Cyclic Diarsines. Part IV. Derivatives of* 5 : 10-*Dihydro*-5 : 10-*dimethylarsanthren.*

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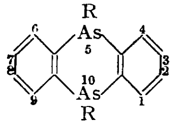
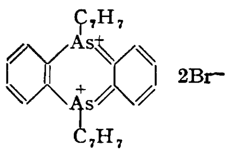
[Reprint Order No. 5708.]

The reaction of the above arsanthren (I; R = Me) with bromine, alkyl halides, ethylene, trimethylene, and *o*-xylylene dibromides, and the formation of novel polycyclic diarsine systems, are discussed. Considerable evidence is adduced for the structure of benzenoid-quinonoid diarsonium salts of type (IV).

5 : 10-Dichloro-5 : 10-dihydroarsanthren (I; R = Cl) was first prepared by Kalb (*Annalen*, 1921, **423**, 39), and the great stability of this ring system was demonstrated by Wieland and Rheinheimer (*ibid.*, p. 10) who showed, for example, that it resisted attempts at nuclear nitration. Chatt and Mann (*J.*, 1940, 1184) prepared the 5 : 10-di-*p*-tolyl derivative (I; R = C_6H_4Me), which they isolated as two geometric isomers: this isomerism arises from the fact that the tervalent arsenic atom has an intervalency angle of *ca.* 100°, and the molecule is therefore folded about the As–As axis. This di-*p*-tolyl derivative formed a highly stable colourless dibromide, which possessed many properties of a salt, and Chatt and Mann suggested that it had the benzenoid-quinonoid structure (II).



(I)



(II)

Although the compound (I; R = C_6H_4Me) did not apparently form diquaternary salts, for only a monomethiodide had been isolated, it appeared probable that the reactivity of the two arsenic atoms would be enhanced if R were an alkyl group; and moreover that the folded structure of the molecule might then, for steric reasons, allow ready diquaternisation by alkylene dibromides with consequent cyclisation across the arsenic atoms. We have therefore investigated the reaction of ethylene, trimethylene, and *o*-xylylene dibromides with 5 : 10-dihydro-5 : 10-dimethylarsanthren (III).

Experiment has confirmed this reasoning. The 5 : 10-dimethyl compound (III) was prepared by the action of methylmagnesium iodide on the chloro-compound (I; R = Cl); no attempt was made to investigate whether this product was also a mixture of geometric isomers, as such isomers would probably undergo reasonably ready interconversion at the temperatures employed in our subsequent reactions. The expected greater reactivity of the arsenic atoms was confirmed, for a solution of (III) in methanolic methyl bromide when heated at 50° for 2 hours gave the monomethobromide, but at 100° for 6 hours furnished the dimethobromide; further, the compound (III) in boiling methyl iodide gave only the monomethiodide, but with methyl toluene-*p*-sulphonate at 180° for 4 hours gave the dimethotoluene-*p*-sulphonate, which was readily converted into the dimethiodide. The stability of the ring system was again demonstrated, in that the compound (III) with a mixture of concentrated sulphuric and fuming nitric acids at 100° for 2 hours gave solely the diarsine di(hydroxynitrate), whose composition was shown by its conversion into the corresponding di(hydroxypicrate).

The interaction of the dihydrodimethylarsanthren (III) with ethylene dibromide depended markedly on the conditions employed, and gave some unexpected products. When equimolecular quantities of (III) and of the dibromide were heated at 125° for 6 hours, or at 100° for 24 hours, the only product isolated (in 60% yield after recrystallisation) was arsanthren dimethobromide (IV), identical in general structure with the compound (II). The allocation of structure (IV) is based on the following evidence. (*a*) The product

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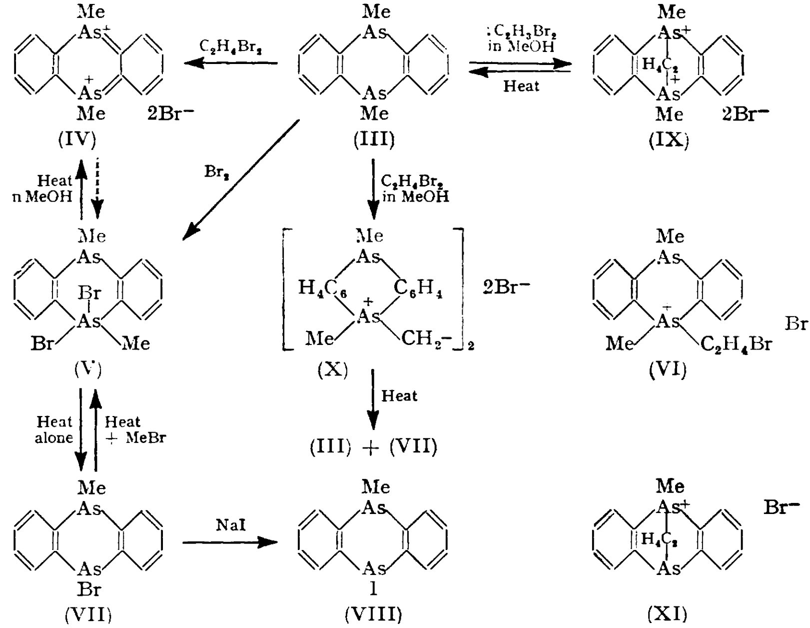
* Part III, preceding paper.

forms stable cream-coloured crystals, m. p. 256°, in which all the bromine is ionic. The bromine can therefore be estimated volumetrically in cold aqueous solution and the dibromide can be readily converted in cold methanolic solution into its di-iodide and dipicrate. (*b*) The compound (III), when heated with an equivalent of bromine in methanol at 100°, again gives the dibromide (IV). It is probable that the first action of the bromine is direct addition to one arsenic atom to give the tertiary arsine dibromide (V) which then undergoes rearrangement to the salt (IV). The mechanism by which ethylene dibromide converts (III) into (IV) is unknown. It is probable, however, that the first action is quaternisation at one arsenic atom to give (VI) : the positive pole on this arsenic atom partly deactivates the second arsenic atom, and in the absence of strongly quaternising conditions (discussed below) the salt (VI) decomposes with loss of ethylene and the formation of (IV).



It is noteworthy that although the dibromide (IV) is colourless, the corresponding di-iodide, obtained from (IV) by double decomposition in solution, forms deep orange crystals; these in turn give pale yellow methanolic and ethanolic solutions, which on treatment with sodium picrate deposit the dipicrate. This indicates that the di-iodide in these solutions may exist as an equilibrium mixture of the ionic and the covalent form [as (IV) and (V) respectively], and that in the crystalline state it assumes solely the covalent form, for tertiary arsine di-iodides are normally orange to brown.

The structure of the cation in (IV) is of great interest, because it will clearly exist as a resonance hybrid closely akin in structure to anthracene; it should then have considerable stability, and in particular the whole cation, including the methyl groups, should be uniplanar. This planar factor is of importance in the structure of the *o*-xylylene derivatives (see below).

