1179. *Cyclic Diarsines. Part IX.*[1] o-*Terphenyl Derivatives containing Nine-, Ten-, Eleven-, and Twelve-membered Diarsine Ring Systems*

By FREDERICK G. MANN, IAN T. MILLAR, and F. C. BAKER

o-Terphenyl-2,2''-ylenebisdimethylarsine combines by cyclic diquaternisation with dibromomethane, 1,2-dibromoethane, 1,3-dibromopropane, and *o*-xylylene dibromide to give diarsonium dibromides having nine-, ten-, eleven-, and twelve-membered diarsine ring systems, respectively.

These dibromides on thermal decomposition react very similarly to the corresponding salts obtained from 2,2'-biphenylylenebisdimethylarsine, namely the first and last lose methyl bromide to give the nine- and twelve-membered cyclic ditertiary arsines, respectively, but the second and third undergo ring contraction to give 7-methyl-7-arsa-1,2:3,4:5,6-tribenzocycloheptatriene. Other products arising from the thermal decomposition of the last three of the dibromides were also identified.

The diarsonium dibromide arising from the union with 1,2-dibromoethane has been isolated in two forms; structural models indicate that the homologous dibromide from 1,3-dibromopropane might exist in two isomeric forms.

THE interaction of *o*-bromoiodobenzene in ether at 0° with magnesium (3 equivs.), followed by iododimethylarsine, gives a mixture of four arsines, of which the highest-boiling component (and the only one solid at room temperature) is *o*-terphenyl-2,2''-ylenebisdimethylarsine (I).[2] We have characterised this diarsine by the preparation of its dimetho-bromide, -iodide, and -picrate. Oxidation with nitric acid readily gives a crystalline dihydroxynitrate, which with alkali gives the dioxide, m. p. 191—194°. Oxidation with hydrogen peroxide in acetone gives a product, m. p. 166°, of composition $C_{22}H_{24}As_2O_2,H_2O_2,2H_2O$, which is apparently analogous in type to those similarly obtained from 1,4-diphenylpiperazine,[3] 1,4-diphenyl-1-aza-4-phosphacyclohexane,[4] and 5,10-diethyl-5,10-dihydrophosphanthren,[5] and may have the hydrogen peroxide unit bridged by hydrogen bonding to the oxygen atoms of the dioxide.[5]

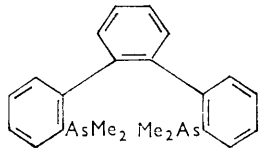
---

[1] Part VIII, F. G. Mann, *J.*, 1963, 4266.
[2] H. Heaney, F. G. Mann, and I. T. Millar, *J.*, 1957, 3930.
[3] G. M. Bennett and E. Glynn, *J.*, 1950, 211.
[4] F. G. Mann and I. T. Millar, *J.*, 1952, 3039.
[5] M. Davis and F. G. Mann, *J.*, 1964, 3770.

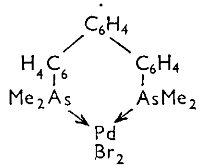
The preparation of the monomeric cyclic palladobromide (II) shows that the rotation of the appropriate component units of the diarsine (I) can bring the two arsenic atoms in reasonably close proximity.[2]

We have studied the cyclic diquaternisation of the diarsine (I) with dibromomethane, 1,2-dibromoethane, 1,3-dibromopropane, and *o*-xylylene dibromide, as in our earlier study of the similar condensation of 2,2′-biphenylylenebisdimethylarsine with these reagents.[6]

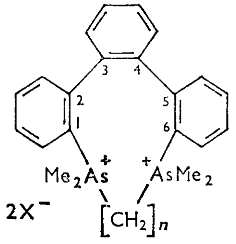
An equimolecular mixture of the diarsine (I) and dibromomethane, when heated under nitrogen, gives the dibromide (III; $n = 1$, X = Br), which is insoluble in most organic solvents, but is moderately soluble in hot dioxan and dimethylformamide. A similar mixture of the diarsine (I) and 1,2-dibromoethane gives two apparently isomeric products (III; $n = 2$, X = Br) according to the conditions employed. The mixture, if heated alone at 110° for 5 hr., or (more satisfactorily) in 10% methanolic solution at 100° for 10 hr., gives the dibromide, m. p. 201—202°, soluble in boiling methanol; the mixture, when heated alone at 150—155° for 5 hr., gives a second form, m. p. 272—275°, insoluble in most organic solvents. The ionic nature of these bromides and their low solubility in most solvents precluded molecular weight determinations; they may be true isomers, or one may be the dibromide and the other a dimeric tetrabromide. No reaction of the diarsine (I) and 1,2-dibromoethane occurs in xylene solution heated at 150° (oil-bath) for 1 hr.



