Cyclic Diarsines. Part III. Compounds containing an Eight-membered Diarsine Ring System.*

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o-Phenylenebis(dimethylarsine) and 1 : 4-dimethylethylene-*o*-phenylenediarsine readily undergo cyclisation with *o*-xylylene dibromide and its 4-chloro-derivative to give compounds of types (IV) and (V), the stereochemistry of which is discussed. The thermal decomposition of the salts (IV) and (V) follows a novel course, with the formation of *o*-phenylenebis-(2-*iso*arsindoline), or its chloro-derivative, in each case.

It has been shown in Part I (Mann and Baker, *J.*, 1952, 4142) that *o*-phenylenebis-(dimethylarsine) (I) readily combines with ethylene dibromide to give the cyclic dimethobromide (II) which on thermal decomposition gives 1 : 4-dimethylethylene-*o*-phenylenediarsine (III); the latter retains this power of cyclisation by diquaternisation, for further reaction with ethylene dibromide followed by thermal decomposition gives diethylene-*o*-phenylenediarsine. This reaction is not limited to the formation of six-membered rings, for the diarsine (I) reacts with trimethylene dibromide to form 1 : 4-dimethyltrimethylene-*o*-phenylenediarsine dimethobromide (Glauert and Mann, *J.*, 1950, 682). We have now investigated the action of *o*-xylylene dibromide, $C_6H_4(CH_2Br)_2$, on the diarsines (I) and (III), for the stereochemistry and reactions of the products are of considerable interest.

The diarsines (I) and (III) react readily and exothermally with the powdered dibromide

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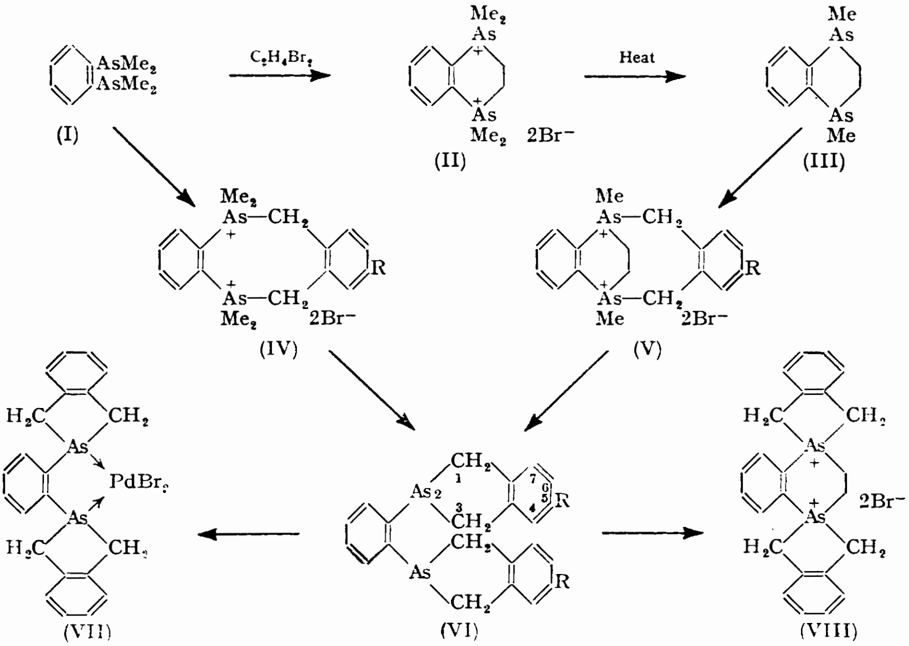
* Part II, preceding paper.

to form 1 : 4-dimethyl-*o*-phenylene-*o*-xylylenediarsine dimethobromide (IV; R = H) and ethylene-*o*-phenylene-*o*-xylylenediarsine dimethobromide (V; R = H) respectively. The fact that each reaction has involved cyclisation by diquaternisation is proved by the precipitation of the corresponding dimethopicrates when cold ethanolic solutions of the bromides are treated with sodium picrate. The readiness of the cyclisation is demonstrated by the rapid formation of (IV; R = H) in an equimolecular solution of (I) and *o*-xylylene dibromide in warm methanol and (more slowly) in cold benzene.