The dibromide (IV) when heated at 0·1 mm. readily lost methyl bromide with the formation of the pale yellow 5-bromo-5 : 10-dihydro-10-methylarsanthren (VII), which with sodium iodide in boiling acetone gave the 5-iodo-analogue (VIII), whose deep yellow colour is characteristic of compounds of type R_2AsI. This formation of the 5-bromo-derivative (VII) again almost certainly proceeds by way of the isomeric dibromide (V). Further, this series of reactions can be reversed, for the bromo-derivative (VII) when heated with methyl bromide at 100° is reconverted into the dibromide (IV). This might appear to be an abnormal reaction, for the methyl bromide might be expected to quaternise the 10-methylarsine group rather than to attack the 5-bromoarsine group in (VII). It is possible that this quaternisation does occur and the product then forms the usual dissociation equilibrium; if, however, addition of methyl bromide to the 5-bromoarsine group occurs as a competing reaction, and the dibromo-derivative (V) so formed readily isomerises to the more stable dibromide (IV), the latter will ultimately be the sole product.

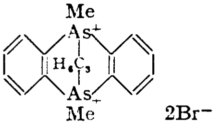
Diquaternisation of the dimethylarsanthren (III) with ethylene dibromide was ultimately achieved in methanolic solution, a condition known powerfully to promote quaternisation (Menschutkin, *Z. physikal. Chem.*, 1890, **6**, 41; Mann and Watson, *J. Org. Chem.*, 1948, **13**, 509). When this solution of (III), containing 2 equivalents of the dibromide, was heated at 100° for 24 hours, the colourless 1 : 4-dimethylethylenedi-*o*-phenylenediarsonium dibromide (IX) was obtained (this compound readily gave a colourless di-iodide, as its structure would indicate). When this dibromide was heated at 0·1 mm. the reaction was reversed, since the dimethylarsanthren (III) was again obtained. All attempts, by modifying the conditions of the thermal decomposition, to induce the alternative loss of methyl bromide and formation of ethylenedi-*o*-phenylenediarsine failed. It must be emphasised that an ethylene group bridging the two arsenic atoms, as in (IX), would apparently entail some strain in the ring system, and there is at present no decisive evidence to show whether the salt has the structure (IX) or is a " dimer " in which two ethylene groups span two arsanthren units, analogous to (XX) (p. 415). No reliable method of molecular-weight determination for such salts is available.

When, however, the methanolic solution of (III) was heated with 1 equivalent of ethylene dibromide, the main product was *s*-ethylenebis-5-(5 : 10-dihydro-5 : 10-dimethylarsanthronium) dibromide (X), which is similar in general type to *s*-ethylenebis(hexahydro-1 : 4-diphenylazarsonium) dibromide and its azaphosphonium analogue (Beeby and Mann, *J.*, 1951, 886; Mann and Millar, *J.*, 1952, 3039). The compound (X) is almost identical in composition with 1-methylethylenedi-*o*-phenylenediarsine monobromide (XI), but its identity is established by decomposition at 250°/0·1 mm. to an equimolecular mixture of the dimethyl- and bromomethyl-arsanthren (III) and (VII); there is no obvious route whereby both these compounds could arise from (XI), whereas fission of (X) could obviously produce them.

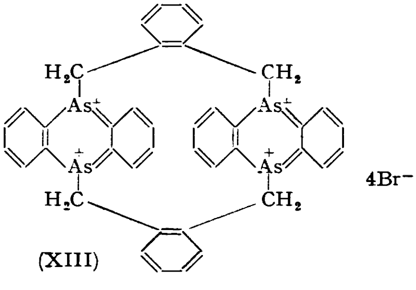
The complexities shown by ethylene dibromide quaternisation do not appear when trimethylene dibromide is used. Equimolecular quantities of the dimethylarsanthren (III) and trimethylene dibromide at 155—160° readily formed 1 : 4-dimethyltrimethylenedi-*o*-phenylenediarsonium dibromide (XII); this salt when heated at 0·1 mm. also smoothly regenerated the arsanthren (III). The ready formation of (XII), compared with that of (IX), is probably due largely to the almost strainless trimethylene bridge.

When equimolecular quantities of dihydrodimethylarsanthren (III) and *o*-xylylene dibromide were heated, two compounds were formed in proportions determined by the temperature. One is 5 : 5′-10 : 10′-bis-*o*-xylylenebisarsanthronium tetrabromide (XIII), a compound analogous to (IV) in the resonance arsanthren structure, its existence as cream-coloured crystals, and in its ready conversion into an orange tetraiodide. If each arsanthronium unit is planar, the As–CH_2 bonds must also be in this plane and must form a direct extension of the As–As axis; if so, the molecule must have the " dimer " structure (XIII), since under these conditions one *o*-xylylene radical could not span the two arsenic atoms of one arsanthren unit. The cation of (XIII) can therefore be shown as (XIIIA), in which the two planar arsanthren ring systems are depicted at right angles to the plane of the paper: for simplicity, the double bonds are shown in the quinonoid but not in the benzenoid rings. The four As–CH_2 groups are in this plane, but models show that in each *o*-xylylenediarsine unit the parallel orientation of the As–CH_2 groups causes the benzene ring of the *o*-xylylene bridge to be markedly tilted towards or away from the observer. This tilt could cause *cis–trans* isomerism: since our products were homogeneous, they probably had the symmetrical (and presumably more stable) *trans*-form. Calculations based on the data provided by Lonsdale (*Proc. Roy. Soc.*, 1929, *A*, **123**, 494; *Trans. Faraday Soc.*, 1929, **25**, 352) and Pauling (" Nature of the Chemical Bond," Cornell University Press, 2nd Edn., 1945, pp. 160 *et seq.*) indicate that the two parallel arsanthren units in

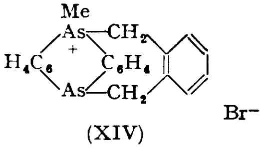
(XIIIA) would be 2·9 Å apart. In view of the shape and considerable size of this cation, it may be significant that the tetrapicrate crystallises as a decahydrate.



(XII)



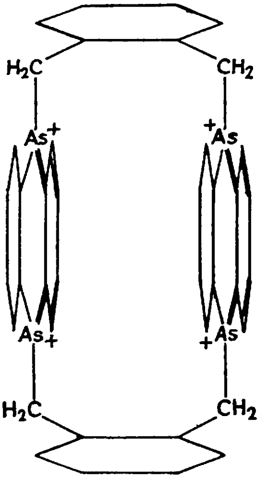
(XIII)

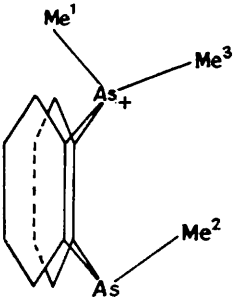


(XIV)

The second product is a colourless salt of empirical formula $(C_{21}H_{19}As_2)Br$, which can readily be converted into a colourless iodide. Several structures (p. 418) could be allocated to this compound, but an *X*-ray crystal investigation, kindly carried out in the Cavendish Laboratory of the University of Cambridge by Dr. W. Schaffer of the University of Cape Town, shows conclusively that it is di-*o*-phenylene-*o*-xylylenediarsine monomethobromide (XIV). This structure is of great interest. A model shows that if the *o*-xylylene group is thus to span the arsenic atoms, the two As–CH_2 bonds must be almost parallel (as in the analogous case of the *o*-xylylene derivatives of *o*-phenylenebis(dimethylarsine) and 1 : 4-dimethylethylene-*o*-phenylenediarsine : Part III). But in the dimethylarsanthren (III) and, for example, its dimethobromide, the C–As–C valency angle, of *ca.* 100° and 109° respectively in these compounds, does not allow any conformation in which the As–Me bonds of the two arsenic atoms are parallel (cf. Chatt and Mann, *loc. cit.*; Mann, *J.*, 1945, 67). In dimethylarsanthren monomethobromide [shown diagramatically as cation in (XV), where Me¹ and Me² represent the original methyl groups and Me³ that inserted by quaternisation], the valency angles at the top and the bottom arsenic atom are now *ca.* 109° and *ca.* 100° respectively, so that, even allowing for some averaging of these angles in the ring system, there is one conformation, as shown, in which these As–Me bonds are almost parallel. Consequently it follows that the tricyclic diarsine structure of (XIV) can exist without marked strain only as a monoquaternary salt, in which the two As–CH_2 bonds have the spatial arrangement of the As–Me³ and As–Me² bonds in (XV).

