The Preparation and Reactions of Dialkyl-(o-dialkylphosphinophenyl)-arsines.

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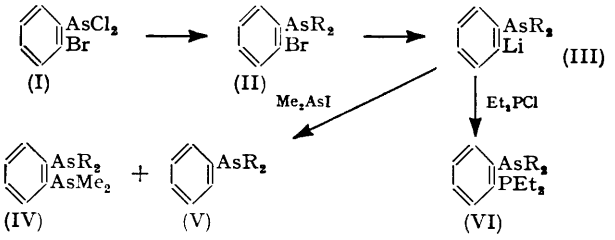
[Reprint Order No. 6607.]

Two members of the above novel type of ditertiary phosphine-arsine have been prepared. They act as strong chelating agents with metals and are thus of considerable stereochemical value. They also undergo diquaternisation with various alkylene dibromides to form cyclic phosphonium-arsonium dibromides, the thermal decomposition of which has been studied. These water-soluble dibromides are of no significant value as schistosomicides.

o-Phenylenebis(dimethylarsine) (IV; R = Me) is a compound of wide application, for it acts as a powerful chelating group with metallic salts (Chatt and Mann, *J.*, 1939, 610: cf. Nyholm, *J.*, 1950, 851 *et seq.*) and also undergoes ready diquaternisation with ethylene, trimethylene, and *o*-xylylene dibromides to give cyclic diarsine dimethobromides, from which in turn various novel types of cyclic arsenic derivatives have been obtained (Glauert and Mann, *J.*, 1950, 682; Mann and Baker, *J.*, 1952, 4142; Jones and Mann, *J.*, 1955, 405, 411).

The diphosphine analogues of this diarsine (IV; R = Me) are unknown. We have therefore investigated the synthesis of the monophosphine analogues, *i.e.*, dialkyl-(*o*-dialkylphosphinophenyl)arsines of type (VI), for such compounds would also be strong chelating agents, but their stereochemical value will be greatly increased by the two unlike co-ordinating atoms: further, quaternisation with alkylene dibromides will now give new types of heterocyclic compounds having arsenic and phosphorus in one ring.

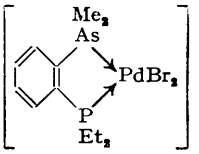


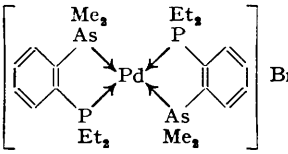
We find that *o*-bromophenyldichloroarsine (I) when treated with methylmagnesium bromide gives *o*-bromophenyldimethylarsine (II; R = Me), which with *n*-butyl-lithium readily affords the *o*-lithio-derivative (III; R = Me). To test the activity of this compound, it was treated with dimethyliodoarsine, whereby *o*-phenylenebis(dimethylarsine) (IV; R = Me) and phenyldimethylarsine (V; R = Me) were obtained in 50% and 5% yield respectively. Treatment of the lithio-derivative with chlorodiethylphosphine gave *o*-diethylphosphinophenyldimethylarsine (VI; R = Me), and repetition of the synthesis, with *o*-bromophenyldiethylarsine (II; R = Et), afforded *o*-diethylphosphinophenyldiethylarsine (VI; R = Et).

The strongly chelating properties of these phosphine-arsines are shown by the ready reaction of the former (VI; R = Me) with potassium palladobromide to give, under appropriate conditions, the covalent dibromo-*o*-diethylphosphinophenyldimethylarsine-palladium (VII) and the salt, bis-(*o*-diethylphosphinophenyldimethylarsine)palladium dibromide (VIII), both highly crystalline yellow compounds. The cation in the salt (VIII), being planar, could clearly exist is *cis*- and *trans*-forms: no indication of a mixture could be detected, and it is highly probable that the salt has the *trans*-configuration (VIII). An *X*-ray crystal structure investigation of this compound is now being carried out by Dr. S. C. Nyburg at the University College of North Staffordshire.

