
Pure *m*-MeO·C_6H_4·PPhH		2·06, 7·51	6·64	—
,, *p*- ,,		2·06, 7·50	6·65	—
,, *o*- ,,		1·87, 7·47	6·60	—
,, Ph_2PH ,,		2·08, 7·53	—	—
,, *m*-MeO·C_6H_4·PPh·Me		—	6·57	8·47, 8·57
,, *p*- ,,		—	6·54	8·48, 8·58
,, *o*- ,, §		—	6·60	8·48, 8·59
,, Ph_2PMe		—	—	8·54, 8·64

* $LiAlH_4$ added to the solution of the compound in tetrahydrofuran. † The compound added to the mixture of the $LiAlH_4$ in tetrahydrofuran. ‡ In benzene solution. § On the supercooled liquid.

(2) *Isolation of Constituents.*—This process depends on the fact that the tertiary diarylmethyl phosphines are comparatively strong bases, whereas the corresponding secondary diaryl phosphines are essentially neutral. A benzene solution of the " reduction distillate " was therefore shaken with 5N-hydrochloric acid, which selectively and completely extracted the tertiary phosphine. The residual benzene solution on distillation gave the pure secondary phosphine. The acid extract was basified and extracted with benzene: the latter, when similarly treated, gave the pure tertiary phosphine. The sharp separation of the two phosphines is shown by their nuclear magnetic resonance spectra (Table 1). The ratio, pure secondary : pure tertiary phosphine, determined by this method corresponds closely to that determined from the area of the respective peaks of these phosphines in the nuclear magnetic resonance spectra of the reduction distillates (Table 2).

Since therefore the secondary phosphines used for the preparation of the propionic ester (II) and the nitrile (III) in Part I were always markedly contaminated with the

TABLE 2.

Boiling points and composition of reduction distillates obtained from *m*-, *p*-, and *o*-methoxyphenylphenylphosphinic acids.

	" Reduction-distillate " (cf. Table 1), b. p./mm.	Pure sec. phosphine, b. p./mm.	Pure tert. phosphine, b. p./mm.	Mol. ratio sec. : tert. phosphine in distillate, determined by	
				N.M.R. spectra	Direct separation
m-Series	112—115°/0·2	115—117°/0·3	114—117°/0·3	1 : 0·28	1 : 0·23
p- ,,	118—121°/0·15	116—119°/0·4 *	116—119°/0·35 †	1 : 0·56	1 : 0·55
o- ,,	106—113°/0·25	116—118°/0·3	122—123°/0·3 ‡	1 : 0·99	1 : 0·86

* M. p. 35·5—38°. † M. p. 16·2—17·5°. ‡ M. p. 45—46·5°.

corresponding tertiary methylphosphines, we have carefully investigated the purity of certain of these " pure " esters to determine whether the methylphosphine had been completely eradicated before hydrolysis.

The earlier sample of ethyl β-*m*-methoxyphenylphenylphosphinopropionate (II; R = Et) (cf. Part I, p. 5466), which had been prepared by the ammonia–sodium–β-bromopropionate ester method, and after fractionation gave excellent carbon and hydrogen analytical values, and on hydrolysis furnished the methylphosphine (V), does in fact show in its infrared spectrum a sharp band at 880 cm.$^{-1}$,[2] with a marked :CO band at 1727 cm.$^{-1}$. In spite of its analytical values, it must have been still contaminated with the methylphosphine (V). The preparation has been repeated, with again the contaminated secondary phosphine, and the ester (II; R = Et) refractionated until both its boiling point and refractive index (n_D^{22} 1·582) were constant and its infrared spectrum did not show a band at *ca.* 880 cm.$^{-1}$. Alkaline hydrolysis of this sample, under various conditions, always furnished the acid (II; R = H) in high yield and only a trace of a pale yellow semi-solid neutral product. The acid, isolated as a thick syrup, was identified by its crystalline benzylthiouronium salt and by its conversion into the crystalline phosphine oxide, previously prepared [1] by hydrolysis of the oxide of the ester (II; R = Et).

The contaminated phosphine has again been combined with vinyl cyanide, and the product on fractionation furnished the methyl phosphine (V) and the nitrile (III), the purity of which was carefully checked. Alkaline hydrolysis of this nitrile also gave the acid (II; R = H) in good yield and only a trace of neutral material.

In the *ortho*-series, the fraction, b. p. 106—113°/0·25 mm., obtained by the reduction of *o*-methoxyphenylphenylphosphinic acid, and later shown to be a mixture of the secondary phosphine and the tertiary phosphine, was treated with ethyl acrylate. The product on fractionation afforded the crystalline tertiary phosphine (as V) and pure ethyl β-*o*-methoxyphenylphenylphosphinopropionate, which on hydrolysis gave solely the corresponding crystalline acid, *o*-$MeO\cdot C_6H_4\cdot PPh\cdot[CH_2]_2\cdot CO_2H$.

It was earlier recorded that the interaction of *m*-methoxyphenylphenylphosphine (I) and methyl acrylate gave the methyl ester (II; R = Me) and the tertiary phosphine (V) in varying proportions. We have repeated this experiment, using the phosphine (I) purified by the hydrochloric acid treatment: the product, apart from polymerised acrylate, was solely the methyl ester (II; R = Me).

From these and many other recent experiments, it is now clear that certain of the results earlier recorded for the propionic acid derivatives were vitiated by the unsuspected presence of the diarylmethyl phosphine (V) in the secondary phosphine (I), and the statement that the *m*- and the *p*-propionic ester (as II) and the propionitrile (III) undergo abnormal hydrolysis with formation of the methylphosphine must be withdrawn.

It was earlier stated that the recorded formation of the methylphosphine (V) during hydrolysis of ethyl and methyl *m*-methoxyphenylphenylphosphinoacetates (IV; R = Et

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[2] Mallion, Mann, Tong, and Wystrach, *J.*, 1963, 1327.

or Me) might constitute a special case, since the phosphino-acetic acid initially formed might undergo decarboxylation to give the phosphine (V).[1] We have therefore now used the highly purified secondary phosphine (I) for the preparation of these esters, which in turn were carefully purified. We find that an alkaline hydrolysis of the ethyl ester gives the crystalline acid (IV; R = H) in almost theoretical yield, but hydrolysis with dilute hydrochloric acid quite decisively gives the methylphosphine (V), the yield of the acid (IV; R = H) falling (under our conditions) to 29%. Acidic hydrolysis of the purified methyl ester (IV; R = Me) also gives the phosphine (V), and a 25% yield of the acid (IV; R = H). Finally, prolonged treatment of the acid (IV; R = H) with hot acid also gives the methylphosphine: in all three cases, prolonged boiling with hydrochloric acid was necessary.

