

97. *Tetra-aryl-phosphonium, -arsonium, and -stibonium Salts. Part III. The Synthesis and Properties of Tetra-aryl-arsonium Salts having Four Dissimilar Aryl Groups.*

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The synthesis of a number of quaternary arsonium iodides having four unlike aryl groups is described. Such salts should be incapable of dissociation to a tertiary arsine and an iodo-hydrocarbon, and consequently should be resolvable into enantiomorphs having high optical stability. All attempts to resolve these salts have failed, however. This is attributed solely to their physical properties, which make the necessary manipulative processes exceedingly difficult.

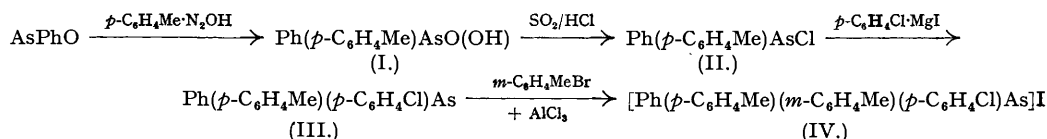
It has been suggested that the considerable difficulty attending the isolation of an asymmetric quaternary arsonium salt in optically stable forms is due to the fact that such salts in solution may form a "dissociation equilibrium" of the type $[abcdAs]X \rightleftharpoons abcAs + dX$ (Burrows and Turner, *J.*, 1921, **119**, 426; Holliman and Mann, *J.*, 1943, 551; Mann, *J.*, 1945, 68). This explanation received strong support from the resolution into optically stable forms of 2-phenyl-2-*p*-chlorophenacyl-1:2:3:4-tetrahydroisoarsinolinium bromide, a salt which possessed considerable chemical stability and therefore would not undergo the above type of dissociation (Holliman and Mann, *loc. cit.*). Further confirmation could be obtained by the preparation and optical resolution of an arsonium salt, $[abcdAs]X$, in which a, b, c, and d were unlike aryl groups: dissociation of such a compound in solution would be exceedingly improbable, and the compound when resolved should possess high optical stability. It should be noted that the configuration of such salts is beyond reasonable doubt, as Mooney (*J. Amer. Chem. Soc.*, 1940, **62**, 2955) has shown by X-ray analysis that tetraphenylarsonium iodide has a tetrahedral cation. The chief object of this paper is to describe the synthesis of such salts: a brief account of their attempted resolution is also included.

Only two reactions are known for the preparation of tetra-arylarsonium salts. Blicke and Monroe (*J. Amer. Chem. Soc.*, 1935, **57**, 720) have shown that triphenylarsine oxide, when treated in turn with phenylmagnesium bromide and hydrobromic acid, yields tetraphenylarsonium bromide, but this reaction appears to have limited application for the synthesis of tetra-arylarsonium salts (Blicke and Cataline, *ibid.*, 1938, **60**, 423) and therefore to be unsuitable for the preparation of salts required in the present work. Chatt and Mann (*J.*, 1940, **1192**) have shown, however, that triphenylarsine reacts with bromobenzene in the presence of aluminium chloride to form tetraphenylarsonium bromide: the mechanism of this reaction has been elucidated by Lyon and Mann (*J.*, 1942, 666), who showed that unlike aryl groups could thus be introduced into the arsonium ion, as, for instance, to form triphenyl-*p*-tolylarsonium and diphenyl-*p*-tolylarsonium salts. We find that arsonium salts containing four dissimilar aryl groups can be prepared by Chatt and Mann's reaction provided the groups be inserted in the appropriate order, and that pure aluminium chloride be used in the final reaction.

This synthesis clearly entails the previous preparation of tertiary arsines, $abcAs$, having three unlike aryl groups: no such arsines had been recorded but they can readily be prepared by the action of a suitable Grignard reagent on the corresponding diarylmonochloroarsines of type $abAsCl$.

Symmetric diarylmonochloroarsines, e.g., diphenylchloroarsine, AsPh_2Cl , are frequently prepared by the action of the requisite diarylmercury on the monoaryldichloroarsine: $\text{AsPhCl}_2 + \text{Ph}_2\text{Hg} = \text{AsPh}_2\text{Cl} + \text{HgPhCl}$. We find that this method cannot safely be used for the preparation of diarylmonochloroarsines having two unlike aryl radicals, because dismutation so readily occurs; for instance, a mixture of diphenylmercury and *p*-tolylidichloroarsine, heated at 220—230° for 5 hours, furnished mainly di-*p*-tolylmonochloroarsine.

In our preliminary experiments, therefore, we utilised a modified Bart's reaction, phenylarsine oxide being treated with sodium *p*-tolylidiazotate in sodium hydroxide solution to form phenyl-*p*-tolylarsinic acid (I) (cf. Kamai, *Trans. Kirov Inst. Chem. Tech. Kazan*, 1935, 3, 49), which on reduction with sulphur dioxide and hydrochloric acid gave phenyl-*p*-tolylchloroarsine (II), the identity of which was thus beyond doubt. This arsine, when treated with *p*-chlorophenylmagnesium iodide, then furnished the viscous liquid *phenyl-p-tolyl-p-chlorophenylarsine* (III).

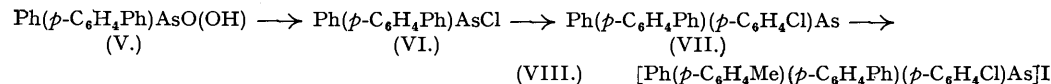


The arsine (III), when heated with *m*-bromotoluene and aluminium chloride followed by aqueous extraction and treatment with potassium iodide, yielded the colourless crystalline *phenyl-p-tolyl-m-tolyl-p-chlorophenylarsonium iodide* (IV), the first salt of the required type to be isolated. This salt was converted by the usual methods into the *d*-bromocamphorsulphonate and the *d*-camphornitronate: both salts formed friable, slightly hygroscopic glasses which could not be recrystallised, and fractional precipitation of the sulphonate gave no evidence of optical resolution. It was thought that this failure might possibly be due to isomerisation of the *m*-bromotoluene when heated with the aluminium chloride at 180—190° to prepare the arsonium salt (IV), whereby the two tolyl groups might become identical. No indication of such isomerisation had ever been obtained, however, and its improbability was shown by the fact that a mixture of triphenylarsine and aluminium chloride, when heated with *m*-bromotoluene and *p*-bromotoluene respectively and subsequently treated in each case with potassium iodide, gave the two distinct salts, *triphenyl-m-tolylarsonium iodide* and *triphenyl-p-tolylarsonium iodide*.

The arsine (III) was then heated with *p*-bromoethylbenzene and aluminium chloride, and thus converted into phenyl-*p*-tolyl-*p*-ethylphenyl-*p*-chlorophenylarsonium iodide. Similarly, the chloro-arsine (II) was treated with *p*-ethylphenylmagnesium bromide to form *phenyl-p-tolyl-p-ethylphenylarsine*, which when heated with *m*-bromotoluene and aluminium chloride, followed by precipitation of the product with potassium thiocyanate, furnished phenyl-*p*-tolyl-*m*-tolyl-*p*-ethylphenylarsonium thiocyanate. Neither of these arsonium salts, however, could be obtained crystalline.