(XIIIA)



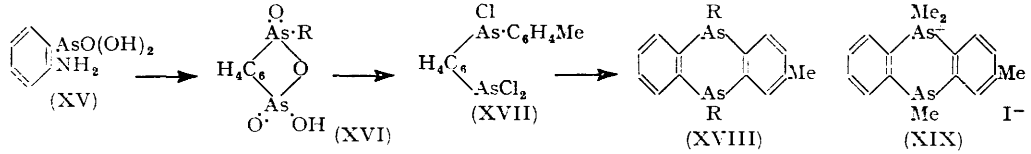


(XV)

This structure is in line with the fact that the bromide (XIV) when heated in a vacuum underwent general decomposition, and no definite product could be isolated; for simple loss of methyl bromide—normally so characteristic of tertiary arsine methobromides—could not occur from (XIV).

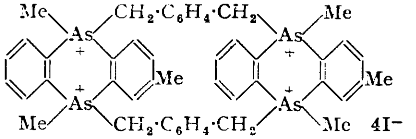
It is noteworthy that when equimolecular quantities of the dimethylarsanthren (III) and *o*-xylylene dibromide were heated together for 2 hours at 130°, the yields of the tetrabromide (XIII) and the monobromide (XIV) were 8% and 65% respectively, and at 160° were 39% and 20%. When two equivalents of the dibromide were used, with heating for 2 hours at 160°, only the tetrabromide (XIII) was isolated; finally, the compound (XIV), when heated with one equivalent of the dibromide for 2 hours at 140—145°, gave (XIII). It is clear therefore that a reasonably ready conversion (XIV) $\longrightarrow$ (XIII) must occur under these conditions: this is not surprising, in view of the great thermal lability shown by " bridged " *o*-xylylene groups in the diarsine derivatives discussed in Part III.

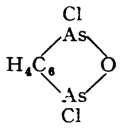
In view of the comparatively ready formation of the bridged salt (IX), we attempted to prepare an analogous compound having one nuclear substituent and consequently possessing molecular dissymmetry. Diazotised *o*-arsanilic acid (XV) was treated with *p*-tolylarsenoxide, C_7H_7AsO, by the Bart reaction, which afforded the anhydride (XVI; $R = C_6H_4Me$) of *o*-arsonophenyl-*p*-tolylarsinic acid; reduction with sulphur dioxide and hydrochloric acid then yielded chloro-(*o*-dichloroarsinophenyl)-*p*-tolylarsine (XVII), a thick oil which with hydrogen peroxide in acetone exothermally regenerated the anhydride (XVI). The chloride (XVII) underwent cyclisation when heated, to give 5 : 10-dichloro-5 : 10-dihydro-2-methylarsanthren (XVIII; R = Cl), a yellow oil, converted by methylmagnesium bromide into 5 : 10-dihydro-2 : 5 : 10-trimethylarsanthren (XVIII; R = Me), which formed a gum. With cold methyl iodide and bromide this gave the monomethiodide [probably (XIX)] and the dimethobromide respectively, both crystalline, this result recalling the work of Mole and Turner (*J.*, 1939, 1720) on the comparative activating effect on chloroarsines of nuclear methyl groups in the formation of phenoxarsines.



(XV) (XVI) (XVII) (XVIII) (XIX)

The trimethylarsanthren (XVIII; R = Me) reacted readily at 100° also with ethylene and trimethylene dibromide, but in each case the product, and the corresponding di-iodide, did not crystallise. The arsanthren also reacted with *o*-xylylene dibromide to give a very hygroscopic bromide, which in turn gave a non-hygroscopic crystalline iodide. The molecular complexity of this salt is uncertain, but the valency distributions about the arsonium atoms [cf. (XIV)] indicate that it is very probably the dimer, *i.e.*, 5 : 10 : 5′ : 10′-tetrahydro-2 : 5 : 10 : 2′ : 5′ : 10′-hexamethyl-5 : 5′-10 : 10′-bis-*o*-xylylenebisarsanthronium tetraiodide (XX). The monomer, in which one *o*-xylylene group bridged the arsenic atoms of one arsanthren unit, would be dissymmetric, but the dimer could exist in several geometrically isomeric forms, at least one of which has a plane of symmetry. The (+)-bromocamphorsulphonate and the antimonyl (+)-tartrate gave no indication of resolution, and other salts with optically active acid radicals were impracticably hygroscopic.

(XX)




(XXI)

The use of *p*-methoxyphenylarsenoxide in the above Bart reaction gave the anhydride acid (XVI; $R = C_6H_4{\cdot}OMe$), which, however, on treatment with sulphur dioxide and hydrochloric acid gave the anhydride (XXI) of *o*-phenylenebis(chlorohydroxyarsine) (cf. Kalb, *loc. cit.*; Chatt and Mann, *loc. cit.*). The use of *p*-nitrophenylarsenoxide gave an azobenzenediarsonic acid, and attempts to synthesise a suitable analogue of (IX) were discontinued.

Compounds of types (XVI) and (XXI) further illustrate the ready formation of five-membered rings containing arsenic atoms (cf. Parts II and III, preceding papers).

EXPERIMENTAL

Unless otherwise stated, all compounds prepared were colourless. The yields stated are those of the once-recrystallised products.

5 : 10-*Dihydro*-5 : 10-*dimethylarsanthren* (III).—A fine suspension of the dichloro-compound (I; R = Cl) (20 g.) in benzene (150 c.c.) was slowly added to a Grignard reagent prepared from methyl iodide (13·2 c.c., 4 mols.) and magnesium (4·8 g., 4 atoms) in ether (100 c.c.). The mixture was boiled under reflux for 1 hr., cooled in ice-water, and hydrolysed with ammonium chloride solution. The organic layer, when separated, dried (Na_2SO_4), and evaporated, gave a residue which when crystallised from ethanol–chloroform afforded the *arsanthren* (III) (16 g., 90%), m. p. 191—192·5° (Found : C, 50·7; H, 4·5. $C_{14}H_{14}As_2$ requires C, 50·6; H, 4·2%).

