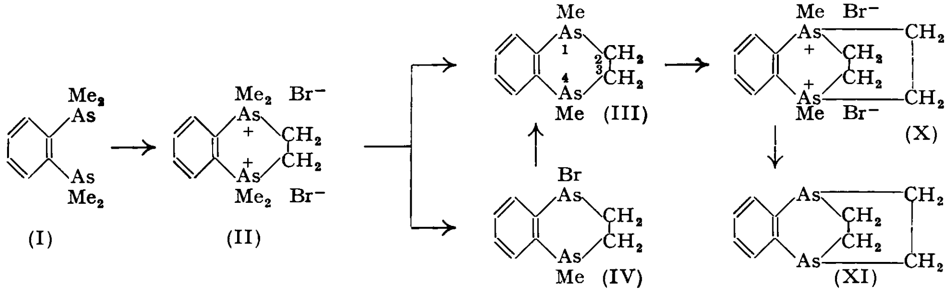
796. *The Preparation and Properties of* 1 : 4-*Dimethylethylene*-o-*phenylenediarsine and of Di-ethylene*-o-*phenylenediarsine.*

By Frederick G. Mann and F. C. Baker.

o-Phenylenebis(dimethylarsine) combines with ethylene dibromide to give 1 : 1 : 4 : 4-tetramethylethylene-*o*-phenylenediarsonium dibromide (II), which on thermal decomposition gives 1 : 4-dimethylethylene-*o*-phenylenediarsine (III) and 1-bromo-4-methylethylene-*o*-phenylenediarsine (IV). The 1 : 4-dimethyl-diarsine in turn combines with ethylene dibromide to give diethylene-*o*-phenylenediarsine dimethobromide (X), which on thermal decomposition gives diethylene-*o*-phenylenediarsine (XI). These three ditertiary arsines show remarkable similarity in their behaviour towards quaternising agents, which is in marked contrast to that of tri-*o*-phenylenediarsine.

The quaternisation of *o*-phenylenebisdimethylarsine (I), originally prepared by Chatt and Mann (*J.*, 1939, 610), shows certain features which are characteristic of the three ditertiary arsines studied in the present investigation. Earlier work (cf. Beeby and Mann, *J.*, 1951, 887) indicated that the diarsine (I) apparently formed only a monomethobromide and a monomethiodide. We find, however, that the diarsine when dissolved in cold methyl bromide readily forms a monomethobromide, m. p. 225—226°, but when heated with methyl bromide at 100° gives a dimethobromide, which decrepitates at *ca.* 150° and subsequently melts at 222—223°. Similarly a solution of the diarsine in an excess of methyl iodide, when boiled under reflux for several hours, forms only a monomethiodide, m. p. 228—230°, but when heated at 100° as before gives the dimethiodide, m. p. 222—224°. In each series, therefore, the quaternisation of the second arsine group requires much more vigorous conditions than that of the first group; moreover, the above melting points indicate that both the diquaternary salts readily lose one molecule of alkyl halide when heated, to give the more stable monoquaternary salts, and that the apparent melting point of each diquaternary salt is probably that of the residual monoquaternary salt.

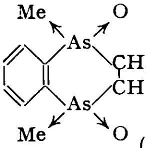


When however the diarsine (I) is heated with one molecular equivalent of ethylene dibromide at 125—130°, *i.e.*, just below the boiling point of the latter, diquaternisation readily occurs with the formation of 1 : 1 : 4 : 4-tetramethylethylene-*o*-phenylenediarsonium dibromide (II), systematically named 1 : 1 : 4 : 4-tetramethyl-1 : 2 : 3 : 4-tetrahydro-1 : 4-diarsonianaphthalene dibromide (Glauert and Mann, *J.*, 1950, 682). A similar derivative is obtained by using trimethylene dibromide. All the above quaternary salts of the diarsine (I) are colourless.

We have investigated in some detail the thermal decomposition of the dibromide (II). The course of this decomposition is markedly affected by the physical conditions employed, and also apparently by slight traces of impurities. When however the pure dry salt is rapidly heated in nitrogen at *ca.* 0·1 mm., the decomposition follows two courses, for the liquid distillate on refractionation yields 1 : 4-dimethylethylene-*o*-phenylenediarsine (III) and 1-bromo-4-methylethylene-*o*-phenylenediarsine (IV).

