222. *The Stereochemistry of 3-Covalent Arsenic. Isomeric Forms of 5 : 10-Di-*p*-tolyl-5 : 10-dihydroarsanthren.*

By JOSEPH CHATT and FREDERICK G. MANN.

Physical evidence indicates that the 3-covalent arsenic atom has a pyramidal configuration with an intervalency angle of *ca.* 97°. 5 : 10-*Di*-p-*tolyl*-5 : 10-*dihydroarsanthren* (III) should therefore be folded along the As–As axis, and should exist in two isomeric forms, a third form being impossible owing to the position of the tolyl groups. These two isomeric forms have now been isolated.

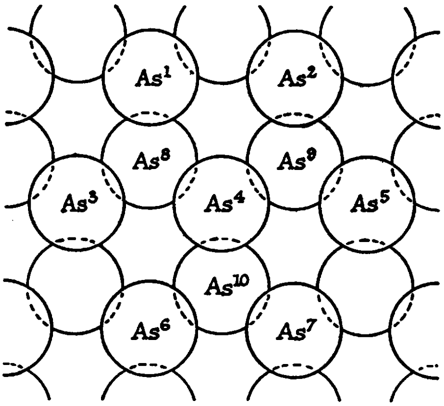
They both give the same tetrabromide and *tetrahydroxide*, since these have planar molecules in which isomerism cannot persist. They give, however, distinct isomeric *monomethiodides*.

The arsenic atoms in the ditolyl compounds show a marked reluctance to assume simultaneously the 4-covalent condition. The dimethiodide, disulphide, and monosulphide-monomethiodide could not be prepared, but a very stable *dibromide*, which probably has the quinonoid structure (V), and a *monosulphide* were obtained.

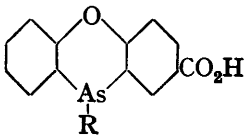
THERE is considerable evidence—mainly physical in character—to show that stereochemically the 3-covalent arsenic atom can be regarded as being at the top apex of a partially flattened tetrahedron, the intervalency angles at the arsenic atom being about 100° instead of the normal value (60°). For instance, Sutherland, Lee, and Wu (*Trans. Faraday Soc.*, 1939, **35**, 1373) have shown by spectroscopic investigation that arsine has a pyramidal molecule, in which the height of the pyramid is 0·75 A., and the intervalency angle H–As–H is 97° ± 3°. Furthermore, electron-diffraction studies of gaseous arsenious compounds have given the following intervalency angles: $AsCl_3$, Cl–As–Cl = 103° ± 3°; $AsBr_3$, Br–As–Br = 100° ± 2°; AsI_3, I–As–I, 100° ± 2°; $AsMe_3$, C–As–C = 96° ± 5° (Pauling and Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 2684; Gregg, Hampson, Jenkins, Jones, and Sutton, *Trans. Faraday Soc.*, 1937, **33**, 852; Springall and Brockway, *J. Amer. Chem. Soc.*, 1938, **60**, 996).

The essential stereochemistry of 3-covalent arsenic is, however, implicit in the crystal structure of the element, a fact which emerges from a consideration of the results obtained by Bradley (*Phil. Mag.*, 1924, **47**, 657). Crystalline arsenic consists of parallel planes of atoms; consecutive planes are not equidistant, however, but are arranged in pairs, the distance between two planes forming such a pair being markedly smaller than that between two such pairs. For example, in Fig. 1 the arsenic atoms As^1—As^7 are in the upper, and the atoms As^8—As^{10} are in the lower plane of one of these pairs, and the distance between the atom As^4 and the nearest atoms in the plane below (As^8, As^9, As^{10}) is 2·51 A.; the distance, however, between the atom As^4 and the nearest three atoms in the plane *above* is 3·15 A. Furthermore, the distance between the atom As^4 and the six nearest atoms in the same plane (As^1—As^3, As^5—As^7) is 3·77 A. In view of these distances, it necessarily follows that the atom As^4 is covalently linked only to the three nearest *lower* atoms As^8, As^9, and As^{10}, and that an atom in the lower plane (*e.g.*, As^8) is linked only to the three similarly situated in the upper plane (As^1, As^3, As^4). The arsenic molecule has therefore infinite length and breadth, but has a depth corresponding only to that of the above two atomic planes. Moreover, the intervalency angle (*e.g.*, As^8–As^4–As^9) is 97°. (It is noteworthy that although antimony and bismuth are isomorphous with arsenic, the distances between consecutive planes tend to become equal as the element becomes more metallic in character; *e.g.*, the distances corresponding to 2·51 and 3·15 in arsenic are 2·87 and 3·37 in antimony, and 3·11 and 3·47 in bismuth.)

