326. *The Stereochemistry of Organic Derivatives of Phosphorus. Part II. The Synthesis of 2 : 2-Disubstituted 1 : 2 : 3 : 4-Tetrahydro*iso*phosphinolinium Salts and the Optical Resolution of 2-Phenyl-2-*p*-hydroxyphenyl-1 : 2 : 3 : 4-tetrahydro*iso*phosphinolinium Bromide.*

By FREDERICK G. HOLLIMAN and FREDERICK G. MANN.

Numerous attempts to synthesise the tetrahydro*iso*phosphinoline ring system by the use of *o*-2-bromoethylbenzyl bromide (cf. Holliman and Mann, *J.*, 1942, 737; 1943, 547, 550) and by other methods having failed, a general synthesis for 2 : 2-diaryl-1 : 2 : 3 : 4-tetrahydro*iso*phosphinolinium salts has been developed and applied to the preparation of 2-*phenyl*-2-p-*bromophenyl*- and 2-*phenyl*-2-p-*hydroxyphenyl*-1 : 2 : 3 : 4-*tetrahydro*iso*phosphinolinium bromides.* Whilst the former salt resisted all attempts at resolution into optically active forms, the dextrorotatory form of the latter, having $[M]_D + 32{\cdot}9°$, was isolated on one occasion : the corresponding lævorotatory form could not be obtained nor could the successful resolution be repeated, these failures being attributed to the formation of partial racemates. This represents the first recorded example of an asymmetric quaternary phosphonium salt showing optical activity.

THE ready resolution of 2-phenyl-2-*p*-chlorophenacyl-1 : 2 : 3 : 4-tetrahydro*iso*arsinolinium bromide (I) and the high optical stability of the isomers obtained (Holliman and Mann, *J.*, 1943, 550), in contrast to the fleeting rotation displayed by other optically active arsonium salts (Burrows and Turner, *J.*, 1921, **19**, 426; Kamai, *Ber.*, 1933, **66**, 1779; *J. Gen. Chem. Russia*, 1934, **4**, 184), was attributed to the great chemical stability of the above heterocyclic ring system and the consequent inability for racemisation to proceed by a dissociation equilibrium :

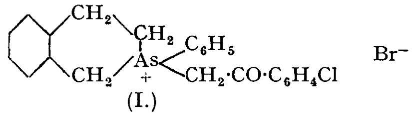
$$[\text{abcdAs}]\text{I} \rightleftharpoons \text{abcAs} + \text{dI}.$$

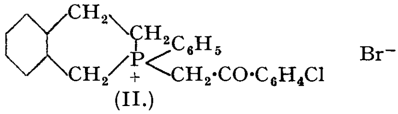
It was pointed out that such an equilibrium was almost certainly responsible for the many previous unsuccessful attempts to resolve quaternary arsonium salts, particularly since these salts always contained at least one alkyl group which would lend itself very readily to the above dissociation.

It would seem that similar arguments could be put forward to explain the lack of success attending some of the many attempts to resolve quaternary phosphonium salts [*e.g.*, Pope and Gibson (*J.*, 1912, **101**, 735) failed to resolve phenyl-*p*-tolylbenzylmethylphosphonium iodide, Wedekind (*Ber.*, 1912, **45**, 2933) failed with phenyl-*p*-tolylmethylethylphosphonium iodide, and Meisenheimer *et al.* (*Annalen*, 1926, **449**, 213) had no success with phenylbenzylmethylethylphosphonium iodide] but in the majority of cases, investigators have been handicapped by the inherent difficulties involved in the crystallisation of phosphonium salts with optically active anions (Michaelis, *Annalen*, 1901, **315**, 43; Pope and Gibson, *loc. cit.*; Wedekind, *loc. cit.*; Radcliffe and Brindley, *J. Soc. Chem. Ind.*, 1923, **42**, 64; Kamai, *J. Gen.*

Chem. Russia, **1932**, **2**, 526; Davies and Mann, *J.*, 1944, 276). On the other hand, evidence has been produced that phosphonium salts do not undergo dissociation in solution as postulated above (Wedekind, *loc. cit.*, but cf. Davies and Lewis, *J.*, 1934, 1600) and it may be that when crystalline salts have been obtained, they have been in the form of partial racemates : if such a form is less soluble than either of the two diastereoisomerides, resolution is obviously impossible.

As a sequel to the successful resolution of the asymmetric arsonium salt (I) it seemed highly probable that, could the analogous phosphorus compound, 2-phenyl-2-*p*-chlorophenacyl-1 : 2 : 3 : 4-tetrahydro*iso*phosphinolinium bromide (II), be prepared it would be possible to

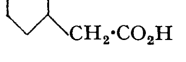

(I.)

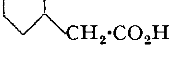

(II.)

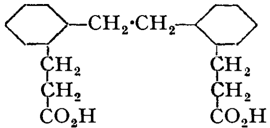
resolve it into optically active forms : crystallisation difficulties would be overcome since derivatives of (II) would probably be isomorphous with corresponding derivatives of (I), and in addition a dissociation equilibrium would be unlikely to operate.

The application of similar methods for the synthesis of (II) to those employed for the arsenic analogue (I) gave only poor yields in the first stage (*i.e.*, the Michaelis reaction between *o*-2-bromoethylbenzyl bromide, phenyldichlorophosphine and sodium in an ethereal medium with ethyl acetate as a catalyst to give 2-phenyl-1 : 2 : 3 : 4-tetrahydro*iso*phosphinoline) as has already been reported (Holliman and Mann, *J.*, 1943, 548) and subsequent attempts to improve the yields by varying the solvent, the proportions of the reactants, and the catalyst all met with no success. The reasons for this failure are not difficult to formulate. The Michaelis reaction is known to proceed much more slowly in the case of phosphorus halides than with those of arsenic : for example, bromobenzene, phosphorus trichloride, and sodium in ether require 48 hours' refluxing to obtain a small yield of triphenylphosphine (Michaelis and Gleichman, *Ber.*, 1882, **15**, 801) whilst the analogous reaction with arsenic trichloride proceeds vigorously and is complete in a short time to give high yields of triphenylarsine (Michaelis and Reese, *ibid.*, p. 2876). On the other hand, the rate of quaternary phosphonium salt formation by the interaction of tertiary phosphines with alkyl halides is many times more rapid than the similar formation of quaternary arsonium salts : the reaction between phenyldiethylphosphine and ethyl iodide in acetone is more than 90% complete after 60 hours, whilst the corresponding reaction with the arsenic analogue is only 20% complete in the same time (Davies and Lewis, *loc. cit.*). Hence, as fast as the phenyl*iso*phosphinoline is formed, phosphonium salt formation takes place with the unreacted *o*-2-bromoethylbenzyl bromide. In another investigation, it was apparent that *p*-tolyldichloroarsine took part in the Michaelis reaction with greater ease than did phenyldichloroarsine. Consequently, the reaction of *p*-tolyldichlorophosphine with *o*-2-bromoethylbenzyl bromide and sodium was investigated in the hope that the rate of phosphine formation would be markedly increased relative to the rate of subsequent phosphonium salt formation, and that a possibly small but workable yield of 2-*p*-tolyl-1 : 2 : 3 : 4-tetrahydro*iso*phosphinoline would result. This, however, proved not to be the case, only a small amount of distillate being obtained. The latter did in fact appear to be the required tertiary phosphine since it reacted in benzene solution with *p*-chlorophenacyl bromide to give the crystalline 2-p-*tolyl*-2-p-*chlorophenacyl*-1 : 2 : 3 : 4-*tetrahydro*iso*phosphinolinium bromide* (as II), but the yield was too small to justify prolonged experimental work to accumulate sufficient of the phosphonium salt for resolution purposes.