The *monomethobromide*, prepared by use of an excess of methyl bromide in methanol in a sealed tube at 50° for 2 hr., had m. p. 219° (effervescence) after crystallisation from methanol (Found : C, 42·3; H, 4·1. $C_{15}H_{17}BrAs_2$ requires C, 42·15; H, 4·0%). The *dimethobromide*, prepared similarly at 100° (6 hr.), had m. p. 302° (effervescence) after crystallisation from water (Found : C, 36·65; H, 4·1. $C_{16}H_{20}Br_2As_2$ requires C, 36·8; H, 3·8%). Its aqueous solution, treated with aqueous sodium picrate, deposited the *dimethopicrate*, yellow crystals, m. p. 282° (decomp.) after crystallisation from dimethylformamide (Found : C, 41·3; H, 3·2; N, 10·55. $C_{28}H_{24}O_{14}N_6As_2$ requires C, 41·05; H, 2·9; N, 10·3%). The *monomethiodide*, prepared by boiling a solution of (III) in methyl iodide for 1 hr., had m. p. 222° (effervescence) after crystallisation from ethanol (Found : C, 38·1; H, 3·6. $C_{15}H_{17}IAs_2$ requires C, 38·0; H, 3·6%). The *dimethotoluene*-p-*sulphonate*, prepared by use of methyl toluene-*p*-sulphonate (2 mols.) at 180° for 4 hr., had m. p. 316° (decomp.) after crystallisation from methanol (Found : C, 51·4; H, 4·8. $C_{30}H_{34}O_6S_2As_2$ requires C, 51·15; H, 4·8%). Since, however, the monomethotoluene-*p*-sulphonate has C, 51·0; H, 4·6%, the identity of the salt was confirmed by adding it to sodium iodide, each in aqueous solution, thus precipitating the *dimethiodide*, m. p. 263° (decomp.) after crystallisation from water (Found : C, 31·2; H, 3·0. $C_{16}H_{20}I_2As_2$ requires C, 31·1; H, 3·25%).

The powdered arsanthren (III) was added cautiously to a stirred mixture of fuming nitric acid and concentrated sulphuric acid (1 : 1 by vol.), which was then kept at 100° for 2 hr., cooled, and poured on ice. The white precipitate, when recrystallised from water, furnished the *di*(*hydroxynitrate*), pale yellow crystals, m. p. 224° (effervescence) with immediate resolidification and remelting at 373° (decomp.) (Found : C, 33·9; H, 3·1; N, 5·4. $C_{14}H_{14}O_2As_2,2HNO_3$ requires C, 34·3; H, 3·3; N, 5·7%). The *di*(*hydroxypicrate*) formed yellow crystals, m. p. 210° (decomp.) from water (Found : C, 37·9; H, 2·7; N, 10·2. $C_{14}H_{14}O_2As_2,2C_6H_3O_7N_3$ requires C, 37·9; H, 2·4; N, 10·2%).

Reaction of the Arsanthren (III) *with Ethylene Dibromide*.—(*A*) The arsanthren (1·541 g.) and the dibromide (0·432 c.c., 1 mol.) were heated in a sealed tube at 125—130° for 6 hr. The tube, although cooled to 0° before being opened, still contained gas (probably ethylene). The cold stone-hard residue, when recrystallised from methanol, gave the cream-coloured *arsanthren dimethobromide* (IV) (1·49 g., 60%), m. p. 256° (effervescence) (Found : C, 34·1; H, 3·0; total Br, 32·4; ionic Br, 32·6; As, 30·8. $C_{14}H_{14}Br_2As_2$ requires C, 34·1; H, 2·9; Br, 32·5; As, 30·5%). From methanolic solution it readily deposited the yellow *dimethopicrate*, m. p. 244° (decomp.) after crystallisation from ethanol (Found : C, 39·35; H, 2·5; N, 10·25. $C_{26}H_{18}O_{14}N_6As_2$ requires C, 39·5; H, 2·5; N, 10·6%).

The *dimethiodide* was prepared (*a*) by adding the methobromide to sodium iodide, each in methanolic solution, (*b*) by boiling a solution of the methobromide in an excess of methyl iodide for 2 hr. It formed deep orange crystals, m. p. 214° (decomp.), from methanol (Found : C, 28·9; H, 2·2. $C_{14}H_{14}I_2As_2$ requires C, 28·7; H, 2·4%).

A solution of the arsanthren (III) (0·395 g.) and of bromine (0·061 c.c., 1 mol.) in methanol (1 c.c.) when heated at 100° for 6 hr., gave the dimethobromide (IV), m. p. and mixed m. p. 256° (effervescence), after crystallisation from methanol; this in turn gave the above dimethopicrate, m. p. and mixed m. p. 243—244° (decomp.).

When the pure dimethobromide (0·52 g.) was heated gently with a " brush " flame at 0·1 mm., effervescence occurred smoothly and the residual pale yellow liquid solidified on cooling. Recrystallisation from benzene afforded 5-*bromo*-5 : 10-*dihydro*-10-*methylarsanthren* (VII) (0·34 g., 81%), pale yellow crystals, m. p. 175—177° (Found : C, 39·15; H, 2·7%; *M*, cryoscopic in benzene, 414. $C_{13}H_{11}BrAs_2$ requires C, 39·3; H, 2·75%; *M*, 397). An acetone–ethanol solution of (VII) and of sodium iodide, when boiled for 5 min. and cooled, deposited the 5-*iodo*-

derivative (VIII), deep yellow crystals, m. p. 174—178°, from acetone (Found : C, 34·7; H, 2·8. $C_{13}H_{11}IAs_2$ requires C, 35·1; H, 2·5%).

When a solution of the bromo-compound (VII) in an excess of methyl bromide was heated in a sealed tube at 100° for 2 hr., it afforded the dimethobromide (IV), m. p. and mixed m. p. 256° (effervescence) after crystallisation from methanol (Found : C, 33·9; H, 3·1%). Repetition of this experiment, with methyl iodide and 1 hour's heating, afforded the dimethiodide (as IV), deep orange crystals, m. p. 214° (decomp.) alone and mixed, after crystallisation from methanol (Found : C, 28·9; H, 2·3%).

(*B*) A solution of the arsanthren (III) (1·36 g.) in ethylene dibromide (0·71 c.c., 2 mols.) and methanol (1·5 c.c.) in a sealed tube at 100° (24 hr.) afforded 1 : *4-dimethylethylenedi-*o*-phenylenediarsonium dibromide monohydrate* (IX), m. p. 272° (effervescence) (from methanol) (1·2 g., 63%) (Found : C, 35·9; H, 3·7; Br, 30·0. $C_{16}H_{18}Br_2As_2,H_2O$ requires C, 35·7; H, 3·75; Br, 29·7%). Concentration of the mother-liquor ultimately yielded a trace of the dimethobromide (IV), m. p. 256° (effervescence), alone and mixed.

A methanolic solution of the dibromide (IX) readily gave the *dipicrate*, which separated from ethanol–dimethylformamide as yellow crystals, m. p. 273° (decomp.), having dimethylformamide of crystallisation (Found : C, 41·85; H, 3·0; N, 11·0. $C_{28}H_{22}O_{14}N_6As_2,C_3H_7ON$ requires C, 41·8; H, 3·3; N, 11·0%).

The dibromide (IX), when added to an excess of sodium iodide, each in methanol, deposited the *di-iodide* (as IX), m. p. 248° (effervescence) after crystallisation from methanol (Found : C, 31·3; H, 3·4. $C_{16}H_{18}I_2As_2$ requires C, 31·3; H, 3·0%).

