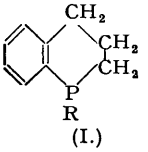
91. *The Preparation of* 1-*Substituted* 1 : 2 : 3 : 4-*Tetrahydrophosphinolines and* 2-*Substituted* 1 : 2 : 3 : 4-*Tetrahydro*isophosphinolines.

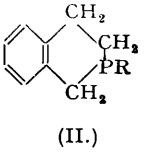
By M. H. Beeby and Frederick G. Mann.

The syntheses of 1-ethyl-1 : 2 : 3 : 4-tetrahydrophosphinoline and of 2-ethyl-1 : 2 : 3 : 4-tetrahydro*iso*phosphinoline are described by methods which can undoubtedly be applied to many other alkyl(or aryl)-substituted derivatives. The *iso*phosphinoline is both more basic and more readily oxidised than the phosphinoline isomeride.

It is noteworthy that although 1-substituted 1 : 2 : 3 : 4-tetrahydrophosphinolines (I) and 2-substituted 1 : 2 : 3 : 4-tetrahydro*iso*phosphinolines (II) have not hitherto been recorded, their arsenic analogues have been prepared and investigated in detail. Thus Burrows and Turner (*J.*, 1921, **119**, 430) have shown that methyl-3-phenylpropylchloroarsine, $Ph{\cdot}[CH_2]_3{\cdot}AsMeCl$, undergoes ready cyclisation by aluminium chloride to 1 : 2 : 3 : 4-tetrahydro-1-methylarsinoline (III). Holliman and Mann (*J.*, 1943, 547) and Beeby, Cookson, and Mann (*J.*, 1950, 1917) have shown that *o*-2-bromoethylbenzyl bromide, $Br{\cdot}CH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2Br$, reacts with phenyldichloroarsine in the presence of sodium, and also with phenylarsinebis-(magnesium bromide), $Ph{\cdot}As(MgBr)_2$, to give 1 : 2 : 3 : 4-tetrahydro-2-phenyl*iso*arsinoline (as II). Holliman and Mann showed that their reaction when applied to phenyldichlorophosphine gave only traces of the tetrahydro*iso*phosphinoline, which was characterised solely as the crystalline quaternary salt. Later, Holliman and Mann (*J.*, 1947, 1634) developed an alternative synthesis of 2 : 2-disubstituted 1 : 2 : 3 : 4-tetrahydro*iso*phosphinolinium salts: since, however, for the stereochemical purpose of their investigation the 2-substituents were both aryl groups, these



(I.)



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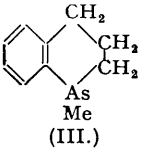


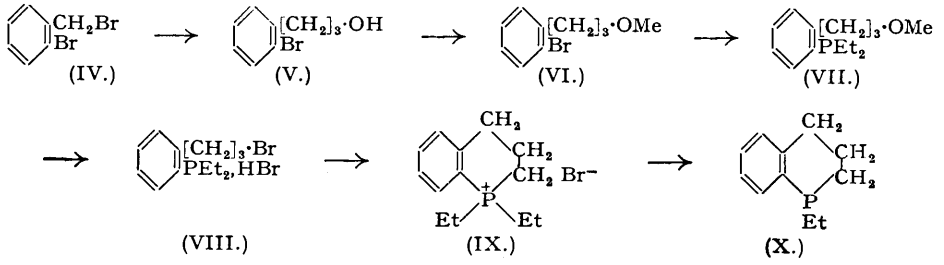
(III.)

compounds did not lend themselves to the preparation of the cyclic tertiary phosphines. The object of the present investigation was therefore to devise practicable syntheses of tertiary phosphines of types (I) and (II).

