539. *Cyclic Diarsines. Part VI.*[1] *The Thermal Decomposition of Some Cyclic Quaternary Diarsonium Dihydroxides and Dibromides.*

By M. H. Forbes, Denys M. Heinekey, Frederick G. Mann, and Ian T. Millar.

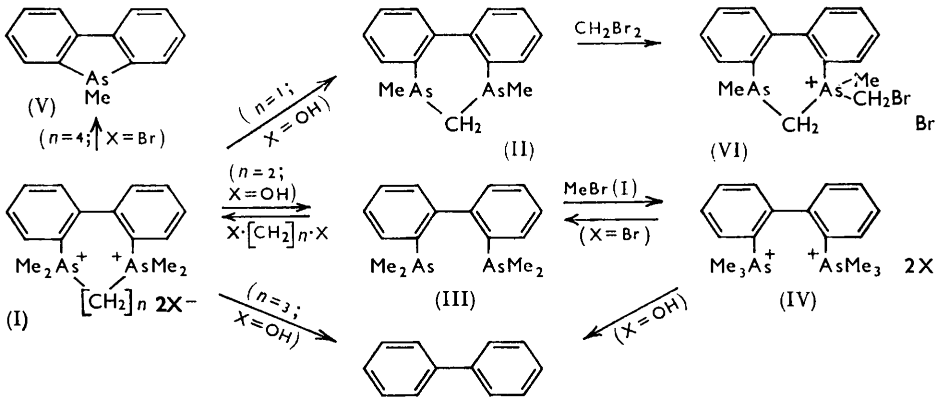
The thermal decomposition of some cyclic quaternary diarsonium dihydroxides (I; *n* = 1, 2, or 3; X = OH), derived from 2,2′-biphenylylenebisdimethylarsine (III), has been found to proceed in a manner markedly dependent on the value of *n*. When *n* = 1, the arsenical product is 5,7-dimethyl-5,7-diarsa-1,2:3,4-dibenzocycloheptadiene (II); when *n* = 2, the diarsine (III) results; when *n* = 3, thermal decomposition yields biphenyl, which is also obtained by heating the dimethohydroxide (IV; X = OH) of the diarsine (III).

The thermal decomposition of certain diarsonium dibromides derived from 2,2′-biphenylylenebisdimethylarsine, and a brief investigation of the quaternising properties of the nitrogen analogue of this diarsine, 2,2′-bisdimethylaminobiphenyl, are described; the preparation and nuclear magnetic resonance characteristics of some quaternary arsonium bromides having a vinyl group attached to arsenic are also noted.

In Part V, the formation and thermal decomposition of some cyclic diarsonium dibromides derived from 2,2′-biphenylylenebisdimethylarsine (III) by diquaternisation with, *e.g.*, methylene, ethylene, and trimethylene dibromides, giving dibromides (I; *n* = 1, 2, and 3 respectively; X = Br), were described.[1] We have now investigated the thermal decomposition of the corresponding dihydroxides.

In contrast with the thermal decomposition of quaternary arsonium halides, that of quaternary arsonium hydroxides has been little investigated. Michaelis[2] reported that methyltriphenylarsonium hydroxide decomposes at 100° to give triphenylarsine and methanol.

The dihydroxide (I; *n* = 1; X = OH), when heated at 150°/0·01 mm. under nitrogen, decomposes smoothly to give the diarsine (II), behaviour resembling that of Michaelis's hydroxide: it is noteworthy that the diarsine (II) is similarly formed by the thermal decomposition of the dibromide (I; *n* = 1; X = Br).[1]



Thermal decomposition of the dihydroxides (I; *n* = 2 or 3; X = OH) is of particular interest, since the corresponding dibromides (I; *n* = 2 or 3; X = Br) decompose with contraction of the heterocyclic rings to give 9-methyl-9-arsafluorene (V).[1] We find that

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[1] Part V, Heaney, Heinekey, Mann, and Millar, *J.*, 1958, 3838.

[2] Michaelis, *Annalen*, 1902, **321**, 166.

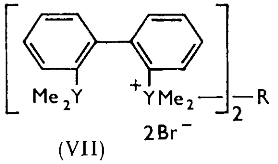
the diarsonium dihydroxide (I; $n = 2$; X = OH) decomposes smoothly at 160°/0·05 mm., giving 2,2′-biphenylylenebisdimethylarsine (III). When, however, the dihydroxide (I; $n = 3$; X = OH) was heated at 165°/0·5 mm., the only product identified was biphenyl; this is also a product of the thermal decomposition of 2,2′-biphenylylenebisdimethylarsine dimethohydroxide (IV; X = OH).