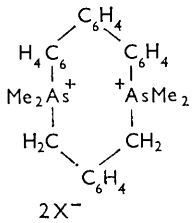
(I)



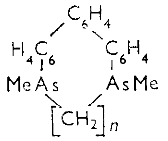
(II)



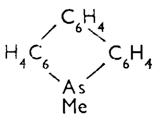
(III)



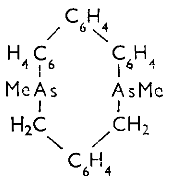
(IV)



(V)



(VI)



(VII)

The diarsine reacts with 1,3-dibromopropane to give the dibromide (III; $n = 3$, X = Br), which is also insoluble in the common organic solvents.

o-Xylylene dibromide differs notably from 1,2-dibromoethane in that it rapidly combines with the diarsine in boiling xylene solution to give the dibromide (IV; X = Br), which, although apparently insoluble in all organic solvents investigated, is readily soluble in cold water.

The ionic nature of the bromine in all these salts has been demonstrated by their conversion into the corresponding di-iodides or dipicrates.

The thermal decomposition of the dibromides (III) and (IV) shows very interesting differences.

The dibromide (III; $n = 1$, X = Br), when heated at 243°/0·1 mm., lost methyl bromide, giving the crystalline nine-membered cyclic ditertiary arsine (V; $n = 1$). This gave a palladobromide of composition $C_{21}H_{20}As_2,PdBr_2$, in which the palladium has presumably formed another ring system by co-ordination with the two arsenic atoms; the low solubility of the compound precluded molecular weight determinations.

The low-melting form of the dibromide (III; $n = 2$, X = Br), when heated at 200°

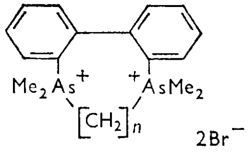
---

[6] H. Heaney, D. M. Heinekey, F. G. Mann, and I. T. Millar, *J.*, 1958, 3838.

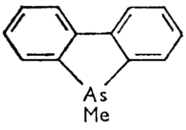
rising to 225°/14 mm., underwent contraction of the ring system with formation of the crystalline cyclic monoarsine (VI), identified by analysis, molecular weight determination, and preparation of the methiodide and methopicrate. The high-melting form of the dibromide (III; $n = 2$) when heated at 250—260°/14 mm. also gave the monoarsine (VI), but when heated at 200° rising to 220°/0·1 mm. gave a syrupy distillate which could not be obtained crystalline but which with methyl iodide gave a dimethiodide identical with that obtained by treating the dibromide with lithium iodide; this syrup was therefore almost certainly the cyclic ditertiary arsine (V; $n = 2$). The difference in the two types of decomposition of this high-melting dibromide may be caused primarily by the difference in temperature, but the pressure may have a significant influence, for the lower pressures would facilitate the rapid volatilisation from the hot zone of the larger ring systems which might otherwise undergo disintegration.

This factor apparently affected the thermal decomposition of the dibromide (III; $n = 3$, X = Br), which when heated at 220—225°/14 mm. gave a golden syrupy distillate, which could not be solidified but with methyl iodide gave the dimethiodide of the uncyclised diarsine (I). The dibromide heated at 220°/0·1 mm. gave a similar distillate which in ethanol deposited the cyclic monoarsine (VI) in small yield. Finally the dibromide heated at 220°/0·002 mm. gave a distillate consisting mainly of the cyclic diteriary arsine (V; $n = 3$), for with methyl iodide it gave the di-iodide (III; $n = 3$, X = I). It is not suggested that these three modes of decomposition were sharply differentiated under the above conditions, but on the small scale of these experiments the products identified in the viscous syrups represent those which could be isolated in the crystalline condition or as crystalline derivatives; the monoarsine (VI) for example represented a small proportion of the total distillate from which it was isolated.

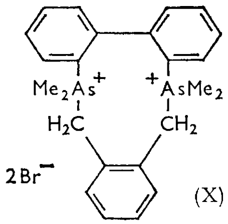
The dibromide (IV; X = Br) when heated at 185—190°/14 mm. for 4 hr. gave only a trace of distillate, but the residue when recrystallised from methanol gave the twelve-membered cyclic ditertiary arsine (VII), resulting from simple loss of methyl bromide from the dibromide. The corresponding di-iodide (IV; X = I) when heated at 245—250°/14 mm. gave, however, an oily distillate from which the crystalline monoarsine (VI) was isolated. There is at present no evidence to show if this different type of decomposition was caused by the change in temperature or anion employed, or both.