FIG. 1.



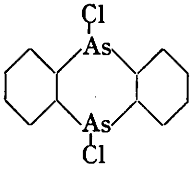
The evidence for the stereochemistry of 3-covalent arsenic arising from a study of its organic derivatives is less conclusive. The resolution of 10-alkyl(or aryl)phenoxarsine-2-carboxylic acids (I; R = Me, Et, or Ph) by Lesslie and Turner (J., 1934, 1170; 1935, 1051, 1268; 1936, 730) can be reasonably interpreted only on the assumption either that the three rings are coplanar and the group R projects above or below this plane, or (far more probably) that the intervalency angle C–As–C within the ring has a value which necessitates a folding of the molecule about the O–As axis. In the latter case, a planar distribution of the valencies of the arsenic atom, although unlikely, is not excluded. It should be noted that Allen, Wells, and Wilson (*J. Amer. Chem. Soc.*, 1934, **56**, 233) have investigated certain derivatives of 7-chloro-7 : 12-dihydro-γ-benzophenarsazine, but their results are too scanty and inconclusive to have any reliable significance.

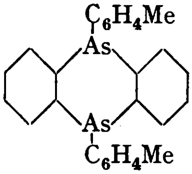


(I.)

To obtain decisive evidence for the non-planar valency disposition of the 3-covalent arsenic atom in its organic compounds, we have studied certain derivatives of 5 : 10-dichloro-5 : 10-dihydroarsanthren ("arsanthrene dichloride") (II), the preparation of which by Kalb's method (*Annalen*, 1921, **423**, 74) we have improved. This compound on treatment with a Grignard reagent prepared from pure *p*-bromotoluene readily gave 5 : 10-*di*-p-*tolyl*-5 : 10-*dihydroarsanthren* (III). We selected this compound because it is more stable than the original (and stereochemically very similar) dichloro-compound, and *p*-tolyl groups were inserted rather than phenyl or alkyl groups because it was thought that a marked dipole at the arsenic atoms might enhance the physical differences between the isomeric forms which we hoped to obtain.

(II.)

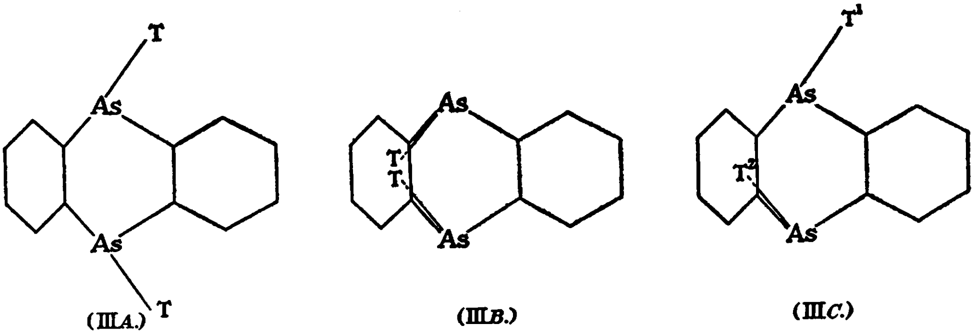




(III.)

Consideration of formula (III) shows at once that if the valencies of each arsenic atom are to be mutually inclined at an angle of *ca.* 97°, the molecule cannot be planar, and in particular, that it must be folded across the As–As axis in order to maintain this value for the two C–As–C angles within the central ring. This folding can apparently lead to the production of three isomeric forms : these are shown diagramatically in (IIIA), (IIIB), and (IIIC), (Fig. 2), in all of which the arsenic atoms and the right-hand benzene ring are in the plane of the paper, whilst the left-hand benzene ring and its two *o*-valencies project above this plane, *i.e.*, *towards* the observer. In (IIIA) the two *p*-tolyl groups (denoted by T) are in the *cis*-position relative to one another, and both project towards the observer, *i.e.*, they are within the angle subtended by the two wings of the molecule; valency considerations now demand that these groups should also project away from the centre of the molecule as shown. In (IIIB), the tolyl groups are again in the *cis*-position, but now both project *below* the plane of the paper; to maintain the requisite intervalency angles at the arsenic atoms, these groups must now also project towards one another. In (IIIC), the tolyl groups are in the *trans*-position, so that the upper group T^1 projects above the plane of the paper (as in IIIA), and the lower group T^2 projects below this plane (as in IIIB). [The general type of isomerism is thus very similar to that of the thianthren disulphoxides (Taylor, J., 1935, 625), except for the smaller intervalency angle at the arsenic atoms.] If, however, models of the three isomers (IIIA, B, and C) are constructed, it becomes at once evident that, owing to this small angle, the two *cis*-tolyl groups in (IIIB) become almost coincident in space, and that this form cannot therefore exist. On the other hand, satisfactory models for the two forms (IIIA) and (IIIC) can be readily constructed.