Attention was now directed to a fuller investigation of the conditions under which *o*-2-bromoethylbenzyl bromide would react with magnesium with a view to the use of the di-Grignard reagent from the dibromide for the synthesis of tetrahydro*iso*phosphinolines. Employing the entrainment method, *i.e.*, admixture of the dibromide with ethyl bromide, it was found that reaction with magnesium would take place. Treatment of the reagent so produced

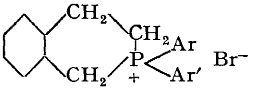

(III.)


(IV.)


(V.)

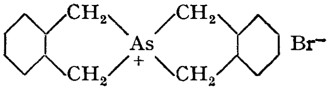
with carbon dioxide was used as a diagnostic method for the presence of the required Grignard reagent, it being anticipated that β-*o*-carboxymethylphenylpropionic acid (III) would be obtained. However, the alkali-soluble fraction of the reaction product was a mixture from which were isolated *o*-ethylphenylacetic acid (IV) and a *compound*, $C_{20}H_{22}O_4$, which was probably either (V) or an isomer thereof. The isolation of these two acids would indicate that the di-Grignard reagent had, in fact, been produced; it then underwent coupling reactions and subsequent reaction with carbon dioxide to give acids of the type (V), or only partly reacted with carbon dioxide to give (IV). Obviously, it is only the yield of (III) and (IV) which is the measure of the degree to which this type of reaction could be employed in the synthesis of tetrahydro*iso*phosphinolines, and the low yield actually obtained caused this method to be abandoned in favour of other syntheses, which, at the time, showed greater promise of success.

The impracticability of synthesising the phenyl*iso*phosphinoline necessary for the preparation of the phosphorus analogue of our arsonium salt led us to consider possible routes for the synthesis of a somewhat different type of phosphinolinium salt. The stability of this type of heterocyclic system has already been discussed and it has been pointed out (Davies and Mann, *loc. cit.*) that a quaternary phosphonium salt with four *aryl* groups attached to the phosphorus atom would not be susceptible to a dissociation equilibrium of the type postulated above. A 2 : 2-diaryl-1 : 2 : 3 : 4-tetrahydro*iso*phosphinolinium salt of type (VI) would combine both these features and would probably be resolvable provided difficulties of crystallisation could be overcome: it was of course realised that such a pronounced change in constitution from that of our arsinolinium salt would no longer offer the possibility of isomorphism, and the absence of the *p*-chlorophenacyl group, to which we have ascribed the high rotation characteristic of that salt and similar salts with sulphur, selenium, or tellurium as the hetero-atom (Holliman and Mann, *J.*, 1945, 37), might lead to a very pronounced decrease in any optical activity which might be observed.

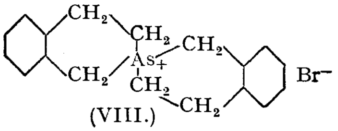


(VI.)

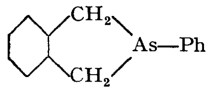
The pyrolysis of quaternary arsonium salts carrying a methyl group leads to the elimination of that group as methyl halide and the formation of a tertiary arsine. With quaternary arsonium salts of a suitable type this reaction may be employed for the synthesis of heterocyclic systems. For example, Lyon and Mann (*J.*, 1945, 30) have used this reaction for the preparation of *As-spiro*-bis*iso*arsindolinium bromide (VII), Holliman and Mann (*J.*, 1945, 45) have analogously prepared the spirocyclic arsonium salt (VIII), and Lyon, Mann, and Cookson (this vol., p. 662) have synthesised the simpler heterocyclic system of 2-phenyl*iso*arsindoline (IX).



(VII.)

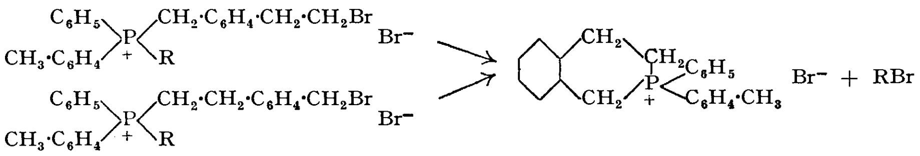


(VIII.)



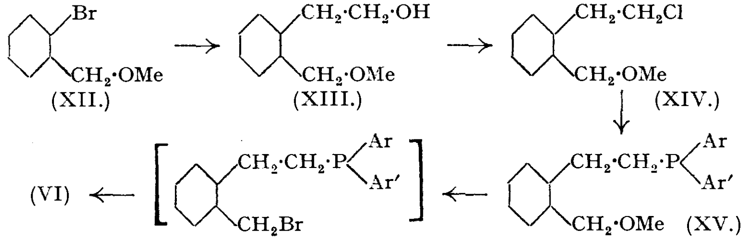
(IX.)

The application of this method to the synthesis of 2 : 2-diaryl-1 : 2 : 3 : 4-tetrahydro*iso*-phosphinolinium salts was therefore investigated. Meisenheimer *et al.* (*loc. cit.*) have shown that the ease with which radicals are split from quaternary phosphonium chlorides is in the order Et > CH_2Ph > Me > Pr > *iso*amyl > Ph. Accordingly, phenyl-*p*-tolylethylphosphine was brought into reaction with an equimolecular proportion of *o*-2-bromoethylbenzyl bromide to give a crystalline, homogeneous quaternary phosphonium salt which was almost certainly *phenyl*-p-*tolyl*-o-(*2-bromoethyl*)*benzylethylphosphonium bromide* (X, R = Et) and not the isomeric

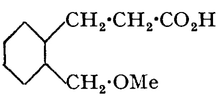


salt (XI, R = Et). However, when this salt was heated under varying conditions, although extensive decomposition took place, none of the desired cyclised product could be isolated and examination of the volatile products evolved during the decomposition failed to show any ethyl bromide. Similar experiments involving the use of the corresponding methyl compounds (X or XI; R = Me) also proved fruitless.