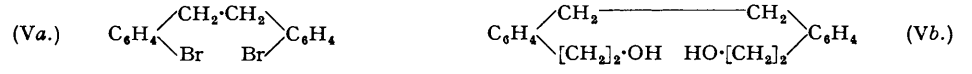
Our initial experiments on the preparation of the phosphinoline showed that an approach similar to that of Burrows and Turner's synthesis of the arsenic analogue was not apparently practicable. The latter workers prepared their methyl-3-phenylpropylchloroarsine by the thermal decomposition of dimethyl-3-phenylpropylarsine dichloride, $Ph{\cdot}[CH_2]_3{\cdot}AsMe_2Cl_2$, involving loss of methyl chloride, a reaction which has subsequently been widely used with other compounds of similar type. We found, however, that the conversion of diethyl-3-phenylpropylphosphine, $Ph{\cdot}[CH_2]_3{\cdot}PEt_2$, into the pure dichloride was difficult (we did not effect it), and the crude dichloride did not undergo the required decomposition; moreover, the crystalline phosphine dibromide, when heated, did not afford the required bromophosphine. It is probable however that if the chlorophosphine, $Ph{\cdot}[CH_2]_3{\cdot}PEtCl$, could be prepared, the desired cyclisation could then be achieved.

An alternative synthesis was therefore developed, which was based essentially on the fact that many quaternary ethylphosphonium chlorides undergo smooth thermal decomposition, an ethyl group breaking off as ethylene with the formation of the tertiary phosphine hydrochloride. This reaction proceeds particularly well when there are two ethyl groups in the phosphonium chloride, but secondary reactions may occur if benzyl or certain other groups are present (Collie, *J.*, 1888, **53**, 714; Meisenheimer *et al.*, *Annalen*, 1926, **449**, 213). The starting material of our successful synthesis was *o*-bromobenzyl bromide (IV), prepared by Holliman and Mann's modification (*loc. cit.*) of Kenner and Wilson's method (*J.*, 1927, 1110). This bromide, when suitably treated with one atomic proportion of magnesium, gave *o*-bromobenzylmagnesium bromide, which then reacted with ethylene oxide to give 3-*o*-bromophenylpropan-1-ol (V). The successful preparation and manipulation of this Grignard reagent required considerable care. The preparation was carried out under an atmosphere of nitrogen, otherwise oxidation readily occurred with the subsequent formation of *o*-bromobenzyl alcohol. Moreover a number of side reactions occurred, and among the by-products were identified

2 : 2′-dibromodibenzyl (V*a*) and 2 : 2′-di-(2-hydroxyethyl)dibenzyl (V*b*), while a low-boiling fraction which was apparently ethylene bromohydrin was also obtained. Since however the required propanol (V) was obtained in 47% yield, the method was satisfactory. The propanol

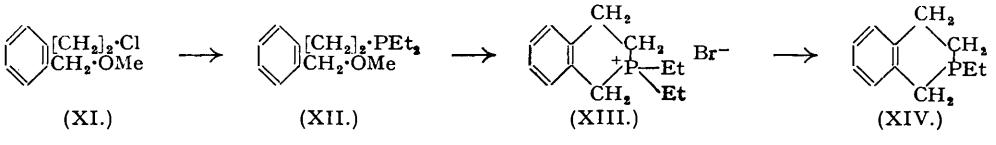


(V) was then converted by phosphorus tribromide into the corresponding bromide, which on treatment with sodium methoxide gave 3-*o*-bromophenylpropyl methyl ether (VI). The bromine atom in this compound does not react readily with magnesium; a Grignard reagent was however successfully prepared by the entrainment method, *i.e.*, by treating an ethereal mixture of the bromo-ether (VI) and ethyl bromide with specially activated magnesium. Diethylchlorophosphine, prepared by an extension of Kharasch, Jensen, and Weinhouse's tetraethyl-lead method (*J. Org. Chem.*, 1949, **14**, 429), reacted with this Grignard reagent to give diethyl-(*o*-3-methoxypropylphenyl)phosphine (VII), a liquid which was characterised by the preparation of its crystalline methopicrate and its dibromopalladium derivative, $[(C_{14}H_{23}OP)_2PdBr_2]$.