The dibromide (IX), when heated at 0·1 mm., effervesced smoothly; the colourless liquid residue solidified on cooling, and when recrystallised from ethanol–chloroform gave the dimethylarsanthren (III), m. p. and mixed m. p. 191—192·5°.

(*C*) A mixture of the arsanthren (III) (1·31 g.), ethylene dibromide (0·34 c.c., 1 mol.), and methanol (1·5 c.c.) was heated at 100° for 9 hr. in a sealed tube which was occasionally shaken vigorously. Recrystallisation of the product from methanol yielded solvated s-*ethylenebis-5-(5 : 10-dihydro-5 : 10-dimethylarsanthronium) dibromide* (X), (0·80 g., 47%), m. p. 195° (effervescence) (Found : C, 41·9; H, 4·1; Br, 17·1. $C_{30}H_{32}Br_2As_4,2CH_4O$ requires C, 42·1; H, 4·2; Br, 17·5%). Concentration of the earlier mother-liquors furnished the dibromide (IX), m. p. 272° (effervescence) alone and mixed, in low yield.

The *dipicrate* (as X) separated from methanol in yellow crystals, m. p. 237° (decomp.) (Found : C, 44·15; H, 3·3; N, 7·2. $C_{42}H_{36}O_{14}N_6As_4$ requires C, 43·8; H, 3·3; N, 7·3%). The *di-iodide dihydrate* (from methanol) had m. p. 185° (effervescence) (Found : C, 36·9; H, 3·75. $C_{30}H_{32}I_2As_4,2H_2O$ requires C, 36·7; H, 3·5%).

The dibromide (X) (0·60 g.) was heated at 0·1 mm. for 5 min. in a hard-glass tube at 210°. Smooth effervescence occurred, and on cooling and recrystallisation from ethanol–chloroform the residue gave pale yellow mixed crystals (0·39 g., 76%), m. p. 142—147°, of the dimethyl derivative (III) and the 5-bromo-derivative (VII) in equimolecular proportions (Found : C, 44·7; H, 3·45. Calc. for $C_{14}H_{14}As_2 + C_{13}H_{11}BrAs_2$: C, 44·45; H, 3·4%). The following evidence confirms this composition. (*a*) A mixture of equimolecular amounts of (III) and (VII) was dissolved in hot chloroform, which was diluted with ethanol and cooled. Pale yellow crystals were deposited, of m. p. 142—147°, unchanged by admixture with the above product, and also by recrystallisation from acetone. (*b*) A solution of the above product in an excess of methyl iodide was boiled under reflux for 4 hr., a pale orange deposit being formed. Fractional recrystallisation of this from ethanol separated it into the less soluble arsanthren dimethiodide (as IV), deep orange crystals, m. p. 214° (decomp.) (Found : C, 28·85; H, 2·6%), and the more soluble 5 : 10-dihydro-5 : 10-dimethylarsanthren monomethiodide, m. p. 222° (effervescence) (Found : C, 37·9; H, 3·8%). Both m. p.s were unchanged on admixture with authentic samples. It is clear therefore that these two products are formed from (VII) and (III) respectively.

Reaction of the Arsanthren (III) *with Trimethylene Dibromide.*—A mixture of the powdered arsanthren (III) (1·55 g.) and the dibromide (0·476 c.c., 1 mol.) was heated at 155—160° for 1·5 hr., and the cold stone-hard product, when recrystallised from methanol, furnished the dihydrated 1 : *4-dimethyltrimethylenedi-*o*-phenylenediarsonium dibromide* (XII) (1·05 g., 52%), m. p. 267—268° (effervescence) (Found : C, 35·75; H, 4·3. $C_{17}H_{20}Br_2As_2,2H_2O$ requires C, 35·8; H, 4·25%). It formed a *dipicrate*, yellow crystals, m. p. 252° (decomp.) from acetic acid (Found : C, 42·3; H, 2·95; N, 10·1. $C_{29}H_{24}O_{14}N_6As_2$ requires C, 42·0; H, 2·9; N, 10·1%).

The dibromide (XII) (0·25 g.) when heated at 0·1 mm., underwent the normal smooth decomposition with effervescence, and the residue, after cooling and solidifying, afforded the arsanthren (III), m. p. and mixed m. p. 191—192·5° after crystallisation from ethanol–chloroform (Found : C, 50·9; H, 3·85%) : 0·13 g., 82% yield.

Reaction of the Arsanthren (III) *with* o-*Xylylene Dibromide*.—(*A*) A powdered mixture of the arsanthren (1·10 g.) and the dibromide (0·875 g., 1 mol.) was heated at 160° for 2 hr. and the hard solid product was then recrystallised from much ethanol, two fractions being isolated. The less soluble fraction, when further recrystallised from ethanol, afforded 5 : 5′-10 : 10′-*bis*-o-*xylylenebisarsanthronium tetrabromide* (XIII), cream-coloured crystals (0·73 g., 39%), m. p. 273° (decomp.) (Found : C, 42·8; H, 3·0; Br, 28·5. $C_{40}H_{32}Br_4As_4$ requires C, 42·4; H, 2·8; Br, 28·2%). The more soluble fraction, when recrystallised from methanol, and dried at 70°/ 0·1 mm., furnished *di*-o-*phenylene*-o-*xylylenediarsine monomethobromide* (XIV) (0·33 g., 20%), m. p. 200° (Found : C, 50·1; H, 3·85. $C_{21}H_{19}BrAs_2$ requires C, 50·3; H, 3·8%). A sample of this salt (XIV), slowly crystallised from methanol–ethanol to obtain suitable crystals for *X*-ray examination (see below) separated apparently as a dimethanol solvate or a monohydrated monoethanol solvate (Found : C, 49·0, 48·8; H, 5·1, 4·7. $C_{21}H_{19}BrAs_2,2CH_4O$ requires C, 48·9; H, 4·8%).

Repetition of this experiment, but with heating at 130° for 1 hr., gave the tetrabromide (XIII), m. p. 273° (decomp.), in 8% yield, and the monobromide (XIV), m. p. 200°, in 65% yield.

(*B*) A mixture of the arsanthren (III) (1·65 g.) and the dibromide (2·60 g., 2 mols.) was heated at 160° for 2 hr. Recrystallisation of the product from methanol afforded solely the tetrabromide (XIII), m. p. 273° (decomp.) (1·80 g., 64%).

Derivatives of the Tetrabromide (XIII).—The addition of this salt to an excess of sodium iodide, both in cold methanol, precipitated the *tetra-iodide*, deep orange crystals, m. p. 244° (decomp.) from methanol (Found : C, 36·4; H, 2·1. $C_{40}H_{32}I_4As_4$ requires C, 36·3; H, 2·4%).

The yellow tetrapicrate was similarly deposited from methanolic sodium picrate solution, and when collected, washed with water, and dried in a vacuum at room temperature for 24 hr. formed a *decahydrate*, m. p. 232° (decomp.) (Found : C, 40·3; H, 3·5; N, 8·7. $C_{64}H_{40}O_{28}N_{12}As_4,10H_2O$ requires C, 40·3; H, 3·25; N, 8·8%). Attempted dehydration of this salt caused the colour to change to orange, and the substance became very hygroscopic; the pure anhydrous salt could not be obtained. Attempted recrystallisation from methanol caused decomposition.