It is noteworthy that the introduction of *p*-alkyl substituents larger than the ethyl group into such salts is apparently not practicable. *p*-Bromo-*n*-propylbenzene would not react with triarylarsonium in the presence of aluminium chloride: even had it so reacted, the constitution of the product would have been uncertain, because the *n*-propyl group might well have isomerised under the influence of the aluminium chloride.

Heavier aryl groups were now employed in the hope that their presence would induce readier crystallisation. For this purpose, phenylarsine oxide was treated with sodium *p*-phenyldiazotate to obtain phenyl-*p*-phenylarsinic acid (V), which Blicke and Smith (*J. Amer. Chem. Soc.*, 1929, 51, 3481) had formerly made by the action of *p*-phenylmagnesium bromide on phenylarsine oxide, followed by treatment first with chlorine and then with sodium hydroxide. The acid (V) was reduced to phenyl-*p*-phenylchloroarsine (VI), which was then

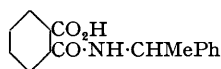


converted by *p*-chlorophenylmagnesium iodide into *phenyl-p-phenyl-p-chlorophenylarsine* (VII). The latter, when heated with *p*-bromotoluene and aluminium chloride, furnished after the usual extraction *phenyl-p-tolyl-p-phenyl-p-chlorophenylarsonium iodide* (VIII). This salt was then converted into the corresponding *d*-camphorsulphonate and *d*-bromocamphorsulphonate, but both salts could be isolated only as the usual friable, unrecrystallisable glasses. The arsine (VII) was also converted by the aluminium chloride reaction into *phenyl-m-tolyl-*

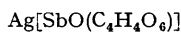
and *phenyl-p-ethylphenyl-p-phenyl-p-chlorophenylarsonium iodide*, but neither salt could be readily recrystallised.

The above results showed clearly that the chief obstacle to success was the physical nature of these asymmetric arsonium salts. Two further steps were therefore taken in the hope of obtaining salts which would crystallise more readily and thus be physically better defined. First, salts were prepared in which three of the phenyl groups carried *para*-substituents, two of which were chloro- and bromo-groups, since the presence of *p*-halogenophenyl groups appeared to promote crystallisation. Secondly, a much wider variety of optically active acids was employed in the resolution experiments. Three of these acids require brief comment, as their use in optical resolution experiments has not apparently been previously recorded.

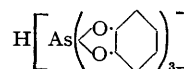
When equimolecular quantities of phthalic anhydride and *l*- α -phenylethylamine were boiled in ethereal solution, *l*-N- α -phenylethylphthalamic acid (IX) was obtained: this acid had $[M]_D$ 130° in ethyl-alcoholic solution, and gave a *silver* salt, which, being soluble in warm aqueous alcohol, could in turn readily be converted into the arsonium salts of the acid. It is noteworthy that the *l*-acid (IX) had m. p. 133°, whereas the *dl*-acid had m. p. 181°.



(IX.)



(X.)



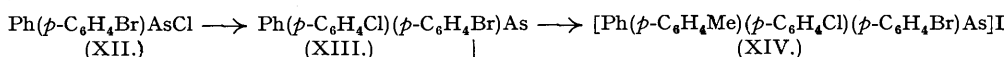
(XI.)

Secondly, Brinnard, Dyke, Jones, and Jones (*J.*, 1932, 1815) have shown that a number of quaternary phosphonium, arsonium, and stibonium halides react with silver *d*-antimonyl tartrate (X) to give well-crystallised salts freely soluble in water. The use of this complex optically active radical in our work therefore appeared very promising, because it might again induce ready crystallisation, and moreover water, instead of organic solvents, could now be used.

Thirdly, Rosenheim and Plato (*Ber.*, 1925, 58, 2000) have shown that tricatechylarsenic acid (XI), originally prepared by Weinland and Heinzler (*Ber.*, 1919, 52, 1316), can be readily resolved with cinchonine. The *l*-barium salt of this acid is soluble in water, has a high rotation, $[M]_D -2330^\circ$, and has reasonable optical stability in the absence of acids. By double decomposition with an arsonium sulphate, therefore, the quaternaryarsonium *l*-tricatechylarsenate could be obtained for resolution purposes.

We have also employed *l*-menthoxyacetic acid, derivatives of which Read and Grubb (*J. Soc. Chem. Ind.*, 1932, 51, 330r) have successfully employed for optical resolutions.

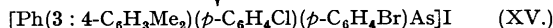
We have therefore reduced phenyl-*p*-bromophenylarsinic acid to the crystalline *phenyl-p-bromophenylchloroarsine* (XII), and converted this by means of *p*-chlorophenylmagnesium iodide into *phenyl-p-chlorophenyl-p-bromophenylarsine* (XIII). This arsine was then converted by the aluminium chloride reaction into *phenyl-p-tolyl-p-chlorophenyl-p-bromophenylarsonium*



(XII.)

(XIII.)

(XIV.)



iodide (XIV), which could be readily recrystallised from aqueous alcohol. This salt was then converted by the usual methods into the *d*-bromocamphorsulphonate, the *d*-camphornitronate, and the *l*-N- α -phenylethylphthalamate, but these salts formed only friable glasses, and the *l*-menthoxyacetate was obtained only as a viscous oil. The *d*-antimonyl tartrate was, however, obtained crystalline, but after it had been repeatedly recrystallised from water, treatment with potassium iodide furnished the inactive iodide (XIV).

Finally, the arsine (XIII) was heated with aluminium chloride and 4-bromo-*o*-xylene, whereby *phenyl-4-o-xyl-yl-p-chlorophenyl-p-bromophenylarsonium iodide* (XV) was ultimately isolated. This iodide was converted into the *d*-bromocamphorsulphonate, the *l*-menthoxyacetate, the *l*-N- α -phenylethylphthalamate, and the *d*-hydrogen tartrate, but none of these salts could be recrystallised. The *d*-antimonyl tartrate was obtained in the crystalline condition, but recrystallisation proved unsatisfactory. Finally, the *l*-tricatechylarsenate was obtained as a white solid, but many attempts at fractional crystallisation or precipitation failed to give any trustworthy evidence of optical resolution.