This result with acidic hydrolysis, and its marked difference from that obtained by alkaline hydrolysis, are not altogether unexpected. Denney and Smith[3] have shown that the phosphonium salt, $[Ph_3P\cdot CH_2\cdot CO_2H]Cl$, when heated to 180°, or when treated with aqueous sodium carbonate below 45°, undergoes decarboxylation to form the salt $[Ph_3PMe]Cl$. Considine[4] has shown that the salt $[Ph_3P\cdot CH_2\cdot CO_2Et]Cl,2H_2O$ in boiling benzene gives the salt $[Ph_3PMe]Cl$, carbon dioxide, ethanol, and water, in cold dilute hydrochloric acid gives the salt $[Ph_3P\cdot CH_2\cdot CO_2H]Cl$, and in aqueous sodium hydroxide gives the phosphorane, $Ph_3P{:}CH\cdot CO_2Et$. This ready decarboxylation is almost certainly associated with the positive charge on the quaternary phosphonium atom.

Our acetate esters, and the acid itself, in dilute hydrochloric acid must be in equilibrium with a salt having a cation of type *m*-$MeO\cdot C_6H_4\cdot \overset{+}{P}PhH\cdot CH_2\cdot CO_2R$. The proportion of molecules having the positive charge must be less than that of Considine's completely charged phosphonium salts, and the decarboxylation of our compounds is therefore much slower.

These acetate esters are, by virtue of this decarboxylation, the only esters to which the previously recorded " abnormal hydrolysis " does in fact apply.

It is noteworthy that methyl γ-*m*-methoxyphenylphenylphosphinobutyrate (VI) boils sufficiently high for any contaminating methylphosphine from the impure phosphine (I) to have been readily removed during normal purification: normal hydrolysis was therefore found.[1]

We are now investigating the mechanism of the reduction of a simple phosphinic acid such as diphenylphosphinic acid to a secondary phosphine, and also the more complex mechanism when the reduction is accompanied by transfer of a methyl group, as in our methoxyphenyl acids.

The methyl group which becomes linked to the phosphorus in the final tertiary PMe phosphine (V) can come only from the methoxyl group. We find in all our reductions that a considerable proportion of the phosphinic acid remains unreduced, presumably by the formation of an insoluble aluminium salt. In a preliminary investigation, the aqueous phase left after the reduction of *o*-methoxyphenylphenylphosphinic acid and subsequent hydrolysis was acidified, and the gummy precipitate was extracted with ether. The insoluble residue afforded the phosphinic acid. The extract gave a crude solid, m. p. 120—144°, which on repeated recrystallisation gave the pure ether-insoluble *o*-hydroxyphenylphenylphosphinic acid, m. p. 156—157·5°; this appeared to have arisen by atmospheric oxidation, possibly of the corresponding secondary phosphine oxide, but its formation provides clear evidence of demethylation of the methoxyl group.

We suggest that the demethylating agent is probably the anion $MeO\cdot C_6H_4\cdot \overset{-}{P}Ph$, the formation of which may cause the deep orange colour which develops in these reductions by lithium aluminium hydride and appears immediately sodium is added to a solution of our secondary phosphines in liquid ammonia. The formation of such anions has been

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[3] Denney and Smith, *Chem. and Ind.*, 1961, 290.

[4] Considine, *J. Org. Chem.*, 1962, **27**, 647.

well established. Issleib and Tzschach [5] isolated a yellow crystalline compound of composition $Ph_2PLi,C_4H_8O_2$ by the interaction of diphenylphosphine and phenyl-lithium in ether-dioxan, and a similar yellow compound, $Ph_2PNa,C_4H_8O_2$ by the action of sodium on diphenylphosphinous chloride in dioxan. Our preliminary evidence is two-fold.

The addition of diphenylphosphine to a suspension of lithium aluminium hydride in tetrahydrofuran gave the usual deep orange colour. The addition of anisole, followed by heating of the mixture, gave a considerable yield of methyldiphenylphosphine. The replacement of the anisole by phenetole gave no detectable tertiary phosphine. The anion Ph_2P^- has thus demethylated the methoxyl group but failed to attack the ethoxyl group. This is in harmony with our earlier [1] and our present results that the methoxyphenylphenylphosphinic acids similarly treated give the secondary phosphine and the tertiary diarylmethylphosphine, whereas the ethoxyphenyl acids give solely the secondary phosphine.

Although there is at present no evidence for the intermediate products in the reduction of the methoxyphenylphenylphosphinic acids, it is possible that the secondary phosphine oxide, $MeO\cdot C_6H_4\cdot PPh(\colon O)H$, is one of these. We find that the pure *o*-methoxy-phosphine oxide, when reduced under our standard conditions, gives the usual mixture of secondary phosphine and tertiary phosphine. More striking, however, is the fact that, when the pure *o*-methoxyphenylphenylphosphine is treated with lithium aluminium hydride in tetrahydrofuran, the tertiary phosphine is again produced, by a process of self-methylation. In our reduction experiments, a standard time of 4 hours' boiling was observed throughout: had this period been considerably extended, all the normal secondary phosphine would thus have been lost.

We have some evidence that these reactions proceed most readily in tetrahydrofuran, and the effect of the nature of the solvent and of the reducing agent is also being investigated.

EXPERIMENTAL

All compounds are colourless unless otherwise stated. Consistent m. p.s were obtained for certain substances only when they were heated in a sealed tube, denoted as (S.T.) or in an evacuated tube, denoted as (E.T.), or in a preheated block, in which case the immersion temperature is denoted as (I.T. —°).

All operations involving the preparation or manipulation of secondary or tertiary phosphines were performed under nitrogen.

The nuclear magnetic resonance spectra were obtained at 40 Mc./sec. in a Perkin-Elmer spectrometer with a permanent magnet and sample spinning. Positions of reference are quoted as chemical shifts on the τ scale [τ ($SiMe_4$) = 10·00] and have been measured against tetramethylsilane as an internal reference.

Refractive indices were measured with a Bellingham and Stanley Abbé refractometer.

m-*Methoxyphenylphenylphosphinic Acid*.—This acid was prepared as described earlier,[1] with certain modifications. Concentrated hydrochloric acid (117 c.c.) and *m*-anisidine (70 g., 1 mol.) were added in turn to a filtered, stirred solution of sodium fluoroborate (78 g., 1·3 mol.) in water (220 c.c.). This mixture was cooled in ice–water whilst a solution of sodium nitrite (40 g., 1·02 mol.) in water (80 c.c.) was added so that the temperature did not rise above 10°. The complete mixture was cooled to 0°, and the diazonium fluoroborate collected, and washed in turn with chilled aqueous sodium fluoroborate (30 c.c.), methanol (30 c.c.), and ether (*ca.* 700 c.c.) until the filtrate was colourless. The fluoroborate, when dried in a vacuum-desiccator over sodium hydroxide, formed a fine brown powder (126 g., 100%).