(VIII)



(IX)



(X)

These results are strikingly similar to those obtained by the thermal decomposition of the corresponding cyclic salts of 2,2′-diphenylylenebisdimethylarsine.[6] The dibromides (VIII; $n = 1$) and (X) underwent simple loss of methyl bromide giving the crystalline ditertiary arsines with the heterocyclic ring unaffected, whereas the dibromides (VIII; $n = 2$) and (VIII; $n = 3$) underwent rupture of the ring system with the formation of 9-methyl-9-arsafluorene (IX). This striking difference was attributed to the fact that only the heterocyclic systems of the dibromides (VIII; $n = 2$) and (VIII; $n = 3$) contained methylene groups in the 2 (or β) position to the arsenic atoms, and that the hydrogen atoms of these groups might be essential for the mechanism of the ring contraction to the arsine (IX).

In the derivatives of the diarsine (I), it is again only the dibromides (III; $n = 1$, X = Br) and (IV; X = Br) from which on thermal decomposition the corresponding crystalline cyclic ditertiary arsines have been isolated. The decomposition of the intermediate dibromides (III; $n = 2$ or 3, $X = Br$) is more complex, for there is decisive evidence in each case for the ring contraction to the monoarsine (VI) and some evidence also for simple loss of methyl bromide with retention of the ring system.

Some interesting aspects of the conformation of the cations in the salts (III; $n = 1$, 2, and 3) and (IV) are revealed by the study of modified Dreiding models, constructed to scale, in which the intervalency angles are fixed but the carbon atoms of the methylene groups and the arsenic atoms can (when the structure permits) twist about their valency bonds. Figure 1 shows the " open " conformation of the cation (III; $n = 1$); it has a vertical

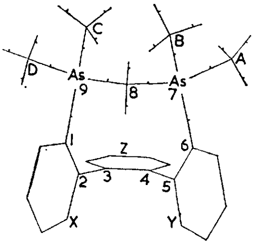


FIGURE 1

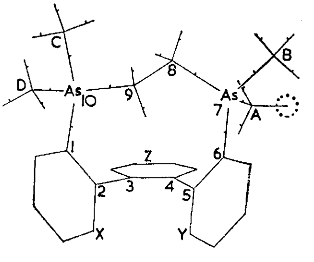


FIGURE 2

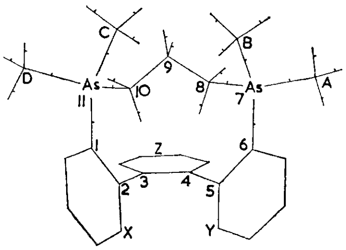


FIGURE 3A

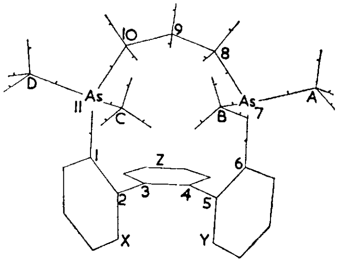


FIGURE 3B

The cations of the salts (III; $n = 1$) (Figure 1), (III; $n = 2$) (Figure 2), and (III; $n = 3$) (Figures 3A and 3B)

Diagrams based on photographs of the scale models. The boundary of the arsenic atoms along the As–C bonds, and that of the carbon atoms along the C–H bonds of the methyl and methylene groups, are indicated by a notch in each bond; the extremity of each C–H bond represents the centre of the hydrogen atom, as shown in the dotted circle in Figure 2. All models are resting on the points X and Y of the outer *o*-phenylene rings and the far edge Z of the middle ring, which projects backwards and downwards

FIGURE 1. The carbon atom 8 of the CH_2 group projects behind the vertical plane of As7—As9, with its two C–H bonds projecting away from the observer; the carbon atoms of the CH_3 groups B and C project in front of this plane and those of groups A and D project obliquely backwards

FIGURE 2. The carbon atoms 8 and 9 of the CH_2 groups project, respectively, in front and behind the vertical plane As7—As10. The C atoms of the CH_3 groups B and C project in front of, and those of the groups A and D obliquely behind, this plane

FIGURE 3A. The carbon atoms 8 and 10 of the outer CH_2 groups project behind the vertical plane As7—As11, with the carbon atom 9 of the central CH_2 group almost directly above them. The two C–H bonds attached to carbon atom 9 both project upwards, the photograph being taken from slightly left of centre to show the front (shorter) and the rear (longer) bond. The C atoms of the CH_3 groups B and C project in front of the As–As plane, those of the groups A and D projecting slightly towards the rear

FIGURE 3B. The carbon atoms 8 and 10 are slightly in front of, and the central atom 9 is behind, the plane As7—As11. The lower C–H bonds attached to carbon atoms 8 and 10 project towards, and that attached to carbon atom 9 projects away from, the observer. The C atoms of the CH_3 groups A and D are very slightly in front of, and those of the CH_3 groups B and C are behind, the As–As plane

plane of symmetry (at right angles to that of the paper) and shows little tendency to twist. Figure 2 shows the similar conformation of the cation (III; $n = 2$). It has no element of symmetry, but the ring system can " twist " considerably, forwards or backwards, from the position depicted; this brings the arsenic atoms nearer together and changes the relative planes of the *o*-phenylene groups, but the cation remains asymmetric throughout. This model does not apparently provide any satisfactory explanation of the two series of salts of the cation (III; $n = 2$) which have been isolated.