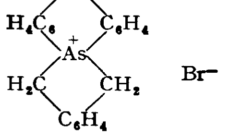
Derivatives from, and Reactions of, the Monobromide (XIV).—The corresponding *picrate*, prepared and recrystallised in ethanol, formed yellow crystals, m. p. 211° (Found : C, 49·6; H, 3·7; N, 6·3. $C_{27}H_{21}O_7N_3As_2$ requires C, 49·9; H, 3·3; N, 6·45%). The *iodide*, when recrystallised from methanol, had m. p. 197° (Found : C, 46·0; H, 3·8. $C_{21}H_{19}IAs_2$ requires C, 46·0; H, 3·5%).

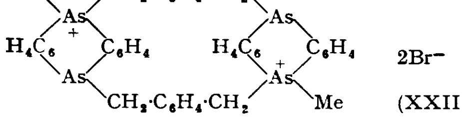
The monobromide (XIV), when heated at 0·1 mm., underwent decomposition with slight effervescence, and the yellow residual liquid on cooling formed a glass containing some apparently crystalline material. No crystalline constituent could be isolated, however, in spite of the use of a variety of solvents.

A mixture of the monobromide (XIV) (0·60 g.) and *o*-xylylene dibromide (0·32 g., 1 mol.) was heated at 140—145° for 2 hr., but did not solidify completely until cold. Recrystallisation from methanol afforded the tetrabromide (XIII) (0·45 g., 66%), m. p. 273° (decomp.), alone and mixed (Found : C, 42·7; H, 2·6%).

Structure of the Monobromide (XIV).—The following report by Dr. W. Schaffer indicates solely the main points by which the essential structure has been determined, with particular reference to the possible alternatives (XXII) and (XXIII; Me groups *cis* or *trans*). The full crystallographic data will be published elsewhere.

(XXII)





(XXIII)

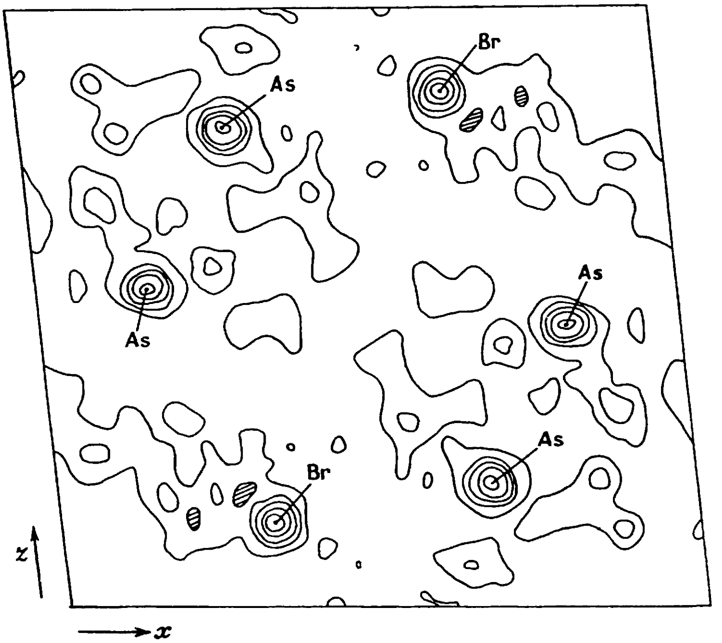
" The immediate object of this investigation was to find the positions of the heavy atoms and (if possible) the benzene rings, rather than to determine bond lengths and angles accurately, in order to eliminate two of the three possible structures.

" *Crystallographic data.* From oscillation photographs and Weissenberg photographs using copper K_α radiation, together with optical measurements of the angles between pairs of faces in a zone, it was found that the crystal was triclinic and the unit cell had the dimensions: $a = 12{\cdot}4$, $b = 7{\cdot}8$, $c = 12{\cdot}0$ Å; $\alpha = 107°$, $\beta = 96°$, $\gamma = 92°$: $a^* = 0{\cdot}127$, $b^* = 0{\cdot}205$, $c^* = 0{\cdot}132$; $\alpha^* = 72°$, $\beta^* = 83°$, $\gamma^* = 86°$. $V = 1110$ Å^3. The crystals have d 1·55, giving 2 molecular units per unit cell.

" By using intensities of reflexions from the (010) projection in the Wilson statistical method (Howells, Phillips, and Rogers, *Acta Cryst.*, 1950, **3**, 210), the crystal was found to be centrosymmetric, space group $P\bar{1}$.

" The signs of the larger unitary structure factors were found by a direct method, based on Harker–Kasper inequalities and a criterion suggested by Cochran and Douglas (unpublished). Electron-density maps then showed clearly the positions of the arsenic and the bromine atoms, in projection on (100) and (010) (see Fig. 1). A ' difference ' density map, from which these heavy atoms had been subtracted out, was then calculated for the (010) projection. Although the random error was expected to be about as large as the contributions of the carbon atoms whose positions were being sought, the benzene rings lying on each side of the As–As axis could be seen (Fig. 2). No decisive indication of the positions of the remaining carbon atoms was found, however, from this map. The positions finally chosen for them were arrived at by the following packing considerations, and are in good agreement with Fig. 2.

