

781. *Cyclic Diarsines. Part V.* Diphenyl Derivatives containing Seven-, Eight-, Nine-, and Ten-membered Diarsine Ring Systems.*

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An improved synthesis of 2 : 2'-diphenylenebisdimethylarsine (I) is described. The diarsine reacts with methyl bromide to form mono- and di-quaternary salts under appropriate conditions. With methylene, ethylene, trimethylene, and *o*-xylylene dibromide the diarsine forms cyclic diquaternary dibromides. These salts decompose on being heated: those derived from methylene and *o*-xylylene dibromide give the expected products having respectively seven- and ten-membered di(tertiary arsine) ring systems; in contrast, the salts derived from ethylene and trimethylene dibromide decompose with contraction of the heterocyclic rings to give 9-methyl-9-arsafluorene.

The quaternising and chelating properties of the above diarsines, and the stereochemistry of the compounds so formed, are discussed.

2 : 2'-DIPHENYLENEBISDIMETHYLARSINE (I) was originally isolated by Heaney, Mann, and Millar¹ from the products of the action of iododimethylarsine on a complex mixture of Grignard reagents, produced by the interaction of *o*-bromoiodobenzene and excess of magnesium at 0°. However, this reaction yields six other arsines and diarsines in addition to the diarsine (I), which moreover was isolated in the lowest yield (*ca.* 1.6%) of all these products. For the further investigation of this diarsine a more convenient method of preparation was therefore sought.

We now find that 2 : 2'-dilithiodiphenyl, conveniently prepared from ethereal 2 : 2'-iododiphenyl and metallic lithium, reacts smoothly with iododimethylarsine to give the diarsine (I) in 63% yield.

We find that 2 : 2'-diphenylenebisdimethylarsine (I) when dissolved in an excess of cold methyl bromide readily forms a monomethobromide, but when this solution contains a trace of methanol the dimethobromide is ultimately formed. The presence of methanol is known powerfully to promote quaternisation.^{2,3} The dimethobromide is also formed, in the absence of methanol, by heating a solution of the diarsine (I) in methyl bromide at 80°. A solution of the diarsine (I) in methyl iodide readily forms a dimethiodide at room temperature.

This behaviour recalls that of *o*-phenylenebisdimethylarsine, C₆H₄(AsMe₂)₂, and

* Part IV, Jones and Mann, *J.*, 1955, 411.

¹ Heaney, Mann, and Millar, *J.*, 1957, 3930.

² Menshutkin, *Z. phys. Chem.*, 1890, **6**, 41.

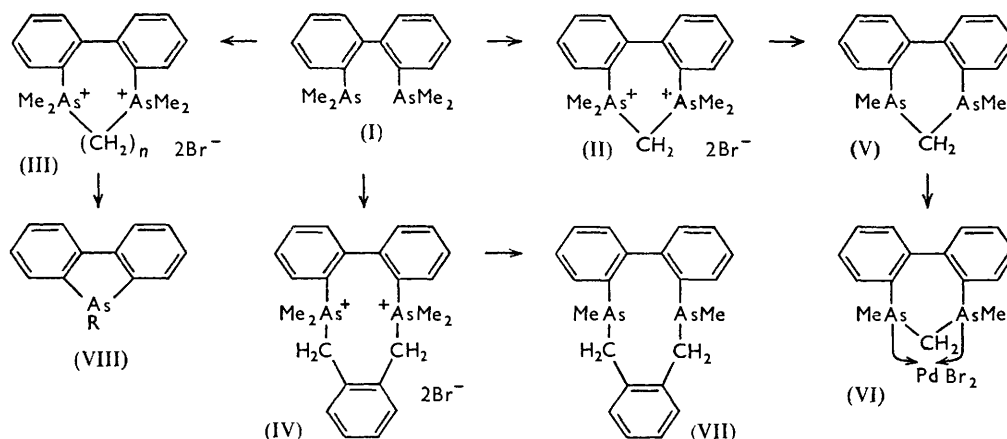
³ Mann and Watson, *J. Org. Chem.*, 1948, **13**, 509.

certain related diarsines. Mann and Baker⁴ have shown that this diarsine in cold methyl bromide readily forms a monomethobromide, but with methyl bromide at 100° gives a dimethobromide. Similarly a solution of this diarsine in an excess of boiling methyl iodide forms only a monomethiodide, but when heated at 100° gives the dimethiodide. In each case the quaternisation of the second tertiary arsine group requires much more vigorous conditions than those required for the first group; moreover, the melting points of the resulting salts indicate that the diquaternary compounds readily lose methyl halide when heated, to give the more stable monoquaternary salts.