The insertion of a third methylene group into the model (Figure 2) gives the cation (III; $n = 3$). The mode of buckling of the trimethylene chain linking the two arsonium atoms gives rise to two forms (Figures 3A and 3B), each having a plane of symmetry similar to that of the cation (III; $n = 1$). In each form the hererocyclic ring readily shows a considerable degree of strainless twist without losing its isomeric identity. When, however, gentle pressure is suitably applied to the central methylene group of either model, the ring will " spring " over to the other isomeric form; this indicates that the energy barrier between the two forms may be low.

The low solubility of the salts (III; $n = 3$), which usually precluded crystallisation, may have masked the possible occurrence of isomeric forms. The marked difference between the di-iodide (III; $n = 3$, X = I) obtained directly from the cold dibromide (p. 6348), and that obtained by the action of methyl iodide on the syrupy distillate from thermal decomposition (p. 6349) may indicate such isomeric forms, for the cyclic ditertiary arsine may have undergone isomerisation during the distillation.

The insertion of an *o*-phenylene group between the two methylene groups of the model (Figure 2) gives the cation (IV) which also has a plane of symmetry in the " open " conformation, and is capable of possibly an even greater degree of twisting than the cations (III; $n = 3$).

The stereochemistry of this series of salts therefore differs from that of the analogous 2,2′-biphenylylene series (VIII; $n = 1$, 2, or 3) and (X), all of which have been resolved into optically active forms.[7]

No attempt has been made to resolve the more soluble low-melting dibromide (III; $n = 2$, X = Br).

Since this investigation was restricted throughout by inadequate supplies of the diarsine (I), alternative and possibly speedier syntheses were briefly studied. The preparation of *o*-lithiophenyldimethylarsine and its condensation with dimethylarsenous iodide have been recorded.[8] We found, however, that this *o*-lithio-compound reacted with *o*-dibromobenzene to give *o*-bromophenyldimethylarsine, and similarly with *o*-di-iodobenzene to give the *o*-iodophenyldimethylarsine. This synthetic route was not further investigated.

EXPERIMENTAL

All compounds were colourless except the yellow picrates and the palladobromide derivative. Consistent m. p.s for some compounds were obtained only if the material was immersed in a preheated bath; in such cases the immersion temperature is noted as (I.T.—°), room temperature, when significant, being denoted as R.T. Very small quantities of liquid reagents were delivered from a calibrated micrometer pipette.

The diarsonium dihalides (III; $n = 1$, 2, or 3, X = Br or I) resemble the corresponding derivatives (VIII) [7] in that they usually form polyhydrates, which in a vacuum desiccator tend to fall to lower hydrates, and when heated under reduced pressure may give the anhydrous salts. Analysis of each salt, even on repeated preparation, was necessary to identify the particular hydrate formed.

o-*Terphenyl*-2,2″-*ylenebisdimethylarsine* (I).—*o*-Bromoiodobenzene (113·2 g.) in ether (400 ml.) was added to magnesium (29·2 g.) in ether (200 ml.) under nitrogen, followed, after the

---

[7] M. H. Forbes, F. G. Mann, I. T. Millar, and E. A. Moelwyn-Hughes, *J.*, 1963, 2833.

[8] Emrys R. H. Jones and F. G. Mann, *J.*, 1955, 4472.

reaction, by benzene (200 ml.) and dimethylarsinous iodide (185·6 g.) in benzene (200 ml.), as recorded in " Expt. B."[2] After hydrolysis, the organic layer was fractionally distilled until only the crude diarsine (I) remained. This residue in methanol was treated with an excess of methyl iodide with initial cooling and final boiling under reflux for 20 min. The crude dimethiodide was extracted with boiling ethanol (50 ml.), and the residue after recrystallisation from methanol and drying under reduced pressure gave the anhydrous dimethiodide (7·9 g.), m. p. 316° (effer.) (I.T. 260°) (Found: C, 40·0; H, 4·4. Calc. for $C_{24}H_{30}As_2I_2$: C, 39·9; H, 4·2%); the powdered salt on exposure to air formed a crystalline dihydrate, m. p. 296—299° (effer.) (I.T. 270°) (Found: C, 38·1; H, 4·9. Calc. for $C_{24}H_{30}As_2I_2,2H_2O$: C, 38·0; H, 4·5%). This salt (7·8 g.), when heated at 285—290°/0·05 mm., rapidly decomposed giving a distillate which solidified when rubbed with ethanol; recrystallisation from ethanol gave the pure diarsine (I) (2·9 g.), m. p. 92—93° (lit.,[2] 92·5—93·5°).

Increasing the scale of the dimethiodide preparation gave a lower percentage yield.