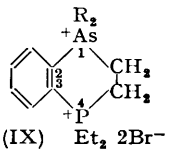
It is noteworthy that, although the phosphine-arsine (VI; R = Me) reacted vigorously when dissolved in an excess of cold methyl iodide, only a monomethiodide could be isolated:

the homologue (VI; R = Et) behaved similarly, with the formation, however, of a mono- and a di-methiodide in the ratio 5 : 1. There is little doubt that these monomethiodides are quaternary phosphonium salts, for Davies and Lewis (*J.*, 1934, 1599) have shown that the speed of quaternisation of tertiary phosphines is greater than that of the corresponding arsines. The stability of the monomethiodides is undoubtedly due to the fact that the positive charge on the quaternised phosphorus atom partially deactivates the tertiary arsine group : the same effect is shown by the diarsine (IV; R = Me), a solution of which in methyl iodide, when boiled under reflux for several hours, forms only a monomethiodide but when heated with methanol at 100° gives a dimethiodide (Mann and Baker, *loc. cit.*).

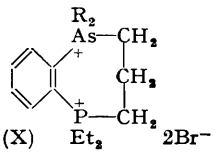
(VII) 

 (VIII)

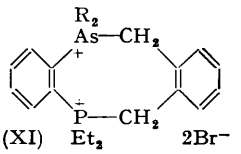
When, however, the phosphine-arsine (VI; R = Me) was heated with ethylene dibromide, trimethylene dibromide, or *o*-xylylene dibromide, ready cyclisation by diquaternisation occurred, with the formation of the diquaternary dibromides (IX, X, and XI; R = Me). The use of the phosphine-arsine (VI; R = Et) gave the corresponding 1 : 1 : 4 : 4-tetraethyl salts. The structure of all these salts was confirmed by the fact that treatment in cold ethanolic solution with sodium picrate gave the corresponding dipicrates, and hence diquaternisation involving cyclisation must have occurred.



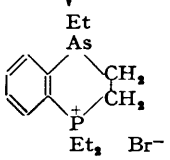
(IX) Et_2 $2Br^-$



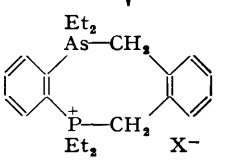
(X) Et_2 $2Br^-$



(XI) Et_2 $2Br^-$



(XII)



(XIII)

The thermal decomposition of the salts (IX and XI; R = Et) has been investigated. It is known that the 1: 1 : 4 : 4-tetramethyldiarsonium analogue of (IX) when heated loses methyl bromide (2 mols.) with the formation of 1 : 4-dimethylethylene-*o*-phenylenediarsine, whereas the same analogue of (XI) undergoes a complex reaction, with the formation of *o*-phenylenebis-(2-*iso*arsindoline). It was expected that the phosphine-arsine salts (IX and XI; R = Et) would similarly lose ethyl bromide readily from the quaternary arsonium group, but that the decomposition of the quaternary phosphonium group, involving the loss of ethylene and hydrogen bromide, would require a higher temperature, and might thus involve general decomposition. This has proved to be the case. The dibromide (IX; R = Et) when heated at 270°/15 mm. for 5 minutes lost ethyl bromide and gave the crystalline 1 : 4 : 4-triethylethylene-*o*-phenylene-1-arsine-4-phosphonium bromide (XII) : when this initial effervescence had ceased, the temperature was increased to 350°/2 mm., causing a slow secondary effervescence, accompanied by general decomposition, liberation of elementary arsenic, and the production of a very small intractable distillate which had no reactions of a tertiary phoshine or arsine. The identity of the bromide (XII) was confirmed by the reconversion of the salt, when heated with ethanolic ethyl bromide, into the dibromide (IX; R = Et).

Similarly the dibromide (XI; R = Et) when heated at 270°/15 mm. lost ethyl bromide, forming 1 : 4 : 4-triethyl-*o*-phenylene-*o*-xylylene-1-arsine-4-phosphonium bromide (XIII;

X = Br), identified as the crystalline iodide (XIII; X = I), but further heating to 330°/2 mm. caused charring and deposition of arsenic, and no distillate was obtained. Further attempts to prepare the cyclic ditertiary phosphine-arsines were therefore abandoned.