This repeated failure to resolve so wide a variety of tetra-arylarsonium salts immediately raises the question whether the "dissociation-equilibrium" theory is an incomplete or inaccurate explanation of the prime difficulty involved, or whether the failure is due solely to the physical properties of these tetra-aryl salts. We incline strongly to the latter view. It is

noteworthy that tetraphenyl- and tetra-*p*-tolyl-arsonium iodides are highly crystalline salts that can be readily recrystallised (Chatt and Mann; Lyon and Mann, *loc. cit.*): this is to be expected, since the large but symmetric cation will pack conveniently into the crystal lattice. Our tetra-arylarsonium iodides having four unlike aryl groups usually crystallise with reluctance, whilst the corresponding salts with optically active acid radicals almost invariably form apparently amorphous glasses. This is also to be expected: the very large and now asymmetric cation would clearly not pack readily into the crystal lattice even in the iodides, but when the cation is also accompanied by an asymmetric anion, crystallisation appears to be almost completely inhibited, with the consequent formation of the familiar amorphous glasses. The fact that these glasses when pulverised are also slightly hygroscopic and therefore become sticky on exposure to air makes the necessary experimental manipulation even more difficult. It would appear that in these quaternary arsonium salts, the constitutional factor which would inhibit dissociation and thus give optical stability, namely, the presence of four unlike aryl groups, simultaneously makes the physical process of optical resolution almost impossible to achieve.

EXPERIMENTAL.

All rotations were determined in a 4-dm. tube, the sodium-D line ($\lambda = 5893$) being used as the source of light.

The aluminium chloride was always freshly prepared by the action of dry hydrogen chloride on heated aluminium, and then finely powdered: immediately before use it was confined in a desiccator over sodium hydroxide, as free hydrogen chloride can have a markedly harmful effect on the arsonium salt formation stage of our syntheses.

p-Bromoethylbenzene. *p*-Bromoacetophenone was prepared by the action of acetic anhydride on bromobenzene in the presence of aluminium chloride (Adams and Noller, *Org. Synth.*, 5, 17), and then converted by a Clemmensen reduction into *p*-bromoethylbenzene.

p-Bromo-*n*-propylbenzene. *p*-Bromopropiophenone was prepared similarly by using propionic anhydride and obtained in 78% yield as colourless crystals, m. p. 47°, b. p. 138–140°/18.5 mm. For reduction, zinc (210 g.) was amalgamated by 5 minutes' immersion in water (250 c.c.) containing concentrated hydrochloric acid (10 c.c.) and mercuric chloride (16 g.). The solution was then decanted, and the zinc covered with concentrated hydrochloric acid (225 c.c.) diluted with water (175 c.c.). The bromo-ketone (115 g.) was added, and the mixture refluxed for 10 hours, hydrochloric acid (*ca.* 30 c.c.) being added at hourly intervals. After 14 hours' further refluxing, the mixture was distilled in steam, and the *p*-bromo-*n*-propylbenzene was extracted from the distillate with benzene, dried, and distilled; colourless liquid, b. p. 223–226°; 46 g. (45%). Meyer (*J. pr. Chem.*, 1886, 34, 101) prepared this compound, b. p. 220°; by bromination of *n*-propylbenzene, and Copenhaver, Roy, and Marvel (*J. Amer. Chem. Soc.*, 1935, 57, 1313) by the interaction of *p*-bromophenylmagnesium bromide and *n*-propyl *p*-toluenesulphonate.

Triphenyl-m-tolylarsonium iodide. This preparation was undertaken to determine whether any indication of isomerisation of tolyl groups during the aluminium chloride reaction could be observed. Its description serves essentially for all similar preparations subsequently cited. Triphenylarsine (3 g.), aluminium chloride (1.35 g., 1 mol.), and *m*-bromotoluene (3.3 g., 2 mols.) were heated together at 180–190° for 1.25 hours, the hot melt being then slightly dark but transparent. The cold product was extracted with much boiling water, and the cold filtrate treated in turn with 2 or 3 drops of acetic acid and an excess of potassium iodide. The pale brown precipitate was recrystallised from hot water containing small quantities of potassium iodide (to decrease the solubility) and sodium sulphite (to reduce any tri-iodide; cf. Chatt and Mann, *loc. cit.*). The *iodide* separated as an emulsion which rapidly gave colourless crystals, m. p. 185–187° (Found: C, 57.4; H, 4.5. $C_{26}H_{22}IAs$ requires C, 57.3; H, 4.2%). The m. p., determined at a constant rate of heating, was depressed to 176.5–181.5° by admixture with an equal weight of triphenyl-*p*-tolylarsonium iodide of m. p. 178–179°; since, moreover, the latter iodide separates as a monohydrate (Lyon and Mann, *loc. cit.*), the two iodides were clearly distinct.

Triphenyl-p-ethylphenylarsonium iodide. This preparation was carried out to determine whether *p*-bromoethylbenzene would react with triarylarsonines under the influence of aluminium chloride. Triphenylarsine (3 g.), aluminium chloride (1.35 g., 1 mol.), and *p*-bromoethylbenzene (2.4 c.c.) were heated together at 180–190° for 1.5 hours. The usual extraction and aqueous recrystallisation ultimately yielded the *monohydrated iodide* as colourless crystals, whose m. p. varied greatly with the speed of heating (Found: C, 56.5; H, 4.9. $C_{26}H_{24}IAs \cdot H_2O$ requires C, 56.1; H, 4.7%).

Phenyl-p-tolylarsinic acid (I). The yield of diarylarsonic acids prepared by the Bart reaction depends largely on the pH at which the reaction is carried out. Many experiments showed that the following conditions afforded the highest yield. A solution of *p*-toluidine (10.7 g.) in water (250 c.c.) containing concentrated hydrochloric acid (25.5 c.c.) was diazotised by addition of a solution of sodium nitrite (7.2 g., 1.04 mols.) in water (25 c.c.). The stirred solution was maintained below 5° whilst a solution of phenylarsine oxide (17 g., 1 mol.) in *n*-sodium hydroxide (180 c.c.) was added dropwise during 1.5 hours, followed by the similar addition of *n*-sodium hydroxide (100 c.c.) during 20 minutes. Effervescence occurred during the later stages of this treatment. After 12 hours, the solution was filtered to remove red tarry matter and then made just acid to Congo-red. A red gum separated first, followed by colourless crystals. The mixture was boiled (whereby only the crystals dissolved) and filtered, and the residual molten red gum extracted again with boiling water. The two filtrates when chilled deposited the arsinic acid (I), m. p. 150–152° (Found: C, 56.0; H, 5.2. Calc. for $C_{12}H_{13}O_2As$: C, 56.5; H, 4.75%); 11 g. (40%). A sample after recrystallisation from water had m. p. 156–157°; Kamai (*loc. cit.*) gives m. p. 159–160°. When the quantities used above were increased *ca.* tenfold, the yield fell to 32%.

Phenyl-p-tolylchloroarsine (II). A solution of the above acid (8.1 g.) in a mixture of methanol (40 c.c.) and concentrated hydrochloric acid (16 c.c.) containing a crystal of potassium iodide was heated on a steam-bath whilst sulphur dioxide was passed through for 2 hours. The mixture was cooled, diluted with water (150 c.c.), and the yellow oil extracted with light petrol, dried, and distilled after removal of the solvent. The *chloro-arsine* was obtained as a pale yellow oil, b. p. 175—180°/0.05 mm. (Found: Cl, 12.7. $C_{15}H_{12}ClAs$ requires Cl, 12.7%; 6.2 g. (76%).