This fluoroborate (126 g., 1·05 mol.) was suspended in ethyl acetate (400 c.c.), in a 5-l. flask in the apparatus earlier described,[1] and about 20 drops of the required phenylphosphonous dichloride (96·7 g., 1 mol.) and purified cuprous chloride (3·5 g.) were added in turn: the remainder of the dichloride was then added dropwise. The preparation was continued as before (although the induction period was now much shorter), giving the phosphinic acid (71 g., 53%); this was purified by dissolution in aqueous sodium carbonate, which was boiled

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[5] Issleib and Tzschach, *Chem. Ber.*, 1959, **92**, 1118.

with charcoal, filtered, and cooled; the phosphinic acid, when precipitated by concentrated hydrŏchloric acid, had m. p. 147—147·5° (lit.,[1] 142—144°).

The *p*-methoxy-acid, when similarly prepared and purified, had m. p. 183·5—185·5° [lit.,[1] 184° (E.T.)] (yield 70%). It gave a *benzylthiouronium salt*, m. p. 158° (from water) (Found: N, 6·9. $C_{21}H_{23}N_2O_3PS$ requires N, 6·8%). o-*Methoxyphenylphenylphosphinic acid*, similarly prepared and purified, was obtained in 44% yield: a sample crystallised from acetone and dried at 114°/0·5 mm., had m. p. 214—216° (Found: C, 62·7; H, 5·0. $C_{13}H_{13}O_3P$ requires C, 62·9; H, 5·3%). It gave a *benzylthiouronium salt*, m. p. 176° (Found: N, 7·0. $C_{21}H_{23}N_2O_3PS$ requires N, 6·8%).

Ethyl m-*Methoxyphenylphenylphosphinate.*—Phosphorus pentachloride (52·2 g., 1·02 mol.) was added portionwise to a slurry of the powdered acid (60·7 g.) in dry benzene (100 c.c.) and phosphorus trichloride (79 c.c.); the warm clear solution was stirred for *ca.* 30 min. and then heated under reflux at 85—95° for 90 min. After the solution had been concentrated at 15 mm., the residue on distillation gave the *phosphinic chloride* (56·9 g., 87%), b. p. 171—174°/0·25 mm. (Found: C, 57·7; H, 5·1. $C_{13}H_{12}ClO_2P$ requires C, 58·5; H, 4·5%).

A solution of dry pyridine (18·55 g., 1·1 mol.) in dry benzene (25 c.c.) was added to a stirred solution of the chloride (56·8 g.) in benzene (30 c.c.), followed dropwise by a solution of absolute ethanol (10·8 g., 1·1 mol.) in benzene (25 c.c.); the mixture became hot, and pyridine hydrochloride was precipitated. The mixture was heated at 100° for 30 min., then cooled and filtered. The filtrate was washed with 2N-hydrochloric acid (50 c.c.) and with water (50 c.c.) and was then dried and fractionally distilled, giving the *ethyl ester* (51·2 g., 87% on the chloride), b. p. 158—164°/0·03 mm., n_D^{21} 1·5704 (Found: C, 65·0; H, 6·1. $C_{15}H_{17}O_3P$ requires C, 65·2; H, 6·2%).

Ethyl o-*Methoxyphenylphenylphosphinate.*—This ester was prepared as above, except that the clear solution after the addition of the pentachloride was boiled under reflux, cooled, and poured into light petroleum (b. p. 40—60°); the solid phosphinic chloride separated rapidly and, when collected, washed with light petroleum, and dried, had m. p. 78—82° (84%). Treatment of this chloride was also as described above, except that the complete mixture without heating was set aside overnight. The benzene was distilled from the filtrate, and the liquid residue when rubbed with light petroleum gave the solid *ethyl ester* (84%), having m. p. 78·5—80·5° after crystallisation from cyclohexane (Found: C, 65·2; H, 6·35%).

Purified *p*-ethoxyphenylphenylphosphinic acid was prepared as the *m*-methoxy-acid in 55% yield and had m. p. 148—149·5° (lit.,[1] 148—149°).

Reductions.—(A) m-*Methoxyphenylphenylphosphinic acid.* A stirred mixture of the powdered acid (122 g.) and dry tetrahydrofuran (400 c.c.) was cooled in ice–water under nitrogen, whilst powdered lithium aluminium hydride (15 g.) was slowly added. The mixture was boiled under reflux for 4 hr., becoming dark brown. About half the solvent was distilled off, and the stirred residue cooled in ice–water while undried ether (400 c.c.) was added, followed slowly by 20% aqueous potassium sodium tartrate (300 c.c.). After the heavy white precipitate had settled in the aqueous layer, the clear ether layer was blown out of the reaction flask under nitrogen, dried (Na_2SO_4), and distilled, giving a fraction (25 g.), b. p. 112—115°/0·2 mm. This fraction was initially used as the phosphine (I) for the preparation of esters of type (II). Later, its nuclear magnetic resonance spectrum (Table 1) showed the presence of the phosphine (I) and the methylphosphine (V): the proportions of these compounds were determined by cutting out the areas under the P–H and P–Me peaks in an enlarged tracing of the spectrum, weighing these portions, and allowing for the fact that there were three protons absorbing in the P–Me peaks and only one in the P–H peaks. The molecular ratio, secondary : tertiary phosphine was 1 : 0·28.

The cloudy aqueous layer from the reduction was treated with hydrogen peroxide (100-vol.) and the white solid, m. p. >200°, was collected and added to hot aqueous sodium carbonate. The mixture was filtered through Supercel to remove a gelatinous solid. The filtrate, on acidification, deposited the initial phosphinic acid (57·5 g.), m. p. and mixed m. p. 146—147·5°.

Repetition of the reduction, in which however the powdered phosphinic acid (90 g.) was added slowly to a stirred cooled mixture of lithium aluminium hydride (10 g.) in tetrahydrofuran (400 c.c.), gave a distillate (12·7 g.), b. p. 119—121°/0·35 mm.; the nuclear magnetic resonance spectrum showed that it was a mixture of the phosphine (I) and the methylphosphine (V) in the ratio of 1 : 0·39. Phosphinic acid (60 g.) was recovered as before.

(B) *Ethyl* m-*methoxyphenylphenylphosphinate.* This reduction was carried out as in (A), the hydride (9·5 g.) being added slowly to the cooled stirred solution of the ester (48 g.) in tetrahydrofuran (200 c.c.). Very little reaction occurred initially, but after addition of about half the hydride a very violent reaction occurred, with some loss of the foaming mixture, which had become deep orange. The complete mixture was worked up as before, but the addition of the tartrate gave a voluminous precipitate of aluminium hydroxide, and very slow separation of the aqueous and organic layers. Ether (70 c.c.) and water (50 c.c.) were therefore added, and the ether layer was separated (with difficulty), dried, and distilled, giving a fraction (1·7 g.), b. p. 128—133°/0·4 mm., which contained the phosphine (I) and the methylphosphine (V) in the ratio 1 : 5·2. This ratio may have been affected by partial oxidation of the phosphine (I) during the long period of separation.