FIG. 2.

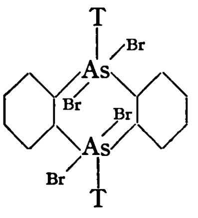


(IIIA.) (IIIB.) (IIIC.)

These theoretical conclusions are in complete accord with our experimental results. We have subjected the ditolyl compound to a prolonged and exhaustive process of fractional crystallisation and have succeeded in isolating two isomeric forms; the *α-isomer* crystallises in small colourless leaflets, m. p. 178—179°, and the *β-isomer* in large colourless bipyramidal crystals, m. p. 179—181°, a mixture of equal quantities of both forms having m. p. 144—158°. Each form shows a normal molecular weight in boiling acetone solution and, moreover, possesses high stability, since it can be maintained in a molten condition about 10° above its m. p. for 10 minutes without undergoing either decomposition or conversion into the other form. No trace of a third isomeric form could be detected.

The crystal habit of the α- and the β-form, and their mixed m. p., prove that they are true isomers, in spite of their almost identical m. p.'s. The method of preparation shows beyond reasonable doubt that they must have the same structure, *i.e.*, that the tolyl groups are united to the arsenic atoms in both compounds. Their isomerism is further proved by a study of the following derivatives.

Tetrabromide and tetrahydroxide. An *X*-ray crystal analysis of trimethylstibine dichloride, dibromide, and di-iodide (Wells, *Z. Krist.*, 1938, **99**, 367) has shown that in these compounds the antimony atom is in the centre of an equilateral triangle having the methyl groups at its apices, and that the halogen atoms lie at equal distances above and below the antimony atom on an axis perpendicular to the plane of the triangle. Now both the α- and the β-form of the ditolyl compound react readily in chloroform solution with 2 mols. of bromine to give 5 : 10-ditolyl-5 : 10-dihydroarsanthren 5 : 5 : 10 : 10-tetrabromide (IV); if Wells's results apply equally to arsenic derivatives, it follows that the C–As–C angles within the ring have now become 120°, and that in consequence all three rings and the two tolyl groups are now in the plane of the paper, and that the bromine atoms lie vertically above and below the arsenic atoms. Hence each form of the ditolyl isomers should give the same tetrabromide. Since, however, the tetrabromide was readily affected by damp air and was difficult to purify, it was converted by the action of aqueous ammonia into the corresponding *tetrahydroxide*, which clearly must have the same structure. This was a stable and well-crystallised compound, and in accordance with expectation the same tetrahydroxide (and therefore the same tetrabromide) was obtained both from the α- and the β-form of the original ditolyl compound. The tetrahydroxide on heating underwent dehydration to the corresponding *dioxide*: this proves its constitution, since it could not therefore be a trihydrated monoxide, which would have an almost identical composition.



(IV.)

The tetrabromide afforded further evidence for the non-existence of a third isomeric form of the ditolyl compound (III). When the tetrabromide in chloroform solution was reduced with sulphur dioxide, the bromine atoms were readily removed, and the ditolyl compound regenerated in almost theoretical yield. In these circumstances a mixture of all possible isomeric forms might well be formed, particularly if these forms did not possess any marked difference in stability. The product was found actually to be an isomeric mixture of m. p. 140—160°. Since identification of the components by fractional crystallisation was too difficult and uncertain, an *X*-ray powder photograph was taken of this mixture; comparison with a similar photograph of a mixture of equal quantities of the pure α- and β-ditolyl compounds showed that the two mixtures had identical components (although present in different proportions) and that the first mixture, obtained by reduction of the tetrabromide, did not contain a third isomeric form.