Phenyl-p-tolyl-p-chlorophenylarsine (III). A solution of the chloro-arsine (II) (12 g.) in ether (40 c.c.) was added during 45 minutes to an ice-cold, stirred Grignard reagent which had been prepared by the interaction of magnesium (1.57 g., 1.5 atoms) and *p*-chloriodobenzene (15.4 g., 1.5 mols.) in ether (40 c.c.) to which a small iodine crystal had been added. The mixture was then refluxed for two hours, cooled, and hydrolysed by addition of a solution of ammonium chloride (12 g.) in water (50 c.c.). The ethereal layer when separated, dried, and distilled ultimately gave the *arsine* (III) as a colourless viscous liquid, b. p. 208—210°/2 mm., which could not be obtained crystalline (Found: C, 64.4; H, 4.3. $C_{18}H_{16}ClAs$ requires C, 64.3; H, 4.5%).

For characterisation, a chilled, agitated solution of the arsine (2.73 g.) in acetic acid (10 c.c.) was treated dropwise with bromine (1.25 g., 1 mol.), instant decolorisation occurring. The solution was then poured into 30% aqueous sodium hydroxide (125 c.c.), the mixture refluxed for 1 hour, and the oily precipitate extracted with chloroform. The extract when dried, filtered, and evaporated, afforded the *arsine oxide* as a viscous residue which rapidly solidified and after recrystallisation (*cyclohexane*) was obtained as very deliquescent, colourless, feathery crystals, m. p. 130° (Found: C, 61.7; H, 4.3. $C_{19}H_{16}OClAs$ requires C, 61.5; H, 4.35%). An alcoholic solution of this oxide, treated with picric acid, gave the *arsine hydroxy-picrate*, greenish-yellow crystals from alcohol, m. p. 174° (Found: C, 50.7; H, 3.2; N, 7.4. $C_{22}H_{19}O_6N_3As$ requires C, 50.0; H, 3.2; N, 7.0%).

It was thought that the tertiary arsine (III) might be better prepared if the aryl groups were introduced in the order: $PhAsO \rightarrow Ph(p-C_6H_4Cl)AsO(OH) \rightarrow Ph(p-C_6H_4Cl)AsCl \rightarrow Ph(p-C_6H_4Me)(p-C_6H_4Cl)As$. *Phenyl-p-chlorophenylarsinic acid* was therefore prepared similarly to (I), a solution obtained from *p*-chloroaniline (12.75 g.), in water (140 c.c.) and concentrated hydrochloric acid (35 c.c.), being first diazotised by addition of a solution of sodium nitrite (7 g.) in water (50 c.c.), and then treated at 5° dropwise with a solution of phenylarsine oxide (17 g., 1 mol.) in water (300 c.c.) containing sodium hydroxide (16 g.). The cold mixture was stirred for 3 hours, set aside for 2 days, filtered, and made just acid to Congo-red. The precipitated arsinic acid (8.2 g., 28%), after two recrystallisations from water, was obtained as colourless needles, m. p. 162—163° (Found: C, 49.2; H, 3.4; Cl, 12.2. $C_{12}H_{10}O_2ClAs$ requires C, 48.6; H, 3.4; Cl, 12.0%). The conversion of this acid into the corresponding chloro-arsine proved unsatisfactory, however, and this alternative route to the arsine (III) was therefore abandoned.

Phenyl-p-tolyl-m-tolyl-p-chlorophenylarsonium iodide (IV). The arsine (III) (16.6 g.), *m*-bromo toluene (11.4 c.c., 2 mols.), and aluminium chloride (6.2 g.) were heated at 180—190° for 2 hours. The usual extraction, followed by potassium iodide treatment, precipitated the *iodide* as an oil which crystallised only after several days: recrystallisation from water was equally slow, and final purification was achieved by cautious addition of ether to a cold alcoholic solution of the iodide. The latter was thus obtained as colourless crystals, m. p. 148—151° (Found: C, 54.2; H, 4.3. $C_{26}H_{23}ClIAs$ requires C, 54.5; H, 4.05%).

The arsonium *d*-bromocamphorsulphonate was prepared by interaction of the iodide and silver *d*-bromocamphorsulphonate (1 mol.) in rectified spirit. The mixture, when boiled for 10 minutes, filtered, and evaporated, afforded the sulphonate as a viscous oil, which was very soluble in cold methyl and ethyl alcohols, acetone, acetic acid and dioxan, and insoluble in ether, *cyclohexane* and petrol. It dissolved in hot benzene and hot ethyl carbonate, but separated as an oil as each solution cooled. Repeated extraction with cold petrol, however, ultimately gave the residual *monohydrated* sulphonate as a very hygroscopic, brittle, white solid (Found: C, 55.9; H, 5.6. $C_{26}H_{23}O_4ClBrSAs \cdot H_2O$ requires C, 55.8; H, 5.1%), which, however, could not be recrystallised from pure or mixed solvents. A solution of the sulphonate in ethyl acetate was therefore cautiously treated with petrol (b. p. 40—60°) until about 50% of the salt has been precipitated as the usual syrup: the latter was collected, redissolved in ethyl acetate, and the fractional precipitation repeated. This process was performed four times, and the final oily precipitate then converted into the brittle solid by treatment with cold petrol. The solid sulphonate could not be converted into a picrate, and was therefore converted into the mercuritri-iodide: the latter, however, was inactive.

The arsonium *d*-camphornitronate was similarly prepared by the interaction of the iodide and silver *d*-camphornitronate in hot methyl-alcoholic solution, boiling being avoided to prevent possible decomposition. Filtration of the mixed solutions followed by evaporation in a vacuum gave the arsonium nitronate as a syrup which also formed a brittle hygroscopic glass on treatment with petrol, but could not be crystallised.

When the arsine (III) was heated with *p*-bromoethylbenzene (1.7 mols.) and aluminium chloride (1 mol.) at 180—190° for 1.5 hours, the usual treatment afforded ultimately a crystalline iodide which, however, on exposure to damp air rapidly formed a sticky semi-solid mass. This could not be recrystallised, and was not further investigated.