In view of the novel mode of thermal decomposition displayed by the cyclic diarsonium dibromides (I; $n = 2$ or 3; X = Br), the formation and thermal decomposition of certain other cyclic and non-cyclic diarsonium dibromides derived from 2,2′-biphenylylenebisdimethylarsine (III) have been investigated.

Ethylidene dibromide, unlike methylene dibromide, fails to give a heterocyclic diquaternary salt with 2,2′-biphenylylenebisdimethylarsine, giving instead ethylidenebis-(2′-dimethylarsino-2-biphenylyldimethylarsonium) dibromide (VII; Y = As, R = $>$CHMe).

2,2′-Biphenylylenebis(allyldimethylarsonium) dibromide (VIII), prepared from 2,2′-biphenylylenebisdimethylarsine and allyl bromide, decomposes at 250°/0·05 mm. to give 2,2′-biphenylylenebisdimethylarsine (III). (The dimethiodide[3] and dimethobromide of this diarsine decompose similarly to regenerate the diarsine.) This decomposition almost certainly involves the intermediate formation of the monoquaternary bromide (IX); it is therefore unlikely that thermal decomposition of the dibromide (I; $n = 3$; X = Br) to 9-methyl-9-arsafluorene (V) occurs by initial fission of the ring with β-elimination of hydrogen bromide to give the bromide (IX) followed by further elimination and ring-closure to give the arsafluorene (V).

5,5,10,10-Tetramethyl-5,10-diarsonia-1,2:3,4-dibenzocyclodecadiene dibromide (I; $n = 4$; X = Br), prepared from 2,2′-biphenylylenebisdimethylarsine and 1,4-dibromobutane, decomposes when heated, with contraction of the ten-membered heterocyclic ring, giving a mixture of 9-methyl-9-arsafluorene (V) and 9-bromo-9-arsafluorene; it thus resembles the similar dibromides in which $n = 2$ or 3. It has previously been noted that in such quaternary diarsonium dibromides the arsonium groups are bridged by a flexible carbon chain which also bears hydrogen in the β-relation to the arsenic atoms, and this may be significant in their decomposition with ring contraction. In the hope of testing whether the second of these conditions is necessary for the formation of a 9-arsafluorene, attempts were made to quaternise 2,2′-biphenylylenebisdimethylarsine with 1,3-dibromo-2,2′-dimethylpropane, $CH_2Br{\cdot}CMe_2{\cdot}CH_2Br$: the resulting diarsonium dibromide would possess a flexible alkylene bridge, lacking β-hydrogen atoms. As a neopentyl-type halide, 1,3-dibromo-2,2-dimethylpropane was expected to show only very low reactivity as a quaternising agent; it failed to give a dinitrile with potassium cyanide.[4] It required heating with the diarsine at 125° in the presence of methanol for some days for quaternisation to occur; the resulting salt was found to be identical with the dimethobromide (IV; X = Br) of the diarsine (III), as shown by examination of the melting point (alone and mixed), infrared absorption, and analytical composition of specimens prepared by each



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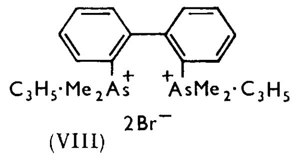

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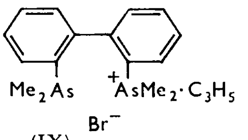

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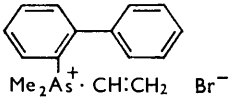

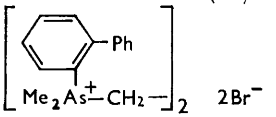

(XI)

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[3] Heaney, Mann, and Millar, *J.*, 1957, **3930**.

[4] Franke, *Monatsh.*, 1913, **34**, 1893.

route, and of the corresponding picrates. Although it was recognised that a system containing the diarsine, 1,3-dibromo-2,2-dimethylpropane, and methanol was potentially complex, since elimination and rearrangement might occur under the forcing conditions required for quaternisation, the formation of the salt (IV; X = Br) is noteworthy.

In order to throw light on the origin of the 9-methyl group in arsafluorenes formed by the thermal decomposition of the dibromides (I; $n = 2$, 3, or 4; X = Br), 2,2′-biphenylylenebisdiethylarsine, prepared from 2,2′-dilithiobiphenyl and chlorodiethylarsine, was heated with ethylene dibromide. However, it is doubtful if cyclising diquaternisation to give the tetraethyl analogue of (I; $n = 2$; X = Br) occurred to any large extent, for the product was a mixture from which no single quaternary salt could be isolated. This marked difference in behaviour between the bisdimethyl- and the bisdiethyl-arsine is probably caused by the greater steric hindrance in the latter.