It is clear, therefore, that in the monoquaternary salts of 2:2'-diphenylenebisdimethylarsine (I) the deactivation of the remaining tertiary arsine group by the positive charge on the quaternary group is much less than that in corresponding salts of *o*-phenylenebisdimethylarsine, and it may be ascribed to a similar inductive effect transmitted in the diarsine (I) by a longer path.

It is of interest that 2:2'-diphenylenebisdimethylamine, the nitrogen analogue of the diarsine (I), forms only a monomethiodide when heated with methyl iodide in a sealed tube at 100°.⁵

It has been shown that *o*-phenylenebisdimethylarsine undergoes ready diquaternisation with alkylene dibromides yielding cyclic diarsonium dibromides; the reaction is not limited to the formation of six-membered rings.^{4,6} This reaction is clearly promoted by



the fact that the tertiary arsine groups in this diarsine are rigidly held in a favourable position by the *o*-phenylene group. Similar reactions using 2:2'-diphenylenebisdimethylarsine (I) have now been investigated.

It is improbable for steric reasons that the molecule of this diarsine (I) can be coplanar: a model indicates that the angle between the planes of the benzenoid rings cannot be less than *ca.* 25°, and in conformity the ultraviolet absorption spectrum (see Figure) lacks almost entirely the characteristic diphenyl band in the 252 mμ region. Nevertheless, the rotation of the benzenoid planes beyond this angle might allow the two tertiary arsine groups to adopt suitable relative positions for diquaternisation with a range of alkylene dihalides.

Experiment has confirmed this expectation. When 2:2'-diphenylenebisdimethylarsine is heated with methylene, ethylene, trimethylene, or *o*-xylylene dibromide at 100° for some hours, the corresponding tricyclic dimethobromides (II), (III; *n* = 2 or 3), and (IV), respectively, are formed in high yields. In all four cases, evidence that cyclisation

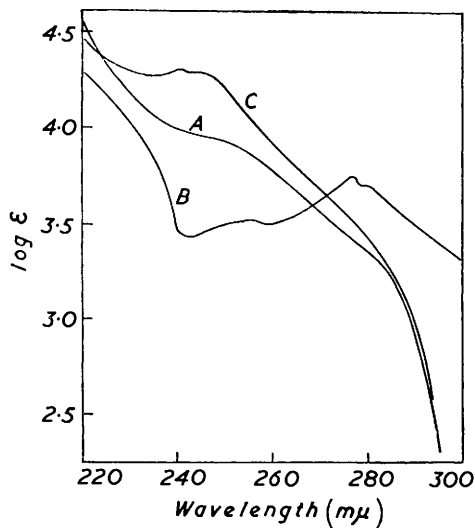
⁴ Mann and Baker, *J.*, 1952, 4142.

⁵ Shaw and Turner, *J.*, 1933, 135.

⁶ Glauert and Mann, *J.*, 1950, 682.

had occurred and that the products were not the isomeric monoarsonium bromides was provided by the formation of the corresponding dipicrates when cold ethanolic solutions of the dibromides were treated with ethanolic sodium picrate.

The stereochemistry of cyclic diarsonium salts of the types (II), (III; $n = 2$ or 3), and (IV) is noteworthy. Construction of models of the cations indicates that the heterocyclic rings are buckled and almost strainless; and that the benzenoid rings of the diphenyl system are not coplanar, and could not become so without great distortion of normal bond angles and lengths. This lack of coplanarity, and the twisted heterocyclic rings which it entails, causes these salts to possess molecular dissymmetry, and they should therefore be resolvable into optically active forms. These resolutions are now under investigation.



Ultraviolet absorption spectra, in *n*-hexane, of:

- (A) 2 : 2'-diphenylenebisdimethylarsine (I).
 (B) 9-methyl-9-arsafluorene (VIII; R = Me).
 (C) 5 : 7-dimethyl-5 : 7-diarsa-1 : 2-3 : 4-dibenzo-
 cycloheptadiene (V).