Phenyl-p-tolyl-p-ethylphenylarsine. This arsine was prepared by the interaction of a solution of phenyl-*p*-tolylchloroarsine (12 g.) in ether (40 c.c.) and a Grignard reagent prepared from *p*-bromoethylbenzene (12 g., 1.5 mols.) and magnesium (1.57 g., 1.5 atoms) in ether (40 c.c.). After the usual treatment, the *arsine* was isolated initially as a liquid, b. p. 196—198°/0.2 mm., which rapidly solidified, and after recrystallisation from alcohol formed colourless crystals, m. p. 73° (Found: C, 72.0; H, 5.9. $C_{21}H_{21}As$ requires C, 72.4; H, 6.0%). A solution of this arsine in acetic acid rapidly united with 1 equiv. of bromine: the resultant dibromide was hydrolysed by boiling with aqueous sodium hydroxide, and the arsine oxide extracted with chloroform. Removal of the solvent gave an oil which ultimately solidified, and on recrystallisation from *cyclohexane* furnished the hygroscopic *diarsine oxide-dihydroxide*, $(C_{21}H_{21}AsOH)_2O$ (Found: C, 67.4; H, 5.8. $C_{42}H_{44}O_3As_2$ requires C, 67.5; H, 5.9%). This compound

in alcohol gave the *arsine hydroxy-picrate*, yellow needles from alcohol, m. p. 133° (Found: C, 54.5; H, 4.5; N, 7.4. $C_{27}H_{24}O_8N_3As$ requires C, 54.6; H, 4.1; N, 7.1%).

When phenyl-*p*-tolyl-*p*-ethylphenylarsine was heated with *m*-bromotoluene and aluminium chloride as usual, the ultimate aqueous extract gave solid precipitates with both potassium iodide and thiocyanate: neither precipitate could be recrystallised, however, and was not further investigated.

Phenyl-p-phenylarsinic acid (V). *p*-Aminodiphenyl was prepared by nitration of diphenyl, followed by purification and reduction of the *p*-nitrodiphenyl (Morgan and Walls, *J. Soc. Chem. Ind.*, 1930, 49, 15r). Several experiments showed the following to give the highest yield of the arsenic acid. A solution of *p*-aminodiphenyl (16.9 g.) in hot water (500 c.c.) containing concentrated hydrochloric acid (25.5 c.c.) was cooled and stirred, so that the amine hydrochloride separated in fine crystals. Ice (200 g.) was added, and the mixture well stirred whilst a solution of sodium nitrite (7.2 g., 1 mol.) in water (25 c.c.) was slowly added. A solution of sodium hydroxide (7.2 g.) and phenylarsine oxide (17 g., 1 mol.) in water (180 c.c.) was then added dropwise during 1.5 hours to the stirred diazonium solution kept between 4° and 8°: each drop produced effervescence and a red precipitate. When the addition was complete, the solution was stirred for 1 hour longer, then diluted with a solution of sodium hydroxide (4 g.) in water (100 c.c.) and set aside for 12 hours. The filtered solution was then made just acid to Congo-red. The precipitated arsenic acid (7.3 g., 22%) was collected and recrystallised from alcohol (charcoal): the pure acid (4 g., 12%) had m. p. 221—225° (Found: C, 64.5; H, 4.7. Calc. for $C_{18}H_{15}O_2As$: C, 63.9; H, 4.5%). Blicke and Smith (*loc. cit.*) give m. p. 218—220°. When the above quantities were increased seven-fold, the yield was 14%.

Phenyl-*p*-phenylchloroarsine (VI) was prepared from this acid by the usual hydrochloric acid-sulphur dioxide reduction at 100°; colourless needles from alcohol, m. p. 87—88°, b. p. 211—212°/0.4 mm.; yield, 87% (Found: C, 63.7; H, 4.5; Cl, 10.5. Calc. for $C_{18}H_{14}ClAs$: C, 63.5; H, 4.1; Cl, 10.4%). Blicke and Smith (*loc. cit.*) give m. p. 83—85°.

Phenyl-p-phenyl-p-chlorophenylarsine (VII). A Grignard reagent prepared from *p*-chloriodobenzene (29.5 g., 1.7 mols.) and magnesium (3 g., 1.7 atoms) in ether (100 c.c.) under a nitrogen atmosphere, was chilled to 0° and stirred whilst a solution of the chloro-arsine (VI) (25.3 g.) in benzene (90 c.c.) was slowly added. The mixture was refluxed for 2 hours, chilled, and hydrolysed with a solution of ammonium chloride (25 g.) in water (125 c.c.). The usual procedure then furnished the *arsine* (VII) as a clear yellow syrup, b. p. 279—290°/0.3 mm., which could not be induced to crystallise (Found: C, 69.05; H, 4.4; Cl, 9.3. $C_{24}H_{18}ClAs$ requires C, 69.15; H, 4.4; Cl, 8.5%); 28 g. (90%).

The *arsine oxide* was prepared by the usual bromine addition followed by hot alkaline hydrolysis; evaporation of the chloroform extract gave the oxide as an oil which solidified when extracted with cold petrol, and then, when recrystallised from ethyl acetate, formed colourless crystals, m. p. 163° (Found: C, 66.4; H, 4.2. $C_{24}H_{18}OClAs$ requires C, 66.6; H, 4.2%). This in turn furnished the *hydroxy-picrate*, greenish-yellow crystals, m. p. 146.5—148.5°, from alcohol (Found: C, 54.0; H, 3.5; Cl, 6.0. $C_{30}H_{21}O_5N_3ClAs$ requires C, 54.4; H, 3.2; Cl, 5.4%).

Phenyl-p-tolyl-p-phenyl-p-chlorophenylarsonium iodide (VIII). A mixture of *arsine* (VII) (13.2 g.), *p*-bromotoluene (10.8 g., 2 mols.), and aluminium chloride (4.2 g.) was heated at 185—190° for 1.5 hours, cooled and twice extracted with 600 c.c. of boiling water. Potassium iodide, added to the cold, united, filtered extracts, precipitated the above *monohydrated arsonium iodide* (11.5 g., 56%), which was then recrystallised from a large volume of water containing a small amount of alcohol and a trace of sodium sulphite; colourless solid, m. p. indefinite 90—125° (efferv.) (Found: C, 57.0; H, 4.2. $C_{31}H_{25}ClIAs, H_2O$ requires C, 57.0; H, 4.2%).

The arsonium *d*-bromocamphorsulphonate, prepared in the usual way, was obtained after evaporation of its alcoholic solution in a desiccator as a syrup which was converted into a brittle solid by repeated extraction with cold petrol. Although this solid dissolved in many organic liquids, it could not be recrystallised and usually separated from these solutions as a viscous syrup. For purification, a sample was dissolved in alcohol, precipitated as a syrup by addition of petrol, and the syrup again extracted with cold petrol until the *dihydrate* became solid (Found: C, 57.7; H, 5.4. $C_{41}H_{39}O_4ClBrSAs, 2H_2O$ requires C, 57.6; H, 5.1%).

A similar preparation of the *d*-camphorsulphonate gave a syrupy residue which ultimately formed a friable glass which could not be recrystallised.