The diarsine (III) is a colourless liquid which on quaternisation behaves precisely as does (I), *i.e.*, with an excess of methyl bromide in the cold it forms a monomethobromide but at 100° regenerates the dibromide (II), and with an excess of boiling methyl iodide forms a monomethiodide, but at 100° forms a dimethiodide. The dimetho-bromide and -iodide have, however, considerably greater stability than the corresponding salts of the diarsine (I), for they can be heated in a vacuum to at least 100° without loss of alkyl halide.

The diarsine (III) was readily oxidised by hydrogen peroxide to the diarsine dioxide (V), which was isolated as the bishydroxypicrate. It is notable however that whereas the diarsine (I) readily co-ordinates with palladous bromide to form the cyclic compound (VI) (Chatt and Mann, *J.*, 1939, 1622), the diarsine (III) gives a compound of composition $(C_{10}H_{14}As_2)_2PdBr_2$, in which only one arsenic atom in each molecule of the diarsine has co-ordinated with the palladium. This composition is undoubtedly determined primarily by the stereochemistry of the diarsine (III), the effect being probably reinforced by the greater reluctance of the second arsenic atom to increase its valency.



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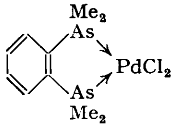

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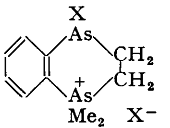

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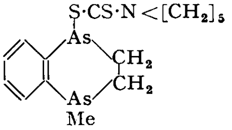


(VIII)

Although the above fractional distillation gave the pure diarsine (III), b. p. 106—108°/0·3 mm., the bromo-arsine (IV), b. p. 120°/0·3 mm., could not by these means be obtained entirely free from the diarsine. The identity of the bromoarsine (IV) rests, however, on the following evidence. A solution in an excess of methyl bromide when heated at 100° gave the colourless crystalline monomethobromide (VII; X = Br), and a similar solution in methyl iodide when boiled under reflux gave the deep yellow crystalline 1-iodo-4-methylethylene-*o*-phenylenediarsine monomethiodide (VII; X = I). The colour of this salt was a strong indication of an As–I link, and the presence of a similar As–Br link in the parent arsine (IV) was shown by the fact that the arsine reacted readily with piperidine *N*-pentamethylenedithiocarbamate to give the dithiourethane (VIII), the identity of which was confirmed by both analysis and molecular-weight determinations. It might be considered however that the above evidence does not distinguish decisively between the bromo-arsine (IV) and the compound (IX) which might conceivably arise from the thermal decomposition of (II) and would differ in composition from (IV) only by two hydrogen atoms. When however the bromo-arsine was treated with methylmagnesium iodide it gave the diarsine (III), which was characterised by its crystalline derivatives, whereas the compound (IX) would have given the original tetramethyldiarsine (I).

Once the two components (III) and (IV) of the original mixture arising from the thermal decomposition of (II) had been identified, refractionation was clearly unnecessary when only the diarsine (III) was required : for this purpose the crude distillate was treated with an excess of methylmagnesium iodide, and the product on distillation readily yielded the pure diarsine (III).

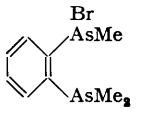
The diarsine (III), when in turn heated with one molecular equivalent of ethylene dibromide at 120—125°, gave the crystalline dimethobromide (X) of diethylene-*o*-phenylenediarsine; this salt when treated with ethanolic sodium picrate readily gave the corresponding dimethopicrate, thus proving that both bromine atoms in (X) were ionic, and that cyclisation by the second molecule of ethylene dibromide had actually occurred.

The dibromide (X), when heated under the conditions described for (II), also underwent a smooth thermal decomposition, giving a crude distillate which on careful fractionation gave pure diethylene-*o*-phenylenediarsine (XI), a colourless liquid of b. p. 95°/0·01 mm., and a higher-boiling bromo-derivative, of which supplies were too small for satisfactory identification.

The identity of the tricyclic diarsine (XI) was confirmed by analysis, molecular-weight determinations, and the fact that methyl bromide in the cold gave the monomethobromide and at 100° regenerated the dimethobromide (X). Again, as in case of the diarsines (I) and (III), boiling methyl iodide furnished only the monomethiodide, whereas at 100° the dimethiodide was formed. Furthermore, this diarsine, like (III), when treated with hydrogen peroxide gave the corresponding diarsine dioxide (XII) which was also characterised as the bishydroxypicrate.