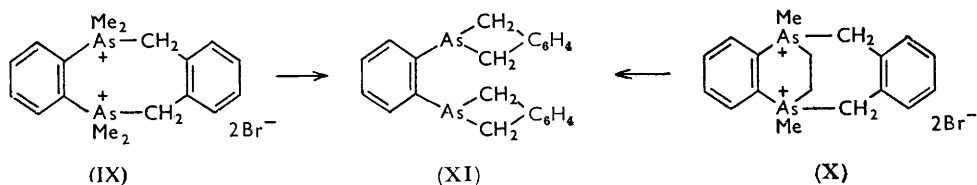
The thermal decomposition of the diarsonium dibromides (II), (III; $n = 2$ or 3), and (IV) reveals features of great interest. Thus the seven-membered ring dibromide (II) decomposes smoothly above its melting point, at 0.15 mm., with loss of methyl bromide to give the seven-membered ring ditertiary diarsine (V). This diarsine has been identified by (a) analysis, (b) molecular-weight determination, and (c) by its ready reaction with potassium palladobromide to give the chelated covalent compound (VI).

Thermal decomposition of the *o*-xylylene salt (IV) follows a similar course, yielding the cyclic diarsine (VII) in which the ten-membered heterocyclic ring has remained intact.

The diarsines (V) and (VII) were converted into their quaternary dimethopicrates, which were identical with those prepared directly from the parent dimethobromides (II) and (IV) respectively. This affords strong evidence that these methobromides have the structure indicated and are not in fact the "dimeric" tetra-arsonium tetrabromides.

However, thermal decomposition of the eight-membered ring dibromide (III; $n = 2$) follows a novel course; smooth decomposition at the melting point gives 9-methyl-9-arsafluorene (VIII; R = Me) in high yield, together with traces of a bromoarsine, almost certainly 9-bromo-9-arsafluorene (VIII; R = Br). The presence of a bromoarsine was shown by the intense yellow colour developed when the crude product, dissolved in acetone, was mixed with a solution of sodium iodide in the same solvent.⁴ However, the small proportion of the bromoarsine present, together with the high tendency of the 9-methyl-9-arsafluorene to crystallise during distillation, rendered separation of these two compounds difficult. The crude product was therefore treated with ethereal methylmagnesium iodide, which readily gave the pure 9-methyl-9-arsafluorene (VIII; R = Me), m. p. 41—41.5°, in overall yield of 69%.

Aeschlimann, Lees, McClelland, and Nicklin ⁷ have prepared 9-methyl-9-arsafluorene, and give m. p. 46°; however, they were unable to obtain fully satisfactory analytical values. The identity of the arsine prepared by thermal decomposition of the dibromide (III; $n = 2$) was established as 9-methyl-9-arsafluorene by (a) analysis, (b) the formation of derivatives, in particular the quaternary methiodide and the corresponding methopicate, and (c) by the similarity of the ultraviolet absorption spectrum of this arsine (Figure) with that of 9-*p*-tolyl-9-arsafluorene, recorded by Campbell and Poller.⁸



This formation of a bromo-arsine during the thermal decomposition of a heterocyclic methylarsonium bromide is not novel. The *o*-phenylene analogue of (III; $n = 2$) yields both 1:4-dimethyl- and 1-bromo-4-methyl-ethylene-*o*-phenylenediarsine (Mann and Baker ⁴); 5:10-dihydro-5:10-dimethylarsanthren dimethobromide similarly gives 5-bromo-5:10-dihydro-10-methylarsanthren (Jones and Mann ⁹).

The contraction of an eight-membered ring containing two quaternary arsonium groups in a 1:4-position on thermal decomposition, to yield a product having the arsenic atoms contained in five-membered rings, has been recorded previously by Jones and Mann,¹⁰ who showed that the dibromides (IX) and (X) readily gave *o*-phenylenebis-(2-*iso*-arsindoline) (XI), but the formation of this product necessarily involved intermolecular reactions.

This contrasts with the ring contraction (III; $n = 2$) \rightarrow (VIII) now recorded, which furthermore involves an unusually ready fission of an aryl carbon-arsenic bond. The second arsenic atom is eliminated in this transformation ultimately as trimethylarsine, which has been characterised as its dinuclear complex with palladium dibromide.

The nine-membered ring dibromide (III; $n = 3$) also decomposes with the formation of 9-methyl-9-arsafluorene in 49% yield, and contamination with a bromoarsine is barely detectable. In this decomposition the second arsenic atom is eliminated almost certainly as dimethylvinylarsine.