It was felt that the readiness with which tertiary phosphines form quaternary salts with alkyl halides could be advantageously employed for closing the tetrahydro*iso*phosphinoline ring, and ultimately the following general synthesis of 2 : 2-diaryl-tetrahydro*iso*phosphinolinium salts was successfully developed.



The compounds (XII) and (XIII) are, of course, analogous to intermediates in the synthesis of *o*-2-bromoethylbenzyl bromide and were prepared by similar methods: *o*-bromobenzyl bromide when treated with a methyl-alcoholic solution of sodium methoxide gave o-*bromobenzyl methyl ether* (XII) which was in turn converted into the Grignard reagent by the entrainment method and then treated with ethylene oxide to give o-2-*hydroxyethylbenzyl methyl ether* (XIII). Replacement of the hydroxyl group of the alcohol (XIII) was first attempted using phosphorus tribromide, but fission of the ether grouping also occurred and *o*-2-bromoethylbenzyl bromide together with *iso*chroman were the main products of the reaction; by the use of the theoretical quantity of thionyl chloride in the presence of one molecular proportion of pyridine good yields of o-2-*chloroethylbenzyl methyl ether* (XIV) were obtained. Conversion of the chloro-compound into the Grignard reagent followed by treatment with a diarylchlorophosphine then gave the tertiary phosphine (XV). At first, difficulty was experienced in the formation of the Grignard reagent from (XIV), and again the carbon dioxide method was employed so that the yields of β-o-*methoxymethylphenylpropionic acid* (XVI) isolated gave an indication of the yields of the Grignard reagent under various conditions. By far the best reproducible yields were obtained by running a mixture of the chloro-compound with ½ mol. of ethyl bromide in ethereal solution on to ordinary magnesium turnings, although the chloro-compound alone would react with activated magnesium.



(XVI.)

When the tertiary phosphine (XV) was heated in a mixture of constant-boiling hydrobromic acid and glacial acetic acid, the three stages, *i.e.*, cleavage of the ether grouping, esterification, and ring closure, necessary to complete the synthesis were accomplished in one operation, giving good yields of the *iso*phosphinolinium salt (VI): a stream of hydrogen bromide mixed with hydrogen was passed through the solution in order that the hydrogen bromide concentration should be maintained and that the methyl bromide produced in the ether cleavage should be removed as fast as it was formed, thus being prevented from reacting with the tertiary phosphine.

The above synthesis was first employed to prepare 2-*phenyl*-2-p-*bromophenyl*-1 : 2 : 3 : 4-*tetrahydro*iso*phosphinolinium bromide* (VI; Ar = Ph, Ar′ = p-C_6H_4Br) as a crystalline solid which with an aqueous solution of sodium picrate gave the *phosphinolinium picrate*. The intermediate *phenyl*-p-*bromophenyl*-2-(o-*methoxymethylphenyl*)*ethylphosphine* (XV; Ar = Ph, Ar′ = p-C_6H_4Br) was obtained as a colourless, viscous, high-boiling liquid which readily reacted with methyl iodide in ethereal solution to give the crystalline *methiodide*.

For resolution, the bromide was converted by the usual method into the *d*-bromocamphorsulphonate, the *d*-hydrogen tartrate and the *l*-*N*-1-phenylethylphthalamate,* but all these salts were non-crystalline glasses or syrups: the d-*camphorsulphonate* was obtained crystalline but repeated recrystallisation from alcoholic ether failed to produce any evidence that a mixture of diastereoisomerides was present.

The introduction of a hydroxyl group into one of the two aryl groups was considered to be a likely means of increasing the probability that crystalline phosphonium salts with optically active anions would be obtained: should these derivatives not prove suitable, benzoylation of the hydroxyl group or some similar procedure might again increase the crystallisability. Accordingly, employing phenyl-*p*-anisylchlorophosphine in place of the phenyl-*p*-bromophenylchlorophosphine previously used, we were able to prepare *phenyl*-p-*anisyl*-2-(o-*methoxymethylphenyl*)*ethylphosphine* (XV; Ar = Ph, Ar′ = p-C_6H_4·OMe), again characterised by the formation of the *methiodide*. The demethylation–ring closure procedure also resulted in the demethylation

---

* For the preparation of the phthalamic acid and its conversion into the silver salt, see Mann and Watson, this vol., p. 510.

of the *p*-anisyl group and the crystalline *2-phenyl-2-*p*-hydroxyphenyl-1 : 2 : 3 : 4-tetrahydro*iso*-phosphinolinium bromide* (VI ; Ar = Ph, Ar′ = *p*-C_6H_4·OH) was thus readily obtained in high yield. That this product did in fact contain a free hydroxyl group was shown by its conversion into the *acetyl* derivative.

The effect of the introduction of the hydroxyl group was soon apparent, as the d-*bromocamphorsulphonate* prepared from the bromide was readily obtained in the crystalline state. Again, however, repeated recrystallisation from a variety of solvents failed to produce any indication that resolution was proceeding.

Similarly, the d-*camphorsulphonate*, originally obtained as a glass, readily crystallised from an acetone solution, and then had m. p. 153—158° and $[M]_D$ + 102° in alcoholic solution. Slow recrystallisation from ethyl acetate–ethyl alcohol gave a first crop having m. p. 171—172·5° and $[M]_D$ + 110°, whilst a second and a third crop had respectively, m. p. 153—157° and 142—151°, $[M]_D$ + 104° and + 98·4°. That the first crop was virtually the optically pure d-*phosphonium* d-*camphorsulphonate* was evident since three more recrystallisations of this crop raised the m. p. to a constant value of 174—175° and the $[M]_D$ to + 113·5°.

An alcoholic solution of the optically pure camphorsulphonate, treated at 0° with an alcoholic solution of calcium bromide, furnished the d-*phosphinolinium bromide*, m. p. 268—270°, with $[M]_D$ + 32·9° in aqueous alcoholic solution : it is noteworthy that the *dl*-phosphinolinium bromide had m. p. 287—287·5° and that the optically active salt was considerably more soluble than the racemic compound. A curious solvent effect was observed in methyl alcohol, solutions of the bromide in this solvent having very low activity : this was not due to racemisation, for the bromide recovered from such solutions had the normal activity when again dissolved in aqueous ethyl alcohol. The optical stability and purity of the active bromide is shown by the fact that recrystallisation from boiling ethyl alcohol failed to affect the rotatory power.