The use of 4-chloro-*o*-xylylene dibromide gave precisely similar salts (IV and V; R = Cl).

The reactions of these salts initially appeared to indicate that they were each formed by the union of two molecules of the diarsine with two of the dibromide. An *X*-ray



crystal investigation of the salt obtained by the reaction of (I) and the dibromide, kindly performed by Dr. W. Cochran in the Cavendish Laboratory of the University of Cambridge, has shown conclusively, however, that it has the " monomer " structure (IV; R = H). Moreover, crystals of (IV; R = H) and (V; R = H) are isomorphous, and the two salts have therefore essentially the same structure. A scale model of the cation of (IV; R = H) shows that the distances apart of the two arsenic atoms and of the two methylene groups are almost identical, and that the two As–CH_2 bonds are therefore almost parallel : furthermore, the tetrahedral angle at the methylene groups will cause the cyclic nucleus of the *o*-xylylene group to be tilted above or below the plane of the two As–CH_2 bonds, and geometric isomerism is therefore possible. This is shown in the schematic Figs. 1 and 2 of the *trans*- and *cis*-cations, in which hydrogen atoms have been omitted for simplicity. In each model, the benzene ring A, the arsenic atoms 1 and 4, and the methyl groups 2 and 2′ can be regarded as being in the plane of the paper, but the methyl groups 3 and 3′ are projecting towards, and the methylene groups 5 and 5′ projecting away from, the observer. In the *trans*-form (Fig. 1), the benzene ring B projects away from A : it is, however, almost parallel to A, but lies of course below the plane of the paper. In the *cis*-form (Fig. 2) the ring B is bent backward towards A, and is inclined at an angle to A, again below the plane of the paper.

Similar models of (V; R = H) can be constructed; they differ from those shown in

FIG. 1.

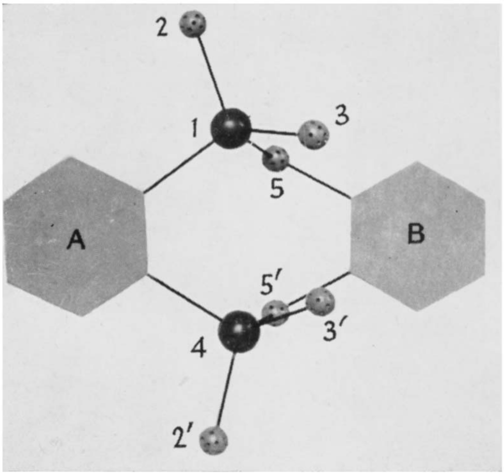
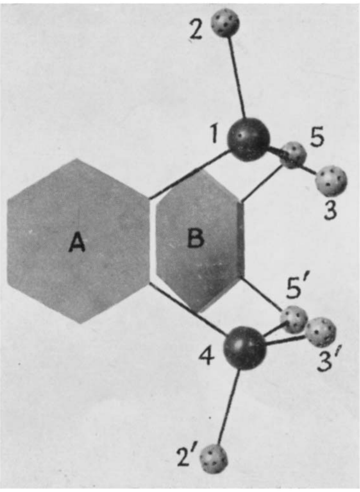


FIG. 2.



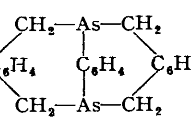
The trans- (Fig. 1) *and the* cis-*form* (Fig. 2) *of the cation of* 1 : 4-*dimethyl*-o-*phenylene*-o-*xylylenediarsine dimethobromide* (IV; R = H).

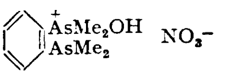
Figs. 1 and 2 only in that the methyl groups 3 and 3′ now become methylene groups which, being linked, are therefore rather closer together; this constriction tends to bring the methyl groups 2 and 2′ very slightly above the plane of the paper.