A methanolic solution of the diarsine, containing an excess of methyl bromide, was heated in a sealed tube at 60° for 4 hr., chilled, and exposed to air. The deposited *dimethobromide*, after recrystallisation from methanol and drying at 70°/0·1 mm. for 4 hr., formed a hygroscopic *monohydrate*, m. p. 296° (effer.) (I.T. 290°) (Found: C, 44·4; H, 5·0. $C_{24}H_{30}As_2Br_2,H_2O$ requires C, 44·6; H, 5·0%), which on exposure to the air for 12 hr. formed a crystalline *trihydrate* (Found: C, 42·1; H, 5·4. $C_{24}H_{30}As_2Br_2,3H_2O$ requires C, 42·25; H, 5·3%). This salt when added to sodium picrate, both in aqueous solution, deposited the *dimethopicrate*, m. p. 198° (I.T. 160°) from water (Found: C, 47·0; H, 4·0; N, 9·4. $C_{36}H_{34}As_2N_6O_{14}$ requires C, 46·8; H, 3·7; N, 9·1%).

A suspension of the powdered diarsine in dilute nitric acid (1 : 1 v/v) was gently warmed until clear; cooling deposited the *bishydroxynitrate*, m. p. 207° (effer.) (I.T. 160°) from aqueous ethanol (Found: C, 44·6; H, 4·5; N, 4·4. $C_{22}H_{26}As_2N_2O_8$ requires C, 44·3; H, 4·4; N, 4·7%). An aqueous solution was treated with sodium hydroxide (2 mols.) and evaporated to dryness; the residue was extracted with chloroform, which when taken to dryness afforded the *dioxide*, m. p. 191—194° (I.T. 170°), readily soluble in water (Found: C, 54·4; H, 6·2. $C_{22}H_{24}As_2O_2,H_2O$ requires C, 54·1; H, 5·4%). Aqueous solutions of the bishydroxynitrate and of the dioxide, treated with aqueous sodium picrate and picric acid, respectively, deposited the same *bishydroxypicrate*, m. p. and mixed m. p. 199—202° (decomp.) (I.T. 190°) (Found: N, 8·5. $C_{34}H_{30}As_2N_6O_{16}$ requires N, 9·05%); insufficient material precluded decisive identification.

An acetone solution of the diarsine was diluted with an excess of hydrogen peroxide (" 20 vols."), set aside at 35—40° for 12 hr., and evaporated in a desiccator. A suspension of the crude residue in boiling ethyl acetate was treated dropwise with ethanol until clear, and then cooled, the *dioxide hydrogen peroxide* adduct separating; recrystallisation gave crystals, m. p. 166° (vigorous effer.) (I.T. 150°) after drying at 15 mm. over phosphoric anhydride (Found: C, 48·9; H, 6·0. $C_{22}H_{24}As_2O_2,H_2O_2,2H_2O$ requires C, 48·9; H, 5·6%). Tests for hydrogen peroxide in this compound gave faint positive results.

7,7,9,9-*Tetramethyl*-7,9-*diarsonia*-1,2:3,4:5,6-*tribenzocyclononatriene Dibromide* (III; $n = 1$, X = Br).—A mixture of the diarsine (I) (0·5 g.) and dibromomethane (0·08 ml., 1 mol.) was heated in a sealed tube at 100° for 8 hr. The hard residual pellet, when thoroughly triturated under ether, collected, washed with ether, and dried at 100°/0·1 mm. for 5 hr. gave the *dibromide*, m. p. 258—264° (I.T. 240°) (Found: C, 44·85; H, 4·5. $C_{23}H_{26}As_2Br_2$ requires C, 45·1; H, 4·3%). A hot aqueous-acetone solution, added to aqueous sodium picrate, deposited the *dipicrate*, m. p. 266° (decomp.) (I.T. 250°) after three recrystallisations from aqueous ethanol (Found: C, 46·0; H, 3·2; N, 9·1. $C_{35}H_{30}As_2N_6O_{14}$ requires C, 46·2; H, 3·3; N, 9·25%).

7,7,10,10-*Tetramethyl*-7,10-*diarsonia*-1,2:3,4:5,6-*tribenzocyclodecatriene Dibromide* (III; $n = 2$, X = Br).—*Low-melting form.* A mixture of the diarsine (I) (0·5 g.), 1,2-dibromoethane (1 mol.) in 10% methanolic solution (1·06 ml.) and methanol (1 ml.) was heated in a sealed tube at 100° for 10 hr. The clear solution in the cold tube on scratching deposited the crystalline *dibromide dihydrate*, m. p. 201—202° (effer.) after recrystallisation from methanol, m. p. 208° (effer.) after heating at 80°/0·2 mm. for 10 hr. (Found: C, 43·8; H, 5·3. $C_{24}H_{28}As_2Br_2,2H_2O$ requires C, 43·5; H, 4·9%).