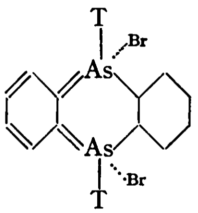
Methiodides. The α-isomer gives a *monomethiodide*, crystallising from alcohol with a molecule of solvent, and from water in the anhydrous state, m. p. 176—179°. The β-isomer gives an isomeric *monomethiodide*, of different crystalline habit, crystallising from alcohol without combined solvent (m. p. 176—179°) and from water as a *monohydrate*. A mixture of the two methiodides had m. p. 167—175°.

It is noteworthy that all our attempts to convert either of these monomethiodides into a dimethiodide have failed; *e.g.*, they are unaffected by 6 hours' boiling with methyl iodide in methyl alcohol. There is no apparent *steric* reason for this inability to form a dimethiodide, for if the upper arsenic atom in (IIIA) were to combine with methyl iodide, it would obtain a tetrahedral configuration and consequently cause a partial unfolding of the ringed system. Furthermore, the increase in intervalency angle of this arsenic atom from *ca.* 97° to *ca.* 109°, whilst leaving the tolyl group in the same general position relative to the now more open ring system, would cause the methyl group to be projected below the plane of the paper and slightly away from the centre of the molecule. The lower arsenic atom is thus clearly exposed to attack by a second molecule of methyl iodide. Similar reasoning may be applied to the isomeric form (IIIc).

The reason for the inertness of the monomethiodide is probably electronic rather than steric; *e.g.*, if the upper arsenic atom in either (IIIA) or (IIIc) were to unite with methyl iodide, the arsonium ion as formed would exert a very strong inductive effect (compare Ingold, Shaw, and Wilson, J., 1928, 1280), which would be readily transmitted through the neighbouring *o*-phenylene groupings. Consequently, there would be a marked electron drag away from the lower arsenic atom, which in these circumstances might well be unable to combine with methyl iodide. Phenazine shows a similar behaviour (Kehrmann and Havas, *Ber.*, 1913, **46**, 343).

The reluctance of both arsenic atoms in the isomeric ditolyl compounds (III) to assume simultaneously a covalency of four is shown also in other derivatives. When the tetrabromide (IV) was treated with an excess of sodium sulphide, sulphur was liberated and 5 : 10-*di*-p-*tolyl*-5 : 10-*dihydroarsanthren monosulphide* was formed; this monosulphide, when mixed with excess methyl iodide, slowly liberated sulphur and gave a mixture of the isomeric α- and β-monomethiodides. All our attempts to prepare a disulphide or a monosulphide-monomethiodide failed. The monosulphide could also exist in two isomeric forms: a pure single compound was, however, readily obtained by recrystallisation of the crude product, which therefore could have contained very little (if any) of a second isomeric form.

When, however, the tetrabromide was treated with hydrogen sulphide, the monosulphide was again formed but was always accompanied by 5 : 10-*di*-p-*tolyl*-5 : 10-*dihydroarsanthren dibromide*. This compound is of great interest; it can readily be obtained by treating the tetrabromide with excess acetone, or by treating the monosulphide with bromine. Its properties, however, afford strong evidence that the two bromine atoms are not joined to one arsenic atom, but that the compound has assumed the planar quinonoid structure (V) and hence is an ionised bis(arsonium bromide) salt. The evidence for this structure is: (1) the dibromide is moderately soluble in hot water, alcohol, and most polar solvents, but not in benzene and ether; (2) it can be readily purified by recrystallisation from rectified spirit, whereas arsine dibromides of type R_3AsBr_2 in these conditions usually give the corresponding hydroxybromide, $R_3AsBr(OH)$; (3) it reacts very slowly with hydrogen sulphide to give the monosulphide, whereas arsine dibromides usually react readily with hydrogen sulphide; (4) it has a very high m. p. (298—300°), which one would expect of a salt, and is moreover stable up to this temperature. Its great stability is also shown by the fact that it is unaffected by moist air, although its aqueous solution is acid to litmus. It is very unlikely that a true arsine dibromide would possess either this high m. p. or this marked stability. Furthermore, the stability normally associated with an ionic arsonium bromide would be enhanced in the compound (V) by its existence as a resonance hybrid.



(V.)

EXPERIMENTAL.