The stereochemical features of the *o*-xylylene salt (XI) are of particular interest. *X*-Ray crystal evidence showed that the corresponding 1 : 1 : 4 : 4-tetramethyl-diarsonium dibromide has the simple structure (as XI), *i.e.*, that no question of a " dimer " with a central 16-membered ring arises: this structure (as XI) can theoretically exist in *cis*- and *trans*-forms, which should not be interconvertible, and the above evidence also indicates strongly, but not conclusively, that this salt has the *trans*-structure (for diagrams and detailed discussion of the stereochemistry see Jones and Mann, *loc. cit.*). There is little doubt that the phosphine-arsine salt (XI) has the same structure, in which, however, the cation, if *cis* or *trans*, is now dissymmetric. We have therefore converted the dibromide (XI; R = Et) into the di-(+)-camphorsulphonate and the di-(+)-bromocamphorsulphonate, but neither salt on recrystallisation gave evidence of optical resolution. The (+)-tartrate and the di-(−)-*N*-1-phenylethylphthalamate were isolated only as viscous syrups.

Very little is known about the therapeutic action of cyclic arsenic compounds and even less about that of similar phosphorus compounds. Since furthermore, the water-soluble salts (IX, X, and XI; R = Et) represent new cyclic systems, their action as possible schistosomicides has kindly been investigated by Mr. O. D. Standen at the Wellcome Laboratories of Tropical Medicine: they prove to be of no significant value for this purpose. The compound (XII) has apparently some schistosomicidal action, the assessment of which, however, is made difficult by the relatively high toxicity.

The co-ordinated derivatives of the phosphine-arsines (VI) with various metals, particularly copper, silver, and gold, have been investigated and will be recorded later.

Experimental

All compounds, unless otherwise stated, were colourless except the yellow picrates. All rotations were measured at 16° in a 4 dm. tube, with Na_D light (λ 5893).

o-*Bromophenyldichloroarsine* (I).—This compound was prepared by Kalb (*Annalen*, 1921, **423**, 69) and by Burton and Gibson (*J.*, 1926, 457) but without analytical identification. Sulphur dioxide was passed through a suspension of *o*-bromophenylarsonic acid (75 g.) (Burton and Gibson, *loc. cit.*) in concentrated hydrochloric acid (750 c.c.) containing potassium iodide (0·5 g.) for 3 hr. at room temperature. The *arsine* (I) separated as a purple oil which solidified (76 g., 95%) and when collected, dried, and distilled (b. p. 110°/0·5 mm.) formed pale yellow crystals, m. p. 62—64° (Found: C, 23·7; H, 1·5. $C_6H_4Cl_2BrAs$ requires C, 23·8; H, 1·3%).

o-*Bromophenyldimethylarsine* (II; R = Me).—A solution of the arsine (I) (40 g.) in ether (200 c.c.) was slowly added under nitrogen to a well-stirred Grignard reagent prepared from methyl iodide (18 c.c., 2·2 mols.) and magnesium (7·0 g., 2·2 atoms) in ether (200 c.c.). After the vigorous reaction had subsided, the mixture was stirred for 15 min. and then hydrolysed by adding ammonium chloride (50 g.) in aqueous solution. Distillation of the dried ethereal layer gave the *arsine* (II; R = Me) (26 g., 76%), b.p. 85—86°/0·8 mm. (Found: C, 37·2; H, 4·2. $C_8H_{10}BrAs$ requires C, 36·8; H, 3·8%). It has a characteristic radish-like odour, and is fairly readily oxidised by air. o-*Bromophenyltrimethylarsonium iodide* readily crystallised from a mixture of the arsine and methyl iodide at room temperature, and when recrystallised from methanol decomposed at *ca.* 240° without melting (Found: C, 27·1; H, 3·3. $C_9H_{13}BrIAs$ requires C, 26·8; H, 3·2%).

o-*Bromophenyldiethylarsine* (II; R = Et), similarly prepared by using the arsine (I) (105 g.), ethyl bromide (78 c.c.; 3 mols.), and magnesium (25·0 g., 3 atomic equivs.), had b. p. 109—110°/1 mm. (Found; C, 41·85; H, 5·0. $C_{10}H_{14}BrAs$ requires C, 41·5; H, 4·8%): 84 g., 84%. It gave o-*bromophenyldiethylmethylarsonium iodide*, m. p. 114—115° after crystallisation from ethanol (Found: C, 30·4; H, 4·1. $C_{11}H_{17}BrIAs$ requires C, 30·6; H, 3·9%).