When (VII) in acetic acid was boiled with hydrogen bromide, the methoxy-group was replaced by bromine. There is little doubt, however, that no appreciable cyclisation occurred at this stage, and that the product was almost solely the hydrobromide of *o*-3-bromopropylphenyl-diethylphosphine (VIII), for the residue, after evaporation of the acetic acid, was entirely soluble in water : neutralisation with sodium hydrogen carbonate, however, liberated an oil (the free phosphine) which was extracted with chloroform, in which solvent an exothermic reaction rapidly occurred. This reaction was almost certainly the cyclisation to 1 : 1-diethyl-1 : 2 : 3 : 4-tetrahydrophosphinolinium bromide (IX) which then promptly dissolved in the aqueous layer, leaving the chloroform layer almost solute-free. Addition of sodium picrate solution to this aqueous layer precipitated the phosphinolinium picrate, which after purification was converted by the usual method into the quaternary chloride (as IX).

This chloride without purification was then subjected to thermal decomposition under reduced pressure, whereby a distillate consisting of 1-ethyl-1 : 2 : 3 : 4-tetrahydrophosphinoline (X) and its crystalline hydrochloride was obtained. This mixture ultimately furnished the pure liquid phosphine, b. p. 141—143°/18 mm., in 78% yield, further characterised as the crystalline methiodide, methopicrate, and dibromopalladium derivative, $[(C_{11}H_{15}P)_2PdBr_2]$.



In the *iso*phosphinoline series, our synthesis has been an extension of the earlier work of Holliman and Mann (*loc. cit.*). *o*-2-Chloroethylbenzyl methyl ether (XI) was converted into a Grignard reagent, which with diethylchlorophosphine gave diethyl-2-*o*-methoxymethylphenylethylphosphine (XII). This compound, like its isomeride (VII), was then cyclised by treatment in boiling acetic acid solution with hydrogen bromide. In this case, however, cyclisation to the quaternary phosphonium bromide (XIII) appeared to occur almost immediately after the concentrated acidic solution was neutralised with sodium hydrogen carbonate. The addition of sodium picrate to the aqueous layer then precipitated 2 : 2-diethyl-1 : 2 : 3 : 4-tetrahydro-*iso*phosphinolinium picrate (as XIII). This difference in the two series is not surprising, for

the bromomethyl group formed by the action of the hydrogen bromide on (XII) would be more reactive than the 3-bromopropyl group similarly formed from (VII); moreover the trialkylphosphine group in (XII) would also be more reactive than the aryldialkylphosphine group in (VII).

The quaternary picrate was then converted into the corresponding chloride (as XIII), which on thermal decomposition gave 2-ethyltetrahydro*iso*phosphinoline (XIV), solely however in the form of its hydrochloride, from which the free phosphine, b. p. 129—132°/15 mm., was subsequently obtained. Again, the fact that the decomposition of this quaternary chloride gave only the hydrochloride of the tertiary phosphine, whereas that of the isomeric chloride (as IX) gave a mixture of the free tertiary phosphine and its hydrochloride, is not surprising, for it would be expected that the phosphine group in (XIV) would be both more reactive and more strongly basic than that in the isomeride (X). It was noted moreover that the *iso*phosphinoline (XIV) was considerably more susceptible to aerial oxidation than the phosphinoline (X).

We are now engaged in the detailed investigation of the chemistry of the two phosphines (X) and (XIV), particularly with regard to their possible use in the synthesis of *spiro*cyclic quaternary phosphonium salts. We are also applying similar syntheses to the preparation of 1-substituted phosphindolines and 2-substituted *iso*phosphindolines.

Experimental.

Ethyldichlorophosphine.—The crude dichlorophosphine, obtained in 80% yield by the method of Kharasch *et al.* (*loc. cit.*), was distilled from the reaction flask during 3 hours, and on redistillation gave the pure phosphine, b. p. 111—113° (65%).