The following values for the rotatory dispersion in the visible spectrum were obtained for a 1·029% solution of the *d*-bromide in aqueous-alcoholic solution. The calculated rotations are obtained from the equation $\alpha = k/(\lambda^2 - \lambda_0^2)$, where k = 0·0885 and λ_0^2 = 0·0948, λ_0 = 3078 A.

Source of light.	Li.	Na.	Hg.	Hg.	Cu.	Zn.	Hg.
λ, A.	6104	5893	5780	5461	5219	4810·5	4358
α, obs.	+0·31°	0·36°	0·37°	0·435°	0·48°	0·64°	0·93°
$[M]_D$	+30·05°	34·9°	35·9°	42·2°	46·5°	62·0°	90·1°
α, calc.	+0·32°	0·35°	0·37°	0·435°	0·50°	0·65°	0·93°
α, obs. − α, calc.	−0·01°	+0·01°	0·00°	0·00°	−0·02°	−0·01°	0·00°

The close agreement between the observed and the calculated values indicates that the bromide probably possesses simple dispersion, although readings for a much greater number of wave-lengths would have to be obtained to establish this beyond doubt.

In order to obtain the *l*-bromide, the phosphinolinium bromide was recovered from the second and third fractions of the *d*-camphorsulphonate and then converted into the l-*camphorsulphonate*. This salt, like its isomer, was initially obtained as a glass which was crystallised from an acetone solution and then had m. p. 152—157°. When recrystallisation of this salt from ethyl acetate–ethyl alcohol was attempted, the hot solution rapidly began to deposit crystalline material and a much greater proportion of alcohol than was used in the case of the *d*-camphorsulphonate had to be employed before solution was again obtained. In this case, on cooling, practically the whole of the salt was recovered with m. p. 170—172° and $[M]_D$ − 102° : further recrystallisation failed to change either the m. p. or the rotatory power. The salt was much less soluble than had been anticipated for the *l*-phosphinolinium *l*-camphorsulphonate and conversion into the phosphinolinium bromide gave only an optically inactive product, m. p. 286—288° : it therefore became apparent that the *l*-camphorsulphonate was now crystallising as a partial racemate. Numerous attempts to re-obtain the low-melting form were of no avail : the less soluble, high-melting form was always obtained in the presence of nuclei, whilst, if steps were taken to ensure that nuclei were excluded, solutions remained supersaturated indefinitely. Similarly, further preparations of the *d*-camphorsulphonate always gave a product, m. p. 170—172°, which, by treatment with calcium bromide, furnished the optically inactive bromide. Attempts to extend the resolution were therefore abandoned.

It is noteworthy that the above 2-phenyl-2-*p*-hydroxyphenyl-1 : 2 : 3 : 4-tetrahydro*iso*-phosphinolinium bromide is the first quaternary phosphonium salt to be resolved into optically active forms. The only other types of organic phosphorus derivatives (*i.e.*, derivatives containing C–P links) to be obtained in optically active forms are the tertiary phosphine oxides, such as phenylbenzylmethylphosphine oxide, resolved by Meisenheimer *et al.* (*Ber.*, 1911, **44**, 356; *Annalen*, 1926, **449**, 224), and the tertiary phosphine sulphide, phenyl-*p*-carboxymethoxyphenyl-*n*-butylphosphine sulphide, resolved by Davies and Mann (*loc. cit.*).

EXPERIMENTAL.

(All rotations were taken by use of a 4-dm. tube. M. p.s are uncorrected.)

2-p-*Tolyl*-2-p-*chlorophenacyl*-1 : 2 : 3 : 4-*tetrahydro*iso*phosphinolinium Bromide* (as II).—*o*-2-Bromoethylbenzyl bromide (29 g.) and *p*-tolyldichlorophosphine (19·3 g., 1 mol.) in absolute ether (350 c.c.) were treated with sodium wire (18 g., 8 atoms), and the mixture refluxed on the water-bath in a stream of dry nitrogen for 4 hours. After this time no apparent change had taken place and ethyl acetate (2·5 c.c.) was added to catalyse the reaction. After a further 4 hours' refluxing, ethyl acetate (2·5 c.c.) was again added and the refluxing continued for 11 hours, by which time the sodium wire had broken up and a heavy white precipitate had collected. The mixture was filtered and the ether removed by distillation in an apparatus similar to that described for 2-phenyl-1 : 2 : 3 : 4-tetrahydro*iso*arsinoline (Holliman and Mann, *loc. cit.*). The residual oil was distilled under reduced pressure : after a preliminary, low-boiling fraction, a small amount of distillate was collected at 150—180°/0·1 mm. The latter possessed a pronounced phosphine-like odour and reacted with methyl iodide to give an oily product. When dissolved in benzene and treated with *p*-chlorophenacyl bromide, no precipitation took place, but evaporation to dryness, dissolution in alcohol, and subsequent addition of ether caused the precipitation of a white solid which was purified by precipitation with ether from an alcoholic solution. The *phosphinolium bromide* then had m. p. 227—230° (Found: C, 60·65; H, 5·1; Cl, 7·7; Br, 17·5. $C_{24}H_{23}OClBrP$ requires C, 60·8; H, 4·8; Cl, 7·5; Br, 16·9%. The Cl and Br were calculated from a total halogen estimation on the assumption that they were present in equi-atomic proportions).

From the low-boiling distillate, unchanged *p*-tolyldichlorophosphine, b. p. 70—80°/0·25 mm., was isolated, together with a fraction at 30°/0·5 mm. The latter boiled at 162° at atmospheric pressure and proved to be *o*-ethyltoluene (Found : C, 89·6; H, 9·6. Calc. for C_9H_{12} : C, 90·0; H, 10·0%).

Reaction of o-2-*Bromoethylbenzyl Bromide with Magnesium*.—Preliminary experiments showed that the dibromide would not react with magnesium under the usual conditions of the Grignard reaction. The dibromide (13·9 g.) and ethyl bromide (5·45 g., 1 mol.) were dissolved in dry ether (60 c.c.), and a portion (5 c.c.) of this solution was added to magnesium turnings (3·6 g., 3 atoms) under ether (20 c.c.). After the addition of a crystal of iodine reaction soon set in and the rest of the bromide solution was added so that the ether was kept gently boiling without external chilling. When the whole of the solution had been added, the mixture was refluxed for 6 hours in an atmosphere of nitrogen, after which time only a small amount of magnesium remained. The cooled mixture was poured, in small portions, on powdered solid carbon dioxide (100 g.) covered with dry ether (100 c.c.). After being set aside overnight the product was hydrolysed with dilute sulphuric acid, the ethereal layer separated, and washed with water. The ethereal solution was shaken with 5% sodium hydroxide solution, and the alkaline extract then boiled to remove ether. Acidification of the cooled solution caused precipitation of an oil which crystallised after 2 hours' keeping at 0°. The solid was collected, washed with water, and dried (5·4 g.). Extraction of this solid with boiling petrol (b. p. 80—100°) gave an insoluble residue (1·4 g.), m. p. 168—185°, which after repeated crystallisation from ethyl acetate gave a white, micro-crystalline *solid*, m. p. 198—200·5° (Found : C, 72·5; H, 6·8. $C_{20}H_{22}O_4$ requires C, 73·5; H, 6·8%). Evaporation of the petrol filtrate left an oil (3·9 g.) which readily crystallised, and when recrystallised twice from water afforded colourless crystals, m. p. 84—85°, raised by another recrystallisation from petrol (b. p. 60—80°) to 85—86°. This compound was evidently *o*-ethylphenylacetic acid (Found : C, 73·0; H, 6·9. Calc. for $C_{10}H_{12}O_2$: C, 73·1; H, 7·4%); Mayer and English (*Annalen*, 1918, **417**, 72) give m. p. 83·5°.