The three ditertiary arsines (I), (III), and (XI) form a series in which both the intensity of odour and the susceptibility to atmospheric oxidation decrease markedly in the above order.

The tricyclic diarsine (XI) is clearly of the same general type as tri-*o*-phenylenediarsine (XIII), prepared by McCleland and Whitworth (*J.*, 1927, 2753; see also Chatt and Mann, *J.*, 1940, 1184). The diarsine (XIII) appeared to differ strikingly from (XI) in one respect, however, because McCleland and Whitworth state that although it forms a dioxide and a tetrabromide, it does not form quaternary salts. This is unexpected, because the fixed disposition of the three valencies of each arsenic atom in (XIII) would appear to be almost ideal for allowing the arsenic atoms to become tetrahedral by valency increase, and the ingress of small groups (such as methyl) by quaternisation should therefore occur as readily as that of oxygen atoms by oxidation : furthermore, whereas quaternisation would thus place no strain on the valencies of the arsenic atoms, the formation of the tetrabromide would involve very considerable strain.



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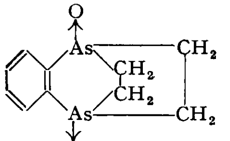
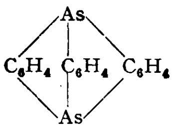


(XII)



(XIII)

Experiments, in which we have been kindly assisted by Mr. Emrys R. H. Jones, have shown that the diarsine (XIII) is in fact unaffected when heated with an excess of methyl bromide or iodide, even at 100° for 10 hours. When, however, the diarsine was heated with an excess of methyl toluene-*p*-sulphonate at 180° for 4 hours, it was converted into the monomethotoluene-*p*-sulphonate, and no further quaternisation occurred even at 210° during 6·5 hours. [This recalls the behaviour of 5 : 10-dihydro-5 : 10-di-*p*-tolylarsanthren, of which Chatt and Mann (*J.*, 1940, 1184) were able to prepare the monomethiodide but not the dimethiodide.] Since therefore no steric factor strongly influences the quaternisation of the diarsine (XIII), it appears that the combined electronic effect of the three *o*-phenylene groups considerably diminishes the normal reactivity of both tertiary arsine groups, and that, when one has undergone quaternisation, the full positive charge on this arsenic atom (as distinct from the modified positive charge in the arsine oxide) deactivates the second arsine group sufficiently to inhibit further quaternisation.

We are now investigating the reaction of the diarsine (III) with *o*-xylylene dibromide and similar compounds.

EXPERIMENTAL

Quaternary Salts of o-*Phenylenebisdimethylarsine* (I).—A solution of the arsine (1 g.) in methyl bromide (10 c.c.) was set aside in a sealed tube at room temperature for 12 hours with occasional shaking, crystals rapidly separating. The methyl bromide was allowed to evaporate, and the residue, when recrystallised from acetone containing a small proportion of methanol, gave the *monomethobromide*, m. p. 225—226° (Found : C, 34·9; H, 5·2. $C_{11}H_{19}BrAs_2$ requires C, 34·9; H, 5·2%).

A similar solution of the arsine (1 g.) in methyl bromide (7 c.c.) and methanol (3 c.c.) was heated in a sealed tube at 100° for 3 hours. The excess of solvent was then evaporated, and the heavy residual crystals, when crushed under acetone, collected, and dried in a vacuum, gave the pure *dimethobromide*, m. p. 222—223° with decrepitation at *ca.* 150° (Found : C, 29·8; H, 4·9. $C_{12}H_{22}Br_2As_2$ requires C, 30·3; H, 4·7%).

A solution of the arsine in an excess of methyl iodide was boiled under reflux in a nitrogen atmosphere for 1 hour, salt formation rapidly occurring. The residual crystals, after evaporation of the iodide, were recrystallised from ethanol and furnished the *monomethiodide*, m. p. 228—230° (Found : C, 30·9; H, 4·1. $C_{11}H_{19}IAs_2$ requires C, 30·85; H, 4·4%). The monomethiodide was also readily formed when the original solution was set aside at room temperature.

The previous solution, diluted with methanol, was heated in a sealed tube at 100° for 4 hours. Removal of the solvent gave a slightly hygroscopic crystalline residue which, when washed with methanol and dried at atmospheric pressure, gave the *dimethiodide*, m. p. 222—224° (Found : C, 24·7; H, 4·0. $C_{12}H_{22}I_2As_2$ requires C, 25·2; H, 3·9%).