Lithiation of o-*Bromophenyldimethylarsine* (II; R = Me).—This arsine did not react with magnesium turnings or activated magnesium powder; it reacted only slowly with metallic lithium in ether, but readily with *n*-butyl-lithium in light petroleum. Whilst the preparation of the compounds described below was in progress, Gilman and Avakian (*J. Amer. Chem. Soc.*, 1954, **76**, 4031) described the lithiation of various dialkyl-*p*-bromophenylarsines and the reaction of the products with quinoline to form the corresponding 2-(*p*-dialkylarsinophenyl)quinolines.

A solution of the arsine (II; R = Me) (2·75 g.) in light petroleum (b. p. 40—60°) (10 c.c.) was added under nitrogen to a 1·31N-solution (8·8 c.c.) of *n*-butyl-lithium (1·1 mols.), also in light petroleum. The mixture was boiled under reflux for 4 hr., cooled, treated with dimethyliodoarsine (2·4 g., 1 mol.), and boiled for 1 hr. more. After cooling and hydrolysis with water, the dried organic layer on distillation gave the fractions: (*a*) phenyldimethylarsine (V), b. p. 95—110°/14 mm. (0·15 g.); (*b*) *o*-phenylenebis(dimethylarsine) (IV; R = Me), b. p. 150—156°/15 mm. (1·5 g., 50%).

Fraction (*a*) gave phenyltrimethylarsonium iodide, m. p. 244—245° (effervescence) after crystallisation from ethanol (Found: C, 33·2; H, 4·6. Calc. for $C_9H_{14}IAs$: C, 33·3; H, 4·3%). Michaelis and Link (*Annalen*, 1881, **207**, 205) give m. p. 244°.

Fraction (*b*) also gave a monomethiodide (at room temperature), m. p. 220—222°, alone and mixed with an authentic sample. Chatt and Mann (*loc. cit.*) give b. p. 156°/20 mm. for the diarsine.

This experiment showed the success of the method, which was applied virtually unchanged to the preparation of the following compound (VI; R = Me) but was modified for that of the homologue (VI; R = Et) (see below).

o-*Diethylphosphinophenyldimethylarsine* (VI; R = Me).—A solution of the arsine (II; R = Me) (14·4 g.) in light petroleum (50 c.c.) was added to one of 1·31N-*n*-butyl-lithium (50 c.c., 1·2 mols. of solute) in light petroleum, which was then boiled under reflux for 5 hr., cooled, and treated with chlorodiethylphosphine (6·9 g., 1 mol.). Working up as in the above experiment gave the fractions: (*a*) b. p. 84—86°/19 mm. (*ca.* 1 g.), phenyldimethylarsine, identified as its methiodide, m. p. and mixed m. p. 244°; (*b*) b. p. 95—130°/19 mm. (2·3 g.) (no component was identified); (*c*) b. p. 152—170°/22 mm. (7·3 g., 49%), crude phosphine-arsine (VI; R = Me). It was noteworthy that this compound and the diethyl analogue (VI; R = Et) on refractionation gave constant b. p.s but consistently poor analyses. Thus fraction (*c*) when carefully refractionated had b. p. 100—102°/0·6 mm. (Found: C, 57·4; H, 8·5. Calc. for $C_{12}H_{20}PAs$: C, 53·3; H, 7·4%); a second fractionation gave b. p. 105—107°/0·6 mm., and a third, b. p. 105—106°/0·6 mm. (Found: C, 56·0; H, 7·4%). No impurity could be detected during the preparation of derivatives. A mixture of the final product and an equal volume of methyl iodide gave a vigorous reaction with deposition of crystals, which on recrystallisation from ethanol gave the P-*methiodide monohydrate*, m. p. 162°—163° (Found: 36·4; H, 5·6. $C_{13}H_{23}IAsP,H_2O$ requires C, 36·3; H, 5·8%).