The dibromide, when added to sodium picrate, both in methanol, deposited the *dipicrate*, m. p. 246° (decomp.) (I.T. 235°), unchanged after recrystallisation from acetic acid and heating at 75°/0·1 mm. for 6 hr. (Found: C, 46·7; H, 3·45; N, 9·5. $C_{36}H_{32}As_2N_6O_{14}$ requires C, 46·9; H, 3·5; N, 9·1%).

The dibromide, similarly treated with lithium iodide, deposited the hygroscopic *di-iodide*, m. p. 256—257° (effer.) (I.T. 250°) from aqueous ethanol, and drying at 90°/0·1 mm. (Found: C, 40·1; H, 4·6. $C_{24}H_{28}As_2I_2$ requires C, 40·0; H, 3·9%); this also gave the dipicrate, m. p. and mixed m. p. 249° (decomp.) (I.T. 235°) (Found: N, 9·2%).

(*b*) *High-melting form.* A mixture of the diarsine (I) (0·5 g.) and 1,2-dibromoethane (0·100 ml., 1 mol.) was heated in nitrogen under reflux at 150—155° (bath temperature) for 5 hr. The powdered product, when triturated with acetone and dried, had m. p. 266—277° (effer.) with softening at 176°. A suspension in hot acetone was treated with methanol until clear and cooled, and the *dibromide dihydrate* carefully precipitated with ether; the collected salt when dried over phosphoric anhydride had m. p. 264—266°, and after heating at 90°/0·1 mm. for 6 hr., 272—275°, both with effervescence (Found: C, 43·9; H, 4·5%).

This dibromide, dissolved in ethanol with a trace of water, was added to a concentrated acetone solution of sodium iodide. The *di-iodide dihydrate* slowly separated as crystals, which when collected, triturated with water, and dried had m. p. 286—289° (effer.) (I.T. 250°), increased to 289—292° (I.T. 250°) by heating at 80°/0·1 mm. for 15 hr. (Found: C, 37·9; H, 4·3. $C_{24}H_{28}As_2I_2,2H_2O$ requires C, 38·1; H, 4·3%).

7,7,11,11-*Tetramethyl*-7,11-*diarsonia*-1,2:3,4:5,6-*tribenzocycloundecatriene Dibromide* (III; $n = 3$, X = Br).—A mixture of the diarsine (I) (0·60 g.) and 1,3-dibromopropane (0·136 ml., 1 mol.) was heated under nitrogen at 120—125° for 6 hr. The cold hard powdered residue, when thoroughly triturated under ether, collected, washed with ether, and dried at 65°/0·1 mm. gave the *dibromide dihydrate*, m. p. 225—226° (effer.) (I.T. 220°) (Found: C, 44·4; H, 5·1. $C_{25}H_{30}As_2Br_2,2H_2O$ requires C, 44·4; H, 5·1%); longer heating at 90°/0·1 mm. gave the hygroscopic anhydrous *dibromide*, of unchanged m. p. (Found: C, 46·4; H, 5·1. $C_{25}H_{30}As_2Br_2$ requires C, 46·9; H, 4·7%). The dihydrate when stirred with cold water formed a gum without apparent dissolution; when stirred with cold ethanol, it became sticky at first and finally formed a fine white apparently insoluble powder. Dropwise addition of water to this suspension gave, however, a clear solution; this solution, when added to ethanolic lithium iodide, deposited the *di-iodide monohydrate*, m. p. 240—242° (effer.) (I.T. 230°) after recrystallisation from water, and unaffected by heating at 80°/0·1 mm. for 6 hr. (Found: C, 39·7; H, 4·0. $C_{25}H_{30}As_2I_2,H_2O$ requires C, 39·9; H, 4·3%). The use of an acetone–sodium iodide solution gave the monohydrate of the same composition and m. p. The salt is almost insoluble in methanol and ethanol.

7,7,12,12-*Tetramethyl*-7,12-*diarsonia*-1,2:3,4:5,6:9,10-*tetrabenzocyclododecatetraene Dibromide* (IV; X = Br).—*o*-Xylylene dibromide (0·1980 g., 1 mol.) was added to a solution of the diarsine (I) (0·330 g.) in cold xylene (5 ml.), which was heated under reflux at 135—140° (oil-bath) for 30 min., crystals rapidly separating. After cooling, the *dibromide*, when collected, well washed with ether, and dried at 100°/0·1 mm., had m. p. 195—197° (effer.) (I.T. 180°) (Found: C, 51·5; H, 5·1. $C_{30}H_{32}As_2Br_2$ requires C, 51·33; H, 4·6%).

An aqueous-ethanolic solution of the dibromide, when added to ethanolic lithium iodide, deposited the *di-iodide*, which after recrystallisation from methanol and drying at 80°/0·1 mm. had m. p. 181—182° (effer.) (I.T. 170°) (Found: C, 45·0; H, 4·7. $C_{30}H_{32}As_2I_2$ requires C, 45·3; H, 4·05%).