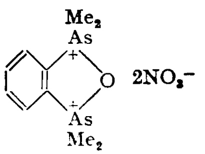
Each of the four dibromides (IV; R = H and Cl) and (V; R = H and Cl) formed homogeneous crystals, and no indication of the above isomerism could be detected. The *X*-ray investigation provides strong indication that (IV; R = H) has the *trans*-form, but a complete structure investigation has not been made. The stereochemistry of the eight-membered ring in (IV; R = H) bears some analogies to that of *s*-dibenzo*cyclo*octadiene (Baker, Banks, Lyon, and Mann, *J.*, 1945, 27), which, although theoretically capable of similar *cis*- and *trans*-isomerism, also occurred in only one form which had a centre of symmetry and hence was the *trans*-isomer.

It will be clear that each form of the compound (IV; R = Cl) and of (V; R = Cl) should be capable of optical resolution: even if *cis*- $\rightleftarrows$ *trans*-interconversion did occur in solution (although no mechanism for this process is apparent) it is highly improbable that the cation could pass through a symmetric phase, particularly in the case of (V; R = Cl). Fractional crystallisation of the di-(+)-camphorsulphonate and di-(+)-bromocamphorsulphonate derived from this salt gave, however, no indication of resolution, and the (+)-antimonyl tartrate, (−)-*N*-1′-phenylethylphthalamate, (+)-tartrate, and (−)-menthoxyacetate were too hygroscopic for effective recrystallisation.

Thermal decomposition of the bromides (IV) and (V) follows an entirely novel course for quaternary arsonium halides. When the bromides (IV and V; R = H) were heated just above their m. p. at *ca.* 20 mm., steady effervescence occurred, the main product in each case being *o*-phenylenebis-(2-*iso*arsindoline) (VI; R = H). The bromides (IV and V; R = Cl) similarly gave *o*-phenylenebis-[2-(5-chloro*iso*arsindoline)] (VI; R = Cl). The identity of (VI; R = H) has been established by: (*a*) analysis and molecular-weight determinations; (*b*) chelation with palladium dibromide to form dibromo-[*o*-phenylenebis-(2-*iso*arsindoline)]palladium (VII), a reaction similar to that shown by the diarsine (I) (Chatt and Mann, *J.*, 1939, 1622); (*c*) its ready condensation with ethylene dibromide to form bis(*iso*arsindoline-*As*-*spiro*)ethylene-*o*-phenylenediarsonium dibromide (VIII), a reaction which is again precisely analogous to that of (I) $\longrightarrow$ (II). These reactions show that this arsine cannot be the isomeric *o*-phenylene-di-*o*-xylylenediarsine (IX); moreover,


(IX)


(X)


(XI)

for structural reasons it is highly improbable that the ring system shown in (IX) can exist, for if the two tertiary arsenic atoms retained their normal intervalency angle (*ca.* 100°) whilst linked through an *o*-phenylene group, they could not also accommodate two " bridging " *o*-xylylene groups, since each group would require two parallel As–CH_2 bonds.

The course of the above thermal decomposition must clearly involve a rupture of the eight-membered ring in both (IV) and (V). It is possible that the first stage is dissociation of the salt to the diarsine (I or III) and *o*-xylylene dibromide, followed by condensation of two molecules of the dibromide and one of the diarsine, with elimination of methyl (and ethylene) groups, to form the diarsine (VI), the remaining diarsine unit (I or III) being discarded in some form. This possibility is supported by the fact that an equimolecular mixture of (IV; R = H) and the dibromide, when subjected to thermal decomposition under the same conditions as those of (IV; R = H) alone, gave twice the yield of the diarsine (VI). In the decomposition of the salt (IV; R = H), no free diarsine (I) could be detected. The mother-liquor from the crystallisation of the crude diarsine (VI) gave, however, a picrate which could not be identified, but which in turn gave a nitrate, the composition of which, after repeated crystallisation, indicated that it was *o*-phenylenebis(dimethylarsine) hydroxynitrate (X). Attempts to oxidise the diarsine (I) for comparison gave, however, the anhydride (XI) of the di(hydroxynitrate), and insufficient supplies of the decomposition product were available for complete identification.