Reaction of o-2-*Bromoethylbenzyl Bromide with Diarylalkylphosphines*.—Phenyl-*p*-tolylethylphosphine (Wedekind, *Ber.*, 1912, **45**, 2935) in ethereal solution was treated with o-2-bromoethylbenzyl bromide (1 mol.) also in ethereal solution. The oily precipitate which gradually formed eventually crystallised and was filtered off and cautiously washed with alcohol. The *phosphonium bromide* (X; R = Et) melted at 146—148° with softening from 143° (Found : C, 56·3; H, 5·3; Br, 31·4. $C_{24}H_{27}Br_2P$ requires C, 56·9; H, 5·3; Br, 31·6%). The thermal decomposition of this salt gave only non-crystalline products from which no crystalline derivative could be prepared.

By a similar method, the *phosphonium salt* (X; R = Me) was prepared from phenyl-*p*-tolylmethylphosphine (Radcliffe and Brindley, *loc. cit.*) and the dibromide. It was recrystallised from alcohol–ether and then melted at 185—186° (Found : C, 55·9; H, 5·2; Br, 31·9. $C_{23}H_{25}Br_2P$ requires C, 56·1; H, 5·1; Br, 32·5%). Again thermal decomposition under different conditions always gave glassy products which could neither be crystallised nor converted into crystalline derivatives.

o-*Bromobenzyl Methyl Ether* (XII).—*o*-Bromobenzyl bromide (200 g.) was cautiously added to a thoroughly chilled solution of sodium (20 g., 1·08 atoms) in methyl alcohol (600 c.c.). The mixture was refluxed on the water-bath for a short time, and the methyl alcohol then distilled off, a current of air being drawn through the mixture to avoid serious bumping. Sodium bromide was dissolved from the residue by the addition of water (500 c.c.), and the insoluble oil extracted with ether. The aqueous layer was again extracted, the combined extracts washed with water, and dried ($CaCl_2$). After removal of the solvent the residue was fractionated under reduced pressure : yield 145 g. (90%), b. p. 106—107°/16 mm. (Found : C, 47·9; H, 5·5; Br, 40·5. C_8H_9OBr requires C, 47·75; H, 4·5; Br, 39·8%).

o-2-*Hydroxyethylbenzyl Methyl Ether* (XIII).—The Grignard reagent from *o*-bromobenzyl methyl ether was prepared by running a solution of the bromo-compound (145 g.) and ethyl bromide (26 g., 0·33 mol.) in dry ether (300 c.c.) on to magnesium (35 g., 2·02 atoms) under ether (100 c.c.), the rate of addition being adjusted so that gentle refluxing was maintained whilst the mixture was vigorously stirred. [The magnesium used in this preparation was activated by heating with iodine as described by Holliman and Mann (*loc. cit.*).] When the addition was complete, the mixture was refluxed on the water-bath for 2 hours, then chilled in an ice–salt freezing mixture, and a solution of ethylene oxide (100 g., 3·15 mols.) in ether (600 c.c.) slowly added during 4 hours. The product was set aside overnight at room temperature, and then chilled in ice-water and hydrolysed cautiously with dilute sulphuric acid (850 c.c., 1 vol. acid : 9 vols. water). The ethereal layer was separated, washed with water, and dried (Na_2SO_4). Removal of the solvent left an oil which was fractionated under reduced pressure yielding the ether (XIII), b. p. 152—154°/14 mm., as the main fraction: yield 64 g. (53%). The product was refractionated several times but even so gave an unsatisfactory analysis (Found: C, 74·9; H, 8·2. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·4%). For characterisation a sample was therefore warmed with phenyl *iso*cyanate to give 2-o-*methoxymethylphenylethyl* N-*phenylcarbamate* as an oil which crystallised on treatment with petrol (b. p. 60—80°). Two recrystallisations from petrol gave colourless crystals, m. p. 64—65° (Found: 72·4; H, 6·5; N, 4·95. $C_{17}H_{19}O_3N$ requires C, 71·6; H, 6·7; N, 4·9%). As in the synthesis of the corresponding ethyl ether (Holliman and Mann, *loc. cit.*), a forerun of 2-bromoethyl alcohol was also obtained.

o-2-*Chloroethylbenzyl Methyl Ether* (XIV).—A solution of *o*-2-hydroxyethylbenzyl methyl ether (182 g.) and dry pyridine (87 g., 1 mol.) in chloroform (220 c.c.) was vigorously stirred and chilled in ice-water whilst thionyl chloride (131 g., 1 mol.) was slowly added during 2 hours. The mixture was then transferred to the water-bath and refluxed with vigorous stirring for 2·5 hours; during the initial stages of this process the mixture became cloudy, an oil separated, and sulphur dioxide was evolved, but after 1·5 hours a clear solution had again been produced. After chilling, the chloroform solution was repeatedly washed with water, then with a 1% solution of sodium hydroxide, and finally with water before drying over calcium chloride. The solvent was removed by distillation at atmospheric pressure, and the residue then fractionated under reduced pressure, the fraction, b. p. 131°/14 mm., being collected (146 g., 72%). Upon refractionation the pure o-2-*chloroethylbenzyl methyl ether* was obtained, b. p. 131°/14 mm. (Found: C, 65·0; H, 7·5. $C_{10}H_{13}OCl$ requires C, 65·05; H, 7·0%).