Preparation and Purification of Arsanthren Dichloride.—Kalb (*loc. cit.*) prepared this compound by reducing *o*-arsonodiphenylarsonic acid, $C_6H_5\cdot AsO(OH)\cdot C_6H_4\cdot AsO(OH)_2$, in hot concentrated hydrochloric acid solution with sulphur dioxide and a trace of potassium iodide. The oil which separated was dried and distilled under reduced pressure, affording two main fractions: (*a*) b. p. 130—200°/12 mm., and (*b*) b. p. 200—290°/12 mm.; the second partly solidified and was separated by crystallisation into $C_6H_5\cdot AsCl\cdot C_6H_4\cdot AsCl_2$ and arsanthren dichloride (II). This distillation is unsatisfactory and the fraction (*b*) contains only a minor proportion of the required compound (II). We have found it advantageous after the fraction (*a*) has been collected to boil the residual liquid under reflux at 12 mm. pressure for 3 hours. The evolution of hydrogen chloride was thus completed and much of the trichloro-compound was converted into arsanthren dichloride. The fractionation was now repeated, and the fraction (*b*) which was collected without difficulty readily solidified on cooling. Slow fractional crystallisation of this product from chloroform gave first the arsanthren dichloride, then tri-*o*-phenylenediarsine (see McCleland and Whitworth, J., 1927, 2753), and the final mother-liquors yielded impure *o*-dichloroarsinodiphenylchloroarsine. The arsanthren dichloride so obtained, m. p. 178—185°, was twice recrystallised from chloroform (to remove traces of the phenylenediarsine), and then twice from benzene containing a trace of dry hydrogen chloride (to remove any *o*-dichloroarsinodiphenylchloroarsine or arsanthren oxide); it then had m. p. 179—184° (Found: Cl, 18·9. Calc. for $C_{12}H_8Cl_2As_2$: Cl, 19·0%). This m. p. was unaffected by further recrystallisation from carbon tetrachloride, and may indicate that the dichloride itself contains a small proportion of an isomeric form. Our modification of Kalb's method nearly doubles the small yield of the triphenylenediarsine, but considerably decreases that of the unchanged *o*-dichloroarsinodiphenylchloroarsine.

Preparation and Isolation of α- *and* β-5 : 10-*Di*-p-*tolyl*-5 : 10-*dihydroarsanthren* (III).—*p*-Bromotoluene was purified by repeated melting and partial solidification, with rejection of the liquid portion, until a solid fraction of sharp m. p. was obtained. Powdered arsanthren dichloride (18 g.) suspended in benzene (100 c.c.) was added to a vigorously stirred Grignard reagent prepared from the *p*-bromotoluene (25 g.), magnesium (3·6 g.), and ether (70 c.c.). Only a slight evolution of heat occurred. More benzene (100 c.c.) was added, and the mixture, after 30 minutes' stirring, was boiled under reflux for the same period, cooled, and then hydrolysed by a solution of ammonium chloride (40 g.) in water (200 c.c.). The ether–benzene layer was collected, dried (Na_2SO_4), the solvent distilled off, and the residue dissolved in hot chloroform (65 c.c.); hot alcohol (100 c.c.) was added, and the solution boiled (charcoal), filtered, and cooled. The mixed di-*p*-tolyldihydroarsanthrens separated as white crystals (16 g.); m. p. 133—158°.

To isolate the two isomeric forms, this product was dissolved in hot acetone (*ca.* 200 c.c.) and the solution set aside to cool in a closed flask. When the slow crystallisation ceased, the first crop of crystals was collected; they had m. p. 175—177°, and were later shown to be almost pure α-isomer. Crops of approximately this quality and composition will be designated A. About one-quarter of the mother-liquor was now removed by evaporation, and the crystallisation repeated under the same conditions. A second crop of crystals was thus obtained identical with the first, except that it contained two small clusters of leaflets which were quite distinct from the rest of the crop and were removed by hand. After this removal, the main bulk of the crop had m. p. 171—175° (A), and together with the first crop weighed 7 g. The leaflets which had been removed had m. p. 151—165° [mixed m. p. with a sample of the rest of the second crop (A), 133—150°], and were later shown to be mainly the β-isomer contaminated with an impurity; crops of this quality are designated B.

It was now possible by very careful manipulation to concentrate the solution by about one-seventh of its volume by evaporation, allow it to cool slowly in a closed vessel, and then seed it with the crystals B. After a third crop, consisting entirely of B, had been collected with minimum disturbance of the filtrate, the latter was again concentrated as before and allowed to cool slowly; it was now more supersaturated with respect to A than to B, and on seeding with A, gave a crop of the A crystals. The process was repeated with alternate seedings with A and B crystals, and seven crops (including those above) thus obtained: their m. p.'s and quality were (1) 175—177°, A; (2) 171—175°, A; (3) 164—167°, B; (4) 173—177°, A; (5) 161—165°, B; (6) 175—177°, A; (7) 161—166°, B. The mother-liquor was now too small for further fractionation to be possible.