Diethylchlorophosphine.—A mixture of the above phosphine (130 g.) and tetraethyl-lead (97 g., 0·3 mol.) was stirred and heated for 36 hours at 140—145° in a nitrogen atmosphere. Distillation of the mixture then gave the crude *monochlorophosphine* (89 g., 70%) which on careful fractionation afforded the pure phosphine, b. p. 131—132° (Found: C, 38·1; H, 7·9. $C_4H_{10}ClP$ requires C, 38·5; H, 8·1%) (47 g., 38%). An earlier fraction, b. p. 125—131° (36 g.), was discarded.

Diethyl-3-phenylpropylphosphine.—3-Phenylpropyl bromide was prepared from the alcohol by the method of Rupe and Burgin (*Ber.*, 1910, **43**, 178). A Grignard reagent, prepared by the action of the bromide (12·4 g.) in ether (40 c.c.) on magnesium (1·55 g.) under nitrogen, was boiled under reflux for 30 minutes, cooled in ice-water and vigorously stirred whilst a solution of diethylchlorophosphine (5·8 g., 0·75 mol.) in benzene (50 c.c.) was added dropwise during 20 minutes. The solution was then boiled for 1·5 hours, cooled, and hydrolysed with saturated aqueous ammonium chloride. The ethereal solution was separated, dried, and distilled (in a nitrogen atmosphere throughout), and furnished the phosphine as a colourless liquid, b. p. 108—109°/0·3 mm. (7·25 g., 75%). It was characterised as its *methiodide*, colourless crystals (from alcohol), m. p. 87—88° (Found: C, 48·4; H, 7·0. $C_{14}H_{24}IP$ requires C, 48·0; H, 6·9%).

When it was desired to convert this phosphine into the phosphine dichloride, considerable difficulty was encountered in finding a solvent which would be unaffected both by the phosphine and by chlorine. The phosphine readily reacted even with cold carbon tetrachloride to give a dark oil, which was presumably the salt $Cl{\cdot}C(PEt_2Cl{\cdot}[CH_2]_3{\cdot}Ph)_3$, comparable to the compound $Cl{\cdot}C(PEt_3Cl)_3$ (Hofmann, *J.*, 1861, 488; Hantzsch and Hibbert, *Ber.*, 1907, **40**, 1516). Consequently, direct union without a solvent was attempted by passing a stream of chlorine greatly diluted with nitrogen over the chilled and agitated phosphine. Even so, the vigorous reaction made quantitatively controlled addition difficult, and subsequent distillation gave no useful product. The addition of bromine (1 mol.) to a chloroform solution of the phosphine followed by evaporation of the solvent gave a solid residue, presumably of the phosphine dibromide, but again destructive distillation gave no well-defined product.

3-o-*Bromophenylpropan*-1-*ol* (V).—This preparation was performed throughout in an atmosphere of nitrogen. *o*-Bromobenzyl bromide (160 g.) in ether (500 c.c.) was added dropwise to a stirred mixture of magnesium (16 g., 1·03 mol.) and ether (50 c.c.); after the reaction had been started by the addition of an iodine crystal, the rate of bromide addition was adjusted so that formation of the Grignard reagent proceeded without ebullition of the ether. When the formation of the Grignard reagent had been completed by 2·5 hours' stirring, a solution of ethylene oxide (63 c.c., 2 mols.) in ether (200 c.c.) was slowly added, a sticky solid slowly separating. The mixture, after being set aside overnight, was hydrolysed by dilute sulphuric acid. The ethereal layer, on drying and distillation, gave the fractions: (*a*) b. p. 50°/17 mm. (73 g.), the properties of which indicated that it was ethylene bromohydrin; (*b*) b. p. 110—113°/0·5 mm. (64·5 g.); (*c*) b. p. 113—139°/0·5 mm.; (*d*) b. p. 139—145°/0·5 mm.; and (*e*) b. p. 145—*ca.* 220°/0·5 mm.