It should be noted that simple loss of methyl bromide, *i.e.*, loss without ring fission, from (IV) and (V) would give the ditertiary arsines, 1 : 4-dimethyl-*o*-phenylene-*o*-xylylenediarsine and ethylene-*o*-phenylene-*o*-xylylenediarsine respectively. Again, it is improbable that the latter compound could exist, for the two arsenic atoms, when linked through an ethylene and an *o*-phenylene group, could not accommodate an *o*-xylylene group. These considerations do not apply to the former diarsine, which has a strainless ring system. The reason for its non-formation during the thermal decomposition of (IV) is presumably that rupture of the eight-membered ring precedes loss of methyl bromide. We have, therefore, prepared *o*-phenylenebis(dibenzylarsine) in order to obtain the tetrabenzyl analogue of (IV), from which a readier loss of benzyl bromide might have been effected. The bis(dibenzylarsine) was isolated solely as a gum, which gave a crystalline monomethiodide, but only hygroscopic syrups and gums by reaction with *o*-xylylene dibromide and its 4-chloro-derivative.

EXPERIMENTAL

Compounds were colourless unless otherwise stated. M. p.s of the dibromides (IV) and (V) depended on the temperature of immersion, denoted as (I.T.); these salts all melted with effervescence. Molecular weights were determined in boiling benzene. The yields stated are throughout those of the once-recrystallised material.

The diarsine (I) was prepared by Chatt and Mann's method (*J.*, 1939, 610). The identity of the purified diarsine (III), b. p. 99—101°/0·5 mm., was checked by conversion into its dimethobromide, m. p. and mixed m. p. 253° (effervescence).

1 : 4-*Dimethyl*-o-*phenylene*-o-*xylylenediarsine Dimethobromide* (IV; R = H).—(*A*) A stirred mixture of the diarsine (I) (27·2 g.) and finely powdered *o*-xylylene dibromide (25·2 g., 1 mol.) rapidly became warm and within 30 min. had solidified; it was then heated at 100° for 1 hr. to ensure complete reaction, and the cold product, when recrystallised from methanol, furnished the hygroscopic *dimethobromide monohydrate*, m. p. 214—216° (I.T. 160° or 200°) (Found : C, 38·4; H, 4·9. $C_{18}H_{24}Br_2As_2,H_2O$ requires C, 38·1; H, 4·6%) : 39·5 g., 75%. Treatment with sodium picrate, each in methanolic solution, yielded the *dimethopicrate*, yellow crystals (from water), m. p. 219—220° (decomp.) (Found : C, 42·45; H, 3·2; N, 10·1. $C_{30}H_{28}O_{14}N_6As_2$ requires C, 42·6; H, 3·3; N, 9·9%).

(*B*) Solutions of the diarsine (2·99 g.) and the dibromide (2·76 g., 1 mol.), each in warm methanol (30 c.c.), when mixed under nitrogen, gave within 1—2 min. a crystalline deposit (3·6 g.) of the dimethobromide, m. p. and mixed m. p. 213—215° (I.T. 160°), which gave the the dimethopicrate, m. p. 219° (decomp.), alone and mixed. Similarly, solutions of the diarsine (1·32 g.) and the dibromide (1·22 g., 1 mol.), each in benzene (100 c.c.), were mixed under nitrogen and set aside for several days; the dimethobromide (1·15 g.) slowly separated, and gave the dimethopicrate (Found : C, 42·8; H, 3·3; N, 10·3%), m. p. and mixed m. p. 218° (decomp.), after recrystallisation.

Dr. W. Cochran reports on the monohydrated dimethobromide (IV; R = H) : "The crystals are orthorhombic, with unit-cell dimensions $a = 17·5$, $b = 11·3$, $c = 10·2$ Å (±2%). (h00) Reflections were absent for h odd, (0k0) for k odd, and (00l) for l = 1, 3, and 5; there were no other absences. The space group is therefore $P2_12_12_1$. The density is $1·66MZ/V$, where M is the molecular weight, Z is the number of molecules per unit cell (4 for $P2_12_12_1$), and $V = abc$. Hence density = 1·86 for the monomer (as IV; R = H), and 3·72 for the dimer. The density experimentally determined = 1·79 ± 0·1 g./c.c. and the compound is therefore the monomer.