It must be emphasised that this separation requires very delicate manipulation. It is complicated by the fact that the α- and the β-isomer readily crystallise together from concentrated acetone solution in massive plates of m. p. 130—136°. Should such crystals appear in the above separation, it indicates that the previous concentration of the mother-liquor has been carried too far, and the solution must be diluted until the alternate separation of crops A and B can once again be resumed.

The α-*isomer*. The above A crops were united (9 g.) and then recrystallised repeatedly from acetone until fine white leaflets of pure α-5 : 10-*di*-p-*tolyl*-5 : 10-*dihydroarsanthren*, m. p. 178—179°, were obtained (Found: C, 64·2; H, 4·5; *M*, ebullioscopic in 1·96% acetone solution, 508; in 2·51% solution, 494. $C_{26}H_{22}As_2$ requires C, 64·5; H, 4·6%; *M*, 484).

The β-*isomer*. The united B crops weighed 2·5 g., much having apparently been lost in the separation of the two forms. This quantity was dissolved in hot acetone (*ca.* 30 c.c.), and slow crystallisation gave bipyramidal crystals of the β-isomer, m. p. 179—181°. The mother-liquor was now twice in turn concentrated by evaporation and seeded with these crystals, and a second and third crop of the β-isomer thus obtained. The three crops were united and twice recrystallised from acetone, without change of m. p., however. The β-*isomer* was thus obtained in bipyramidal crystals which could readily be grown to a very large size;

m. p. 179—181° (Found: C, 64·3; H, 4·7%; *M*, ebullioscopic in 1·51% acetone solution, 472; in 2·18% solution, 452).

After the above three crops of the β-isomer had been collected, further concentration of the mother-liquor gave a small quantity of needle-shaped crystals (m. p. 166—170°) of impure β-isomer (mixed m. p.). The mother-liquor was therefore allowed to evaporate very slowly to dryness, and the colourless needles removed carefully from the residue by hand. They had m. p. 166—171°, mixed m. p. with the β-isomer, 168—176°; when recrystallised from *cyclo*hexane, they gave a small crop of crystals (Found: C, 66·85; H, 5·55%), of m. p. 176—188°, unchanged by admixture with the pure β-isomer. These needles clearly consist of the β-isomer contaminated with an unknown by-product. The latter must be present in very small proportion in the original mixture, but is presumably responsible for the initial separation of the β-isomer in the characteristic crystals of type B.

Although the pure α- and β-isomers have such close m. p.'s, their non-identity is clearly shown by the fact that a mixture of equal quantities of the two forms has m. p. 144—158°, and by their widely different crystalline habit when they separate from acetone under almost identical physical conditions. Their stability was shown by keeping a small quantity of each isomer molten at *ca.* 10° above its m. p. for 10 minutes, cooling it, and powdering it. The m. p. of the α-isomer was virtually unchanged at 177—179°, and that of the β-isomer at 178—181°; neither had been converted into the other, since a mixed m. p. determination gave 140—160°.

A repetition of the above preparation of the ditolyl compound indicated that the relative proportion of the α- and β-isomers may vary considerably in successive preparations.

There remained a possibility that a third much more soluble isomer had been formed and had stayed in the alcohol–chloroform mother-liquor from which the 16 g. of mixed α- and β-isomers had been collected. This mother-liquor was therefore evaporated, and the dry residue taken up in hot acetone, from which on standing small white crystalline nodules, of m. p. 200—211°, separated. A second similar crop was obtained, and the united crops were then recrystallised once from acetone and twice from benzene. The white crystals finally had m. p. 216—217°. Their identity is uncertain: analysis (Found: C, 60·2; H, 4·15; *M*, ebullioscopic in 1·00% chloroform solution, 412; in 1·60% solution, 405. $C_{21}H_{18}As_2$ requires C, 60·0; H, 4·3%; *M*, 420) indicates a *tri*-p-*tolylenediarsine*, $(CH_3{\cdot}C_6H_3)_3As_2$, homologous to McCleland and Whitworth's compound, but it is very difficult to see how such a compound could have been formed.

