Synthesis and Reactions of 2,2′-Biphenylylenebisdiethylphosphine. Formation of Cyclic Diquaternary Dibromides with Alkylene Dibromides, and the Nature and Probable Mechanism of their Thermal Decomposition

By **David W. Allen** and **Ian T. Millar**, Department of Chemistry, The University, Keele, Staffordshire
F. G. Mann, University Chemical Laboratory, Cambridge

The synthesis of the above diphosphine is described. It forms cyclic diquaternary dibromides by union with the alkylene dibromides, $Br{\cdot}[CH_2]_n{\cdot}Br$, where n = 1—4, and a similar salt with *o*-xylylene dibromide. These salts, and the dimethiodide of the diphosphine, when heated, undergo a novel degradation to give 9-alkyl-9-phosphafluorenes. These reactions are compared with those shown by the analogous cyclic tetramethyl diarsonium dibromides, in which the dibromides formed from $Br{\cdot}[CH_2]_n{\cdot}Br$ where n = 2—4 undergo a similar degradation to give the 9-alkyl-9-arsafluorenes, but the other members lose alkyl bromide with retention of the heterocyclic ring as a ditertiary arsine. The strictly analogous tetraethyl diarsonium dibromides undergo thermal decomposition with degradation of the heterocyclic ring. It is suggested that the ring contraction reactions shown by all these series of salts when heated are examples of a general internal nucleophilic displacement mechanism; other examples of this are discussed.

Alkaline hydrolysis of certain of the above heterocyclic phosphonium salts occurs with ring-opening to give phosphine oxides.

Few ditertiary phosphines are known in which the phosphorus atoms are suitably disposed for the formation of a heterocyclic ring by co-ordination or diquaternisation. A very few *o*-phenylene ditertiary phosphines have been synthesised [1-3] and used as strongly chelating ligands for the stabilisation of unusual co-ordination numbers and oxidation states. They have also been used as intermediates from which heterocyclic compounds can be obtained by quaternisation with alkylene dihalides. Thus *o*-phenylenebisdiethylphosphine undergoes quaternisation with ethylene dibromide to form a heterocyclic diphosphonium salt,[2] and 2-diethylphosphino-5-methylbenzyldiethylphosphine quaternises with dibromomethane to form a salt which is apparently the first phosphorus analogue of the quinazoline system to be recorded.[3] The ethylene ditertiary phosphines $R_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PR_2$ (R = alkyl or aryl) quaternise readily with ethylene dibromide to form quaternary derivatives of the 1,4-diphosphoniacyclohexane system; these dibromides are decomposed by heat to give the original diphosphine.[4] In certain cases the cyclic diphosphines have been obtained by reduction of the diquaternary salts with lithium aluminium hydride.[5]

The ditertiary phosphine, 2,2-biphenylylenebisdiethylphosphine (I) offers possibilities both as a ligand and as an intermediate for the synthesis of quaternary derivatives of heterocyclic phosphorus compounds, from which free cyclic diphosphines might be obtained by thermal decomposition, by analogy with 2,2′-biphenylylenebisdimethylarsine.[6] The synthesis of (I) and a preliminary account of certain novel cyclisation reactions undergone by various diquaternary salts derived therefrom have been reported briefly.[7]

2,2′-Biphenylylenebisdiethylphosphine (I) was readily synthesised in high yield from 2,2′-dilithiobiphenyl and diethylphosphinous chloride in ether; the product was distilled to give a viscous liquid, which when set aside in the refrigerator under nitrogen slowly crystallised to a low-melting solid. Oxidation of the diphosphine (I) with hydrogen peroxide in acetone solution readily gave the corresponding dioxide.

The co-ordinating ability of the diphosphine (I) was demonstrated by the ready formation of a chelate dibromopalladium complex and a bis(aurous chloride) complex when potassium tetrabromopalladate(II) or sodium chloroaurate was added to the diphosphine in hot aqueous ethanol. The investigation of the co-ordination chemistry of the diphosphine is currently being extended, and will be reported elsewhere.