Thermal Decompositions.—For this purpose the finely powdered salts were usually placed at the sealed end of a hard glass tube of 7 mm. internal bore, connected at the other end to a vacuum pump. The sealed end was placed in a heating block with the open end very slightly raised. The heating was continued until either the condensation of a syrupy distillate was complete, or until the residue was halogen-free.

The Dibromide (III; $n = 1$, X = Br).—This salt was heated at 245°/0·1 mm., the oily distillate on cooling forming a glass which was readily soluble in boiling ethanol, acetone, benzene, and chloroform, but not in methanol. A solution in boiling ethanol, treated dropwise with methanol until faintly cloudy and then allowed to cool slowly, deposited the crystalline 7,7,9,9-*tetramethyl*-7,9-*diarsa*-1,2:3,4:5,6-*tribenzocyclononatriene* (V; $n = 1$), m. p. 137—140° (R.T.), 137—138° (I.T. 100°) (Found: C, 59·6; H, 5·0%; *M*, in boiling ethanol, 430. $C_{21}H_{20}As_2$ requires C, 59·7; H, 4·8%; *M*, 422).

A hot ethanolic solution of the diarsine was added dropwise to a warm stirred solution of potassium palladobromide in aqueous ethanol. The precipitated flocculent bright yellow *dibromodiarsinepalladium*, when collected, washed with water and ethanol, and dried at 100°/0·1 mm., had m. p. 300° (R.T.), 304° (I.T. 290°), both with effervesence (Found: C, 38·0; H, 3·3.

$C_{21}H_{20}As_2Br_2Pd$ requires C, 36·6; H, 2·9%). Low solubility and insufficient material precluded recrystallisation.

The Dibromide (III; $n = 2$, X = Br).—(*a*) *Low-melting form.* The salt in a small flask, when heated in a silicone bath at 200—205°/14 mm. under a nitrogen stream, underwent vigorous foaming followed by a gentle effervescence. When the latter had completely ceased, the residual liquid on cooling formed a hard halogen-free glass. Recrystallisation from ethanol gave 7-*methyl*-7-*arsa*-1,2:3,4:5,6-*tribenzoheptatriene* (VI), m. p. 159—160° after drying at 70°/0·1 mm. (Found: C, 71·55; H, 4·85%; *M*, in boiling ethanol, 310. $C_{19}H_{15}As$ requires C, 71·7; H, 4·75%; *M*, 318). The dibromide, when heated in a tube at 220—230°/14 mm., slowly gave a clear distillate, which from ethanol deposited the arsine (VI), m. p. 159° (Found: C, 71·7; H, 4·8%).

A methanolic solution of the arsine (VI) was boiled with methyl iodide for 2 hr. and evaporated to dryness; the residue afforded the *methiodide monohydrate*, m. p. 218—221°, from ethanol with drying at 80°/0·1 mm. (Found: C, 50·3; H, 4·4. $C_{20}H_{18}AsI,H_2O$ requires C, 50·2; H, 4·2%). The iodide when set aside slowly formed a black mass. A mixture of the arsine and methyl toluene-*p*-sulphonate, when heated at 125° for 3 hr. and cooled, gave a solid mass, which after extraction with cold ether afforded the residual crude methotoluene-*p*-sulphonate, m. p. 174—182°. This was converted into the *methopicrate*, which, after recrystallisation from hot water containing just sufficient ethanol to give a clear solution, and drying at 90°/0·1 mm. for 6 hr., had m. p. 190—191° (Found: C, 55·7; H, 3·7; N, 7·5. $C_{26}H_{20}AsN_3O_7$ requires C, 55·6; H, 3·6; N, 7·5%).

(*b*) *High-melting form.* (i) The dibromide, when heated in a tube at 250—270°/14 mm., slowly gave a viscous distillate; a hot ethanolic solution deposited the arsine (VI), m. p. and mixed m. p. 156—158°. (ii) The dibromide, when similarly heated at 200° rising slowly to 220°/0·1 mm., gave a pale yellow oily distillate, which did not solidify when seeded with the diarsine (I). Its solution in methanolic methyl iodide when gently boiled deposited the di-iodide dihydrate (III; $n = 2$, X = I), which after recrystallisation from methanol and drying had m. p. 296° (I.T. 270°), increased by heating at 90°/0·1 mm. for 6 hr. to 298° (I.T. 270°), both with effervescence (Found: C, 37·9; H, 4·15%). It is noteworthy that a mixture of this di-iodide with the apparently identical salt, of m. p. 289—292° (I.T. 250°), prepared by the action of sodium iodide on the high-melting dibromide, had m. p. 292—294°, but mixtures of each of these salts with the dimethiodide of the arsine (I) also showed reasonably sharp intermediate m. p.s (all with effervescence). If the above oily distillate had, however, been the diarsine (I), it would almost certainly have crystallised on seeding.