Attempts to construct "Catalin" models of salts derived from the cyclic diarsine (II) by further cyclising diquaternisation with $\alpha\omega$-alkylene dihalides suggest that such bridging of the arsenic atoms would be stereochemically unlikely. In accord with this prediction, it was found that the diarsine (II), even when treated with methylene dibromide under forcing conditions, gave only the monoquaternary salt (VI) and not the isomeric doubly bridged dibromide. In addition to the stereochemical difficulty of further quaternisation to give the latter salt, it is clear that deactivation of the tertiary arsine group by the arsonium group resulting from initial monoquaternisation, transmitted through both the biphenyl system and the single methylene group, is probably marked in the bromide (VI).

We have prepared triethylvinylarsonium bromide and 2-biphenylyldimethylvinylarsonium bromide (X) in order both to recognise the ·CH:CHAs group by nuclear magnetic resonance spectra, and to establish the absence of this group in the foregoing heterocyclic diarsines, since the small scale of the early experiments on the thermal decomposition of the compound (I; $n = 2$; X = OH) and the difficulty of purification of the resulting diarsine and its quaternary salts made it initially seem possible that the thermal decomposition product might be 5,8-dimethyl-5,8-diarsa-1,2:3,4-dibenzocyclo-octa-1,3,6-triene. Triethylvinylarsonium bromide was readily prepared by interaction of equimolecular quantities of triethylarsine and ethylene dibromide to give 2-bromoethyltriethylarsonium bromide which on treatment with silver oxide in aqueous solution, followed by filtration and neutralisation with hydrobromic acid, gave the vinylarsonium bromide.

Considerable care was required, however, in the preparation of 2-biphenylyldimethylvinylarsonium bromide (X). When an equimolecular mixture of 2-biphenylyldimethylarsine and ethylene dibromide was heated under nitrogen at 100° for 6 hr., the only crystalline product was ethylenebis-(2-biphenylyldimethylarsonium) dibromide (XI), which has a very low solubility in ethanol. When, however, a mixture of the arsine and an excess (3·75 mols.) of ethylene dibromide was heated at 50° for 72 hr., it afforded the required 2-bromoethyl-2-biphenylyldimethylarsonium bromide, which was readily purified by utilising its high solubility in ethanol. This salt, when treated as before with silver oxide and then hydrobromic acid, gave 2-biphenylyldimethylvinylarsonium bromide (X).

Nuclear magnetic resonance spectra of hydrogen nuclei were obtained at 40 Mc. by using a Varian Associates 4300B spectrometer and 12″ electromagnet, with flux stabilisation and sample spinning. Positions of the resonances are quoted as chemical shifts on the tetramethylsilane scale. The τ values for the D_2O solutions were measured by using t-butyl alcohol as a subsidiary internal standard. The following values were obtained for the above vinylarsonium bromides and for tri-2-chlorovinylarsine:

Compound	Solvent	τ
$[Et_3As\cdot CH{:}CH_2]Br$	D_2O	3·47
$[C_{12}H_9\cdot AsMe_2\cdot CH{:}CH_2]Br$	D_2O	3·34, 3·11
$As(CH{:}CHCl)_3$	CCl_4	3·62

The presence of the ·CH: group directly linked to the arsenic atom can thus be clearly detected. It could not be similarly detected in the dibromide (I; $n = 2$; X = Br), or the diarsine (III) or its dimethobromide.

The ultraviolet absorption spectra of certain of the above arsonium salts and of 5,10-dimethyl-5,10-diarsa-1,2:3,4:7,8-tribenzocyclodecatriene dimethobromide[1] are recorded in Figs. 1 and 2. The broad absorption centred at 317 mμ ($\log_{10} \varepsilon$ 3·403) in the spectrum of the methiodide of the arsafluorene (V) (Fig. 1, C) has no counterpart in this region in the spectra of any other of these arsonium salts, and is probably to be attributed to the central 5-membered monoarsine ring system.

The optical resolution of the four cyclic diarsonium salts (Fig. 2) will be described in another paper.