The structural factors in the dibromides (II), (III; $n = 2$ and 3), and (IV) which determine their type of thermal decomposition (*i.e.*, with or without ring contraction) remain uncertain. It appears significant, however, that decomposition with ring contraction occurs only in the dibromides (III; $n = 2$ or 3) which have flexible bridging groups, whereas the heterocyclic ring, which is rigid in the dibromide (II) and has very limited flexibility in the dibromide (IV), remains intact during the decomposition. Furthermore, the ethylene and the trimethylene bridge in the dibromides (III; $n = 2$ or 3) both possess a methylene group containing hydrogen atoms in the β -relation to the arsenic atoms: such hydrogen atoms may be essential if this exceptional ring-contraction involves an elimination mechanism similar in general type to that shown, for example, by several cyclic quaternary phosphonium bromides.¹¹ This mechanism is of course quite different from that of the normal thermal dissociation of arsonium halides containing at least one alkyl group.

It is clearly unlikely that the decomposition of the dibromide (III; $n = 2$) proceeds by

⁷ Aeschlimann, Lees, McClelland, and Nicklin, *J.*, 1925, **127**, 66.

⁸ Campbell and Poller, *Chem. and Ind.*, 1953, 1126; *J.*, 1956, 1195.

⁹ Emrys R. H. Jones and Mann, *J.*, 1955, 411.

¹⁰ *Idem*, *J.*, 1955, 405.

¹¹ Beeby and Mann, *J.*, 1951, 411; Mann and Millar, *J.*, 1951, 2205; Hart and Mann, *J.*, 1955, 4107; Mann, Millar, and Watson, *J.*, 1958, 2516.

initial decomposition to ethylene dibromide and 2 : 2'-diphenylenebisdimethylarsine (I) followed by loss of trimethylarsine and ring closure of the diarsine (I), since the dimethiodide of the diarsine (I) decomposes smoothly and normally at 260°/0.05 mm. to give the diarsine (I).¹ It is also noteworthy that the formation of the arsafluorene, under these relatively vigorous conditions of thermal decomposition, affords further evidence for the high stability of this ring system.

We are now investigating the formation and thermal decomposition of salts formed by the quaternisation of the cyclic diarsines (V) and (VII) with alkyl halides and with alkylene and other dibromides.

EXPERIMENTAL

Compounds are colourless unless otherwise described. M. p.s were determined on a Kofler hot stage.

2 : 2'-*Di-iododiphenyl*.—Diphenyleneiodonium iodide (58.5 g.), prepared as described by Lothrop¹² in 56% yield, was heated in an oil-bath at 215—220° for 30 min. The residue was extracted with ether (Soxhlet), and the extract percolated through a short column of chromatographic alumina to remove coloured impurities not readily removable by charcoal: evaporation of the solvent followed by recrystallisation from ethanol gave 2 : 2'-di-iododiphenyl, m. p. 110° (40 g., 68%).

2 : 2'-*Diphenylenebisdimethylarsine* (I).—This preparation was performed throughout under nitrogen. A solution of 2 : 2'-di-iododiphenyl (7.84 g.) in ether (100 c.c.) was added dropwise to fine lithium foil (1 g.) covered by ether (10 c.c.) at such a rate that the mixture boiled gently, and the complete mixture was then boiled under reflux for 30 min. The resulting solution of 2 : 2'-dilithiodiphenyl was decanted from insoluble material. Iododimethylarsine (9.4 g., 2 mols.) in benzene (50 c.c.) was added dropwise during 15 min. to the cooled solution, which was then boiled under reflux for 1 hr., cooled, and hydrolysed with cold air-free water. The organic layer was separated and dried (Na₂SO₄), the solvents were evaporated, and the residue was distilled under reduced pressure in nitrogen, giving the fractions: (a) diphenyl, b. p. 80—85°/0.7 mm. (0.6 g., 20%), m. p. and mixed m. p. 66—67° after two recrystallisations from methanol; (b) 2 : 2'-diphenylenebisdimethylarsine, b. p. 146—152°/0.7 mm. (4.4 g., 63%). The diarsine prepared in this way may be used for the preparation of quaternary salts, but gives high carbon values on analysis, owing to contamination with diphenyl. It may be purified by conversion into the dimethiodide, followed by thermal decomposition of the recrystallised salt, and then has b. p. 110°/0.05 mm., m. p. 46—46.5°.¹

Quaternary Salts of 2 : 2'-Diphenylenebisdimethylarsine.—A solution of the diarsine (I) in an excess of methyl bromide was set aside in a sealed tube at room temperature for 1 hr. with occasional shaking, crystals rapidly separating. The excess of methyl bromide was allowed to evaporate and the residue when recrystallised from ethanol-light petroleum (b. p. 80—100°) gave the *monomethobromide monohydrate*, m. p. 240—241° (decomp.) (Found: C, 42.55; H, 5.0. C₁₇H₂₃BrAs₂·H₂O requires C, 42.9; H, 5.3%).