Preparation of Tetrabromide and Tetrahydroxide.—Bromine (0·66 g., 0·21 c.c., 4 mols.) was slowly added to a solution of the pure α-isomer (1 g.) in chloroform (20 c.c.); addition of ether with ice-cooling then precipitated the tetrabromide as pale yellow crystals which readily evolved hydrogen bromide on exposure to air. They were therefore at once added to aqueous ammonia solution (5 c.c. of *d* 0·880 diluted with 35 c.c. of water), and the mixture boiled under reflux for 30 minutes. After cooling, the 5 : 10-*di*-p-*tolyl*-5 : 10-*dihydroarsanthren tetrahydroxide* was collected, twice recrystallised from 30% alcohol, and thus obtained as beautiful white crystals, which on heating lost water and finally melted at *ca.* 318—325° (decomp.), the range depending on the rate of heating (Found: C, 56·6; H, 4·8. $C_{26}H_{26}O_4As_2$ requires C, 56·55; H, 4·7%).

This preparation was repeated exactly as above with the pure β-isomer, and the same tetrahydroxide obtained (Found: C, 56·75; H, 4·9%). The identity of the two samples was shown by their identical behaviour on crystallisation and on heating, by mixed m. p. determinations, and by *X*-ray powder photographs. Dehydration of the tetrahydroxide by heating at 250° for 1½ hours gave the *dioxide* as a hygroscopic white powder (Found: C, 60·7; H, 4·7. $C_{26}H_{22}O_2As_2$ requires C, 60·5; H, 4·35%).

Reduction of the above tetrabromide was performed in order to determine whether a third isomeric ditolylarsanthren was formed by this process. For this purpose, the α-isomer in chloroform solution was converted as above into the tetrabromide; instead of ether, however, dilute hydrochloric acid (20 c.c.) and potassium iodide (0·05 g.) were added, and sulphur dioxide was passed through the solution for 4 hours to complete reduction of the tetrabromide. The aqueous layer was separated, extracted with chloroform, and the extract added to the main chloroform layer. The combined extracts were washed with water, sodium carbonate solution, and water (twice), the separated chloroform layer allowed to evaporate spontaneously, and the residue recrystallised from alcoholic chloroform (containing 20% of chloroform); ice cooling gave an almost complete separation of the mixed isomeric ditolyldihydroarsanthrens, m. p. 140—160° (Found: C, 64·3; H, 4·7%).

A mixture of equal quantities of the pure α- and β-isomers was now recrystallised from alcoholic chloroform as above, and then had m. p. 138—161°. *X*-Ray powder photographs were taken of each sample of mixed isomers so obtained. In general, the same lines appeared on both photographs, but a particular set of lines on the first photograph was much more intense than on the second, and certain faint lines on the first did not appear on the second. Both samples clearly consisted solely of α- and β-isomers, and the minor differences in the two photographs were caused solely by a difference in their proportions in the two samples. No third isomer was therefore present in the sample obtained from the tetrabromide.

Preparation of the Monomethiodides.—(A) Methyl iodide (4 c.c.) was added to solution of the α-isomer (2 g.) in benzene (10 c.c.) and ether (10 c.c.), and the mixture set aside for 3 days, during which considerable crystallisation occurred. The crystals (3·8 g.) were collected, washed with ether, and dried in a vacuum; they clearly contained much solvent of crystallisation, which was partly lost during the drying. The product was then crystallised from alcohol, and the α-5 : 10-*di*-p-*tolyl*-5 : 10-*dihydroarsanthren monomethiodide* separated with 1 mol. of alcohol of crystallisation as large pale yellow crystals (1·2 g.), m. p. 140—177° with loss of alcohol (Found: C, 52·0; H, 4·9; I, 18·8. $C_{27}H_{25}IAs_2,C_2H_5\cdot OH$ requires C, 51·8; H, 4·7; I, 18·9%). The crystals slowly effloresced at room temperature. This product when recrystallised from much boiling water gave the anhydrous α-*monomethiodide* as small white crystals, m. p. 176—179° (slight effervescence) (Found: C, 52·25; H, 4·0; I, 20·4. $C_{27}H_{25}IAs_2$ requires C, 51·8; H, 4·0; I, 20·3%).

A solution of this monomethiodide in a mixture of equal volumes of methyl alcohol and methyl iodide was boiled under reflux for 6 hours, and the solvent then allowed to evaporate spontaneously. The residue recrystallised from water in characteristic crystals of the unchanged monomethiodide (Found: I, 20·1%).