Phenyl-p-tolyl-p-phenyl-p-chlorophenylarsonium iodide. By using *m*-bromotoluene, this salt was prepared as the previous iodide, but in much smaller yield. A solution of the crude iodide in hot water containing a small proportion of alcohol on cooling gave an emulsion, which ultimately, on chilling and scratching, deposited the crystalline *iodide monohydrate*, melting indefinitely 75—135° (Found: C, 56.7; H, 4.2. $C_{31}H_{25}ClIAs, H_2O$ requires C, 57.0; H, 4.2%).

Phenyl-p-ethylphenyl-p-phenyl-p-chlorophenylarsonium iodide. This salt was prepared by interaction of the above tertiary arsine (2.1 g.), *p*-bromoethylbenzene (1.6 g., 1.7 mols.), and aluminium chloride (0.7 g., 1 mol.) at 185—190° for 1.25 hours. The cold product was extracted six times with boiling water (300 c.c. in all), and the cold filtered extracts precipitated by potassium iodide. The *arsonium iodide monohydrate* was ultimately purified by slowly cooling a solution in hot water containing a small proportion of alcohol, potassium iodide, and sodium sulphite; the viscous syrup which initially separated crystallised after the solution had been kept at 0° for 12 hours (Found: C, 57.5; H, 4.5. $C_{32}H_{27}ClIAs, H_2O$ requires C, 57.6; H, 4.4%). The iodide has an indefinite m. p.

The preparation of certain optically active acids and their salts used in subsequent experiments is now described.

1-*N*-*a*-Phenylethylphthalamic acid (IX). A solution of 1-*a*-phenylethylamine (5.4 g.) in ether (30 c.c.) was added rapidly to a solution of phthalic anhydride (6.6 g., 1 mol.) in boiling ether (200 c.c.), the mixture refluxed for 30 minutes, and cooled. The syrupy acid which had separated slowly recrystallised; after filtration, a second crop was obtained either by concentration or by careful addition of light petrol. The united crops were recrystallised from ether, and furnished the colourless *acid*, m. p. 134° (Found: C, 71.2; H, 5.3. $C_{16}H_{15}O_2N$ requires C, 71.3; H, 5.6%). A 0.394% alcoholic solution had $\alpha - 0.76^\circ$, $[M] - 131^\circ$; a 0.559% solution had $\alpha - 1.08^\circ$, $[M] - 130^\circ$.

The *dl*-acid was similarly prepared from the *dl*-amine, and recrystallised from acetone; colourless crystals, m. p. 181° (efferv.) (Found : C, 71.0; H, 5.7%).

Silver l-N- α -phenylethylphthalamate. The *l*-acid was dissolved in aqueous *N*-NaOH solution (1 equiv.), and a small excess of aqueous silver nitrate solution added. After 3 hours, the precipitated silver salt was collected and washed with water, alcohol, and ether; it formed a colourless powder (Found : Ag, 28.6. $C_{18}H_{14}O_2NaAg$ requires Ag, 28.7%) moderately soluble in hot aqueous alcohol.

Silver d-antimonyl tartrate monohydrate (X). When solutions of tartar emetic (24.5 g.) in water (400 c.c.) and silver nitrate (15 g., 1.2 mols.) in water (100 c.c.) were mixed, the above monohydrate separated as hard white granules, which were collected, washed in turn with water, alcohol and ether, and dried. The salt is soluble in hot aqueous alcohol.

Silver l-menthoxyacetate. *l*-Menthoxyacetic acid was prepared by the method of Leffler and Calkins (*Org. Synth.*, 1943, 23, 52), but although it was thrice distilled (b. p. 188—190°/17 mm., 119—122°/0.05 mm.), it could not be induced to crystallise. It was therefore dissolved in aqueous *N*-sodium hydroxide solution (1 equiv.), and silver nitrate (1 mol.) in aqueous solution added; the silver salt was precipitated as a white powder, which was collected, washed with water, and dried (Found : Ag, 33.5. $C_{12}H_{21}O_3Ag$ requires Ag, 33.6%). This salt is soluble in chloroform, slightly soluble in water, and almost insoluble in alcohol, acetone or methanol: boiling alcohol slowly decomposes it.

Barium l-tricatechylarsenate. (i) Tricatechylarsenic acid (XI) was prepared by adding catechol (100 g.) to a solution of arsenic acid (40 g.) in hot water (100 c.c.), boiling the mixture for 1—2 minutes, and then allowing it to cool. Crystallisation of the required acid was initially slow, but became rapid later. In subsequent preparations, seeding the solution caused crystallisation. The monohydrated acid was collected, washed with a small volume of water, and dried (cf. Weinland and Heinzler, *loc. cit.*). (ii) The arsenic acid (48 g.) was added to a solution of cinchonine (34 g., 1 mol.) in boiling alcohol (1100 c.c.), and the solution immediately filtered through a preheated filter. On cooling, colourless crystals of the cinchonine *l*-tricatechylarsenate (33 g.) rapidly separated; a 0.304% acetone solution had $\alpha - 3.15^\circ$, $[\alpha] - 259^\circ$ (cf. Rosenheim and Plato, *loc. cit.*). (iii) This *l*-anion is optically stable only in alkaline solution, and the following preparation of the barium salt was developed in order to avoid removal of excess barium by carbon dioxide or sulphuric acid. A mixture of cinchonine *l*-tricatechylarsenate (26.5 g.), methanol (125 c.c.), and barium hydroxide (8 g.) was refluxed for 30 minutes; water (125 c.c.) was then added, and the alcohol slowly distilled off. When 100 c.c. of distillate had been collected, more water (75 c.c.) was added, and a further 50 c.c. of distillate collected. The residue was filtered hot to remove cinchonine, and the filtrate evaporated to dryness at 25 mm. The dry residue (consisting of the required barium salt and barium hydroxide) was extracted with cold absolute alcohol, the undissolved hydroxide removed by filtration, and the barium *l*-tricatechylarsenate precipitated from the filtrate by addition of light petrol as a colourless granular powder: a 0.213% aqueous solution had $\alpha - 3.74^\circ$, $[\alpha] - 438^\circ$.

Phenyl-p-bromophenylchloroarsine (XII). Phenyl-*p*-bromophenylarsinic acid was prepared by interaction of diazotised *p*-bromoaniline and phenylarsine oxide in alkaline solution (Blicke and Webster, *J. Amer. Chem. Soc.*, 1937, 59, 534) and obtained as colourless crystals, m. p. 174—176° (Found : C, 42.7; H, 3.2. Calc. for $C_{12}H_{10}O_2BrAs$: C, 42.25; H, 3.0%). A solution of this acid (82 g.) in methyl alcohol (350 c.c.) and concentrated hydrochloric acid (125 c.c.) was reduced at 100° by a stream of sulphur dioxide, and the crude product cooled, poured into water, and extracted with petrol. Distillation of the dried extract gave the *monochloro-arsine* (XII) as a mobile yellow oil, b. p. 184—186°/0.3 mm., which slowly crystallised when set aside (53.5 g., 65%); crystallisation from alcohol gave colourless needles, m. p. 46—47° (Found : C, 42.3; H, 2.95. $C_{12}H_9ClBrAs$ requires C, 41.9; H, 2.6%).