Reaction of o-2-*Chloroethylbenzyl Methyl Ether with Magnesium.*—*o*-2-Chloroethylbenzyl methyl ether (9·2 g.) and ethyl bromide (2·72 g., 0·5 mol.) in dry ether (40 c.c.) were slowly added to magnesium turnings (1·8 g., 1·5 atoms). The reaction was started by gentle warming and then proceeded vigorously whilst the bromide solution was slowly added. After the addition was complete, the mixture was refluxed during 2 hours. The cooled solution was carefully poured on powdered solid carbon dioxide (80 g.) under ether (40 c.c.). The mixture was allowed to attain room temperature, treated with a further quantity of solid carbon dioxide (40 g.), and then set aside during 24 hours. Hydrolysis was performed at 0° with dilute sulphuric acid (100 c.c., 1 vol. acid : 9 vols. water), the ethereal layer separated, washed with water, and extracted with 5% sodium hydroxide solution (100 c.c.). The alkaline filtrate was evaporated to about half bulk, boiled with charcoal, and filtered. Acidification of the chilled filtrate gave a white precipitate which was collected on the filter, washed with water, and dried: yield 5·6 g. (58%) of the practically pure *β*-o-*methoxymethylphenylpropionic acid*, m. p. 76—78°. Recrystallisation from petrol gave colourless crystals, m. p. 77—78° (Found: C, 68·35; H, 6·95. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·2%).

Phenyl-p-*bromophenyl*-2-(o-*methoxymethylphenyl*)*ethylphosphine* (as XV).—The Grignard reagent was prepared from *o*-2-chloroethylbenzyl methyl ether (9·2 g.), ethyl bromide (2·72 g., 0·5 mol.) in ether (40 c.c.), and magnesium turnings (1·8 g., 1·5 atoms) as described above. With a stream of dry nitrogen passing through the apparatus, the mixture was refluxed for 2·5 hours and then chilled in ice-water, whilst, with vigorous stirring, a solution of phenyl-*p*-bromophenylchlorophosphine (16·5 g., 1·1 mols.) (Davies and Mann, *J.*, 1944, 279) in dry ether (60 c.c.) was slowly added during 20 minutes. After refluxing for 3 hours the mixture was set aside overnight with a stream of nitrogen passing through the apparatus to minimise atmospheric oxidation. The mixture was chilled and vigorously stirred whilst being hydrolysed by addition of a solution of ammonium chloride (25 g.) in water (100 c.c.). The nitrogen was now replaced by carbon dioxide and, using a suitable apparatus, the contents of the reaction flask were forced over by gas pressure, through a sintered-glass funnel into a separating funnel from which the air had been displaced by the passage of carbon dioxide. The aqueous layer was run off, and the ethereal layer washed with water and then dried (Na_2SO_4) in an inert atmosphere. The solution, filtered from the drying agent in carbon dioxide, was distilled from the water-bath in a stream of nitrogen. When all the ether had been removed, the residue was fractionated under reduced pressure, the fractions, b. p. 130—160°/0·1—0·2 mm. and 200—230°/0·1—0·2 mm., being collected. The former was a colourless oil, presumably phenyl-*p*-bromophenylethylphosphine (3·1 g., representing 42·5% of the theoretical based on the ethyl bromide used). The high-boiling fraction was a viscous, green, highly refractive oil which upon redistillation gave the pure *phenyl*-p-*bromophenyl*-2-(o-*methoxymethylphenyl*)*ethylphosphine* as a viscous, almost colourless oil, b. p. 214—216°/0·1 mm. (Found: C, 63·1; H, 5·5; Br, 18·65. $C_{22}H_{22}OBrP$ requires C, 63·9; H, 5·4; Br, 19·3%): yield, 12 g., 59%.

Methiodide. An ethereal solution of the tertiary phosphine, treated with methyl iodide, rapidly deposited a colourless, sticky semi-solid. The solvent was decanted off, and the gum dissolved in alcohol, ether then being added until a slight cloudiness was produced. On standing for some days, a colourless crystalline precipitate collected; this was filtered off and recrystallised from alcohol, two recrystallisations sufficing to give the pure *methiodide* as colourless crystals, m. p. 167—168° (Found: C, 49·6; H, 4·8; Br, 14·2; I, 22·5. $C_{23}H_{25}OBrIP$ requires C, 49·7; H, 4·5; Br, 14·4; I, 22·9% The Br and I were calculated from a total halogen estimation, it being assumed they were present in equi-atomic proportion).

2-*Phenyl*-2-p-*bromophenyl*-1 : 2 : 3 : 4-*tetrahydro*iso*phosphinolinium Bromide* (as VI).—A stream of anhydrous hydrogen bromide was generated by passing a mixture of bromine vapour with excess of hydrogen through a heated combustion tube and completely freed from free bromine by passage over metallic copper. This gas stream was passed through a solution of phenyl-*p*-bromophenyl-2-(*o*-methoxymethylphenyl)ethylphosphine (6·7 g.) in glacial acetic acid (275 c.c.) and constant-boiling hydrobromic acid (275 c.c.) maintained at 120° in an oil-bath. After 2 hours the acetic acid and hydrobromic acid were distilled off in a vacuum, leaving a brown viscous mass. The latter was dissolved in alcohol (25 c.c.) and again evaporated to dryness under reduced pressure, finally being dried in a vacuum over concentrated sulphuric acid and sodium hydroxide. The gum failed to crystallise and was therefore dissolved in alcohol (100 c.c.), boiled with charcoal, and filtered. The filtrate was concentrated

(40 c.c.), and chilling in ice-water then gave a crystalline precipitate which was collected, washed with alcohol, and dried: m. p. 125—130°. Recrystallisation from ethyl alcoholic ethyl acetate gave colourless crystals of the pure *bromide*, m. p. 137—149° to a viscous cloudy liquid which resolidified and melted at 218—221°, this behaviour persisting in spite of repeated recrystallisation (Found: C, 54·3; H, 4·3; Br, 35·4. $C_{21}H_{19}Br_2P$ requires C, 54·55; H, 4·1; Br, 34·6%). A sample was heated in an oil-bath to the lower m. p. and the heating continued until solidification set in: analysis then indicated that no significant change had taken place (Found: C, 53·6; H, 4·21; Br, 35·7%).

A hot aqueous solution of the phosphonium bromide, treated with an aqueous solution of sodium picrate, gave an emulsion from which a crystalline precipitate was readily obtained. Recrystallisation from alcohol gave the pure *picrate* as glistening, elongated, yellow plates, m. p. 186—187° (Found: C, 53·3; H, 3·4; N, 6·9. $C_{27}H_{21}O_7N_3BrP$ requires C, 53·1; H, 3·4; N, 6·9%).