Fraction (*b*) was the colourless *propanol* (47% yield), which on refractionation had b. p. 106—108°/0·5 mm. (Found: C, 50·4; H, 5·2. $C_9H_{11}OBr$ requires C, 50·2; H, 5·2%). It gave a 3 : 5-*dinitrobenzoate*, colourless crystals, m. p. 96—97°, from light petroleum (Found: C, 47·2; H, 3·0; N, 6·9. $C_{16}H_{13}O_6N_2Br$ requires C, 46·95; H, 3·2; N, 6·85%). It also reacted with phenyl *iso*cyanate to give 3-o-*bromophenylpropyl* N-*phenylcarbamate*, colourless crystals, m. p. 75·5—76°, from light petroleum (Found: C, 57·7; H, 4·85; N, 4·3. $C_{16}H_{16}O_2NBr$ requires C, 57·5; H, 4·8; N, 4·2%). The structure of the propanol was further confirmed by alkaline permanganate oxidation to *o*-bromobenzoic acid, m. p. 148—149°, alone and mixed.

Fraction (*d*) slowly deposited crystals, which, after repeated crystallisations from alcohol, furnished 2 : 2′-dibromodibenzyl (V*a*), m. p. 84° (Found : C, 49·4; H, 3·7. Calc. for $C_{14}H_{12}Br_2$: C, 49·4; H, 3·6%). Kenner and Wilson (*loc. cit.*) give m. p. 84·5°.

Fraction (*e*), which became semi-solid, was recrystallised repeatedly from *cyclo*hexane, and furnished colourless crystals of 2 : 2′-*di*-(2-*hydroxyethyl*)*dibenzyl* (V*b*), m. p. 98—99° (Found : C, 80·1; H, 8·35. $C_{18}H_{22}O_2$ requires C, 79·95; H, 8·2%).

3-o-*Bromophenylpropyl Bromide.*—This *compound*, prepared by the addition of the propanol to chilled phosphorus tribromide followed by 1 hour's heating at 100°, was obtained in 83% yield as a colourless liquid, b. p. 84—85°/0·3 mm. (Found : C, 38·6; H, 3·4. $C_9H_{10}Br_2$ requires C, 38·9; H, 3·6%).

3-o-*Bromophenylpropyl Methyl Ether* (VI).—This was prepared by the cautious addition of the foregoing compound (120 g.) to a chilled solution of sodium (11 g.) in methyl alcohol (300 c.c.). The product, after 1 hour's boiling, was worked up and gave the *ether* as a colourless liquid, b. p. 127—129°/15 mm. (Found : C, 52·2; H, 5·95. $C_{10}H_{13}OBr$ requires C, 52·4; H, 5·7%) (83 g., 84%).

Diethyl-(o-3-*methoxypropylphenyl*)*phosphine* (VII).—A solution of the ether (VI) (48·4 g.) and ethyl bromide (11·55 g., 0·5 mol.) in ether (150 c.c.) was slowly added to magnesium turnings (8·2 g., 1·58 atoms) which had been previously activated by heating with iodine (Holliman and Mann, *loc. cit.*) and then covered with ether (20 c.c.). The reaction soon started, and the rate of addition of the mixed bromides was then adjusted so that the ether boiled only gently without external cooling. The complete mixture was boiled for 3 hours in a nitrogen atmosphere, cooled, and stirred whilst a solution of diethylchlorophosphine (33 g., 1·25 mols.) in benzene (150 c.c.) was slowly added, and then boiled again for 2 hours. After hydrolysis with ammonium chloride, the usual treatment furnished the *phosphine*, b. p. 155—158°/15 mm. (Found : C, 70·7; H, 9·8. $C_{14}H_{23}OP$ requires C, 70·5; H, 9·7%) (37 g., 73%). The phosphine always frothed vigorously on distillation.

Addition of methyl iodide to an ethereal solution of the phosphine precipitated the methiodide as a gum, an aqueous solution of which, when treated with sodium picrate, gave the *methopicrate*, yellow crystals, m. p. 99—99·5°, from alcohol (Found : C, 52·6; H, 6·0. $C_{21}H_{28}O_8N_3P$ requires C, 52·4; H, 5·9%).