Thermal Decomposition of the Dibromide (II).—The pure powdered dibromide (65 g.) was placed in a simple distilling-flask fitted with a capillary intake, a water-condenser, and receiver, and evacuated to 0·03 mm. pressure whilst nitrogen was led through the capillary. The dibromide was then heated carefully with the " brush " flame of a Bunsen burner, whereupon decomposition occurred smoothly; the distillate (41 g.), at first quite clear, became ultimately slightly cloudy. To ensure the elimination of traces of unchanged dibromide, the distillate was redistilled without fractionation under similar conditions. The new distillate, when carefully fractionated in nitrogen at 0·5 mm. through a column, gave the fractions : (A) b. p. 80—108°, very small quantity; (B) b. p. 110—130°, 10·6 g., colourless; (C) b. p. 130—140° (mainly at 136—138°), 22·9 g., very faintly golden; (D) a small semisolid residue. No sharp distinction between fractions (B) and (C) could be obtained.

Fraction (B) was twice refractionated, and 1 : 4-*dimethylethylene*-o-*phenylenediarsine* (III) ultimately obtained as a colourless liquid of moderate odour, b. p. 94—97°/0·015 mm. (Found : C, 42·0; H, 5·2%; *M*, ebullioscopic in 1·235% ethanol solution, 289. $C_{10}H_{14}As_2$ requires C, 42·3; H, 5·0%; *M*, 284).

Fraction (C), even after four refractionations, gave impure 1-bromo-4-methylethylene-*o*-phenylenediarsine (IV), b. p. 120°/0·3 mm. (Found : C, 32·3; H, 3·8. $C_9H_{11}BrAs_2$ requires C, 30·95; H, 3·2%).

In later experiments, when only the diarsine (III) was required, the crude distillate was added slowly with stirring to an excess of methylmagnesium iodide in ether under nitrogen. The ethereal product, when hydrolysed with aqueous ammonium chloride and worked up in the usual way, furnished on one distillation the pure diarsine (III), b. p. 106—108°/0·3 mm. (Found : C, 42·6; H, 5·3%), giving the same crystalline derivatives as the above sample.

When the thermal decomposition of the dibromide (II) was carried out by heating the dibromide either slowly in a metal-bath at a high vacuum, or in a vigorous stream of nitrogen at atmospheric pressure, various other products of uncertain constitution were obtained.

1 : 4-*Dimethylethylene*-o-*phenylenediarsine* (III).—This diarsine gave the following derivatives, the quaternary salts being prepared under the same conditions as those of the diarsine (I) : *Monomethobromide*, very soluble in methanol but separating readily from ethanol as colourless crystals, m. p. 228° (effervescence) (Found : C, 35·0; H, 4·5. $C_{11}H_{17}BrAs_2$ requires C, 34·85; H, 4·5%). Dimethobromide, prepared to check the identity of (III), and forming colourless crystals, m. p. 254° (effervescence), unchanged by admixture with the original dibromide. *Monomethiodide*, m. p. 250° (effervescence) after recrystallisation from methanol and drying at 100°/0·1 mm. (Found : C, 31·45; H, 4·15. $C_{11}H_{17}IAs_2$ requires C, 31·0; H, 4·0%). *Dimethiodide*, m. p. 245—246°, when recrystallised from methanol and dried at 75°/0·1 mm. for 2 hours (Found : C, 24·95; H, 3·7. $C_{12}H_{20}I_2As_2$ requires C, 25·4; H, 3·55%).

Dioxide (V).—A mixture of the diarsine (III) and an excess of aqueous hydrogen peroxide (" 20-vol.") was diluted with sufficient acetone to give a clear solution, which was kept at 35° for 4 hours, then concentrated on a water-bath, and finally evaporated in a vacuum to a sticky residue of the dioxide (V). An aqueous solution of the latter, when treated with aqueous picric acid, deposited the *bishydroxypicrate*, yellow crystals, m. p. 179—180°, after recrystallisation from methanol (Found: C, 33·8; H, 2·6; N, 10·9. $C_{22}H_{20}O_{16}N_6As_2$ requires C, 34·1; H, 2·6; N, 10·9%) : it was too soluble in water and ethanol for satisfactory recrystallisation.