Phenyl-p-chlorophenyl-p-bromophenylarsine (XIII). This arsine was prepared in the usual way, a solution of the monochloroarsine (XII) (26 g.) in benzene (100 c.c.) being slowly added to a chilled, agitated Grignard reagent prepared from *p*-chloriodobenzene (29.5 g., 1.65 mols.) and magnesium (3 g., 1.65 atoms) in ether (80 c.c.). The final mixture was refluxed for 2 hours, cooled, and hydrolysed with ammonium chloride (25 g.) dissolved in water (125 c.c.). The usual working up ultimately gave the *arsine* (XIII) as a pale yellow oil, b. p. 248—252°/0.5 mm., which crystallised after several days (27 g., 85%); recrystallisation from methanol gave colourless crystals, m. p. 64—65° (Found : C, 51.9; H, 2.9. $C_{18}H_{13}ClBrAs$ requires C, 51.5; H, 3.1%).

This arsine by the usual reactions gave the *arsine oxide*, colourless crystals from cyclohexane or cyclohexane-acetone, m. p. 154—156° (Found : C, 49.9; H, 3.2. $C_{18}H_{13}OClBrAs$ requires C, 49.6; H, 3.0%). The *hydroxy-picrate* formed yellow crystals from alcohol, m. p. 184° (Found : C, 43.7; H, 2.4. $C_{24}H_{16}O_8N_3ClBrAs$ requires C, 43.3; H, 2.4%).

Phenyl-p-tolyl-p-chlorophenyl-p-bromophenylarsonium iodide (XIV). A mixture of the above arsine (27.7 g.), *p*-bromotoluene (22.5 g., 2 mols.), and aluminium chloride (8.8 g., 1 mol.) was heated at 185—190° for 1.25 hours. The clear brown salt was then allowed to cool, extracted with cold benzene to remove any unchanged organic reagent, and the residue then extracted with a large volume of boiling water. The latter was filtered, allowed to cool, and poured into a solution of potassium iodide (50 g.) in water (ca. 200 c.c.). The pale yellow precipitated iodide was collected and recrystallised from a mixture of water (1200 c.c.) and alcohol (400 c.c.) containing small quantities of potassium iodide and sulphite; the emulsion which formed on cooling finally deposited the colourless crystalline *iodide* (27 g., 64%). A portion was further purified by addition of ether to its alcoholic solution, whereby the iodide separated as a syrup which slowly crystallised; colourless crystals, m. p. 206—208° with preliminary sintering (Found : C, 47.0; H, 2.8. $C_{26}H_{20}ClBrIAs$ requires C, 47.1; H, 3.2%).

A portion of this iodide was converted by the usual method into the *d*-bromocamphorsulphonate; an acetone solution of the latter on evaporation in a desiccator furnished a syrup which slowly formed a hygroscopic brittle glass. This was soluble in many solvents, but separated always as a viscous oil, and could not be crystallised. It was eventually dissolved in alcohol and precipitated by addition of petrol; the syrup thus obtained, when extracted with petrol, again furnished the *sulphonate monohydrate* as a friable glass (Found : C, 49.7; H, 4.4. $C_{35}H_{24}O_4ClBr_2SAs \cdot H_2O$ requires C, 50.1; H, 4.3%).

The *d*-camphornitronate, similarly prepared, also formed a brittle glass which could not be crystallised.

The *l*-*N*-*α*-phenylethylphthalamate was prepared by interaction of an alcoholic solution of the iodide (1.276 g.) and the silver phthalamate (0.7526 g., 1 mol.) dissolved in 50% aqueous alcohol (60 c.c.). The filtered solution on evaporation gave an oil which formed a brittle glass on extraction with cold petrol, but which, although freely soluble in many solvents, could not be obtained crystalline.

The *l*-menthoxyacetate was similarly prepared, but the final brown viscous syrup could not be crystallised.

The *d*-antimonyl tartrate. Preliminary experiments showed that this salt was the most promising of those investigated, but that although it was soluble in many organic liquids it could be recrystallised only from water. It was therefore prepared by the interaction of silver *d*-antimonyl tartrate (16.9 g.) and the above iodide (26.17 g., 1 mol.) in a hot mixture of water (3 l.) and alcohol (2 l.). The filtrate was evaporated under reduced pressure, the solid residue dissolved in alcohol (100 c.c.), the solution filtered, and the salt reprecipitated by the addition of much ether; the *d*-antimonyl tartrate was thus obtained as an almost colourless solid (28.9 g., 88% of the theoretical) of indefinite m. p. Three recrystallisations from water (800, 500, 200 c.c.) gave in turn 8.6, 2.6, 0.5 g. of the tartrate, still of indefinite m. p. (Found : C, 43.5; H, 2.7. $C_{29}H_{24}O_7ClBrAsSb$ requires C, 43.7; H, 3.0%). The last fraction was dissolved in hot water (200 c.c.), cooled, and treated with potassium iodide (2 g.), but the reprecipitated arsonium iodide was inactive in alcoholic solution.

4-Bromo-*o*-xylene. A solution of *o*-4-xylidine (30 g.) in hot water (250 c.c.) containing sulphuric acid (49 g.) was rapidly chilled to precipitate the amine sulphate as fine crystals, and then maintained at 5–10° and continuously stirred whilst a solution of sodium nitrite (17.5 g., 1 mol.) in water (30 c.c.) was slowly added. Meanwhile, a solution of hydrated copper sulphate (16 g.) and sodium bromide (38.5 g.) in water (250 c.c.) containing sulphuric acid (7.5 g.) was boiled with copper powder (5 g.) under reflux for 3.5 hours, during which a whitish-grey precipitate of cuprous bromide appeared. The refluxing was now stopped, the diazonium solution added with shaking during 30 minutes, the refluxing then continued for 1.5 hours, and the mixture finally distilled in steam. The *4*-bromo-*o*-xylene was extracted from the distillate with benzene, washed with alkali, dried, and distilled; colourless liquid, b. p. 206–208° (14.3 g., 31%) (Found : C, 51.1; H, 4.9; Br, 44.9. Calc. for C_8H_7Br : C, 51.9; H, 4.9; Br, 43.2%). This compound has previously been prepared solely by bromination of *o*-xylene (Jacobsen, *Ber.*, 1884, 17, 2372; Datta and Chatterjee, *J. Amer. Chem. Soc.*, 1916, 38, 2549).