FIG. 1. (010) *Fourier projection. Contour scale arbitrary.*

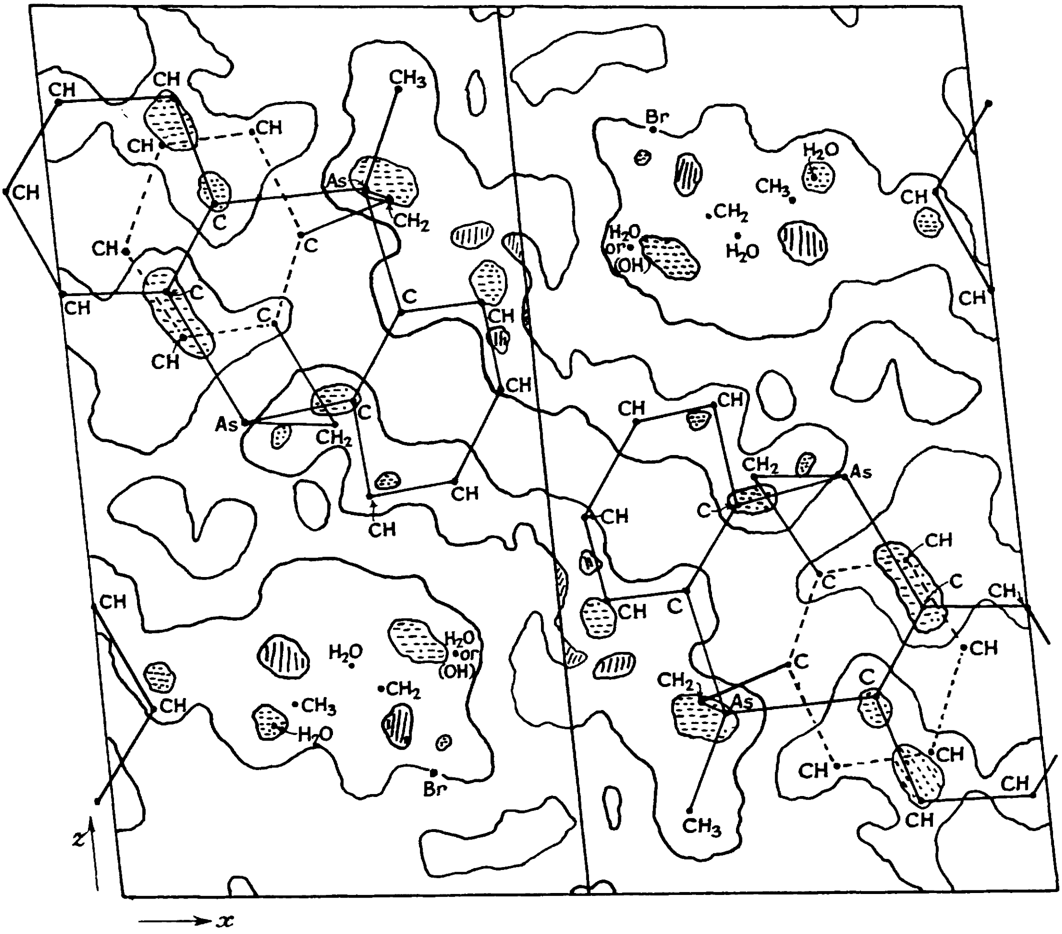


" Wire models of the structures (XIV), (XXII), and (XXIII) were constructed, and attempts made to fit each in turn into the electron-density maps. The structure (XXIII) could be immediately ruled out. The structure (XIV) accounted best for the peaks in the ' difference ' map; the distances between atoms of adjacent molecules were satisfactory, and no serious distortion of bond angles was involved.

" There remained one fairly large cavity between the main molecules into which molecules of solvent of crystallisation could be fitted. The crystals used for the X-ray work had separated from methanol–ethanol containing a trace of water. In agreement with their analytical composition (p. 418), two molecules of methanol per molecular unit were tried in the model, but no positions were found which did not imply improbably small values of some interatomic distances. One molecule of ethanol plus one of water per molecular unit were then tried, but again, although this could not be regarded as impossible, some of the distances involved between carbon atoms of different molecules (a little less than 3·5 Å) were too small to make the arrangement probable.

It was then found that ethanol fitted in, with interatomic distances nearer to accepted values. Furthermore, three molecules of water fitted fairly well into the cavity in the unit cell. A statistical distribution of one ethanol and three water molecules among the available cavities in the structure, about three cavities containing ethanol to each one containing water, would agree well with the chemical analysis, and this is suggested as the arrangement in the crystals used in the experiment. The available evidence, however, is not conclusive on this point.

FIG. 2. (010) *Difference map. Contour scale arbitrary. Horizontal hatching indicates a peak of high electron density, vertical hatching indicates a lower density area.*



" Atomic co-ordinates, expressed as fractions of the corresponding unit cell edges, are given

Br	0·342, 0·667, 0·133
As	0·183, 0·200, 0·533
As	0·333, 0·267, 0·792
CH_3	0·383, 0·150, 0·908
CH_2	0·225, 0·433, 0·533
CH_2	0·366, 0·500, 0·783
Benzene	
C	0·358, 0·083, 0·658
C	0·450, $\overline{0{\cdot}050}$, 0·667
C	0·458, $\overline{0{\cdot}200}$, 0·567
C	0·400, $\overline{0{\cdot}217}$, 0·467
C	0·308, $\overline{0{\cdot}083}$, 0·450
C	0·300, 0·067, 0·558

Benzene	
C	0·117, 0·267, 0·675
C	0, 0·300, 0·675
C	$\overline{0{\cdot}050}$, 0·350, 0·792
C	0·017, 0·366, 0·892
C	0·142, 0·342, 0·900
C	0·175, 0·300, 0·775
Benzene	
C	0·225, 0·575, 0·642
C	0·125, 0·667, 0·625
C	0·075, 0·800, 0·725
C	0·125, 0·817, 0·842
C	0·225, 0·733, 0·858
C	0·267, 0·600, 0·742

in the Table. Atomic co-ordinates for atoms in the solvent molecules of crystallisation are not included in this Table."

5 : 10-*Dihydro*-2 : 5 : 10-*trimethylarsanthren* (XVIII; R = Me) *and its Derivatives.*—A solution of *o*-arsanilic acid (XV) (64 g.) in water (600 c.c.), mixed with concentrated hydrochloric acid (88 c.c.), was diazotised at 0° by the slow addition of a solution of sodium nitrite (20 g.), and then run slowly into vigorously stirred ice-water (1 l.) concurrently with a solution of dichloro-*p*-tolylarsine (78 g., 1·1 mols.) in aqueous 5N-sodium hydroxide (280 c.c.) and N-sodium carbonate (240 c.c.). The mixture was set aside overnight, then diluted with water (1 l.) and heated to 100°, and concentrated hydrochloric acid was cautiously added until precipitation of *p*-tolylarsenoxide was complete. The filtered solution was reheated, and made just acid to Congo-red by further addition of acid, the *anhydride* (XVI; R = C_6H_4Me) (80 g., 68%) of *o*-arsonophenyl-*p*-tolylarsinic acid being precipitated as a microcrystalline powder, m. p. 380° (decomp.); it was purified by boiling its solution in aqueous sodium carbonate (charcoal), and reprecipitating it with acetic acid, and formed a colourless powder, m. p. 382—383° (decomp.) (Found: C, 40·9; H, 2·95. $C_{13}H_{12}O_4As_2$ requires C, 40·85; H, 3·1%).

In an attempt to obtain direct cyclisation to the *p*-tolyl group, a stirred solution of this anhydride (1 g.) in concentrated sulphuric acid (5 c.c.) was heated at 100° for 20 min., poured into water (30 c.c.), made just acid to Congo-red with aqueous sodium carbonate, and concentrated to *ca.* 50 c.c., but only the anhydride, m. p. and mixed m. p. 380° (decomp.), separated.

A solution of the anhydride (80 g.) in concentrated hydrochloric acid (800 c.c.) containing potassium iodide (0·5 g.) was kept at 100° for 8 hr. whilst sulphur dioxide was passed through it, hydrogen chloride being also passed in during the last 2 hr. The mixed gas stream was continued whilst the solution cooled, and the supernatant aqueous layer then decanted. The heavy oily residue (presumably XVII) did not crystallise; its solution in chloroform (350 c.c.) was therefore dried (Na_2SO_4) and distilled, giving fractions (*a*) b. p. 92—188°/0·05 mm. (13 g.) and (*b*) b. p. 188—193°/0·05 mm. (35 g.). Fraction (*b*), which did not crystallise, was impure 5 : 10-dichloro-5 : 10-dihydro-2-methylarsanthren (XVIII; R = Cl).

A solution of fraction (*b*) (1 g.) in acetone (10 c.c.), when treated dropwise with 30% hydrogen peroxide, deposited the pure anhydride (XVI; R = C_6H_4Me), m. p. 382° (decomp.) when washed with acetone (Found: C, 40·6; H, 3·1%). The crude oily residue (XVII) behaved similarly.