Dibromobis-1 : 4-*dimethylethylene*-o-*phenylenediarsine Palladium*.—The arsine, when added to aqueous-ethanolic potassium palladobromide, rapidly deposited a reddish-brown precipitate which became deep orange when the mixture was boiled. The precipitate when recrystallised from methanol gave the above *compound* as deep orange crystals, m. p. 360° (vigorous decomp.) (Found : C, 28·6; H, 3·55; Pd, 12·5. $C_{20}H_{28}Br_2As_4Pd$ requires C, 28·75; H, 3·4; Pd, 12·8%).

1-*Bromo*-4-*methylethylene*-o-*phenylenediarsine* (IV).—This compound gave the following derivatives. *Monomethobromide* (VII; X = Br). (*a*) A solution of (IV) in an excess of methyl bromide in a sealed tube was set aside at room temperature for 3 days. (*b*) A similar solution, containing in addition some methanol, was heated at 100° for 5 hours. In both cases, evaporation of the solvent gave the *monomethobromide*, m. p. 240° (effervescence) after recrystallisation from methanol (Found: C, 27·2; H, 3·5. $C_{10}H_{14}Br_2As_2$ requires C, 27·0; H, 3·2%). 1-*Iodo*-4-*methylethylene*-o-*phenylenediarsine monomethiodide* (VII; X = I) readily separated when a solution of (IV) in methyl iodide was boiled under reflux, and on recrystallisation from methanol formed deep yellow crystals, m. p. 199—200° (Found : C, 22·5; H, 2·7. $C_{10}H_{14}I_2As_2$ requires C, 22·3; H, 2·6%). 4-*Methyl*-1-(N-*pentamethylenethiocarbamylthio*)*ethylene*-o-*phenylenediarsine* (VIII) readily separated when ethanolic solutions of the bromo-arsine (IV) and of piperidine *N*-pentamethylenedithiocarbamate were mixed and warmed: it formed cream-coloured crystals, m. p. 101—101·5°, from ethanol (Found: C, 41·6; H, 5·1; N, 3·2%; *M*, ebullioscopic in 1·08% ethanolic solution, 433. $C_{15}H_{21}NS_2As_2$ requires C, 41·9; H, 4·9; N, 3·3%; *M*, 429·3).

The bromo-arsine (IV) was also added to an excess of ethereal methylmagnesium iodide, and thus converted into the diarsine (III), which was identified by analysis and by conversion into the dimethobromide and dimethiodide previously described.

Diethylene-o-*phenylenediarsine Dimethobromide* (X).—A mixture of the diarsine (III) (11·6 g.) and pure ethylene dibromide (3·5 c.c., 1 mol.) was heated in an oil-bath under reflux in nitrogen at 120—125° for 3 hours. Solidification rapidly started and after *ca.* 2 hours' heating was complete. The cold pulverised material, when recrystallised from methanol, gave the hygroscopic *dimethobromide*, m. p. 240° (effervescence) (Found : C, 30·15; H, 4·0. $C_{12}H_{18}Br_2As_2$ requires C, 30·5; H, 3·8%). Cold aqueous solutions of this salt and of sodium picrate when mixed deposited the *dimethopicrate*, pale yellow needles, m. p. 230° after recrystallisation from water (Found : C, 37·6; H, 3·2; N, 10·6. $C_{24}H_{22}O_{14}N_6As_2$ requires C, 37·5; H, 2·9; N, 10·9%). *X*-Ray powder photographs gave independent evidence that this picrate was structurally distinct from, although similar to, that obtained from (II).

The diarsine (III) combined similarly with trimethylene dibromide, but the hard glassy product could not be satisfactorily recrystallised.

Thermal decomposition of the dibromide (X). The pure dry dibromide (12·8 g.) was heated at 270°/0·5 mm. whilst a fine stream of nitrogen was passed through a capillary tube into the distilling flask. Decomposition occurred smoothly with the formation of a colourless distillate, no residue ultimately remaining. The distillate was redistilled without fractionation, and then carefully refractionated in nitrogen through a short column. Two fractions were obtained at 0·065 mm. : (A) b. p. 120—125°, 3·4 g.; and (B) b. p. 130—135°, 2·3 g.; the separation of the two fractions was apparently distinct.

Fraction (A) on refractionation gave *diethylene*-o-*phenylenediarsine* (XI) as a slightly hygroscopic colourless liquid, b. p. 95—96°/0·01 mm. (Found : C, 42·7; H, 4·6%; *M*, cryoscopic in 0·857% benzene solution, 274. $C_{10}H_{12}As_2$ requires C, 42·6; H, 4·3%; *M*, 282). It had an odour fainter than that of (III).