Repetition of this reduction, in which the ester (45·5 g.) in tetrahydrofuran (100 c.c.) was slowly added to the hydride (6·8 g.), also in tetrahydrofuran (100 c.c.), gave no apparent reaction when half the ester had been added. Removal of the cooling-bath allowed the mixture ultimately to boil; the bath was then replaced, and addition of the ester and the working up continued as before. Even greater trouble was caused by the aluminium hydroxide, which did not dissolve even when sodium hydroxide was added until the final concentration was 35%. After 24 hr., most of the ether layer was separated; it afforded a fraction (7·6 g.), b. p. 120—124°/0·35 mm., which contained the phosphines (I) and (V) in the ratio 1 : 1·2.

(C) p-*Methoxyphenylphenylphosphinic acid.* This was carried out as in (A), the hydride (15 g.) being added to a slurry of the acid (140 g.) in tetrahydrofuran (400 c.c.). The final organic layer on distillation gave a fraction (18·2 g.), b. p. 118—121°/0·15 mm., which began to crystallise during the distillation. It was set aside overnight under nitrogen, and then had m. p. 22—27° (E.T.). The nuclear magnetic resonance spectrum of this fraction in benzene (5 c.c.) showed that it contained the secondary phosphine and the methylphosphine in the ratio 1 : 0·56.

(D) o-*Methoxyphenylphenylphosphinic acid.* The reduction of this acid (99 g.) in tetrahydrofuran (350 c.c.) by the hydride (13·8 g.) was carried out as in (A) and afforded a distillate (17·7 g.), b. p. 106—113°/0·25 mm., which contained the secondary and the tertiary phosphine in the ratio 1 : 0·99.

The by-products present in the aqueous layer from the hydrolysis were briefly investigated. 6N-Hydrochloric acid (1 l.) was added to the aqueous layer, and the rather gummy precipitate collected, dried, and extracted with cold ether. The insoluble residue, on being worked up, afforded the phosphinic acid (31·9 g.), m. p. 206—208°. The ether extract, on evaporation, yielded a solid (3·0 g.), m. p. 120—144°, which after several recrystallisations from ethyl acetate yielded o-*hydroxyphenylphenylphosphinic acid*, m. p. 156—157·5° (Found: C, 62·0; H, 4·75; P, 13·4. $C_{12}H_{11}O_3P$ requires C, 62·05; H, 4·8; P, 13·3%); it gave a *benzylthiouronium salt*, m. p. 180° (from water) (Found: N, 6·8. $C_{20}H_{21}N_2O_3PS$ requires N, 7·0%).

(E) m-*Ethoxyphenylphenylphosphinic acid.* The acid (24·5 g., m. p. 134—136°) in tetrahydrofuran (100 c.c.) was reduced with the hydride (3 g.), the mixture being boiled under reflux for 6 hr. The product gave a fraction (3·56 g.), b. p. 111—113°/0·2 mm. The nuclear magnetic resonance spectrum showed the peaks: τ P–H, 2·10, 7·52; τ O·CH_2·CH_3, 6·11, 6·29, 6·46, 6·63; τ O·CH_2·CH_3, 8·72, 8·89, 9·07. A sample of pure ethyldiphenylphosphine showed the peaks: τ P·CH_2·CH_3, 7·83, 7·98, 8·18, 8·34, 8·66, 8·82, 9·08, 9·23, 9·43. The spectrum of the fraction showed no significant peaks that could indicate any tertiary ethylphosphine; its infrared spectrum showed a medium band at 2280 and a very small broad band at 886 cm.$^{-1}$, these being typical values of a secondary phosphine.[2] The aqueous layer from the reduction on oxidation afforded the phosphinic acid (13 g.), m. p. 135—136°.

(F) p-*Ethoxyphenylphenylphosphinic acid.* The reduction of this acid (90 g.) with the hydride (10 g.) as in (E) gave a fraction (16·4 g.), b. p. 119—124°/0·2 mm. This was the pure secondary phosphine, for its spectrum showed peaks: τ P–H, 2·08, 7·51; τ O–CH_2·CH_3, 6·04, 6·20, 6·39, 6·57; τ O–CH_2·CH_3, 8·67, 8·83, 9·00. Its infrared spectrum showed a medium band at 2290 and a smaller band at 890 cm.$^{-1}$.[2] The aqueous layer afforded the phosphinic acid (50 g.), m. p. 148—149·5°.

Separation of the Secondary Phosphine (I) *and the Tertiary Phosphine* (V).—The mixed phosphines (24·4 g.), b. p. 112—115°/0·2 mm., prepared in experiment (A), were dissolved in benzene (50 c.c.) under carbon dioxide, and extracted with 5N-hydrochloric acid (2 × 100 c.c.). The benzene layer was separated, dried, and distilled, giving the pure phosphine (I) (15·7 g.), b. p. 115—117°/0·3 mm. (Found: C, 71·1; H, 5·8; P, 14·0. Calc. for $C_{13}H_{13}OP$: C, 72·2;

H, 6·1; P, 14·3%. Low carbon values were obtained with all secondary phosphines, owing to their rapid oxidation). The nuclear magnetic resonance spectrum showed the peaks: τ P–H; 2·06, 7·51: τ O–Me: 6·64: the infrared spectrum showed medium bands at 2280 and 895 cm.$^{-1}$.

The aqueous extract was basified, and then extracted with benzene (2 × 50 c.c.) and the combined extracts, when dried and distilled, gave the pure methylphosphine (V) (3·84 g.), b. p. 106—113°/0·1 mm., n_D^{22} 1·6173, $\nu_{max.}$ 878 cm.$^{-1}$. It was also identified by an improved conversion into the tribromogold compound, performed by adding sodium bromide to tetrachloroauric acid, each in aqueous-ethanolic solution, and then adding the ethanolic phosphine until the red solution became straw-coloured: bromine was added to the warmed solution to give complete precipitation of the gold compound, which was recrystallised from benzene, collected, washed with ether, and dried under reduced pressure over paraffin wax. The deep orange crystals had m. p. 147—147·5° (lit.,[1] 151—152°) (Found: C, 25·1; H, 2·1. Calc. for $C_{14}H_{15}AuBr_3OP$: C, 25·2; H, 2·3%).

A portion of this pure phosphine (I) (5·4 g.) in liquid ammonia (*ca.* 150 c.c.), cooled in acetone–carbon dioxide, was treated in turn with sodium (0·575 g., 1 equiv.) and with methyl iodide (3·7 g., 1·05 mol.) in ether (25 c.c.) as previously described.[1] After working up, distillation of the residue gave the pure methylphosphine (V) (3·3 g., 57%), b. p. 114—117°/0·3 mm., n_D^{22} 1·6173 (Found: C, 73·1; H, 6·9. Calc. for $C_{14}H_{15}OP$: C, 73·0; H, 6·6%), τ O–Me 6·57, τ P–Me 8·47, 8·57 (no peaks attributable to P–H).