2,2'-Biphenylylenebisdimethylamine was first prepared by Shaw and Turner,[5] who found that it forms a monohydriodide and monomethiodide, and established the non-planarity of the biphenyl system in the cation of the latter salt by resolving it. This di(tertiary amine) would be expected to show the effect of inhibition of basicity at one basic centre as a result of salt formation at the other, an effect shown, *e.g.*, by the arsenic analogue, 2,2'-biphenylylenebisdimethylarsine.[1] Such inhibition of basicity in the diamine might be expected to be not much greater than in the diarsine (which under very mild conditions undergoes monoquaternisation with methyl bromide but readily diquaternises with methyl iodide) since a unit positive pole is involved in both cases, and non-planarity in the biphenyl system, which might affect mesomeric transmission of the effect, would be comparable in the two cases. However, a " Catalin " model of the cation of 2'-dimethylamino-2-biphenylyltrimethylammonium iodide reveals that the formation of a dimethiodide would be very difficult; owing to the comparatively small size of the nitrogen atoms, the attachment of a second methyl group to form the dimethiodide is impeded

FIG. 1.

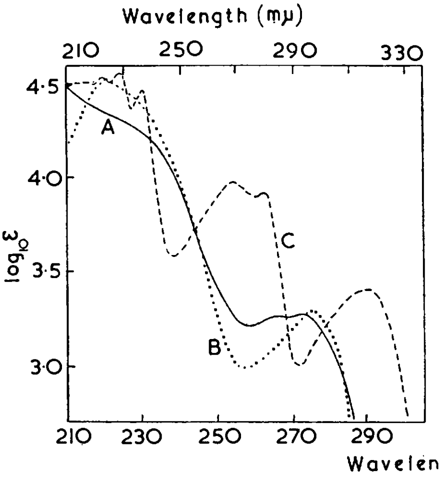

FIG. 2.

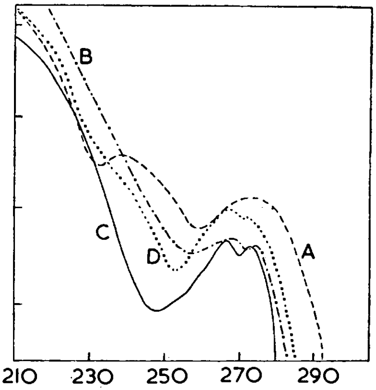

FIG. 1. *Ultraviolet spectra of* 2-*biphenylyl-dimethylarsine methiodide* (A), 2,2'-*biphenylylenebisdimethylarsine dimethiodide* (IV; X = I) (B), *and* 9-*methyl*-9-*arsafluorene methiodide* (C) (*all in water*).
The lower scale of mμ *values applies to* (A) *and* (B), *and the upper scale to* (C).
(*The iodide ion has an absorption band at* 225 mμ, *of peak-height* $\log_{10} \varepsilon$ 4·017, *and of half-width* 22 mμ.)

FIG. 2. *Ultraviolet spectra of* 5,7-*dimethyl*-5,7-*diarsa*-1,2:3,4-*dibenzocycloheptadiene dimethobromide* (I; $n = 1$, X = Br) (A), 5,8-*dimethyl*-5,8-*diarsa*-1,2:3,4-*dibenzocyclo-octadiene dimethobromide* (I; $n = 2$, X = Br) (B), 5,9-*dimethyl*-5,9-*diarsa*-1,2:3,4-*dibenzocyclononadiene dimethobromide* (I; $n = 3$, X = Br) (C), *and* 5,10-*dimethyl*-5,10-*diarsa*-1,2:3,4:7,8-*tribenzocyclodecatriene dimethobromide* (D) (*all in water*).

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[5] Shaw and Turner, *J.*, 1933, 135.

by steric overcrowding about the nitrogen atom. This effect is less marked in the analogous di(tertiary arsine) since the larger arsonium ion holds the attached groups at greater distances, and the overcrowding effect is reduced. Moreover, a " Catalin " model can be made for the product of cyclic diquaternisation of the diamine with an alkylene dibromide, $Br\cdot[CH_2]_n\cdot Br$, when $n = 1$, but not when $n = 2$—6 or when the bridge is *o*-xylylene, implying steric hindrance to such diquaternisations. When the diamine is heated with an excess of methyl iodide in the presence of methanol or nitromethane (both promoters of quaternisation) for a prolonged period, only the monomethiodide is formed. Similarly, vigorous treatment of the base with ethylene dibromide results only in monoquaternisation, giving ethylenebis-(2′-dimethylamino-2-biphenylyldimethylammonium) dibromide, (VII; Y = N, R = $\cdot CH_2\cdot CH_2$). Similar treatment of the diamine with methylene dibromide failed to give evidence of salt formation, a result indicating either lower reactivity or greater steric obstruction of the group $\cdot CH_2Br$ than of $\cdot CH_2\cdot CH_2Br$.

EXPERIMENTAL

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

The quaternary dihydroxides described below, when isolated by evaporation of their solutions, were hygroscopic glassy solids, which could not be readily crystallised: in each case, therefore, the thoroughly dried material was subjected forthwith to thermal decomposition.