Fraction (B) on refractionation ultimately gave a liquid, b. p. 105—107°/0·014 mm., which was apparently still a mixture (Found : C, 34·6; H, 3·8; Br, 16·1%).

Derivatives of Diethylene-o-*phenylenediarsine* (XI).—The *monomethobromide* was prepared as before at room temperature, and after recrystallisation from ethanol had m. p. 244° (effervescence) (Found : C, 34·9; H, 4·1. $C_{11}H_{15}BrAs_2$ requires C, 35·0; H, 4·0%). The use of an excess of methanolic methyl bromide at 100° regenerated the dimethobromide (X), which, after recrystallisation from ethanol and drying at 100°/0·1 mm. for 6 hours, had m. p. 239—240° (effervescence), unchanged by admixture with the earlier sample (Found : C, 30·2; H, 4·1%). A solution of (XI) in methyl iodide, when boiled under reflux, gave the *monomethiodide*, which after recrystallisation from methanol had m. p. 240° (effervescence, the crystals showing considerable agitation from 210°) (Found : C, 31·5; H, 4·15. $C_{11}H_{15}IAs_2$ requires C, 31·2; H, 3·6%). A similar solution, when heated at 100° for 4 hours, gave the *dimethiodide*, which, recrystallised from methanol and then dried at 60°/0·1 mm. for 4 hours, had m. p. 260° (effervescence) (Found : C, 25·4; H, 3·4. $C_{12}H_{18}I_2As_2$ requires C, 25·5; H, 3·2%). The two diquaternary salts are thus, like those of (III) but unlike those of (I), stable to moderate heat.

A suspension of the diarsine (XI) in cold hydrogen peroxide (" 20-vol.") was set aside overnight, and the clear solution thus obtained was gently evaporated. The residue of the crude dioxide (XII) became sticky on exposure to air : its aqueous solution was therefore treated with aqueous picric acid, the *bishydroxypicrate* being precipitated as yellow crystals, m. p. 184° after recrystallisation from water (Found : C, 34·5; H, 2·5; N, 11·1. $C_{22}H_{18}O_{16}N_6As_2$ requires C, 34·2; H, 2·3; N, 10·9%).

Attempted Quaternisation of Tri-o-*phenylenediarsine* (XIII).—(1) A mixture of the diarsine (0·5 g.), methyl bromide (1 c.c., *ca.* 9 mols.) or methyl iodide (0·6 c.c., *ca.* 14 mols.), and methanol (1 c.c.) was heated in a sealed tube in nitrogen at 100° for 10 hours, and then evaporated to dryness. The residue, when recrystallised from much ethanol, gave the unchanged diarsine (XIII), m. p. 286—287°, unchanged by admixture with the original sample, of m. p. 285—286°. Almost the whole of the original diarsine was thus recovered.

(2) A mixture of the powdered diarsine (0·2 g.) and methyl toluene-*p*-sulphonate (0·6 g., 6 mols.) was heated at 180° for 4 hours, complete solution being obtained at *ca.* 160°. The cold viscous residue when stirred with ether deposited the *monomethotoluene*-p-*sulphonate* as a white powder, very soluble in cold ethanol; recrystallisation from water gave the very stable *monohydrate*, which after drying at 120°/0·1 mm. for 3 hours had m. p. 238° (Found : C, 53·8; H, 3·8. $C_{26}H_{22}O_3SAs_2,H_2O$ requires C, 53·6; H, 4·1%). Since however the carbon and hydrogen content of the mono- and di-metho-salts are closely similar, an aqueous solution of the pure monohydrate was treated with aqueous sodium picrate, thus precipitating the yellow *monomethopicrate*, which after recrystallisation from methanol and drying at 100°/0·1 mm. for 3 hours had m. p. 226—227° (decomp.) (Found: C, 48·8; H, 3·0; N, 6·6. $C_{25}H_{17}O_7N_3As_2$ requires C, 48·4; H, 2·7; N, 6·75%).

(3) Expt. (2) was repeated, with however 16 mols. of the sulphonate at 210° for 6·5 hours. The product, when purified as before, again gave the monohydrate of the monomethotoluene-*p*-sulphonate, which was not affected by being heated at 140°/0·1 mm. for 15 hours, and again had m. p. 238°, unaffected by admixture with that obtained in Expt. (2). This sample gave the same monomethopicrate, m. p. 226—227° (decomp.), mixed and unmixed.

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