The diphosphine (I) reacted vigorously with methyl iodide to give the dimethiodide (II), and when heated with methylene, ethylene, trimethylene, tetramethylene, or *o*-xylylene dibromide at 100° for some hours it gave the corresponding cyclic diphosphonium dibromides (III; $n = 1$—4) and (IV). In these cases, evidence that cyclisation had occurred and that the products were not the isomeric mono(bromoalkyl)phosphonium bromides was provided by the formation of the corresponding dipicrates when a cold aqueous solution of the halide was treated with sodium picrate solution.

The stereochemistry of cyclic diphosphonium salts of the types (III; $n = 1$—4) and (IV) is noteworthy. Models of the cations imply that the heterocyclic rings are buckled and almost strainless, and that the benzenoid rings of the biphenyl system are not coplanar, and could not become so without considerable distortion of normal bond angles and lengths. This lack of coplanarity is in accord with the ultraviolet spectra of the cyclic salts, which lack almost entirely the characteristic biphenyl band in the 250 mμ region. A further consequence of this lack of planarity and the twisted heterocyclic rings which it entails, is that the cations are dis-

---

[1] F. A. Hart and F. G. Mann, *J. Chem. Soc.*, 1957, 3939.

[2] F. A. Hart, *J. Chem. Soc.*, 1960, 3324.

[3] M. Davis and F. G. Mann, *J. Chem. Soc.*, 1964, 3786.

[4] C. H. S. Hitchcock and F. G. Mann, *J. Chem. Soc.*, 1958, 2081.

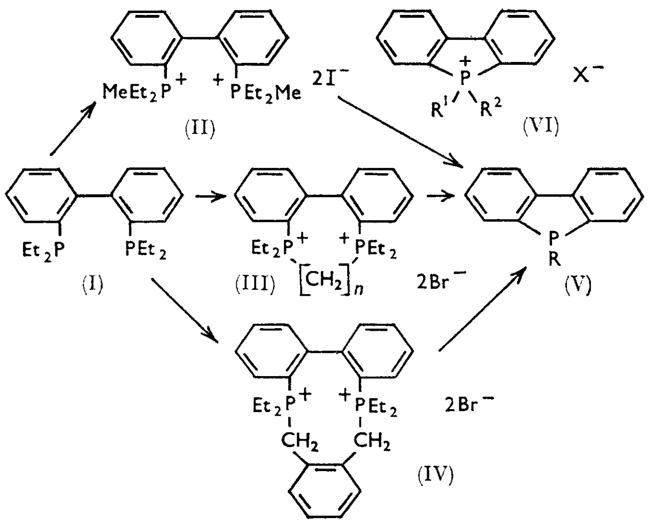
[5] R. C. Hinton and F. G. Mann, *J. Chem. Soc.*, 1959, 2835.

[6] H. Heaney, D. M. Heinekey, F. G. Mann, and I. T. Millar, *J. Chem. Soc.*, 1958, 3838 (see also ref. 22).

[7] D. W. Allen, F. G. Mann, and I. T. Millar, *Chem. and Ind.*, 1966, 196.

symmetric, and the salts should therefore be resolvable into optically active forms. Such resolutions are now under investigation.

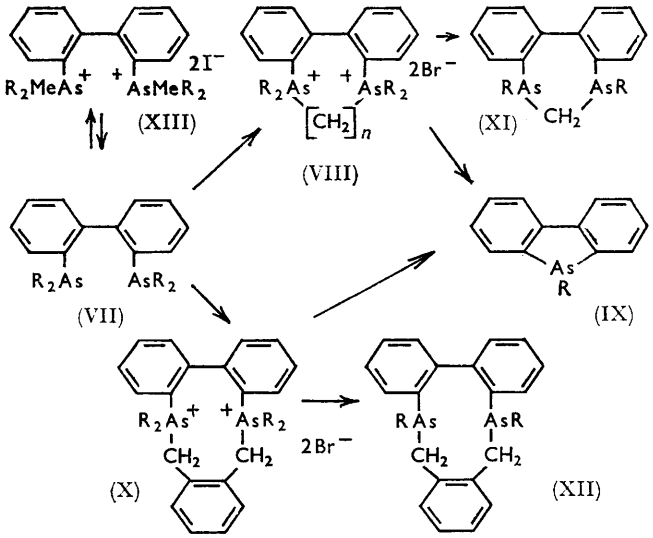
Many quaternary phosphonium halides decompose when heated above 300°, with the loss of one alkyl group and the halogen atom to yield tertiary phosphines.[8] In particular, the decomposition of phosphonium halides containing an ethyl group has been used frequently to prepare cyclic phosphines.[9–11] In such cases it has generally been found that the ethyl group breaks off as ethylene and a tertiary phosphine hydrohalide is formed. (Such observations contrast with those of Fenton *et al.*,[12] who reported no formation of ethylene from the thermal decomposition of an ethyl phosphonium salt but observed the formation of an ethyl halide and the free phosphine.) The decomposition of ethyl phosphonium salts normally proceeds in high yield, but mixtures of phosphines are often obtained in the presence of benzyl or certain other groups.[8,13] An approximate order of ease of cleavage has been given as ethyl ~ benzyl > methyl > propyl > isopentyl > aryl.[13]