When an acetone solution of the phosphine was mixed with an aqueous solution of potassium palladobromide, yellow crystals of *dibromobis*[*diethyl*-(o-3-*methoxypropylphenyl*)*phosphine*]*palladium* separated; these had m. p. 149·5—150° after recrystallisation from alcohol (Found : C, 45·05; H, 6·25. $C_{28}H_{46}O_2Br_2P_2Pd$ requires C, 45·2; H, 6·2%).

1 : 1-*Diethyl*-1 : 2 : 3 : 4-*tetrahydrophosphinolinium Picrate.*—A stream of dry hydrogen bromide was passed for 3 hours through a solution of the phosphine (VII) (17·5 g.) in a mixture of acetic acid (600 c.c.) and constant-boiling hydrobromic acid (600 c.c.) maintained at 120—130°. The solvent was then distilled off under reduced pressure, and the residue, undoubtedly consisting of the hydrobromide (VIII), dissolved in water. The solution was treated with an excess of sodium hydrogen carbonate, whereupon an oil separated. The addition of chloroform dissolved this oil, and the temperature of the chloroform layer soon rose perceptibly. The mixture was then shaken vigorously, so that the cyclised phosphinolinium bromide (IX) was extracted by the aqueous layer. The latter, when treated with sodium picrate solution, deposited the *phosphinolinium picrate* (28·8 g., 90%) which, once recrystallised from alcohol, formed yellow crystals, m. p. 111—111·5° (Found : C, 52·3; H, 5·2. $C_{19}H_{22}O_7N_3P$ requires C, 52·4; H, 5·1%).

1-*Ethyl*-1 : 2 : 3 : 4-*tetrahydrophosphinoline* (X).—The picrate (29 g.) was converted into the chloride by shaking it with concentrated hydrochloric acid (75 c.c.) and water (75 c.c.), the picric acid being then removed by ether-extraction. After distillation of the water, the residual chloride (which tended to crystallise on cooling, but which was not purified) was heated to 350—370° at 20 mm. pressure. Decomposition occurred smoothly, with the separation of a mixture of the liquid phosphine (X) and its crystalline hydrochloride in the receiver : after 2 hours there was no residue in the distillation flask. The mixture was treated with sodium hydrogen carbonate solution, and the free phosphine extracted with chloroform; distillation subsequently gave the pure *phosphine* (X) as a colourless liquid, b. p. 141—143°/18 mm. (Found : C, 73·7; H, 8·4. $C_{11}H_{15}P$ requires C, 74·1; H, 8·5%) (9·3 g., 78%). The identity of the crystalline hydrochloride in the distillate was shown by the fact that the crystals, after decomposition with sodium hydrogen carbonate, and the liquid phosphine, with potassium palladobromide each gave *dibromobis*-(1-*ethyl*-1 : 2 : 3 : 4-*tetrahydrophosphinoline*)*palladium*, orange crystals (from alcohol), m. p. 153·5—154° (Found : C, 42·4; H, 5·1. $C_{22}H_{30}Br_2P_2Pd$ requires C, 42·4; H, 4·9%).

The phosphine was further characterised by the preparation of the *methiodide*, colourless crystals (from alcohol), m. p. 184—185° (Found : C, 44·7; H, 5·6. $C_{12}H_{18}IP$ requires C, 45·0; H, 5·7%), and the *methopicrate*, yellow crystals (from alcohol), m. p. 121° (Found : C, 51·3; H, 4·9; N, 10·1. $C_{18}H_{20}O_7N_3P$ requires C, 51·3; H, 4·8; N, 10·0%). The ethiodide was also prepared and converted into the ethopicrate, which was shown to be identical with that utilised for the preparation of the phosphinolinium chloride.