In the *para*-series, the solid mixture of the secondary phosphine (as I) and the methylphosphine (as V) obtained in experiment (C) was dissolved in benzene and treated as described above. The benzene solution, on extraction with acid and distillation, gave the pure secondary phosphine, b. p. 116—119°/0·4 mm., m. p. 35·5—38° (E.T., the tube being first filled with nitrogen) (Found: C, 70·5; H, 6·0; P, 14·5. Calc. for $C_{13}H_{13}OP$: C, 72·2; H, 6·1; P, 14·3%). The compound in benzene solution showed the peaks: τ P–H, 2·06, 7·50; τ O–Me, 6·65. On exposure to air the crystals rapidly softened and melted, probably by partial oxidation to the phosphine oxide and the consequent fall in m. p.

The acid extracts, treated as above, gave the pure methylphosphine (as V), b. p. 112—117°/0·2 mm., n_D^{20} 1·6204, m. p. 16·2—17·5°, $\nu_{max.}$ 876s cm.$^{-1}$ (no band in the 2280 cm.$^{-1}$ region).

This methylphosphine gave a methiodide, m. p. 134—135° (S.T.) (lit.,[1] 135°), and a benzylphosphonium bromide which, treated with aqueous sodium picrate, gave *benzyl*-p-*methoxyphenylmethylphenylphosphonium picrate*, yellow, m. p. 93·5—95° (from ethanol) (Found: C, 58·9; H, 4·2; N, 7·8. $C_{27}H_{24}N_3O_8P$ requires C, 59·0; H, 4·4; N, 7·6%).

The pure methylphosphine was also prepared by treating the above mixture of secondary phosphine (as I) and methylphosphine (as V) in ammonia with sufficient sodium and methyl iodide to methylate the former; the phosphine (as V) had b. p. 116—119°/0·35 mm., n_D^{21} 1·6205 (Found: C, 72·8; H, 6·8. Calc. for $C_{14}H_{15}OP$: C, 73·0; H, 6·6%): its spectrum showed peaks at τ O–Me 6·54, τ P–Me 8·48, 8·58.

In the *ortho*-series, the mixture (30·5 g.), b. p. 106—113°/0·25 mm., of the secondary phosphine (as I) and the methylphosphine (as V) obtained as in Experiment (D), was dissolved in benzene (60 c.c.) and extracted with 6N-hydrochloric acid, from which the hydrochloride of the methylphosphine rapidly crystallised. Treatment of the benzene solution as before afforded the pure o-*methoxyphenylphenylphosphine* (as I) (11·6 g.), b. p. 116—118°/0·3 mm. (Found: P, 14·15. $C_{13}H_{13}OP$ requires P, 14·3%). The spectrum showed peaks at τ P–H 1·87, 7·47, but a complete absence of the doublet τ P–Me 8·48, 8·59.

Basification of the chilled acid layer dissolved the crystals and deposited the o-*methoxyphenylmethylphenylphosphine* (as V) as an oil (11·0 g.) which rapidly crystallised; a sample after sublimation had m. p. 45—46° (Found: C, 72·8; H, 6·35. $C_{14}H_{15}OP$ requires C, 73·0; H, 6·6%). A spectrum taken on the phosphine before crystallisation showed the peaks: τ P–Me, 8·48, 8·59: peaks at τ P–H 1·87, 7·47 were absent. Its infrared spectrum showed a sharp band at 876 cm.$^{-1}$.

This phosphine gave a pale yellow *aurous bromide derivative*, m. p. 192—194° (from butan-1-ol) (Found: C, 33·5; H, 3·4. $C_{14}H_{15}AuBrOP$ requires C, 33·2; H, 3·0%), and an *auric tribromide derivative*, m. p. 156·5—157·5°, deposited from benzene as deep red crystals which became yellowish-orange when washed with ether (Found: C, 25·4; H, 2·5. $C_{14}H_{15}AuBr_3OP$ requires C, 25·2; H, 2·3%). Oxidation of the phosphine in acetone with hydrogen peroxide (100-vol.) gave the *phosphine oxide*, m. p. 129—130° (from ethyl acetate) (Found: C, 68·1; H, 5·9. $C_{14}H_{15}O_2P$ requires C, 68·2; H, 6·1%).

Preparation of Carboxylic Esters.—The following pure esters were prepared from the mixture, b. p. 112—115°/0·2 mm., of secondary and tertiary phosphines, obtained in Experiment (A), in order to investigate their hydrolysis.

Ethyl β-(m-*methoxyphenylphenylphosphino*)*propionate* (II; R = Et). (i) Sodium (1·52 g.) was added slowly to a solution of the mixture (14·2 g.) in liquid ammonia (*ca.* 150 c.c.) cooled in acetone–carbon dioxide, the initially colourless solution becoming reddish-orange; a little more sodium was added to give the solution a blue colour persisting for 30 min. Ethyl β-bromopropionate (12·0 g.) in dry ether (50 c.c.) was added slowly, followed by more ether (80 c.c.), and the ammonia was then allowed to boil off. The residual liquid was mixed with water (50 c.c.) and blown over under nitrogen pressure into a separatory funnel; the ether layer was collected and dried, and the solvent was removed. The residual ester was repeatedly refractionated, until the refractive index was constant, giving the pure ester (II; R = Et) (8·15 g.), b. p. 173—175°/0·3 mm., n_D^{22} 1·5820 (Found: C, 68·2; H, 6·7. Calc. for $C_{18}H_{21}O_3P$: C, 67·3; H, 6·7%), $\nu_{max.}$ 1732s (C=O) and 895w,br cm.$^{-1}$.

This preparative method appears to remove the methylphosphine (possibly as a quaternary salt with the bromo-ester), for only traces of this phosphine could usually be detected in the foreruns. Nevertheless, we find that, for the preparation of the propionate ester, the acrylic ester method (below) is much quicker, gives a product which on distillation leaves much less black residue, and gives an initial distillate that requires less fractionation; the pure propionate is usually obtained in higher yield than by the sodium–ammonia method.

(ii) Reaction of pure ethyl acrylate (4·9 g.) and the phosphine mixture (10·5 g.), as previously described,[1] followed by repeated fractionation of the product, gave the pure ethyl ester (10·1 g.), b. p. 171—175°/0·3 mm., n_D^{22} 1·5824. The methylphosphine had been eliminated in the earlier lower-boiling fractions, where it was identified by a strong band at 878 cm.$^{-1}$ and as the tribromogold derivative, m. p. and mixed m. p. 146·5—147·5°.

Methyl β-(m-*methoxyphenylphenylphosphino*)*propionate* (II; R = Me). (i) Preparation (i) above was repeated with methyl β-bromopropionate, and considerable refractionation of the product afforded the methyl ester, b. p. 174°/0·5 mm., n_D^{20} 1·5920 (Found: C, 67·1; H, 6·6. Calc. for $C_{17}H_{19}O_3P$: C, 67·6; H, 6·3%), $\nu_{max.}$ 1727s (C=O) and 872w,br cm.$^{-1}$.