Formation and Thermal Decomposition of Quaternary Dihydroxides.—(A) 5,5,7,7-*Tetramethyl*-5,7-*diarsonia*-1,2:3,4-*dibenzocycloheptadiene dihydroxide* (I; $n = 1$; X = OH). A cold solution of the dibromide (3 g.) in water (15 ml.) was shaken overnight with freshly prepared dry silver oxide [from silver nitrate (2 g.) and sodium hydroxide (1·5 g.) in water (25 ml.)]. The mixture was then heated to the b. p. and filtered hot, and the filtrate was evaporated under nitrogen at reduced pressure. The residue, heated at 150°/0·01 mm. in a nitrogen atmosphere, yielded a partly crystalline distillate of the diarsine (II) (1·2 g.), identified by treatment with excess of methyl iodide at 100° for 2 hr., which gave the dimethiodide, m. p. 264° (from ethanol); the latter with sodium picrate in ethanol gave the corresponding dimethopicrate, m. p. and mixed m. p. 274—275° (from water) (lit.,[1] m. p. 283—285°).

(B) 5,5,8,8-*Tetramethyl*-5,8-*diarsonia*-1,2:3,4-*dibenzocyclo-octadiene dihydroxide* (I; $n = 2$; X = OH). This compound was similarly prepared from the corresponding dibromide, or by shaking an aqueous solution of the di-iodide with silver oxide for 1 hr. only. This *di-iodide monohydrate* (I; $n = 2$; X = I), prepared from the dibromide by treatment with sodium iodide in methanol and recrystallised from methanol, had m. p. 222—223° after being heated at 60°/0·1 mm. for 6 hr. (Found: C, 33·1; H, 4·3. $C_{18}H_{24}As_2I_2,H_2O$ requires C, 32·65; H, 4·0%). The dihydroxide decomposed at 160°/0·05 mm., giving a pale yellow distillate which, redistilled under nitrogen, gave 2,2′-biphenylylenebisdimethylarsine (III), b. p. 120°/0·1 mm., identified by comparison of its infrared absorption spectrum with that of an authentic specimen and by analysis, m. p., and mixed m. p. of its dimethiodide and dimethobromide. The dimethiodide with aqueous sodium picrate deposited the yellow *dimethopicrate monohydrate*, m. p. 177° (from water or ethanolic acetone) (Found: C, 42·4; H, 3·8; N, 9·7. $C_{30}H_{30}As_2N_6O_{14},H_2O$ requires C, 41·7; H, 3·85; N, 9·8%).

Heated at 260°/0·05 mm. in nitrogen, the dimethobromide regenerated the diarsine (III); proof of identity was secured by comparison of infrared absorption spectra, which also showed that the diarsine prepared in this way was free from a trace contaminant (almost certainly biphenyl) present in the original specimen. The corresponding dihydroxide (IV; X = OH), prepared from the dimethobromide and silver oxide, decomposed at 170°/0·1 mm., giving biphenyl, m. p. and mixed m. p. 66—67° (after recrystallisation from methanol), and an intractable residue containing arsenic.

(C) 5,5,9,9-*Tetramethyl*-5,9-*diarsonia*-1,2:3,4-*dibenzocyclononadiene dihydroxide* (I; $n = 3$; X = OH), prepared as above from the corresponding dibromide (3 g.), decomposed at 165°/0·5 mm., giving a solid distillate (crude 1·0 g.) of biphenyl, m. p. and mixed m. p. 69° (from methanol). The residue in the flask and the volatile products condensed in a trap cooled in liquid air proved intractable.

Quaternary Salts from 2,2′-*Biphenylylenebisdimethylarsine* (III).—(A) 2,2′-*Biphenylylenebis*(*allyldimethylarsonium*) *dibromide.* The diarsine, heated with an excess of allyl bromide in a sealed tube at 100° for 10 hr., gave the *dibromide,* m. p. 194° (from ethanol–ethyl acetate) (Found: C, 43·8; H, 5·2. $C_{22}H_{30}As_2Br_2$ requires C, 43·8; H, 5·0%). The diarsine, when heated with an equimolecular quantity of allyl bromide, gave a mixture, not readily separated, and almost certainly containing the mono- and di-quaternary salts. The dibromide decomposed at 250°/0·05 mm., giving a colourless distillate of the diarsine (III), identified by conversion into the dibromodiarsinepalladium, m. p. 280° (decomp.) [lit.,[3] m. p. 270° (decomp.)] (Found: C, 31·2; H, 3·1. Calc. for $C_{16}H_{20}As_2Br_2Pd$: C, 30·55; H, 3·2%).