Conversion of the phosphonium bromide into the *d*-bromocamphorsulphonate, the *d*-hydrogen tartrate, the *l*-*N*-1-phenylethylphthalamate and the *d*-camphorsulphonate was accomplished by the usual method employing the silver salt of the appropriate acid. Of these phosphonium salts only 2-*phenyl*-2-p-*bromophenyl*-1 : 2 : 3 : 4-*tetrahydro*iso*phosphinolinium* d-*camphorsulphonate* was obtained crystalline, m. p. 206—212° (Found: C, 60·1; H, 5·8. $C_{31}H_{34}O_4BrSP$ requires C, 60·6; H, 5·6%). A 0·326% solution in ethyl alcohol had $\alpha_D^{15°} = +0·21°$, $[M]_D^{15°} = +98·7°$; the m. p. and rotation underwent no significant change upon recrystallisation of the salt from ethyl-alcoholic ether.

Phenyl-p-*anisyl*-2-(o-*methoxymethylphenyl*)*ethylphosphine* (as XV).—This phosphine was prepared in a precisely similar manner to that described for its *p*-bromophenyl analogue described above, phenyl-*p*-anisylchlorophosphine (13·9 g., 1·1 mols.), prepared according to the method of Davies and Mann (*J.*, 1944, 281), being used in place of the phenyl-*p*-bromophenylchlorophosphine. After the small preliminary fraction of phenyl-*p*-anisylethylphosphine, the required *phosphine* was collected at 215—225°/0·1 mm. Refractionation gave the pure phosphine, b. p. 208°/0·05 mm. (Found: C, 76·1; H, 7·2. $C_{23}H_{25}O_2P$ requires C, 75·75; H, 6·9%): yield, 11·8 g., 65%.

In ethereal solution, the phosphine rapidly combined with methyl iodide at room temperature, the *methiodide* being precipitated as a gummy mass. The supernatant ethereal solution was decanted off, and the residue recrystallised from alcohol to give the pure salt as colourless crystals, m. p. 120·5—121° (Found: C, 57·1; H, 5·4; I, 25·9. $C_{24}H_{28}O_2IP$ requires C, 56·9; H, 5·6; I, 25·1%).

2-*Phenyl*-2-p-*hydroxyphenyl*-1 : 2 : 3 : 4-*tetrahydro*iso*phosphinolinium Bromide* (as VI).—Demethylation, bromination, and ring closure of phenyl-*p*-anisyl-2-(*o*-methoxymethylphenyl)ethylphosphine was carried out in glacial acetic acid–hydrobromic acid mixture as described in the preparation of the 2-phenyl-2-*p*-bromophenyl analogue; in this case, however, the heating at 120° was for 5 hours. Removal of the glacial acetic and hydrobromic acids under reduced pressure left a crystalline solid which was treated with a small amount of alcohol, filtered off, and washed with ether: m. p. 285—286°. Recrystallisation from methyl alcohol gave colourless crystals, m. p. 287—287·5°, of the pure 2-*phenyl*-2-p-*hydroxyphenyl*-1 : 2 : 3 : 4-*tetrahydro*iso*phosphinolinium bromide*, demethylation of the *p*-anisyl group also having taken place (Found: C, 63·4; H, 5·2; Br, 21·0. $C_{21}H_{20}OBrP$ requires C, 63·15; H, 5·1, Br, 20·0%): yield 75%.

A solution of the phosphonium bromide (0·5 g.) in pyridine (8 c.c.) was treated with acetic anhydride (2 c.c.) and the mixture refluxed for 1 hour. The hot solution was filtered from the slight amount of solid which had separated, and the filtrate on cooling gave a crystalline precipitate, which was collected and washed with pyridine followed by ether. The acetyl derivative was much more soluble in alcohol than the original phosphonium bromide, and recrystallisation was accomplished from alcoholic ethyl acetate; the colourless crystals obtained, m. p. 100—103°, were deliquescent when exposed to the air, after 48 hours the m. p. having fallen to *ca.* 50°. The twice recrystallised 2-*phenyl*-2-p-*acetoxyphenyl*-1 : 2 : 3 : 4-*tetrahydro*iso*phosphinolinium bromide* was dried by heating at 80°/1 mm. for 3 hours before analysis (Found: C, 62·2; H, 5·6; Br, 17·2. $C_{23}H_{22}O_2BrP$ requires C, 62·6; H, 5·0; Br, 18·1%).

dl-2-*Phenyl*-2-p-*hydroxyphenyl*-1 : 2 : 3 : 4-*tetrahydro*iso*phosphinolinium* d-*Bromocamphorsulphonate*.—A methyl-alcoholic solution of the bromide was mixed with a similar solution of silver *d*-bromocamphorsulphonate (1 mol.). After boiling for a few minutes, the solution was filtered from the precipitated silver bromide and evaporated to dryness in a vacuum at room temperature. The residual oil was gently warmed with benzene, scratching then readily inducing crystallisation: the m. p. of the unrecrystallised material was 137—147° with softening from 130°, and a 1·015% ethyl-alcoholic solution had $\alpha_D^{17°}$ + 1·94°, $[M]_D^{14°}$ + 300°. Two recrystallisations from ethyl alcohol–ethyl acetate raised the m. p. to 145—152° but no change in rotatory power was observed: for a 1·008% ethyl-alcoholic solution, $\alpha_D^{14°}$ + 1·92°, $[M]_D^{14°}$ + 300° (Found: C, 58·7; H. 6·0; Br, 13·5. $C_{31}H_{34}O_5SBrP$ requires C, 59·1; H, 5·5; Br, 12·7%).

The salt was next recrystallised repeatedly from *iso*propyl alcohol. After five such recrystallisations the m. p. was 116—125° in spite of intensive drying at 80°/0·1 mm. Since a 1·030% ethyl-alcoholic solution had $\alpha_D^{16°}$ + 2·00°, $[M]_D^{16°}$ + 305°, it was considered that resolution was not proceeding.

Repeated recrystallisation from acetone gave a sample which consistently melted at 135—140° with previous softening. After four recrystallisations the salt in 1·080% ethyl-alcoholic solution had $\alpha_D^{15°}$ + 2·005°, $[M]_D^{15°}$ + 313°. The phosphonium bromide was precipitated from an ethyl-alcoholic solution of this sample of the *d*-bromocamphorsulphonate by treatment with an alcoholic solution of sodium bromide at 0°. A methyl-alcoholic solution (0·362%), however, showed no optical activity.