"The crystals grow as needles with the c axis as the needle axis. The growth of a crystal in this way very rarely occurs unless the molecules are rather flat, with the plane of the molecule perpendicular to the needle axis. The *trans*-structure (Fig. 1) gives a much flatter molecule than the *cis* (Fig. 2) and is thus strongly, but not conclusively, indicated."

Ethylene-o-*phenylene*-o-*xylylenediarsine dimethobromide* (V; R = H) was prepared by method (*A*) above, from the diarsine (III) (1·91 g.) and the dibromide (1·77 g., 1·05 mol.) which rapidly solidified with heat evolution, and from methanol gave the crystalline hygroscopic *monohydrate*, m. p. 214—216° (I.T. 160° and 220°) (Found : C, 38·5; H, 4·6. $C_{18}H_{22}Br_2As_2,H_2O$ requires C, 38·2; H, 4·3%) : 1·71 g., 47%. It gave a *dimethopicrate*, yellow crystals (from water), m. p. 221—222° (decomp.) (Found : C, 42·8; H, 3·3; N, 9·9. $C_{30}H_{26}O_{14}N_6As_2$ requires C, 42·65; H, 3·1; N, 9·95%).

A mixture of the salts (IV; R = H) and (V; R = H) had m. p. 212—213° (I.T. 160°) with softening at 207°, and 210—213° (I.T. 200°) with softening at 208°, at the same rate of heating as for the pure salts. The infra-red spectra of the salts in a Nujol mull were almost identical (as would be expected in view of their very similar structures), but in hexachlorobutadiene the dibromide (V; R = H) showed strong sharp bands at 3·36, 2·93, 2·99, and 3·46 μ with intensities decreasing in this order, whereas the dibromide (IV; R = H) showed weak bands at 3·00, 3·37, and 2·94 μ (decreasing intensities) with only a very faint indication of a band at 3·47 μ.

*4'-Chloro-*1 : *4-dimethyl-*o*-phenylene-*o*-xylylenediarsine dimethobromide* (IV; R = Cl) *monohydrate*, similarly prepared and recrystallised, had m. p. 241—242° (I.T. 160°), 243—244° (I.T. 220°) (Found: C, 36·2; H, 4·3. $C_{18}H_{23}ClBr_2As_2,H_2O$ requires C, 35·85; H, 4·2%), which in a vacuum over phosphoric anhydride gave the anhydrous *salt* of unchanged m. p. (Found: C, 36·9; H, 4·3. $C_{18}H_{23}ClBr_2As_2$ requires C, 37·0; H, 4·0%). It gave a *dimethopicrate*, yellow crystals, m. p. 213°, from water (Found: C, 41·1; H, 3·5; N, 9·9. $C_{30}H_{27}O_{14}N_6ClAs_2$ require C, 40·9; H, 3·1; N, 9·5%).

*4'-Chloro-ethylene-*o*-phenylene-*o*-xylylenediarsine dimethobromide* (V; R = Cl) *monohydrate*, m. p. 236° (I.T. 160°) and 240° (I.T. 220°) (Found: C, 35·95; H, 3·8. $C_{18}H_{21}ClBr_2As_2,H_2O$ requires C, 35·7; H, 3·8%), heated at 60°/0·1 mm. for 3 hr., gave the hygroscopic anhydrous *salt* (Found : C, 37·3; H, 4·4. $C_{18}H_{21}ClBr_2As_2$ requires C, 37·1; H, 3·6%). It gave a yellow *dimethopicrate*, m. p. 213—214° (decomp.) (Found : C, 41·2; H, 3·3; N, 9·8. $C_{30}H_{25}O_{14}N_6ClAs_2$ requires C, 41·0; H, 2·9; N, 9·6%).