The thermal decomposition of the diphosphonium dihalides (II), (III; $n = 1$—4), and (IV) reveals features of great interest, and proceeds in a manner not previously recorded in phosphorus chemistry. Thermal decomposition of the dimethiodide (II) gave both 9-methyl-9-phosphafluorene (V; R = Me) and 9-ethyl-9-phosphafluorene (V; R = Et) (1 : 4·8) initially as a mixture of the free phosphines and their hydriodides. The free 9-alkyl-9-phosphafluorenes (V) were identified by analytical vapour-phase chromatography (v.p.c.) by comparison with the authentic phosphines, prepared by the reaction of the appropriate alkylphosphonous dichloride with 2,2′-dilithiobiphenyl in ether.

Thermal decomposition of the methylene-bridged salt (III; $n = 1$) also gave both 9-methyl- and 9-ethyl-9-phosphafluorenes (1 : 2), again initially as a mixture of the free phosphines and their hydrobromides. The remaining alkylene-bridged salts (III; $n = 2$—4) gave only 9-ethyl-9-phosphafluorene (V; R = Et), as a similar mixture. In addition to v.p.c. identification, the product was converted into the corresponding methopicrate (VI; R^1 = Et, R^2 = Me, X = $C_6H_2N_3O_7$) identical with the authentic derivative. The *o*-xylylene dibromide salt (IV) gave mainly 9-ethyl-9-phosphafluorene (V; R = Et) and a small proportion of the original diphosphine (I).

No evidence for the formation of a cyclic diphosphine was observed in the thermal decomposition reactions of the above cyclic diphosphonium salts. Comparable ring contraction reactions have been observed in arsenic chemistry,[6,14] *e.g.*, in the thermal decomposition of the diquaternary salts of 2,2′-biphenylylenebisdimethylarsine (VII; R = Me). Decomposition of the cyclic diarsonium dibromides (VIII; R = Me, $n = 2$—4) proceeded with ring contraction to form 9-methyl-9-arsafluorene (IX; R = Me). However, decomposition of the salts (VIII; R = Me, $n = 1$) and (X; R = Me) gave the cyclic diarsines (XI) and (XII), respectively, and the dimethiodide (XIII; R = Me) gave the original diarsine (VII) without the formation of an arsafluorene.[6,15]



The ease with which five-membered rings containing arsenic are formed has been discussed, and the prediction made that a similar tendency would be found in suitable phosphorus compounds.[16] The formation of

---

[8] N. Collie, *J. Chem. Soc.*, 1888, **53**, 636, 714.

[9] M. H. Beeby and F. G. Mann, *J. Chem. Soc.*, 1951, 411.

[10] F. G. Mann and I. T. Millar, *J. Chem. Soc.*, 1951, 2205.

[11] F. G. Mann, I. T. Millar, and H. R. Watson, *J. Chem. Soc.*, 1958, 2516.

[12] G. F. Fenton, L. Hey, and C. K. Ingold, *J. Chem. Soc.*, 1933, 989.

[13] J. Meisenheimer, J. Casper, M. Höring, W. Lauter, L. Lichtenstadt, and W. Samuel, *Annalen*, 1926, **449**, 213.

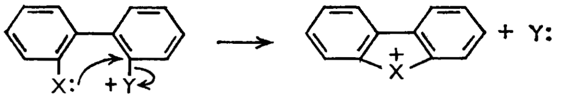
[14] F. G. Mann, I. T. Millar, and F. C. Baker, *J. Chem. Soc.*, 1965, 6342.