The d-*camphorsulphonate* was prepared by a similar method from silver *d*-camphorsulphonate. The gum remaining after the removal of the solvents was thoroughly freed from methyl alcohol by evacuation at 0·1 mm. for a prolonged period and then dissolved in acetone. After boiling with charcoal the filtered solution was set aside at 0°. After several days practically the whole of the solute had separated as a microcrystalline powder insoluble in hot acetone. This salt was apparently the dl-*phosphonium* d-*camphorsulphonate*, m. p. 153—158° (Found: C, 67·0; H, 6·3; S, 5·8. $C_{31}H_{35}O_5SP$ requires C, 67·6; H, 6·4; S, 5·8%). 26 G. of the phosphonium bromide gave 27 g. (representing 75% of the theoretical) of this salt after the above process of isolation, and a 0·991% ethyl-alcoholic solution had α_D^{18} + 0·74°, $[M]_D^{18°}$ + 102°. It was far too soluble in methyl, ethyl, or *n*-propyl alcohol for recrystallisation, and the use of *sec.*-butyl alcohol failed to change either the m. p. or the rotatory power. The salt (25 g.) was boiled with ethyl acetate (150 c.c.), in which it was insoluble, and alcohol carefully added until complete solution was obtained (41·5 c.c. required) : after boiling with charcoal and filtering, the solution was set aside for a few days, whereupon clusters of needles began to separate. Crystallisation was allowed to proceed at 2° for three days, and the salt was then collected and washed, first with ethyl acetate–ethyl alcohol (4 : 1) and then with ethyl acetate : 6·4 g. of colourless needles, m. p. 171—172·5°, were obtained, and a 0·985% solution in alcohol had $\alpha_{\mathrm{D}}^{18^\circ}$ + 0·79°, $[M]_{\mathrm{D}}^{18^\circ}$ + 110°. The mother-liquor upon dilution with ethyl acetate (50 c.c.) gave a second crop (5·3 g.), m. p. 153—157°, a 0·990% alcoholic solution having α_{D}^{17} + 0·75, $[M]_{\mathrm{D}}^{17^\circ}$ + 104°. Evaporation to dryness under reduced pressure gave a third fraction (12 g.), m. p. 142—151°, $\alpha_{\mathrm{D}}^{18^\circ}$ + 0·71°, $[M]_{\mathrm{D}}^{18^\circ}$ + 98·4° for a 0·993% alcoholic solution.

Three more recrystallisations of the first crop from ethyl acetate–ethyl alcohol raised the m. p. of the salt to 174—175°, the optical constants then being $\alpha_{\mathrm{D}}^{17^\circ}$ + 0·81°, $[M]_{\mathrm{D}}^{17^\circ}$ + 113·5° for a 0·983% alcoholic solution. Further treatment failed to alter these values and the salt was evidently the optically pure d-*phosphonium* d-*camphorsulphonate* (Found : C, 68·0; H, 6·46%).

d-2-*Phenyl*-2-p-*hydroxyphenyl*-1 : 2 : 3 : 4-*tetrahydro*iso*phosphinolinium Bromide*.—The *d*-phosphonium *d*-camphorsulphonate (2·2 g.) was dissolved in alcohol (20 c.c.), and the solution cooled to 0° whilst a similarly chilled solution of calcium bromide (5 g.) in alcohol (10 c.c.) was rapidly added. Stirring and scratching caused precipitation of the crystalline bromide, which was collected, and washed with two portions of 5 c.c. and three of 2·5 c.c. of alcohol. 1·5 G. (94%) of the pure *bromide* were obtained, m. p. 268—270° with softening from 263° (Found : C, 62·6; H, 5·0: Br, 20·7. $C_{21}H_{20}OBrP$ requires C, 63·15; H, 5·1; Br, 20·0%). A 1·029% solution in aqueous alcohol (2 vols. alcohol : 1 vol. water) had $\alpha_{\mathrm{D}}^{17^\circ}$ + 0·34°, $[M]_{\mathrm{D}}^{17^\circ}$ + 32·9°.

Recrystallisation from alcohol failed to affect the m. p. or to cause any significant change in the rotatory power : for a 1·010% solution in aqueous alcohol, $\alpha_{\mathrm{D}}^{16^\circ}$ + 0·34°, $[M]_{\mathrm{D}}^{16^\circ}$ + 33·7° (values for other wave-lengths for a 1·029% solution of this recrystallised material are given in the table on p. 1638) (Found : C, 62·7; H, 4·9; Br, 20·15%).

With methyl alcohol as solvent a marked decrease in rotatory power was observed : a 1·032% solution had $\alpha_{\mathrm{D}}^{17^\circ}$ + 0·05°, $[M]_{\mathrm{D}}^{17^\circ}$ + 4·8°. The bromide was recovered from the solution by evaporation in a vacuum and a 0·941% solution of this material in aqueous alcohol had $\alpha_{\mathrm{D}}^{17^\circ}$ + 0·31°, $[M]_{\mathrm{D}}^{17}$ + 32·9°.

The Phosphonium l-*Camphorsulphonate*.—The phosphonium bromide was recovered from the second and the third fraction of the *d*-camphorsulphonate by precipitation with calcium bromide as described above, and was then converted into the *l*-camphorsulphonate by the usual method. The glass obtained by evaporation of the methyl-alcoholic solution was crystallised from acetone and then had m. p. 152—157°. When recrystallisation was attempted from ethyl acetate–ethyl alcohol, in the proportions used for the *d*-camphorsulphonate, the hot solution initially obtained began to deposit a crystalline precipitate and considerably more alcohol was required before solution could be re-obtained [14 g. of the salt in ethyl acetate (90 c.c.) required 47 c.c. of alcohol]. On cooling, a crystalline precipitate of l-*camphorsulphonate* rapidly separated : 11·8 g., m. p. 170—172°. This had $\alpha_{\mathrm{D}}^{18^\circ}$ − 0·73°, $[M]_{\mathrm{D}}^{18}$ − 102° for a 0·950% solution in alcohol (Found : C, 68·1; H, 6·3. $C_{31}H_{35}O_5SP$ requires C, 67·6; H, 6·4%). Evaporation of the mother-liquors left a solid residue, m. p. 165—168°, $\alpha_{\mathrm{D}}^{18^\circ}$ − 0·72°, $[M]_{\mathrm{D}}^{18^\circ}$ − 101° for a 0·945% alcoholic solution.

The phosphonium bromide was regenerated from a sample of the first crop; this had m. p. 286—288° and proved to be optically inactive in aqueous-alcoholic solution, in which solvent it was considerably less soluble than the *d*-phosphonium bromide described above.

Repeated attempts to recrystallise the *l*-camphorsulphonate from ethyl acetate–ethyl alcohol showed that it was much less soluble than the *d*-phosphonium *d*-camphorsulphonate, and a product, m. p. 170—172°, was always obtained. It was redissolved in methyl alcohol, the solution taken to dryness, and the glass crystallised from acetone in the hope that the low-melting form could be again obtained, but such methods led invariably to a product, m. p. 170—172°, evidently a partial racemate of the *dl*-phosphonium *l*-camphorsulphonate. In a similar way, further preparations of the *d*-camphorsulphonate led to a high-melting product from which the inactive bromide, m. p. 286—288°, was regenerated.

We are indebted to Mr. F. C. Baker for a considerable amount of assistance in the preparation of chlorophosphines.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[*Received, February* 10*th*, 1947.]