Phenyl-4-o-xyl-yl-p-chlorophenyl-p-bromophenylarsonium iodide (XV). A mixture of the arsine (XIII) (8.7 g.), *4*-bromo-*o*-xylene (7.7 g., 2 mols.), and aluminium chloride (2.8 g., 1 mol.) was heated at 185–190° for 1.25 hours, and the cold product thrice extracted with boiling water (3 × 250 c.c.). The cold, combined, filtered extracts were slowly added to an aqueous solution of potassium iodide (30 g.), and the arsonium iodide then separated as a colourless precipitate; 7.2 g. (53%). It was purified by dissolution in hot water (700 c.c.) containing alcohol (100 c.c.) and a small amount of potassium iodide and sulphite; cooling gave the *iodide* (XV) as an oil which slowly crystallised but when dry had an indefinite m. p. (Found : C, 47.9; H, 3.45. $C_{25}H_{22}ClBrIAs$ requires C, 47.9; H, 3.4%).

The *d*-bromocamphorsulphonate, prepared in the usual way, formed a friable glass, which had properties very similar to those of the previous sulphonate, and could not be recrystallised.

The *l*-*N*-*α*-phenylethylphthalamate, prepared by interaction of the iodide (3.6950 g.) and the silver phthalamate (2.1310 g., 1 mol.) in aqueous alcohol, was isolated as an oil which was then dissolved in alcohol and reprecipitated by addition of ether; the syrup thus obtained solidified when extracted with cold petrol, but the hygroscopic brittle glass (Found : C, 63.4; H, 5.1. $C_{48}H_{36}O_3NCIBrAs$ requires C, 63.6; H, 4.6%) could not be crystallised.

The *l*-menthoxyacetate was isolated as a syrup which also could not be crystallised.

The *d*-antimonyl tartrate, prepared and purified similarly to the previous antimonyl tartrate, formed a white crystalline mass from water (Found : C, 44.0; H, 3.4. $C_{30}H_{26}O_7ClBrAsSb$ requires C, 44.4; H, 3.2%). It had an indefinite m. p., and recrystallisation from water did not appear promising.

The arsonium sulphate was prepared by interaction of the iodide and silver sulphate (0.5 mol.) in aqueous alcohol. Evaporation of the filtrate gave a syrup, which was dissolved in alcohol and reprecipitated by ether. This purified syrup, when confined in a desiccator, ultimately gave the sulphate as a friable glass which was very hygroscopic and hence was not analysed.

The *d*-hydrogen tartrate was prepared by treating an aqueous alcoholic solution of tartaric acid with barium hydroxide (0.5 mol.) and then with the arsonium sulphate (0.5 mol.). Evaporation of the filtered solution gave a clear gum, which was extracted with cold acetone and then, when confined in a vacuum, gave the *dihydrate* of the arsonium hydrogen tartrate as a brittle glass (Found : C, 51.2; H, 4.4. $C_{30}H_{27}O_6ClBrAs, 2H_2O$ requires C, 50.7; H, 4.4%) which although soluble in various solvents could not be recrystallised.

The *l*-tricatechylarsenate. Acetone solutions of the arsonium sulphate and barium *l*-tricatechylarsenate (1 mol.) were mixed, the barium sulphate allowed to settle, and the supernatant liquid decanted through a filter. Dilution of the filtrate with ether precipitated the *arsonium l*-tricatechylarsenate initially as a syrup which readily formed a white solid when extracted with more cold ether (Found : C, 56.9; H, 3.9. $C_{44}H_{34}O_6ClBrAs_2$ requires C, 57.2; H, 3.7%). It was very soluble in acetone, slightly soluble in hot methyl and ethyl alcohols, and insoluble in water. The following experiments were performed on this material.

(i) The salt (1.9 g.) slowly dissolved when boiled with alcohol (150 c.c.); the solution on cooling deposited 0.65 g., which when recrystallised again from alcohol (80 c.c.) furnished 0.15 g. of the salt. A 0.349% solution of the latter in acetone had α -1.25° , $[M] -830^\circ$. This acetone solution was evaporated to dryness, and the residue taken up in chloroform and shaken with concentrated aqueous potassium iodide solution 6 times to convert the salt into the arsonium iodide. The chloroform solution was then inactive. The low rotation (-830°) of the above salt must presumably have been due to partial racemisation of the anion.

(ii) In view of this result, resolution was now attempted by fractional precipitation of the tri-

catechylarsenate from cold acetone solution by the addition of ether; it was hoped that racemisation of the anion would thus be averted. The following table shows the progress of the fractional precipitation of the arsenate (initial weight, 13.0 g.), the rotation of various fractions being determined in acetone solution.

	Vol. of acetone for dissol- ution, c.c.	Vol. of ether for precipit- ation, c.c.	Wt. of ppt., g.	Rotation of ppt.		
				Concn., g./100 g. soln.	α .	$[M]$.
A	65	200	9.3	0.224	-2.32°	-2380°
B	45	140	5.7			
C	28	95	4.0	0.236	-2.37	-2320
D	20	60	2.8			
E	14	40	1.95	0.226	-2.21	-2260
F	10	30	—			
G	7	20	0.9	0.223	-2.09	-2160

A portion of fraction G was dissolved in chloroform and shaken six times with saturated aqueous sodium picrate solution and then twice with water. The chloroform solution of the arsonium picrate was dried (Na_2SO_4) but was optically inactive. The solution was then evaporated and the sticky residual yellow *picrate*, when rubbed with water, formed a brittle solid (Found: N, 5.0. $\text{C}_{32}\text{H}_{24}\text{O}_7\text{N}_3\text{ClBrAs}$ requires N, 5.6%).

A second portion was stirred with warm concentrated hydrochloric acid until it formed a gum; the acid was decanted, and the treatment repeated to ensure conversion into the arsonium chloride. The gummy residue was dissolved in alcohol, filtered from a trace of unchanged arsenate, the alcohol diluted with water, again filtered, and the solution finally added to a concentrated solution of potassium iodide containing some sulphite. The precipitated arsonium iodide was, however, inactive in acetone solution.

The following new compounds were also prepared in the course of this work: *Di-p-tolyl-p-chloro-phenylarsine*, prepared by the action of *p*-chlorophenylmagnesium iodide on di-*p*-tolylchloroarsine, separated from alcohol as colourless crystals, m. p. 125–126.5° (Found: Cl, 10.0. $\text{C}_{20}\text{H}_{18}\text{ClAs}$ requires Cl, 9.6%). *m-Tolyl-di-p-tolyl-p-chlorophenylarsonium iodide* was prepared by interaction of the above arsine (2 g.), *m*-bromotoluene (2 g., 2 mols.), and aluminium chloride (0.74 g., 1 mol.) at 180–190° for 1 hour; the usual extraction ultimately gave the iodide as a monohydrate, colourless crystals from water containing potassium iodide and sulphite; it was also purified by precipitation by ether from a cold methanol solution (Found: C, 53.7; H, 5.05; Cl, 5.8; I, 20.8. $\text{C}_{27}\text{H}_{25}\text{ClIAs}\cdot\text{H}_2\text{O}$ requires C, 53.6; H, 4.5; Cl, 5.9; I, 21.0%). The salt sintered at ca. 120° but did not melt decisively.

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