(B) A mixture of methyl iodide (3 c.c.) and the pure β-isomer (1 g.) dissolved in benzene (6 c.c.) and ether (6 c.c.) was set aside for 7 days, as the reaction appeared to be markedly slower. The product (0·75 g.) was collected, washed with ether, and then had m. p. 176—179° (slight effervescence). Recrystallisation from alcohol gave, however, pale yellow crystals of the pure β-5 : 10-*di*-p-*tolyldihydroarsanthren monomethiodide*, m. p. 176—179° (slight effervescence) (Found: C, 51·6; H, 4·4; I, 20·0%). When this compound was crystallised from boiling water, it gave white crystals of the *monohydrate*, m. p. 174—179° (slight effervescence) (Found: C, 50·5; H, 4·5; I, 19·6. $C_{27}H_{25}IAs_2,H_2O$ requires C, 50·3; H, 4·2; I, 19·7%). These white crystals differ from those of the above α-monomethiodide in their crystal habit, and in being a monohydrate; further, a mixed m. p. gave 167—175°. The anhydrous β-methiodide was recovered as monohydrate (Found: I, 20·0%, after recrystallisation from water) after an attempt to form a dimethiodide precisely as for the α-compound.

The m. p. of both methiodides is affected slightly by the rate of heating, which was therefore kept approximately constant for all determinations.

The Monosulphide.—(1) *Preparation from the tetrabromide.* Bromine (0·42 c.c., 2 mols.) was slowly added to a solution of the mixed isomeric ditolyl compounds (III, 2 g.) in cold chloroform (20 c.c.), and the solution of the tetrabromide thus obtained was then added to a hot solution of sodium sulphide nonahydrate (1·5 g.) in alcohol (100 c.c.). The solution was allowed to cool and evaporate spontaneously, and was finally taken to dryness in a desiccator. The residue was washed with water and dried (2·2 g., m. p. 191—198°), and was then twice recrystallised from alcohol (charcoal). The *monosulphide* was obtained as white needles, m. p. 198—201° (Found: C, 60·0; H, 4·5; S, 6·0. $C_{28}H_{22}SAs_2$ requires C, 60·5; H, 4·3; S, 6·2%).

(2) *Reaction with methyl iodide.* A solution of the monosulphide (0·5) in methyl iodide (3 c.c.) and ether (3 c.c.) was set aside for 3 days, by which time a red oil had separated. Dilution with more ether then caused a further separation of the oil; the solution was decanted off, and the oil, when mixed with ether, solidified. Recrystallisation from water containing 5% of alcohol gave a mixture of the α- and β-monomethiodides, m. p. 145—165° (Found: I, 19·8%).

The Dibromide.—(1) *From the tetrabromide.* A solution of the tetrabromide in chloroform was prepared as above, and damp hydrogen sulphide then passed through the solution for 7 hours; sulphur was deposited in the early stages and removed by filtration. Complete evaporation at room temperature gave an oil which solidified when stirred with alcohol. The dry solid (2·3 g.) was extracted with hot benzene (20 c.c.), and the filtrate on cooling deposited the monosulphide, which after recrystallisation from alcohol had m. p. 198—201°, unchanged by admixture with an authentic sample. The benzene-insoluble residue, when twice recrystallised from alcohol (charcoal), gave the *dibromide* as white crystals, m. p. 298—300° (decomp.) (Found: C, 48·4; H, 3·5; Br, 24·85. $C_{26}H_{22}Br_2As_2$ requires C, 48·4; H, 3·4; Br, 24·8%).

The dibromide was also formed, dry reagents being used, by boiling a solution of the tetrabromide (1 g.) in chloroform (10 c.c.) under reflux, and gradually adding acetone (10 c.c.). After 2 hours' boiling, ether was added to the warm red solution until a permanent cloudiness appeared; on cooling, the dibromide was deposited (0·6 g.), m. p. *ca.* 300° (Found : Br, 24·7%).

(2) *From the monosulphide.* 6·7 C.c. of a solution of bromine in chloroform (25 g./l.) was slowly added to a solution of the monosulphide (0·54 g., 1 mol.) in chloroform (10 c.c.), sulphur being at once deposited. After 30 minutes, the solution was warmed and filtered, and dilution of the hot filtrate with ether deposited the dibromide (0·4 g.) (Found : Br, 25·2%).

Action of Hydrogen Sulphide on the Dibromide.—A solution of the dibromide was prepared by the addition of bromine (0·32 c.c., 1 mol.) to the isomeric ditolyl compounds (3 g.) in chloroform (30 c.c.). Damp hydrogen sulphide was passed through this solution for 7 hours, and the product was then separated into unchanged dibromide and the monosulphide by the method described above.

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