[15] H. Heaney, F. G. Mann, and I. T. Millar, *J. Chem. Soc.*, 1957, 3930.

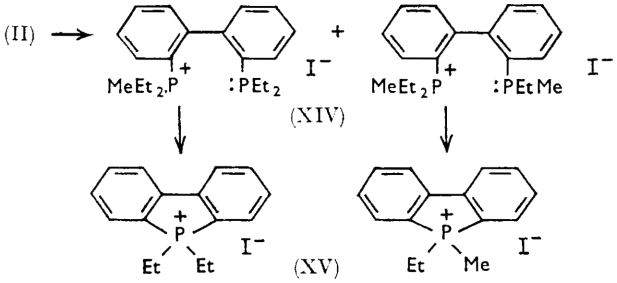
[16] F. G. Mann, *Progr. Org. Chem.*, 1958, **4**, 217.

the 9-phosphafluorene system by thermal decomposition of the cyclic diphosphonium salts might therefore have been anticipated, but the formation of 9-alkyl-9-phosphafluorenes on thermal decomposition of the dimethiodide (II) is remarkable. The high stability of the 9-phosphafluorene system has been demonstrated by recent thermochemical studies.[17]

Such cyclisation reactions appear to be further examples of a general S_Ni mechanism:

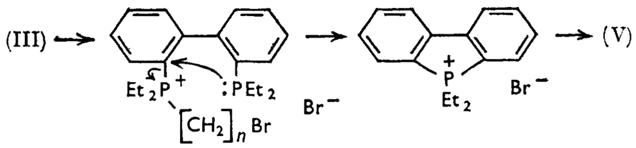


This involves an S_Ni displacement of the leaving group Y (as a neutral species), with the formation of a positively charged cyclic species, which may then react further. Several cyclisation reactions of this type are known, *e.g.*, the formation of cyclic halogenonium salts [18,19] by the decomposition of diazotised 2-amino-2′-halogenobiphenyls with displacement of nitrogen, the decomposition of diazotised 2-amino-2′-aryloxybiphenyl to form a cyclic oxonium salt, and the decomposition of diazotised 2-amino-2′-diphenylaminobiphenyl to form a cyclic quaternary ammonium salt.[20] In the case of the thermal decomposition of the dimethiodide (II) it is proposed that initial loss of ethyl (or methyl) iodide occurs to yield the monophosphonium salts (XIV) which then undergo an S_Ni displacement of diethylmethylphosphine to form quaternary derivatives (XV) of a 9-alkyl-9-phosphafluorene. These would then lose an alkyl group to yield the 9-alkyl-9-phosphafluorenes (V; R = Me or Et).



The quaternary salt (VI; R^1 = Me; R^2 = Et; X = I), identical with one of the postulated intermediates (XV) when decomposed by heat gives both 9-methyl- and 9-ethyl-9-phosphafluorenes (1 : 1·3) (in contrast with the observations of Meisenheimer *et al.*,[13] who reported a preferential elimination of ethyl groups rather than methyl groups in the thermal decomposition of certain monophosphonium salts. In the present example, there is a slight preference for methyl group loss.)

A similar mechanism is proposed for the ring-contraction reaction observed in the thermal decomposition of the cyclic diphosphonium salts (III; *n* = 1—4) and (IV). This involves initial dealkylation with ring opening at one of the phosphorus atoms, to give a tervalent phosphorus derivative similar to (XIV); an S_Ni displacement of the remaining phosphorus fragment ($Et_2P\cdot[CH_2]_n\cdot Br$) would then give the ethobromide of 9-ethyl-9-phosphafluorene. Thermal decomposition of this salt would give 9-ethyl-9-phosphafluorene (V; R = Et).



Such reactions involving nucleophilic displacement of groups attached to aryl rings are interesting because established examples of heterolytic aromatic substitution by phosphorus are rare. It has been claimed recently that the attack of triethyl phosphite on *o*-dinitrobenzene to yield diethyl *o*-nitrophenylphosphonate and ethyl nitrite is evidence of a reaction involving nucleophilic substitution of groups attached to a benzene ring by tervalent phosphorus.[21]

Of the cyclic diphosphonium salts, the methylene dibromide salt (III; *n* = 1) was unique in giving both 9-methyl- and 9-ethyl-9-phosphafluorenes by thermal decomposition. The formation of a methylphosphine from a starting material which does not contain a $P\text{–}CH_3$ group may indicate that a free-radical pathway is here operative. Collie [8] reported that the thermal decomposition of tetramethylphosphonium bromide gave ethylene, which may imply (as Collie suggested) that methylene is involved.