The Dibromide (III; $n = 3$, X = Br).—(i) The dibromide, heated in a tube at 220—225°/14 mm., gave a golden distillate, which in hot acetone-methyl iodide deposited the dimethiodide of the diarsine (I), having, after drying at 110°/0·1 mm., m. p. and mixed m. p. 312—315° (effer.) (I.T. 300°) (Found: C, 39·9; H, 4·3%). (ii) A similar experiment, with heating at 220°/0·1 mm., gave a distillate which from hot ethanol deposited the crystalline arsine (VI), m. p. 149—158°, mixed m. p. 151—158°; there was insufficient for recrystallisation. (iii) A third experiment, with heating at 220°/0·002 mm., gave a distillate, which with hot ethanolic methyl iodide gave very pale yellow crystals, m. p. 270° (effer.) (I.T. 250°) after drying at 120°/0·1 mm., apparently the anhydrous di-iodide (III; $n = 3$, X = I) (Found: C, 40·6; H, 4·3. $C_{25}H_{30}As_2I_2$ requires C, 40·9; H, 4·1%).

The Dibromide (IV; X = Br).—This salt was heated in a tube at 185—190°/14 mm. for 4 hr., when all effervescence had ceased but only a trace of distillate had collected. The residue, recrystallised from methanol, gave 7,12-*dimethyl*-7,12-*diarsa*-1,2:3,4:5,6:9,10-*tetrabenzocyclododecatetraene* (VII), m. p. 67—71° (Found: C, 65·4; H, 5·2%; *M*, in 1,2-dichloromethane, 450. $C_{28}H_{26}As_2$ requires C, 65·6; H, 5·1%; *M*, 412); the absence of bromine was confirmed. At other temperatures and pressures, mixtures of arsines were obtained.

The di-iodide (IV; X = I) was heated as above at 245—250°/14 mm. until effervescence ceased and an oily distillate had collected. A hot ethanolic solution of the latter on cooling deposited halogen-free crystals of the arsine (VI), m. p. and mixed m. p. 154—155°.

Reactions of o-*Lithiophenyldimethylarsine.*—Following the recorded directions,[7] a 1·16 molar solution (34·5 ml.) of n-butyl-lithium (2 mol.) in light petroleum (b. p. 40—60°) was added to a solution of *o*-bromophenyldimethylarsine (10 g.) in the petroleum (15 ml.), causing a slight rise in temperature and deposition of a white powder. The mixture was boiled under reflux for 4 hr. and then cooled. *o*-Di-iodobenzene (5·69 g.) (0·5 mol.) in the petroleum (20 ml.) was slowly added to the cold stirred mixture, which was then again boiled for 1 hr. The cold product contained a heavy dark oily residue and some inorganic matter. The solvent layer was filtered and evaporated, leaving an oil which with methyl iodide deposited *o-iodophenyltrimethylarsonium iodide*, m. p. 240—241° (effer.) after three recrystallisations from ethanol (Found: C, 24·6; H, 2·9. $C_9H_{13}AsI_2$ requires C, 24·0; H, 2·9%). It gave a *picrate*, m. p. 189° from ethanol (Found: C, 33·0; H, 2·75; N, 8·0. $C_{15}H_{15}AsIN_3O_7$ requires C, 32·7; H, 2·7; N, 7·6%). The initial oily residue was washed with water and taken up in chloroform, and the solution dried and distilled; the halogen-containing distillate, b. p. 134—145°/12 mm., showed no arsine properties and was discarded. (When the di-iodobenzene in tetrahydrofuran was added to the solution of the *o*-lithio-compound chilled in CO_2-acetone, working up gave an intractable syrup.)

The above experiment was repeated adding, however, a solution of *o*-dibromobenzene in tetrahydrofuran to the *o*-lithio-solution at room temperature; the reaction caused the mixture to boil. The final cold reaction mixture was shaken with water, and the organic layer, dried and distilled, gave *o*-bromophenyldimethylarsine, b. p. 124—125°/11 mm., identified as its methiodide, m. p. 286° (decomp.) (lit.,[7] decomp. *ca.* 240°) from ethanol (Found: C, 27·0; H, 3·2. Calc. for $C_9H_{13}AsBrI$: C, 26·8; H, 3·25%) and its methopicrate, m. p. 178° (lit.,[9] 181—182°).

We are indebted to Mrs. Olga Kennard for the construction of the structural models.

University Chemical Laboratory, Cambridge.
Department of Chemistry, The University,
Keele, Staffordshire.

[*Received, March* 15*th*, 1965.]

---

[9] H. Heaney, F. G. Mann, and I. T. Millar, *J.*, 1956, 4692.