To prepare the dimethobromide, a similar solution of the diarsine (I) was heated in a sealed tube at 80° for 3 hr. Removal of the excess of methyl bromide and recrystallisation of the residue from ethanol-light petroleum (b. p. 60—80°) gave the dimethobromide dihydrate, m. p. and mixed m. p. 292—294° (decomp.) (lit.,¹ m. p. 292—294°). This salt was also prepared by confining a solution of the diarsine in an excess of methyl bromide containing a trace of methanol in a sealed tube at room temperature for 4 hr.

When a solution of the diarsine (I) in an excess of methyl iodide was set aside at room temperature, salt formation rapidly occurred. The residue, after evaporation of the excess of methyl iodide and crystallisation from methanol, gave the dimethiodide, m. p. and mixed m. p. 289—290° (decomp.) (lit.,¹ m. p. 286—288°) (Found: C, 33.2; H, 3.85. Calc. for C₁₈H₂₆I₂As₂: C, 33.5; H, 4.0%).

5 : 5 : 7 : 7-*Tetramethyl-5 : 7-diarsonia-1 : 2-3 : 4-dibenzocycloheptadiene Dibromide* (II).—The diarsine (I) (1 g.) was heated with methylene dibromide (0.48 g., 1 mol.) in a sealed tube at 100° for 6 hr. The product when washed with ether and recrystallised from ethanol-light petroleum (b. p. 80—100°) gave the *dibromide tetrahydrate*, m. p. 224—225° (decomp.) (Found: C, 36.9; H, 4.85. C₁₇H₂₂Br₂As₂·4H₂O requires C, 36.4; H, 4.95%). The corresponding *dipicrate* was

¹² Lothrop, *J. Amer. Chem. Soc.*, 1941, **63**, 1187.

deposited when cold ethanolic solutions of the above dibromide and of sodium picrate were mixed and formed yellow crystals, m. p. 283—285°, from water or from ethanol containing a small amount of acetone (Found: C, 41.65; H, 3.05; N, 9.95. $C_{29}H_{26}O_{14}N_6As_2$ requires C, 41.9; H, 3.15; N, 10.1%).

5 : 5 : 9 : 9-Tetramethyl-5 : 9-diarsonia-1 : 2-3 : 4-dibenzocyclononadiene Dibromide (III; $n = 3$).—The diarsine (I) (1 g.) was heated with trimethylene dibromide (0.52 g., 1 mol.) in a sealed tube at 100° for 4 hr. The crystalline product, purified as before, gave the hygroscopic *dibromide monohydrate*, m. p. 261—262° (decomp.) (Found: C, 39.2; H, 4.85. $C_{19}H_{26}Br_2As_2 \cdot H_2O$ requires C, 39.2; H, 4.85%). The corresponding *dipicrate*, prepared as above, formed yellow crystals, m. p. 201—203°, from ethanol containing a small amount of acetone (Found: C, 42.8; H, 3.8; N, 9.95. $C_{31}H_{30}O_{14}N_6As_2$ requires C, 43.3; H, 3.5; N, 9.75%).

5 : 5 : 10 : 10-Tetramethyl-5 : 10-diarsonia-1 : 2-3 : 4-7 : 8-tribenzocyclodecatriene Dibromide (IV).—The diarsine (I) (1.04 g.) and *o*-xylylene dibromide (0.76 g., 1 mol.) in methanol (1 c.c.) were heated in a sealed tube at 100° for 4 hr. The methanol was then evaporated, and the crystalline residue washed with ether and recrystallised from ethanol, giving the *dibromide monohydrate*, m. p. 209—210° (decomp.) (1.25 g., 80%) (Found: C, 44.2; H, 4.55. $C_{24}H_{28}Br_2As_2 \cdot H_2O$ requires C, 44.7; H, 4.7%). The corresponding *dipicrate*, prepared as above, formed yellow crystals, m. p. 225—227°, from water or from ethanol containing a small amount of acetone (Found: C, 46.3; H, 3.7; N, 9.1. $C_{36}H_{32}O_{14}N_6As_2$ requires C, 46.8; H, 3.5; N, 9.1%).