(ii) Use of methyl acrylate, as in (ii) above, gave a product which after extensive fractionation gave the pure ester (II; R = Me), b. p. 173—179°/0·45 mm., n_D^{20} 1·5932 (Found: C, 67·3; H, 6·7%). The methylphosphine (as V) was identified in the earlier fractions as before.

It has been recorded that the methyl ester (II; R = Me) gives a red tribromogold derivative, m. p. 94—95° (E.T.),[1] and that the ester, when heated under nitrogen in a sealed tube at 100° for 5 hr., is apparently unchanged but gives a yellowish-orange tribromogold derivative, m. p. 113° (E.T.). We find that the ester gives a tribromogold derivative which separates from benzene as deep red crystals; these become orange when washed with ether; even after thorough drying in a vacuum over paraffin shavings, consistent m. p.s can be obtained only if the derivative is heated in a tube evacuated to 1 mm. The compound then has m. p. 92—94°, both before and after the ester has been heated as described above (Found: C, 27·6; H, 2·65. Calc. for $C_{17}H_{19}AuBr_3O_3P$: C, 27·6; H, 2·6%).

Hydrolysis.—This process was investigated with great care, particularly to detect any methylphosphine (V) which might have been formed: all operations were carried out under nitrogen.

(i) *Ethyl ester* (II; R = Et). The pure ester (1·017 g.) was added under nitrogen to a solution (10 c.c.), prepared from sodium hydroxide (10 g.) in water (35 c.c.) and ethanol (15 c.c.). The mixture was boiled under reflux for 5 hr., and the ethanol removed under reduced pressure. The residual solution was cooled, diluted with freshly boiled water (10 c.c.), and extracted with ether (2 × 10 c.c.) and benzene (10 c.c.). The combined dried extracts, when evaporated under reduced pressure, afforded only a pale yellow, semi-solid residue (42 mg.).

The aqueous solution was just acidified with hydrochloric acid and extracted with ether (2 × 10 c.c.). The dried extract when evaporated, with final warming under reduced pressure to *ca.* 50°, gave a colourless syrup (770 mg.), undoubtedly β-(*m*-methoxyphenylphenylphosphino)-propionic acid (II; R = H); it gave the *benzylthiouronium salt,* m. p. 134—135° (from water) (Found: C, 63·15; H, 6·3; N, 6·15. $C_{24}H_{27}N_2O_3PS$ requires C, 63·4; H, 6·0; N, 6·2%). The acid could not be sublimed or obtained crystalline; its infrared spectrum showed a strong C=O band at 1705 cm.$^{-1}$ and broad absorption in the 3400—2400 cm.$^{-1}$ region, indicating absence of zwitterion formation.

A mixture of the ester (4·78 g.) and 20% aqueous sodium hydroxide (25 c.c.) was heated to 120° and ethanol (5 c.c.) then added to give a clear solution; this was boiled for 5 hr. and, when worked up as above, gave the neutral yellow residue (35 mg.) and the syrupy acid (2·74 g.), identified as before. Other variations of the alkaline hydrolysis gave the same result, the insignificant amounts of the yellow residue being the only by-product isolated.

The pure ethyl ester (4·52 g.) and 10% hydrochloric acid (25 c.c.) were boiled under reflux for 9 hr., a clear solution being obtained in 15 min. The cold solution was made alkaline with aqueous sodium hydroxide, an oil which separated at the neutral point rapidly redissolving. This alkaline solution was extracted with benzene (20 c.c.) and ether (30 c.c.), and the combined dried extracts, when evaporated at reduced pressure, left a yellow oil (200 mg.), identified by its infrared spectrum as the unchanged ester.

The alkaline solution was made slightly acid and extracted with benzene (2 × 30 c.c.). The dried extract, when evaporated, yielded the colourless syrupy acid (3·54 g.), which gave the benzylthiouronium salt, m. p. and mixed m. p., 132·5—133·5°. The acid was further identified by oxidation in alkaline solution with hydrogen peroxide (100-vol.), to give 2-carboxyethyl-(*m*-methoxyphenyl)phenylphosphine oxide, m. p. 156—157° (from water), unchanged by admixture with the oxide earlier obtained by the oxidation of the ethyl ester followed by hydrolysis.[1] This phosphine oxide gave a benzylthiouronium salt having m. p. 92—94° after four recrystallisations from water (Found: C, 61·05, 5·8. Calc. for $C_{24}H_{27}N_2O_4PS$: C, 61·25; H, 5·8%); the two forms, m. p. 84° and 125—126° earlier recorded,[1] were not obtained.

(ii) *Methyl ester* (II; R = Me). The similar alkaline hydrolysis of this ester (0·924 g.) afforded solely the neutral product (29 mg.) and the syrupy acid (694 mg.), identified as before.

2-*Cyanoethyl*-(m-*methoxyphenyl*)*phenylphosphine* (III). Freshly distilled vinyl cyanide (2·9 g.) was added dropwise to a mixture of acetic acid (8 c.c.) and the reduction mixture (11·6 g.), b. p. 112—115°/0·2 mm., obtained in Experiment (A). The mixture was heated at 100° for 10 min., cooled, diluted with more cyanide (2·9 g.), and heated again for 1 hr., and the excess of vinyl cyanide and acetic acid were removed at 15 mm. The viscous residue was repeatedly refractionated until the pure phosphine (III), b. p. 159—162°/0·002 mm., n_D^{19} 1·6130, was obtained (Found: C, 71·2; H, 5·9; N, 5·4. Calc. for $C_{16}H_{16}NOP$: C, 71·4; H, 6·0; N, 5·2%); the infrared spectrum showed no band at 878 cm.$^{-1}$.

An intermediate fraction, b. p. 124·5—126·5°/0·3 mm., contained the methylphosphine (V), identified by a sharp band at 878 cm.$^{-1}$ and by isolation of the tribromogold compound, m. p. and mixed m. p. 147·5—148°.

The pure nitrile (III) (5·33 g.), 20% aqueous sodium hydroxide (25 c.c.), and ethanol (10 c.c.) were boiled under reflux under nitrogen for 5½ hr., then worked up as in the alkaline hydrolysis of the ethyl ester (II; R = Et); they yielded the neutral yellow semi-solid product (57 mg.) and the syrupy acid (II; R = H) (5·43 g.), identified by conversion into the benzylthiouronium salt, m. p. and mixed m. p. 133—134·5°, and by oxidation to the phosphine oxide, m. p. and mixed m. p. 157—158°.