The dimethobromide (V; R = Cl) also gave a *dimetho-*(+)*-camphorsulphonate*, m. p. 298—299° (decomp.) after 3 recrystallisations from ethanol (Found: C, 51·3; H, 5·8. $C_{38}H_{51}O_8ClS_2As_2$ requires C, 51·6; H, 5·8%). A 1·3% aqueous solution had $[M]_D^{17}$ +96°; two camphorsulphonate ions should have $[M]_D$ +100° (cf. Graham, *J.*, 1912, **101**, 746). Further recrystallisation did not change the m. p. or the rotation.

The corresponding *dimetho-*(+)*-bromocamphorsulphonate dihydrate* after one crystallisation from methanol–ethanol had m. p. 267—268° (decomp.), increased to 271° (decomp.) by 4 recrystallisations from ethanol (Found : C, 42·5; H, 5·3. $C_{38}H_{49}O_8ClBr_2S_2As_2,2H_2O$ requires C, 42·25; H, 5·1%). A 1·10% aqueous solution had $[M]_D^{20}$ +551°; two sulphonate ions should have $[M]_D$ +556° (cf. Pope and Read, *J.*, 1910, **97**, 2201). The dimethobromide, precipitated from aqueous solution by concentrated potassium bromide, was inactive.

A mixture of the salts (IV; R = Cl) and (V; R = Cl) had m. p. 241—242° (I.T. 200° or 220°). The infra-red spectra of these salts in Nujol mull were also closely similar, but that of the former had a well-defined sharp band at 9·84 μ which was absent in that of the latter. In hexachlorobutadiene, the salt (IV; R = Cl) showed very weak rather broad bands at 2·9, 3·1, 3·38, 3·47, and 3·57 μ, whereas the salt (V; R = Cl) showed much stronger and sharper bands at 2·87 and 3·36 μ and rather weaker bands at 3·46 and 3·55 μ, but none at 3·1 μ.

Thermal Decomposition.—The dimethobromide (IV; R = H). (*A*) The pure powdered salt (3·88 g.), when cautiously heated with a small " brush " flame, melted and then gave a steady effervescence; when this ceased, the clear residual liquid readily solidified on cooling. Recrystallisation from ethanolic chloroform gave o*-phenylenebis-*(2-iso*arsindoline*) (VI; R = H), m. p. 129—131° (0·80 g., 53%) (Found : C, 61·0; H, 4·7%; *M*, 416. $C_{22}H_{20}As_2$ requires C, 60·9; H, 4·6%; *M*, 434).

(*B*) To ensure the mildest possible conditions for the decomposition, the powdered salt (2 g.) was heated at 0·5 mm. in a large flask (to ensure that most of the salt was in contact with the wall) immersed in a Silicone bath, the temperature being slowly increased until effervescence started and then kept constant (240—245°), the complete decomposition taking 45 min. The product, once recrystallised, gave the same product (VI; R = H), m. p. and mixed m. p. 123—129° (0·25 g., 32%).

(*C*) A powdered mixture of the salt (IV; R = H) (2·0 g.) and *o*-xylylene dibromide (0·93 g., 1 mol.), treated as in (*A*), gave the same product (0·48 g., 61%).

Evaporation of the mother-liquors from the recrystallisation of (VI; R = H) in (*A*) gave a gum, which could not be obtained solid but, treated in ethanol with sodium picrate, gum deposited a bromine-free picrate. The latter, repeatedly recrystallised from methanol, ethanol, acetone, or water, gave in each case yellow crystals, m. p. 181—182° (Found : C, 45·5, 45·65; H, 4·0, 4·05; N, 6·7, 7·1%). Since this product appeared to be mixed crystals of more than one compound, a portion (0·5 g.) was decomposed with cold dilute nitric acid and the mixture then repeatedly extracted with ether. The aqueous solution was evaporated to dryness in a desiccator at room temperature, and the residue, after repeated recrystallisation from ethanol, gave apparently o-*phenylenebis*(*dimethylarsine*) *hydroxynitrate dihydrate* (X), m. p. 196—197° (effervescence) (Found: C, 29·65; H, 4·6; N, 3·6. $C_{10}H_{17}O_4NAs_2,2H_2O$ requires C, 29·9; H, 5·2; N, 3·5%).