Palladium Derivatives.—When solutions of the phosphine-arsine (0·50 g.) in hot ethanol and of potassium palladobromide (1·00 g., 1·06 mol.) in a minimum of water were mixed, an almost insoluble reddish-brown precipitate, probably the salt $[(C_{12}H_{20}PAs)_2Pd][PdBr_4]$, was formed (cf. Chatt and Mann, *loc. cit.*). A mixture of this product, 48% hydrobromic acid (10 c.c.), and ethanol (10 c.c.), when boiled under reflux for 3 hr., gave a deep red solution, which on cooling deposited *dibromo*-o-*diethylphosphinophenyldimethylarsinepalladium* (VII), yellow crystals, m. p. 308° (decomp.) after crystallisation from ethanol (Found: C, 27·3; H, 4·0. $C_{12}H_{20}Br_2PAsPd$ requires C, 26·8; H, 3·75%).

Repetition of the above procedure, using the phosphine-arsine (0·60 g.) and the palladobromide (0·57 g., 0·50 mol.), gave a yellow solution which was evaporated to dryness in a desiccator. The residue, when recrystallised from ethanol, gave *bis*-(o-*diethylphosphinophenyldimethylarsine*)*palladium dibromide monohydrate* (VIII), yellow crystals, m. p. 266—267° (Found: C, 35·1; H, 5·2. $C_{24}H_{40}Br_2P_2As_2Pd,H_2O$ requires C, 34·9; H, 5·1%). This salt gave the deep yellow *dipicrate*, m. p. 236° (decomp.) from aqueous acetone (Found: C, 39·5; H, 4·2; N, 7·9. $C_{36}H_{44}O_{14}N_6P_2As_2Pd$ requires C, 39·2; H, 4·0; N, 7·6%).

Diethyl-o-*diethylphosphinophenylarsine* (VI; R = Et).—The preparation of this compound was investigated more fully than that of its analogue (VI; R = Me). It was found that the use of ether to dissolve the arsine (II; R = Et) accelerated the lithiation (the period of boiling being reduced to 1 hr.), prevented the formation of the arsine (V; R = Et) as a by-product, and increased the yield of the phosphine-arsine (VI; R = Et). The 1·80N-light petroleum solution of *n*-butyl-lithium (220 c.c., 1·05 mols. of solute) was therefore treated in turn with the arsine (II; R = Et) (109 g.) in ether (200 c.c.) and with chlorodiethylphosphine (47 g., 1·0 mol.). After working up as before, distillation gave the fractions: (*a*) b. p. 90—125°/2·5 mm. (14·1 g.), of unidentified composition; (*b*) b. p. 147—152°/3 mm. (70·5 g.). This crude phosphine-arsine (63% yield) on refractionation gave a sample, b. p. 131—132°/0·8 mm. (Found: C, 57·8; H, 8·9. Calc. for $C_{14}H_{24}PAs$; C, 56·3; H, 8·1%), and when again fractionated, a sample, b. p. 136°/1·0 mm. (Found: C, 57·6; H, 7·9%).

The addition of methyl iodide to an equal volume of the cold phosphine-arsine caused the

mixture to boil and to precipitate the *dimethiodide*, m. p. 165° (effervescence) after crystallisation from ethanol (Found: C, 33·0; H, 4·8. $C_{16}H_{30}I_2PAs$ requires C, 33·0; H, 5·2%). Addition of ether to the filtrate from the reaction mixture precipitated the P-*monomethiodide*, m. p. 148—149° after crystallisation from water (Found: C, 41·0; H, 6·2. $C_{15}H_{27}IPAs$ requires C, 40·85; H, 6·2%). The ratio of the weights of these salts was *ca.* 1 : 5.

Cyclic Diquaternisation with Dibromides.—All the following reactions were carried out in a nitrogen atmosphere. (A) *Derivatives of the phosphine-arsine* (VI; R = Me). (1) A mixture of the compound (VI; R = Me) (0·5 g.) and ethylene dibromide (0·16 c.c., 1 mol.) was heated at 90° for 15 min. and at 120° for 2 hr. The mixture solidified considerably during the earlier period, and violent " bumping " was thus avoided. The final hard product, when recrystallised from methanol, afforded 4 : 4-*diethyl*-1 : 1-*dimethylethylene*-o-*phenylene*-1-*arsonium*-4-*phosphonium dibromide dihydrate* (IX; R = Me), m. p. 235—245° (effervescence) (Found: C, 34·5; H, 6·2. $C_{14}H_{24}Br_2PAs,2H_2O$ requires C, 34·1; H, 5·8%). The *dipicrate* formed crystals, m. p. 196—197° from methanol (Found: C, 41·3; H, 3·7; N, 11·1. $C_{26}H_{28}O_{14}N_6PAs$ requires C, 41·2; H, 3·7; N, 11·1%).