The secondary phosphine (I) (7·2 g.), which had been purified by the acid-extraction method, was treated with methyl acrylate (2 × 2·9 g., 2 mol.) as in Experiment (ii) (p. 1163). The product when once distilled at 0·4 mm. gave the fractions: (*a*) b. p. to 172°, n_D^{21} 1·5773 (0·3 g.); (*b*) the pure methyl ester (II; R = Me), b. p. 172—174°, n_D^{21} 1·5923 (8·5 g., 84%). The absence of a band in the 878 cm.$^{-1}$ region in the infrared spectrum of fraction (*a*) showed that no methylphosphine (V) had been formed.

For the preparation of the following ethyl and methyl esters, the *m*-methoxyphenylphenylphosphine (I), b. p. 112—115°/0·2 mm., purified by the acid-extraction method, was used.

A solution of the phosphine (I) (10·4 g.) in liquid ammonia (*ca.* 150 c.c.) was treated with sodium (1·11 g., 1 equiv.) and ethyl bromoacetate (8·1 g., 1·01 mol.) in ether (50 c.c.). The product, when worked up as before, gave, after two fractional distillations, the pure ethyl (*m*-methoxyphenylphenylphosphino)acetate (IV; R = Et) (4·9 g.), b. p. 162—164°/0·8 mm., n_D^{22} 1·5902 (Found: C, 67·5; H, 6·65. Calc. for $C_{17}H_{19}O_3P$: C, 67·6; H, 6·3%). The infrared spectrum showed a strong C=O band at 1728 and a weak band at 872 cm.$^{-1}$. A tribromogold derivative of this ester could not be isolated.

Use of the pure phosphine (I) (11·0 g.) in ammonia (150 c.c.) with sodium (1·17 g., 1 equiv.) and methyl bromoacetate (7·85 g., 1·01 mol.) gave a crude product which after three fractional distillations gave the methyl ester (IV; R = Me) (1·97 g.), b. p. 160—164°/0·6 mm. n_D^{22} 1·6000

(Found: C, 67·3; H, 6·0. Calc. for $C_{16}H_{17}O_3P$: C, 66·65; H, 5·9%). The infrared spectra of the intermediate fractions showed that a compound absorbing in the 2300—2400 cm.$^{-1}$ region was being steadily removed during the distillations: that of the final ester showed a strong C=O band at 1733 and a medium band at 881 cm.$^{-1}$. The ester did not give a tribromogold derivative: the product, m. p. 143° (E.T.), recorded earlier was presumably an impure derivative of the phosphine (V).

Hydrolyses.—(*a*) *Ethyl Ester* (IV; R = Et). (i) A mixture of the ester (1·41 g.) and 20% aqueous-ethanolic sodium hydroxide (15 c.c.) [prepared from the hydroxide (10 g.), water (35 c.c.), and ethanol (15 c.c.)] was boiled under reflux in nitrogen for 5 hr. The mixture formed two approximately equal layers throughout the boiling. The ethanol was removed under reduced pressure, and the cold mixture was diluted with water (20 c.c.) and extracted with benzene (2 × 10 c.c.). The united, dried, filtered extracts were evaporated under reduced pressure, leaving a cloudy yellow residue (44 mg.). The aqueous alkaline layer was just acidified with 5N-hydrochloric acid and extracted with benzene as above. The united extracts, treated as before, left a syrupy residue (1·25 g., 97%) of (m-*methoxyphenyl*)*phenylphosphinoacetic acid* (IV; R = H), m. p. 99—100·5° (E.T.) (after solidification and crystallisation from aqueous ethanol) (Found: C, 65·7; H, 5·5. $C_{15}H_{15}O_3P$ requires C, 65·7; H, 5·5%); it gave a benzylthiouronium salt, m. p. 128—129° from water (lit.,[1] 129—130°).

(ii) A mixture of the ester (3·03 g.) and 10% hydrochloric acid (15 c.c.) was boiled under reflux in nitrogen for 9 hr., some liquid remaining undissolved. The cold product was made alkaline and extracted with benzene (2 × 10 c.c.). The aqueous alkaline layer was made slightly acid and similarly extracted. The extract from the alkaline solution, when dried and evaporated as above, left a fairly mobile pale yellow residue (1·47 g.), the infrared spectrum of which showed a medium band at 880 cm.$^{-1}$, and a C=O band relatively less intense than that of the original ester. A portion of this residue readily gave a copious deposit of the tribromogold derivative, m. p. 143·5—144° (from benzene with washing by ether), mixed m. p. with the authentic derivative of the methylphosphine (V), 143—143·5°. The extract from the acid solution, worked up as usual, gave the syrupy phosphino-acetic acid (IV; R = H) (0·80 g., 29%) which, recrystallised as before, had m. p. 98—100° (E.T.), mixed m. p. 97·5—99·5° (E.T.).

(*b*) *Methyl ester* (IV; R = Me). In view of the clear result obtained above by alkaline hydrolysis of the ethyl ester, the methyl ester (1·68 g.) was subjected only to the above acid hydrolysis. The extract from the solution when made alkaline again on evaporation left a mobile, pale yellow residue (0·85 g.), the infrared spectrum of which showed a weak band at *ca.* 2330 cm.$^{-1}$ and a medium band at 880 cm.$^{-1}$, but no C=O absorption. It gave the tribromogold derivative of the phosphine (V), m. p. and mixed m. p. 144—144·5°. The extract from the acidified solution left a residue of the acid (IV; R = H) (0·40 g., 25%), having m. p. 98·5—100·5° (E.T.) after recrystallisation.

(*c*) *Acid* (IV; R = H). A mixture of the acid (1·55 g.) and 10% hydrochloric acid was boiled as before for 9 hr., some molten acid remaining undissolved. The cold mixture was basified and extracted with benzene (2 × 100 c.c.); the washed and dried extract, when evaporated, left a mobile, pale yellow residue (0·79 g.). A sample readily gave the tribromogold complex of the methylphosphine (V), m. p. and mixed m. p. 144—145° (Found: C, 25·0; H, 2·2%). The infrared spectrum of the residue showed bands at *ca.* 2330w and *ca.* 880 cm.$^{-1}$; hence the residue may also have contained a secondary phosphine or phosphine oxide, the oxidation of which would have accounted for the earlier isolation of the phosphinic acid.[1] The alkaline solution, when just acidified and extracted, yielded the acid (IV; R = H) (0·52 g.), which crystallised when seeded. The earlier failure to effect this decarboxylation was based on 2 hours' boiling.[1]

The infrared spectrum of the acid showed broad absorption in the region 3200—2200 cm.$^{-1}$, typical of a carboxylic acid, and a strong C=O band at 1692 cm.$^{-1}$, a much higher value than that of a carboxylate ion; zwitterion formation therefore does not occur.