The dimethobromide (V; R = H). This was performed as in (*A*) above, and furnished the diarsine (VI; R = H), m. p. and mixed m. p. 129—131°, after crystallisation (Found: C, 60·9; H, 4·9%).

The dimethobromide (IV; R = Cl). This was carried out essentially as in (*A*) above, and gave o-*phenylenebis*-[2-(5-*chloro*iso*arsindoline*)] (VI; R = Cl), m. p. 191—195°, after crystallisation from chloroform (Found: C, 52·8; H, 3·9%; *M*, 525. $C_{22}H_{18}Cl_2As_2$ requires C, 52·5; H, 3·6%; *M*, 503).

The dimethobromide (V; R = Cl). This also gave the diarsine (VI; R = Cl), m. p. and mixed m. p. 190—195°.

Reactions of the Diarsine (VI; R = H).—A solution of the diarsine in excess of methyl iodide, when boiled for 2 hr., gave the *monomethiodide*, m. p. 180—181° (effervescence) after recrystallisation from aqueous ethanol (Found: C, 47·6; H, 4·2. $C_{23}H_{23}IAs_2$ requires C, 47·9; H, 4·0%). When a solution of the arsine (VI; R = H) in methanolic methyl iodide was heated in a sealed tube at 100° for 6 hr., it also afforded this salt, m. p. as above, alone and mixed (Found: C, 47·7; H, 4·05%). It may be noted that under these conditions the diarsine (I) gives the mono- and di-methiodide respectively (Mann and Baker, *loc. cit.*).

When a concentrated aqueous solution of potassium palladobromide was added dropwise to a boiling solution of the diarsine (VI; R = H) in acetone, *dibromo*-[o-*phenylenebis*-(2-iso*arsindoline*)]*palladium* (VII) was deposited; it formed yellow crystals, m. p. 336—337° (decomp.), from dimethylformamide (Found: C, 37·6; H, 3·1. $C_{22}H_{20}Br_2As_2Pd$ requires C, 37·7; H, 2·85%).

A mixture of the diarsine (VI; R = H) (1·44 g.) and ethylene dibromide (0·29 c.c., 1 mol.), when heated at 125—130° for 6 hr., slowly solidified, and when then recrystallised from ethanol furnished *bis*(iso*arsindoline*-As-spiro)*ethylene*-o-*phenylenediarsonium dibromide monohydrate* (VIII), m. p. 223° (effervescence) (Found: C, 45·0; H, 4·1. $C_{24}H_{24}Br_2As_2,H_2O$ requires C, 45·0; H, 4·1%). It gave a *dipicrate*, yellow crystals, m. p. 216—217° (decomp., preliminary softening), from ethanolic acetone (Found: C, 47·3; H, 3·5; N, 8·9. $C_{36}H_{28}O_{14}N_6As_2$ requires C, 47·1; H, 3·1; N, 9·2%).

Oxidation of the Diarsine (I).—Samples of this diarsine were treated with cold concentrated nitric acid, warm dilute nitric acid (1 : 1 by vol.), and with hydrogen peroxide in acetone, followed later by a small quantity of dilute nitric acid. Each solution was evaporated to dryness in a vacuum-desiccator at room temperature, and the residue, when crystallised from ethanol, yielded the *anhydride* (XI), m. p. 213° (effervescence), of *o*-phenylenebis(dimethylarsine) di(hydroxynitrate) (Found: C, 28·1; H, 3·9; N, 6·5. $C_{10}H_{16}O_7N_2As_2$ requires C, 28·2; H, 3·8; N, 6·6%). It gave a *di*(*hydroxypicrate*) (as XI), yellow needles, m. p. 138—140°, after crystallisation from water and drying at 70°/0·1 mm. (Found: C, 34·9; H, 3·05; N, 11·0. $C_{22}H_{20}O_{15}N_6As_2$ requires C, 34·8; H, 2·7; N, 11·1%).

Addition of bromine (1 mol.) to the diarsine (I) in ethanol, followed by hydrolysis with aqueous sodium hydroxide, did not furnish an arsine oxide, and the aqueous solution did not give a picrate. Many other attempts to prepare the salt (X) by the oxidation of (I) failed.

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