(B) *Ethylidenebis*-(2′-*dimethylarsino*-2-*biphenylyldimethylarsonium*) *dibromide* (VII; Y = As, R = $>$CHMe). The diarsine (2 g.) was heated with 1,1-dibromoethane (1·1 g., 1·05 mol.) in a sealed tube at 100° for 48 hr., giving the *dibromide monohydrate,* m. p. 240° [from ethanol–light petroleum (b. p. 80—100°)] (Found: C, 43·9; H, 4·9. $C_{34}H_{44}As_4Br_2,H_2O$ requires C, 43·9; H, 4·95%). With aqueous sodium picrate this gave the corresponding yellow *dipicrate monohydrate,* m. p. 134° (from water) (Found: C, 44·5; H, 3·9; N, 7·1. $C_{46}H_{48}As_4N_6O_{14},H_2O$ requires C, 45·0; H, 4·1; N, 6·9%).

(C) 2,2′-*Biphenylylenebistrimethylarsonium dibromide* (IV; X = Br). 2,2′-Biphenylylenebisdimethylarsine (3 g.) was heated with 1,3-dibromo-2,2-dimethylpropane (1·8 g.) and methanol (1 ml.) in a sealed tube at 125° for 14 days. The resulting dibromide, after recrystallisation from ethanol, had m. p. 270—280° (decomp.), alone or mixed with a specimen prepared from the diarsine (III) and methyl bromide. The infrared absorption spectra were also identical. With sodium picrate it gave the dipicrate, m. p. and mixed m. p. 175° (from ethanol–acetone) (Found: C, 41·8; H, 3·6; N, 9·8. Calc. for $C_{30}H_{30}As_2N_6O_{14},H_2O$: C, 41·7; H, 3·85; N, 9·8%).

A sample of the dibromopropane was heated with methanol in a sealed tube at 125° for 14 days: some darkening occurred, but no evidence was obtained suggesting substantial reaction, and the infrared absorption spectrum of the mixture was unchanged.

(D) 5,5,10,10-*Tetramethyl*-5,10-*diarsonia*-1,2:3,4-*dibenzocyclodecadiene dibromide* (I; n = 4; X = Br). The diarsine (4 g.) was heated with 1,4-dibromobutane (2·1 g., 0·9 mol.) in a sealed tube at 100° for 12 hr. No suitable solvent could be found for recrystallisation of the product; it was therefore purified by precipitation from its ethanolic solution by ether, which gave the hygroscopic and apparently amorphous *dibromide sesquihydrate,* m. p. 210° (decomp.) (Found: C, 39·6; H, 5·4; ionic Br, 25·6. $C_{20}H_{28}As_2Br_2,1\frac{1}{2}H_2O$ requires C, 39·7; H, 5·2; ionic Br, 26·0%). When the dibromide (5 g.) was heated at 215°/0·1 mm. in nitrogen, it decomposed, yielding a pale yellow distillate. A sample of this distillate gave an intense yellow colour with sodium iodide in acetone, indicating the presence of a bromo-arsine; the remainder was therefore treated with excess of methylmagnesium iodide in ether. Hydrolysis with aqueous ammonium chloride and distillation then gave 9-methyl-9-arsafluorene (V), b. p. 110°/0·2 mm. (1·25 g., 60%), identified by conversion into its methiodide monohydrate, m. p. and mixed m. p. 206—207° (decomp.) (lit.,[1] m. p. 206—207°), and thence into the methopicrate, m. p. and mixed m. p. 214·5—215·5° (lit.,[1] m. p. 214·5—215·5°) (from water).

(E) 5-*Bromomethyl*-5,7-*dimethyl*-7-*arsa*-5-*arsonia*-1,2:3,4-*dibenzocycloheptadiene bromide* (VI). The diarsine (II) (1·26 g.) was heated with methylene dibromide (0·6 g.) and methanol (1 ml.) in a sealed tube at 100° for 72 hr. No satisfactory solvent being found for recrystallisation, the salt was purified by precipitation from its ethanolic solution by ether, giving the *bromide monohydrate,* m. p. 202—204° (Found: C, 35·7; H, 4·2. $C_{16}H_{18}As_2Br_2,H_2O$ requires C, 35·7; H, 3·8%). With ethanolic sodium picrate this gave the yellow *picrate monohydrate,* m. p. 145—146° (from water) (Found: C, 38·0; H, 2·9%; M, determined[6] spectrometrically, 690. $C_{22}H_{20}As_2BrN_3O_7,H_2O$ requires C, 38·4; H, 3·2%; M, 687).