Diethyl-2-o-*methoxymethylphenylethylphosphine* (XII).—*o*-2-Chloroethylbenzyl methyl ether (XI) was prepared according to Holliman and Mann's directions (*loc. cit.*). A Grignard reagent was prepared in a nitrogen atmosphere from a solution of the methyl ether (36 g.) and ethyl bromide (10·8 g., 0·5 mol.) in ether (180 c.c.), and magnesium (7·2 g., 1·5 atoms) covered with ether (20 c.c.). The reaction was started by gentle warming, and the halide solution added with stirring at such a rate as to maintain gentle boiling. The preparation was then precisely as that of the phosphine (VII), with addition, however, of a solution of diethylchlorophosphine (33 g., 1·3 mols.) in benzene (250 c.c.). The *phosphine* (XII), worked up in the usual way, had b. p. 117—118°/0·2 mm. (Found : C, 68·6; H, 9·6. $C_{14}H_{23}OP$ requires C, 70·5; H, 9·7%) (34·5 g., 74%). The very ready aerial oxidation prevented accurate analysis.

The phosphine was characterised by the preparation of the *methiodide*, colourless crystals (from alcohol), m. p. 106·5—107° (Found : C, 47·1; H, 7·15. $C_{15}H_{26}OIP$ requires C, 47·35; H, 6·9%), and the *methopicrate*, yellow crystals (from alcohol), m. p. 66·5—67° (Found : C, 52·6; H, 6·0; N, 8·9. $C_{21}H_{28}O_8N_3P$ requires C, 52·4; H, 5·9; N, 8·7%), and also *dibromobis(diethyl*-2-o-*methoxymethylphenylethylphosphine)palladium*, orange crystals, m. p. 106·5—107° (Found : C, 45·4; H, 6·4. $C_{28}H_{46}O_2Br_2P_2Pd$ requires C, 45·2; H, 6·2%).

2 : 2-*Diethyl*-1 : 2 : 3 : 4-*tetrahydro*iso*phosphinolinium Picrate*.—This was prepared precisely as the isomeric picrate. After passage of the hydrogen bromide for 2·5 hours, the solvent was removed, and the residual syrup dissolved in water and neutralised with sodium hydrogen carbonate. The aqueous solution was shaken with chloroform, which now, however, underwent no perceptible rise in temperature. The aqueous layer, treated with sodium picrate, gave the *iso*phosphinolinium picrate (7·15 g.). The chloroform layer was boiled and evaporated, and the residue when dissolved in water gave a further crop of the picrate (5·4 g.; total yield, 50%). Recrystallisation from methyl alcohol gave the pure *picrate*, yellow crystals, m. p. 98—98·5° (Found : C, 52·5; H, 5·3; N, 10·0. $C_{19}H_{22}O_7N_3P$ requires C, 52·4; H, 5·1; N, 9·7%).

2-*Ethyl*-1 : 2 : 3 : 4-*tetrahydro*iso*phosphinoline* (XIV).—The picrate was converted into the crude chloride and the latter subjected to thermal decomposition precisely as the earlier isomeric compounds. The distillate consisted apparently solely of the *iso*phosphinoline hydrochloride, which crystallised very readily. Neutralisation with sodium hydrogen carbonate followed by chloroform extraction ultimately gave the iso*phosphinoline* as a colourless liquid, b. p. 129—132°/15 mm. (Found : C, 72·4; H, 8·5. $C_{11}H_{15}P$ requires C, 74·1; H, 8·5%) (yield 78%). The very ready oxidation caused low carbon values on analysis.

The *iso*phosphinoline was characterised by the preparation of the *ethiodide*, colourless crystals (from acetone), m. p. 93—94° (Found : C, 46·3; H, 6·2. $C_{13}H_{20}IP$ requires C, 46·7; H, 6·0%), which was converted into the ethopicrate, identical with that used in the preparation. The phosphine also gave *dibromobis*-(2-*ethyl*-1 : 2 : 3 : 4-*tetrahydro*iso*phosphinoline)palladium*, deep orange crystals (from alcohol), m. p. 165·5—166° (Found : C, 42·1; H, 5·0. $C_{22}H_{30}Br_2P_2Pd$ requires C, 42·4; H, 4·9%).

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