Thermal Decompositions.—(A) *The dibromide* (II). The dibromide (2.5 g.) was placed in a distillation flask fitted with a capillary intake, air-condenser, and a receiver connected in turn to a trap cooled in liquid oxygen, and evacuated to 0.15 mm. whilst nitrogen was led through the capillary. Heating in an air-bath at 256° caused smooth decomposition, yielding a colourless syrupy distillate (1.26 g.) and no residue. A sample of the distillate dissolved in acetone developed no colour when mixed with a solution of sodium iodide in the same solvent. Crystallisation of the distillate from ethanol gave 5 : 7-dimethyl-5 : 7-diarsa-1 : 2-3 : 4-dibenzocycloheptadiene (V), m. p. 95.5—96° (Found: C, 51.9; H, 4.7%; *M*, ebullioscopic in acetone, 355. $C_{16}H_{16}As_2$ requires C, 52.05; H, 4.65%; *M*, 346). The ultraviolet absorption spectrum of this diarsine in *n*-hexane is given in the Figure.

The diarsine, when boiled with aqueous ethanolic potassium palladobromide, deposited the yellow crystalline *dibromodiarsinepalladium* (VI), m. p. 318—319° (decomp.) (Found: C, 29.8; H, 2.8. $C_{15}H_{16}Br_2As_2Pd$ requires C, 29.4; H, 2.65%). No satisfactory solvent could be found for recrystallisation.

To prove that the ring system had not undergone rearrangement during decomposition, the diarsine (V) was heated with an excess of methyl iodide at 100° for 3 hr. The crude dimethiodide was washed with ether, and its ethanolic solution treated with ethanolic sodium picrate; the dipicrate corresponding to (II) was deposited (m. p. and mixed m. p. 283—285° after recrystallisation from water).

(B) *The 5 : 5 : 8 : 8-tetramethyl-5 : 8-diarsonia-1 : 2-3 : 4-dibenzocyclooctadiene dibromide* (III; $n = 2$). The powdered dibromide (7 g.), prepared as described earlier,¹ was heated in the above-mentioned apparatus at 0.1 mm. in an oil-bath at 210—215°, decomposition of the salt occurring smoothly and being complete in 45 min. The distillate (3.08 g.), at first colourless and ultimately faintly golden, showed a high tendency to crystallise and effective fractionation on redistillation proved impracticable.

Solutions of the distillate and of sodium iodide in acetone when mixed developed an intense yellow colour, indicating the presence of a bromoarsine.

The distillate, dissolved in ether, was therefore mixed with an excess of ethereal methylmagnesium iodide under nitrogen, in order to convert any bromoarsine (VIII; R = Br) into the tertiary arsine (VIII; R = Me). Hydrolysis with aqueous ammonium chloride followed by separation of the organic layer, drying (Na_2SO_4), and one distillation in nitrogen gave 9-methyl-9-arsafluorene, b. p. 125°/0.05 mm., m. p. 41—41.5° (lit.,⁷ m. p. 46°) (2.97 g., 69%) (Found: C, 64.5; H, 4.9. Calc. for $C_{13}H_{11}As$: C, 64.5; H, 4.6%; λ_{max} . (log ϵ) in *n*-hexane (see Figure), 255 (3.52) and 277 (ϵ 3.75); λ_{min} . (log ϵ) 242 (3.43) and 259 $m\mu$ (ϵ 3.51). The maximum and minimum at the longer wavelengths probably correspond to those observed at 279 $m\mu$ (log ϵ_{max} . 4.15) and 264 $m\mu$ (log₁₀ ϵ_{min} . 4.06) in the spectrum of 9-*p*-tolyl-9-arsafluorene in *cyclohexane*, determined by Campbell and Poller.⁸

A solution of 9-methyl-9-arsafluorene in an excess of methyl iodide was set aside at room temperature, salt formation rapidly occurring. The precipitate, when washed with ether and recrystallised from ethanol, gave 9:9-dimethyl-9-arsoniafluorene iodide monohydrate, m. p. 206—207° (decomp.) (lit.,⁷ m. p. 190° for the anhydrous salt) (Found: C, 41.5; H, 3.8. $C_{14}H_{14}IAs_2H_2O$ requires C, 41.8; H, 4.0%). The anhydrous picrate formed yellow crystals, m. p. 214.5—215.5°, on recrystallisation from ethanol containing a small amount of acetone (Found: C, 49.4; H, 3.35; N, 9.2. $C_{26}H_{16}O_7N_3As$ requires C, 49.5; H, 3.35; N, 8.7%).