2,2′-*Biphenylylenebisdiethylarsine.*—Diethyliodoarsine (12 g.) in benzene (50 ml.) was added to a solution of 2,2′-dilithiobiphenyl prepared from 2,2′-dibromobiphenyl (7 g.) and lithium foil (1·5 g.) in ether (150 ml.) under nitrogen. After boiling under reflux for 1 hr., the mixture was hydrolysed with cold air-free water, and the organic layer was separated, dried, and evaporated. Fractionation of the residue in nitrogen gave the *diarsine,* b. p. 150°/0·2 mm. (7 g., 50%) (Found: C, 57·3; H, 6·5. $C_{20}H_{28}As_2$ requires C, 57·4; H, 6·7%). Treatment of the diarsine with excess of methyl bromide either at room temperature or at 100° in a sealed tube for 4 hr. gave the *dimethobromide,* m. p. 240° [ethanol–light petroleum (b. p. 60—80°)]

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[6] Cunningham, Davies, and Spring, *J.*, 1951, 2305.

(Found: C, 42·95; H, 5·6. $C_{22}H_{34}As_2Br_2$ requires C, 43·3; H, 5·6%). With ethylene dibromide (10 mol.) in a sealed tube at 100°, the diarsine gave an apparent mixture from which no quaternary salt was isolated.

Triethylvinylarsonium Bromide.—A mixture of triethylarsine and ethylene dibromide (1 mol.) was heated under nitrogen in a pressure bottle at 100° for 6 hr. The cold crystalline product, when recrystallised from ethanol, gave 2-*bromoethyltriethylarsonium bromide*, m. p. 236—237° (decomp.) (Found: C, 27·5; H, 5·2. $C_8H_{19}AsBr_2$ requires C, 27·5; H, 5·5%).

An aqueous solution of this bromide was shaken with an excess of silver oxide at room temperature for 19 hr., filtered, neutralised with hydrobromic acid, and evaporated to dryness in a desiccator. The crystalline residue, when recrystallised from acetone, gave *triethylvinylarsonium bromide*, m. p. 246° (decomp.) after heating at 160°/0·1 mm. for 8 hr. (Found: C, 35·5; H, 6·95. $C_8H_{18}AsBr$ requires C, 35·7; H, 6·7%): it gave a *picrate*, yellow crystals (from water), m. p. 170° (decomp.) after drying at 100°/0·1 mm. (Found: C, 40·2; H, 4·7. $C_{14}H_{20}AsN_3O_7$ requires C, 40·3; H, 4·83%). Hofmann[7] prepared both the above arsonium bromides in solution, but isolated only the corresponding chloroplatinates, of general formula $[R_4As]_2[PtCl_6]$.

Ethylenebis-(2-*biphenylyldimethylarsonium*) *Dibromide* (XI).—A mixture of 2-biphenylyldimethylarsine (3·5 g.) and 1·25 c.c. (1·1 mol.) of ethylene dibromide was heated under nitrogen in a sealed tube at 100° for 6 hr. The cold solid product, when triturated with ether, collected and recrystallised twice from absolute ethanol, afforded the *dibromide* (XI), m. p. 280° (effervescence) after drying at 60°/0·1 mm. for 6 hr. (Found: C, 51·1; H, 4·5; Br, 22·4. $C_{30}H_{34}As_2Br_2$ requires C, 51·2; H, 4·8; Br, 22·8%). It gave a yellow *dipicrate*, m. p. 225° after crystallisation from acetic acid and drying at 90°/0·1 mm. for 6 hr. (Found: C, 49·9; H, 4·1; N, 8·5. $C_{42}H_{38}As_2N_6O_{14}$ requires C, 50·4; H, 3·8; N, 8·4%). Repetition of the experiment with the original mixture diluted with ethanol (5 c.c.) gave the same product (XI).

2-*Biphenylyl*-2′-*bromoethyldimethylarsonium Bromide*.—A mixture of 2-biphenylyldimethylarsine (1 g.), ethylene dibromide (1·25 ml.) (3·75 mol.), and methanol (1 c.c.) was heated under nitrogen in a sealed tube at 50° for 12 hr. The excess of dibromide and the methanol were then removed under reduced pressure. The residual oil, when triturated with ether, gave a hard, white powder, m. p. 122—128° after washing with ether. This salt was dissolved in a minimum of ethanol, leaving a small residue of the dibromide (XI): the extract was filtered and the bromide precipitated by the addition of ether. This process was repeated twice more to eliminate traces of the dibromide (XI). The final precipitated *bromide* had m. p. 130—132° (effervescence) after drying at 70°/0·1 mm. for 6 hr. (Found: C, 43·1; H, 4·3; Br, 36·15. $C_{16}H_{19}AsBr_2$ requires C, 43·1; H, 4·3; Br, 35·8%). It gave a yellow *picrate*, m. p. 138—140° (from water) (Found: C, 44·7; H, 3·8; N, 7·3. $C_{22}H_{21}AsBrN_3O_7$ requires C, 44·5; H, 3·5; N, 7·1%).