A solution of (*b*) (10·8 g.) in benzene (40 c.c.) reacted vigorously with heat evolution when added dropwise under nitrogen to a stirred Grignard reagent prepared from methyl iodide (9·5 c.c., 6 mols.) and magnesium (3·7 g., 6 atoms) under ether (100 c.c.). The mixture was boiled under reflux for 1 hr., and hydrolysed with ammonium chloride (25 g.) in water (100 c.c.). The organic layer, when dried (Na_2SO_4) and evaporated, gave the crude 5 : 10-dihydro-2 : 5 : 10-trimethylarsanthren (XVIII; R = Me) as a foul-smelling gum (8·6 g., 90%).

A solution of this arsanthren in cold methyl iodide, when set aside for 24 hr., deposited the *monomethiodide* (XIX), m. p. 215—216° after crystallisation from ethanol (Found: C, 39·05; H, 4·15. $C_{16}H_{19}IAs_2$ requires C, 39·35; H, 3·9%). A similar solution in methyl bromide deposited during 48 hr. the dimethobromide, which crystallised from methanol as the *monohydrate*, m. p. 265° (effervescence) (Found: C, 37·2; H, 4·3. $C_{17}H_{22}Br_2As_2,H_2O$ requires C, 36·9; H, 4·3%); it gave a *dimethopicrate*, yellow crystals, m. p. 258° (decomp.) from ethanolic dimethylformamide (Found: C, 42·1; H, 3·4; N, 10·2. $C_{29}H_{26}O_{14}N_6As_2$ requires C, 41·8; H, 3·1; N, 10·1%).

When equimolecular mixtures of the arsanthren (XVIII; R = Me) and ethylene or trimethylene dibromide were set aside for several days, or their methanolic solutions were boiled, no apparent reaction occurred and the foul odour of the arsanthren persisted. When the mixtures were heated at 100°, an odourless hygroscopic gum was readily formed, but this product, and its iodide and picrate, could not be obtained crystalline.

5 : 10 : 5′ : 10′-*Tetrahydro*-2 : 5 : 10 : 2′ : 5′ : 10′-*hexamethyl*-5 : 5′-10 : 10′-*bis*-o-*xylylenebisarsanthronium Tetraiodide* (XX).—A mixture of (XVIII; R = Me) (4·2 g.) and powdered *o*-xylylene dibromide (3·2 g., 1 mol.) was heated at 100° for 1·5 hr., and the highly hygroscopic product, dissolved in ethanol (50 c.c.), was then added to a solution of sodium iodide (8 g.) in ethanol (60 c.c.). The precipitated tetraiodide, recrystallised from methanol, gave the *monohydrate* (6 g., 70%), m. p. 180—181° (decomp.) (Found: C, 38·8; H, 3·9. $C_{46}H_{48}I_4As_4,H_2O$ requires C, 38·75; H, 3·5%); this gave a *tetrapicrate*, yellow crystals, m. p. 171—173° (from aqueous methanol) (Found: C, 46·05; H, 3·3; N, 8·9. $C_{70}H_{56}O_{28}N_{12}As_4$ requires C, 46·3; H, 3·1; N, 9·25%).

When the tetraiodide was heated at 170°/0·1 mm. for 30 min., decomposition with effervescence occurred, but the yellow gummy residue on attempted recrystallisation gave only an oil, which did not yield a solid methiodide.

The tetraiodide gave a *tetra-(+)-bromocamphorsulphonate dihydrate,* m. p. 257—258° (decomp.) from acetone (Found: C, 47·4; H, 5·2. $C_{86}H_{104}O_{16}Br_4S_4As_4,2H_2O$ requires C, 47·4; H, 5·1%). Further recrystallisation did not change the m. p.; the salt, after two and three recrystallisations, had $[M]_D$ +1104° and +1110° respectively in aqueous solution; the value expected for four sulphonate radicals is $[M]_D$ +1112°.

The *tetra[antimony -tartrate] dihydrate* (from aqueous ethanol) had m. p. 239° (effervescence) (Found: C, 37·9; H, 3·4. $C_{64}H_{56}O_{24}As_4Sb_4,2H_2O$ requires C, 37·5; H, 3·25%), $[M]_D$ +1648°; the m. p. and rotation were unaffected by three recrystallisations, and then gave an inactive iodide and picrate.

The (+)-tartrate, (+)-camphorsulphonate, and (−)-*N*-1-phenylethylphthalamate were obtained only as very hygroscopic products.

The Anhydride (XVI; R = C_6H_4OMe) *of* o-*Arsonophenyl*-p-*methoxyphenylarsinic Acid.*—Diazotised *o*-arsanilic acid, when treated with *p*-methoxyphenylarsenoxide as described for (XVI; R = C_6H_4Me), gave this *anhydride* (51%), m. p. 373° (decomp.) after washing with hot water and acetone (Found: C, 38·85; H, 3·45. $C_{13}H_{12}O_5As_2$ requires C, 39·2; H, 3·05%). Treatment with hot sulphuric acid, as described above, again yielded the unchanged anhydride. Treatment with hot hydrochloric acid and sulphur dioxide gave ultimately a heavy oil which solidified, and when recrystallised from *cyclo*hexane (charcoal) gave the oxychloride (XXI) (84%), yellow crystals, m. p. 148—150° (Found: C, 23·4; H, 1·1. Calc. for $C_6H_4OCl_2As_2$: C, 23·0; H, 1·3%).

Diazotised *o*-arsanilic acid, when similarly treated with dichloro-*p*-nitrophenylarsine, gave, on final acidification to Congo-red, a precipitate of a *diarsonoazobenzene* as a white microcrystalline powder, m. p. >450° after crystallisation from much water (Found: C, 33·0; H, 2·7; N, 6·8. $C_{12}H_{12}O_6N_2As_2$ requires C, 33·4; H, 2·8; N, 6·5%). Treatment with hydrochloric acid and sulphur dioxide gave a heavy oil which solidified on cooling, and when recrystallised from benzene–*cyclo*hexane (1 : 1) gave the *bis(dichloroarsino)azobenzene* (78%), yellow crystals, m. p. 129—131° (Found: C, 30·6; H, 2·0; N, 5·8. $C_{12}H_8N_2Cl_4As_2$ requires C, 30·5; H, 1·7; N, 5·9%).

The orientation of the arsenic groups in the above compounds is uncertain, but we suggest that they are in the *op'*-positions, which their synthesis renders probable. Karrer (*Ber.*, 1912, **45**, 2359) describes the *pp'*-diarsonoazobenzene as a dull brown powder (no m. p. recorded); Kalb (*loc. cit.*) and Lieb (*Ber.*, 1921, **54**, 1511) describe the *oo'*-isomer, m. p. 272°, and the *mm'*-isomer, m. p. 240° (decomp.), as orange-yellow and deep orange-yellow respectively. The recorded colours of these compounds may not be those of the pure compounds. Moreover, the strongly acidic arsono-groups may considerably suppress the resonance to which the normal colours of azo-compounds are due, and the fact that our diarsono-compound is colourless does not preclude its having the azo-structure.

We are greatly indebted to Dr. W. Schaffer for the *X*-ray crystal investigation, to Dr. A. G. Maddock for arsenic estimations by activation analysis, and to the Department of Scientific and Industrial Research for a grant (E. R. H. J.).

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[*Received, September 6th,* 1954.]