A solution of 9-methyl-9-arsafluorene in ethanol, when boiled with aqueous-ethanolic potassium palladobromide, rapidly deposited yellow crystals of dibromobis-(9-methyl-9-arsafluorene)palladium, decomp. ca. 320° (Found: C, 41.7; H, 3.15. $C_{26}H_{22}Br_2As_2Pd$ requires C, 41.6; H, 3.0%). No satisfactory solvent could be found for recrystallisation.

The trap, which had been cooled in liquid oxygen during the thermal decomposition, was allowed to warm to room temperature. It was then warmed to 60—70° whilst a stream of nitrogen was passed through it, the effluent gas being passed by means of glass-to-glass connections through gently boiling aqueous-ethanolic potassium palladobromide, extra portions of the latter being occasionally added to ensure an excess, indicated by the deep red colour of the solution. Concentration of the solution and cooling afforded orange-red crystals which, recrystallised from ethanol, gave dibromobis(trimethylarsine)- $\mu\mu'$ -dibromodipalladium, m. p. and mixed m. p. 232° (Found: C, 9.6; H, 2.6. Calc. for $C_6H_{18}Br_4As_2Pd_2$: C, 9.3; H, 2.3%).

(C) *The dibromide* (III; $n = 3$). The powdered dibromide (12 g.), in the above apparatus at 0.05 mm., was heated in an air-bath, initially at 230°; decomposition occurred smoothly to give a pale yellow liquid distillate. The temperature was ultimately raised to 260°, the distillate then becoming more discoloured.

A sample of the crude distillate gave only a slight yellow colour with sodium iodide in acetone.

Fractionation of the distillate in nitrogen gave 9-methyl-9-arsafluorene (VIII; R = Me), b. p. 110°/0.2 mm. (2.5 g., 49%) which readily crystallised and when recrystallised from methanol had m. p. 42°. This compound was identified by its ultraviolet absorption spectrum, and by conversion into its methiodide which in turn afforded the yellow crystalline 9:9-dimethyl-9-arsoniafluorene picrate, m. p. and mixed m. p. 215°. Another sample of the arsine, boiled with aqueous ethanolic potassium palladobromide, gave the yellow crystalline dibromobis-(9-methyl-9-arsafluorene)palladium, decomp. ca. 320°.

The contents of the trap cooled in liquid oxygen were treated as in the previous experiment, giving red-brown crystals (from ethanol), m. p. 270°, probably solvated dibromobis(dimethylvinylarsine)- $\mu\mu'$ -dibromodipalladium (Found: C, 13.3; H, 2.45. $C_8H_{18}Br_4As_2Pd_2 \cdot 0.5C_2H_6O$ requires C, 13.2; H, 2.55%).

Dibromobis(ethyl-dimethylarsine)- $\mu\mu'$ -dibromodipalladium, which in a solvated form would give very similar analytical values, was prepared in the usual way, and formed red-brown crystals, m. p. 207° from ethanol (Found: C, 12.1; H, 3.1. $C_8H_{22}Br_4As_2Pd_2$ requires C, 12.0; H, 3.15%).

(D) *The dibromide* (IV). The powdered dibromide (1.5 g.) contained in a bulb-tube at 0.05 mm. was heated in an oil-bath at 210°; smooth decomposition gave an arsine which distilled when the temperature was raised to 235°. Crystallisation of the solidified distillate from ethanol gave 5:10-dimethyl-5:10-diarsonia-1:2:3:4:7:8-tribenzocyclodecatiene (VII), m. p. 110—111° (Found: C, 60.0; H, 4.95%; *M*, cryoscopic in benzene, 402. $C_{22}H_{22}As_2$ requires C, 60.5; H, 5.05%; *M*, 436). To prove that the ring system had not undergone rearrangement during the decomposition, the diarsine (VII) was heated with an excess of methyl toluene-*p*-sulphonate under nitrogen for 8 hr. Removal of excess of the reagent with ether gave a syrup which failed to crystallise but with ethanolic sodium picrate gave the quaternary dipicrate, m. p. and mixed m. p. 225—227° (from water), analogous to (IV).

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