(2) Repetition of this experiment, using however trimethylene dibromide (0·19 c.c., 1 mol.), gave a product which, recrystallised from methanol–ethanol, afforded 4 : 4-*diethyl*-1 : 1-*dimethyltrimethylene*-o-*phenylene*-1-*arsonium*-4-*phosphonium dibromide monohydrate* (X; R = Me), m. p. 245—257° (effervescence) (Found: C, 36·7; H, 5·6. $C_{15}H_{26}Br_2PAs,H_2O$ requires C, 36·7; H, 5·7%). It gave a *dipicrate*, m. p. 201—202° after crystallisation from acetone–ethanol (Found: C, 42·3; H, 3·9; N, 10·8. $C_{27}H_{30}O_{14}N_6PAs$ requires C, 42·2; H, 3·9; N, 10·9%).

(3) A solution of the compound (VI; R = Me) (0·5 g.) in warm methanol (2 c.c.) was added to one of *o*-xylylene dibromide (0·49 g., 1 mol.) in methanol (5 c.c.) which was set aside overnight. The crystalline hygroscopic deposit, when recrystallised from methanol, gave 4 : 4-*diethyl*-1 : 1-*dimethyl*-o-*phenylene*-o-*xylylene*-1-*arsonium*-4-*phosphonium dibromide hemihydrate* (XI; R = Me), m. p. 208—209° (effervescence) (Found: C, 44·3; H, 5·8. $C_{20}H_{28}Br_2PAs,\frac{1}{2}H_2O$ requires C, 44·25; H, 5·4%). The *dipicrate* formed crystals, m. p. 188° from acetone–ethanol (Found: C, 46·5; H, 3·9; N, 10·2. $C_{32}H_{32}O_{14}N_6PAs$ requires C, 46·25; H, 3·9; N, 10·1%).

(B) *Derivatives of the phosphine-arsine* (VI; R = Et). These were prepared as their above analogues. (1) 1 : 1 : 4 : 4-*Tetraethylethylene*-o-*phenylene*-1-*arsonium*-4-*phosphonium dibromide* (IX; R = Et) had m. p. 223° (effervescence) when crystallised from ethanol (70% yield) (Found: C, 39·3; H, 6·0. $C_{16}H_{28}Br_2PAs$ requires C, 39·5; H, 5·8%); it gave a *dipicrate*, m. p. 215° (decomp.) when crystallised from acetone–ethanol (Found: C, 42·9; H, 4·4; N, 10·95. $C_{28}H_{32}O_{14}N_6PAs$ requires C, 42·9; H, 4·1; N, 10·7%).

(2) The use of trimethylene dibromide afforded 1 : 1 : 4 : 4-*tetraethyltrimethylene*-o-*phenylene*-1-*arsonium*-4-*phosphonium dibromide* (X; R = Et), m. p. 240° (effervescence) after crystallisation from methanol (50% yield) (Found: C, 41·1; H, 6·4. $C_{17}H_{30}Br_2PAs$ requires C, 40·8; H, 6·05%); it gave a *dipicrate*, m. p. 221° (decomp.) after crystallisation from acetone (Found: C, 43·7; H, 4·3; N, 10·5. $C_{29}H_{34}O_{14}N_6PAs$ requires C, 43·7; H, 4·3; N, 10·55%).

(3) *o*-Xylylene dibromide gave 1 : 1 : 4 : 4-*tetraethyl*-o-*phenylene*-o-*xylylene*-1-*arsonium*-4-*phosphonium dibromide* (XI; R = Et), m. p. 234° (effervescence) after crystallisation from aqueous methanol (48% yield) (Found: C, 47·2; H, 5·9. $C_{22}H_{32}Br_2PAs$ requires C, 47·0; H, 5·7%); it gave a *dipicrate*, precipitated from aqueous solution and recrystallised from aqueous dimethylformamide, m. p. 208° (decomp.) (Found: C, 47·5; H, 4·5; N, 9·95. $C_{34}H_{36}O_{14}N_6PAs$ requires C, 47·5; H, 4·2; N, 9·8%).