An aqueous solution of the bromide was shaken with an excess of freshly prepared silver oxide for 24 hr. The filtered solution was carefully neutralised with hydrobromic acid, refiltered, and evaporated in a desiccator. The residue was triturated with ether, and the insoluble residue purified by dissolution in a minimum of cold ethanol and reprecipitation with ether, the process being repeated four times. The pure, slightly hygroscopic 2-*biphenylyldimethylvinylarsonium bromide* (X) had m. p. 194—196° (effervescence) after drying at 70°/0·1 mm. for 8 hr. (Found: C, 52·25; H, 5·2. $C_{16}H_{18}AsBr$ requires C, 52·6; H, 5·0%). It gave a yellow *picrate*, m. p. 129—130° (from 19 : 1 water–ethanol) (Found: C, 51·4; H, 3·9; N, 8·1. $C_{22}H_{20}AsN_3O_7$ requires C, 51·5; H, 3·9; N, 8·2%).

2,2′-*Bisdimethylaminobiphenyl*.—This diamine, prepared and purified as described by Shaw and Turner,[5] had m. p. 70·5° (lit.,[5] m. p. 72—73°) (yield, 76%) (Found: C, 80·4; H, 8·7; N, 11·4. Calc. for $C_{16}H_{20}N_2$: C, 80·0; H, 8·4; N, 11·6%).

When the diamine was heated with an excess of methyl iodide and a small amount of methanol in a sealed tube at 100° for 24 hr., it gave only 2′-dimethylamino-2-biphenylyltrimethylammonium iodide, m. p. 250—251° (from ethanol) (lit.,[5] m. p. 190—192°) (Found: C, 53·8; H, 5·8; N, 7·7; ionic I, 32·7%. Calc. for $C_{17}H_{23}IN_2$: C, 53·4; H, 6·1; N, 7·3; ionic I, 33·2%). The same product, m. p. 250—251°, was formed when the base was boiled under reflux with methyl iodide and nitromethane for 3 days (Found: ionic I, 33·0%).

The diamine (4 g.) was heated with methylene dibromide (3 g.) and methanol (1 ml.) in a sealed tube at 125° for 5 days. No quaternary salt was isolated from the dark red product, and the diamine, m. p. and mixed m. p. 71—72°, was recovered.

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[7] Hofmann, *Phil. Trans.*, 1860, **150**, 409; *Annalen*, 1861, Suppl. I, 156, 275.

When the diamine (4 g.) was heated with ethylene dibromide (3·3 g.) and methanol (1 ml.) in a sealed tube at 100° for 48 hr., quaternisation occurred. Recrystallisation of the product from ethanol–light petroleum (b. p. 80—100°) gave *ethylenebis-*(*2'-dimethylamino-2-biphenylyldimethylammonium*) *dibromide dihydrate* (VII; Y = N, R = $\cdot CH_2\cdot CH_2\cdot$), m. p. 215—216° (Found: C, 56·5; H, 6·35; N, 8·1. $C_{34}H_{44}Br_2N_4,2H_2O$ requires C, 56·5; H, 6·8; N, 7·8%). With aqueous sodium picrate this gave the corresponding yellow *dipicrate*, m. p. 105° (from water) (Found: C, 56·7; H, 5·45; N, 15·0%; *M*, determined spectrometrically, 1010. $C_{46}H_{48}N_{10}O_{14}$ requires C, 57·2; H, 5·0; N, 14·5%; *M*, 965).

When the diamine in ethanol was boiled with an equimolecular quantity of potassium tetrabromopalladate dissolved in the minimum amount of water, the filtered solution on cooling deposited dark red crystals of a *palladium dibromide complex*, m. p. 191—192° (from ethanol) (Found: C, 32·95; H, 3·9; N, 4·6; Pd, 18·5%; *M*, cryoscopic in phenanthrene, 1110; in boiling methylene dichloride, 1114. $C_{32}H_{40}Br_6N_4Pd_2$ requires C, 32·7; H, 3·4; N, 4·8; Pd, 18·2%; *M*, 1174). This complex may therefore be a dinuclear complex of sexicovalent palladium; if so, it is curious that it is formed in conditions which make the oxidation $Pd^{II} \longrightarrow Pd^{III}$ or Pd^{IV} unlikely.

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