In the *ortho*-series, the reduction mixture (19·9 g.), b. p. 106—113°/0·25 mm., obtained in Experiment (D), was treated with pure ethyl acrylate (13·7 g.), and the product was heated under reflux for 45 min., then distilled at 0·35 mm.; this removed the excess of acrylate and gave fractions: (*a*) b. p. 73—75° (39 g.); (*b*) b. p. 131—141° (14·5 g.); (*c*) b. p. 158—173° (13·3 g.). Fraction (*a*) was polymerised acrylate. Fraction (*c*), when twice refractionated, gave pure *ethyl* β-(o-*methoxyphenylphenylphosphino*)*propionate*, b. p. 166—168°/0·25 mm., n_D^{20} 1·5820 (4·6 g.) (Found: C, 68·1; H, 6·9. $C_{18}H_{21}O_3P$ requires 68·3; H, 6·7%). Fraction (*b*) on redistillation gave a fraction, b. p. 119—122°/0·3 mm., which separated into two layers. Treatment with cold light petroleum (b. p. 40—60°) extracted the upper layer, and refractionation of the extract gave the methylphosphine (as V), b. p. 119—122°/0·25 mm., m. p. 45—46·5° (from the light petroleum).

The pure ethyl ester (3·88 g.), when subjected to the normal alkaline hydrolysis, gave solely β-(o-*methoxyphenylphenylphosphino*)*propionic acid* (2·81 g., 80%), m. p. 114·5—116·5° (from cyclohexane) (Found: C, 66·35; H, 6·0. $C_{16}H_{17}O_3P$ requires C, 66·7; H, 5·9%).

A solution in warm aqueous sodium hydroxide, when oxidised with hydrogen peroxide, cooled, and acidified, gave the 2-*carboxyethyl*-(o-*methoxyphenyl*)*phenylphosphine oxide*, m. p. 155·5—157° (Found: C, 63·0; H, 5·65. $C_{16}H_{17}O_4P$ requires C, 63·2; H, 5·65%).

The ethyl ester, when heated under nitrogen in a sealed tube at 160° for 8 hr., had n_D^{20} 1·5845 and an unchanged infrared spectrum.

o-*Methoxyphenylphenylphosphine Oxide.*[6] Lithium aluminium hydride (8·0 g.) was added in 1 hr. to a stirred slurry of *o*-methoxyphenylphenylphosphinic chloride (56·3 g.) in ether (400 c.c.) cooled in ice–salt. Stirring at −19° was then continued for 1½ hr. and followed by addition, at 8—10°, of water (80 c.c.) and 15% sulphuric acid (500 c.c.). After filtration, the aqueous layer was extracted with benzene (2 × 100 c.c.), which was added to the ether layer, washed with 10% aqueous sodium carbonate and with water, dried, concentrated to *ca.* 150 c.c., and poured into light petroleum (b. p. 40—60°) (400 ml.). The crystalline deposit (24·4 g.) was collected and extracted four times with cyclohexane (350 c.c., the filtrate from each extraction being used again). The *phosphine oxide* (10·8 g., 22%) had m. p. 102—104° (Found: C, 67·4; H, 5·9. $C_{13}H_{13}O_2P$ requires C, 67·2; H, 5·6%).

Reduction. The phosphine oxide (8·0 g.) in tetrahydrofuran (50 c.c.) was treated with lithium aluminium hydride (1·3 g., 1 mol.), and the product worked up as in the reduction of the phosphinic acid. Distillation gave a fraction (3·6 g.), b. p. 113—114°/0·05 mm., the nuclear magnetic resonance spectrum of which showed that it contained the secondary phosphine (as I) and the methylphosphine (as V) in the ratio 1 : 5·5.

The *o*-methoxyphenylphenylphosphine (10·0 g.), b. p. 116—118°/0·3 mm., which had been rigorously purified by the acid-extraction treatment, was similarly treated in tetrahydrofuran (50 c.c.) with lithium aluminium hydride (0·9 g., 0·5 mol.). Distillation gave a fraction (6·1 g.), b. p. 118—120°/0·05 mm., which contained the secondary phosphine and the methylphosphine in the ratio 1 : 3·5.

Diphenylphosphine.—This was prepared by Chatt and Hart's method,[7] triphenylphosphine (25 g.) in tetrahydrofuran (75 c.c.) being treated with lithium (1·33 g., 2 atom-equiv.) with subsequent hydrolysis. The phosphine (12·2 g., 69%) had b. p. 95—98°/0·6 mm.; its nuclear magnetic spectrum showed τ (P–H) 2·08, 7·53.

The phosphine (3·0 g.) was added to a suspension of lithium aluminium hydride (1 g.) in tetrahydrofuran (50 c.c.) under nitrogen, giving a deep orange solution. Anisole (3·5 g., 2 mol.) in tetrahydrofuran (15 c.c.) was added and the mixture boiled under reflux for 4 hr., the colour fading considerably. A portion (50 c.c.) of the solvent was distilled off and the cold residue treated in turn with ether (50 c.c.), water, and 15% aqueous sodium hydroxide. Distillation of the dried organic layer gave methyldiphenylphosphine (1·65 g.), b. p. 98—100°/0·35 mm., n_D^{20} 1·6245. It was identified by (*a*) its nuclear magnetic resonance spectrum (τ P–Me, 8·54, 8·64; no P–H group), (*b*) identical infrared spectra of the sample and of an authentic specimen, in particular with a band at 877 cm.$^{-1}$, (*c*) n_D^{20} 1·6241 of the authentic specimen, and (*d*) reaction with benzyl bromide to give the phosphonium bromide, m. p. 248—249°, which with sodium picrate (both in aqueous solution) gave *benzylmethyldiphenylphosphonium picrate*, yellow needles, m. p. 118—119° (from ethanol) (Found: C, 60·3; H, 4·4; N, 8·35. $C_{26}H_{22}N_3O_7P$ requires C, 60·1; H, 4·3; N, 8·1%). Mixed m. p.s with the bromide and picrate prepared from the authentic sample were 247·5—249·5° and 117·5—118·5°, respectively.

This experiment was repeated, with, however, diphenylphosphine (6·4 g.), the hydride (2 g.) in tetrahydrofuran (85 c.c.), and phenetole (8·4 g., 2 mol.), with boiling for 6 hr. Distillation, with heating to *ca.* 200° to ensure collection of any ethyldiphenylphosphine, gave a total fraction (2·78 g.), b. p. 78—130°/0·2 mm., some phenetole contaminating the first portion. The nuclear magnetic resonance showed the peaks: τ P–H, 2·10, 7·53; τ $O{\cdot}CH_2{\cdot}CH_3$, 6·08, 6·25,

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[6] Based on the method of Williams and Hamilton, *J. Amer. Chem. Soc.*, 1952, **74**, 5418.

[7] Chatt and Hart, *J.*, 1960, 1378; modification of the method of Gilman and Wittenburg, *J. Org. Chem.*, 1958, **23**, 1063.

6·42, 6·60; τ $O{\cdot}CH_2{\cdot}CH_3$, 8·71, 8·88, 9·05. Hence the distillate contained the secondary phosphine and some phenetole, but no ethyldiphenylphosphine (for spectrum of the last see p. 1161).

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