Thermal Decomposition of the Dibromides.—(1) *The dibromide* (IX; R = Et). The finely powdered salt, when heated at 270°/15 mm. for 15 min., effervesced, losing ethyl bromide. The residue, when recrystallised from ethanol–acetone, afforded 1 : 4 : 4-*triethylethylene*-o-*phenylene*-1-*arsine*-4-*phosphonium bromide* (XII), m. p. 167—169° (Found: C, 44·9; H, 6·2. $C_{14}H_{23}BrPAs$ requires C, 44·6; H, 6·15%). When, however, the above residue, after the initial effervescence had subsided, was heated at 350°/2 mm., a secondary effervescence occurred, with much general decomposition and deposition of arsenic. The very small distillate consisted of a thick gum and a mobile liquid, but neither would give an ethobromide, a crystalline palladium dibromide derivative, or (after oxidation) a hydroxynitrate, and it is improbable therefore that either was a tertiary arsine or phosphine.

A mixture of the bromide (XII) (0·5 g.), ethyl bromide (1 c.c.), and ethanol (1 c.c.), when heated in a sealed tube at 100° for 6 hr., regenerated the dibromide (IX; R = Et), m. p. and mixed m. p. 223° (effervescence) after recrystallisation.

(2) *The dibromide* (XI; R = Et). This salt when heated at 270°/15 mm. lost ethyl bromide with effervescence, giving a residue of the bromide (XIII; X = Br), which formed a glass which

could not be recrystallised, and did not give a crystalline picrate. Its aqueous solution, when treated with aqueous sodium iodide, deposited 1 : 4 : 4-*triethyl*-o-*phenylene*-o-*xylylene*-1-*arsine*-4-*phosphonium iodide* (XIII; X = I), m. p. 222—224° after crystallisation from ethanol (Found: C, 48·3; H, 5·6. $C_{20}H_{27}IPAs$ requires C, 48·0; H, 5·4%). When the dibromide (XI; R = Et) was heated to 330°/2 mm., extensive charring and deposition of arsenic occurred, and no distillate was obtained.

Attempted Resolution of the Dibromide (XI; R = Et).—(*a*) Aqueous solutions of the dibromide and of silver (+)-camphorsulphonate were mixed, boiled for a few min., filtered, and evaporated to dryness. The residual *di*-(+)-*camphorsulphonate monohydrate* had m. p. 252° (decomp.) after one and after eight recrystallisations from ethanol (Found: C, 56·8; H, 7·2. $C_{42}H_{62}O_8S_2PAs,H_2O$ requires C, 57·1; H, 7·3%), the weight of salt falling from 3·18 g. to 0·35 g. meanwhile. A 1·152% aqueous solution of the final product had α +0·57°, $[M]$ +105°. The two anions have $[M]$ +100° (Graham, *J.*, 1912, **101**, 746) and resolution was therefore not occurring.

(*b*) The *di*-(+)-*bromocamphorsulphonate*, similarly prepared, had m. p. 253° (decomp.) after one and after ten recrystallisations from methanol (Found: C, 49·2; H, 5·7. $C_{42}H_{60}O_8Br_2S_2PAs$ requires C, 49·3; H, 5·9%), the weight falling from 4·17 g. to 1·13 g. A 0·9057% aqueous solution then had α +1·96°, $[M]$ +553°: the two anions alone have $[M]$ +556° (Pope and Read, *J.*, 1910, **97**, 2201).

The (+)-tartrate and the di-(−)-*N*-1-phenylethylphthalamate were similarly prepared by the interaction of the dibromide (XI; R = Et) and the silver salt in aqueous solution and suspension respectively. Each formed a viscous syrup which could not be crystallised.

We are greatly indebted to Mr. O. D. Standen for the therapeutic tests, and to the Department of Scientific and Industrial Research and the Medical Research Council for grants.

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