Similar S_Ni mechanisms might be postulated for the ring-contraction reactions observed in the thermal decomposition of the cyclic diarsonium salts (VIII; R = Me, *n* = 2—4). The difference in the behaviour of the dimethiodide (XIII; R = Me) and the cyclic diarsonium salts (VIII; R = Me, *n* = 1) and (X; R = Me), in comparison with the corresponding phosphorus compounds (II), (III; *n* = 1), and (IV) might be ascribed to steric causes and the less strongly nucleophilic properties of tervalent arsenic under conditions in which the simple loss of methyl halide becomes the favoured process. To investigate the effect of the alkyl groups present in the original diarsine on the course of such reactions, a study was made of the mode of thermal decomposition of various salts derived from 2,2′-biphenylylenebisdiethylarsine (VII; R = Et).

This diarsine has been little investigated. In extension of a previous Report,[22] we find that cyclisation with ethylene dibromide to yield the cyclic diarsonium

---

[17] A. F. Bedford, D. M. Heinekey, I. T. Millar, and C. T. Mortimer, *J. Chem. Soc.*, 1962, 2932.

[18] L. Mascarelli, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1907, **16**, II, 582.

[19] R. B. Sandin and A. S. Hay, *J. Amer. Chem. Soc.*, 1952, **74**, 274.

[20] A. N. Nesmeyanov, *Bull. Soc. chim. France*, 1965, 897, and references therein.

[21] J. I. G. Cadogan, D. J. Sears, and D. M. Smith, *Chem. Comm.*, 1966, 491.

[22] M. H. Forbes, D. M. Heinekey, F. G. Mann, and I. T. Millar, *J. Chem. Soc.*, 1961, 2762.

salt (VIII; R = Et, *n* = 2) does occur when equimolecular quantities of the diarsine and ethylene dibromide are heated for a long time in a sealed tube containing a trace of ethanol. Similarly, cyclisation occurs with *o*-xylylene dibromide to give the cyclic diarsonium salt (X; R = Et). Evidence that cyclisation had occurred was obtained by the determination of ionic bromine, and by conversion into the corresponding dipicrate, respectively.

The thermal decomposition reactions of the cyclic salts of 2,2′-biphenylylenebisdiethylarsine differ from those of the corresponding salts of 2,2′-biphenylylenebisdimethylarsine. Decomposition of the *o*-xylylene bridged salt (X; R = Et) gives a mixture of the ring-contraction product, 9-ethyl-9-arsafluorene (IX; R = Et), and 2,2′-biphenylylenebisdiethylarsine (VII; R = Et), and none of the cyclic diarsine corresponding to (XII). The ethylene bridged salt (VIII; R = Et, *n* = 2) decomposed smoothly to yield only 9-ethyl-9-arsafluorene (IX; R = Et). The corresponding salt of 2,2′-biphenylylenebisdimethylarsine yielded 9-bromo-9-arsafluorene in addition to 9-methyl-9-arsafluorene.[6]

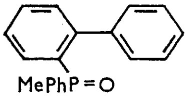
The thermal decomposition of the dimethiodide of the diarsine (VII; R = Et) gave a mixture of arsines of similar boiling point to the parent diarsine, which was also a major product of the reaction. Although the other arsines were not identified, they were probably the products obtained by the loss of ethyl instead of methyl from one or both of the arsonium centres. No arsafluorenes were detected.

Thermal decomposition of the methiodide of 9-ethyl-9-arsafluorene (IX; R = Et) gave a mixture of 9-methyl-9-arsafluorene (IX; R = Me) and 9-ethyl-9-arsafluorene (IX; R = Et) (1 : 2), which again indicates the preferential loss of methyl groups from simple arsonium salts.

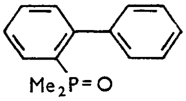
The alkaline hydrolysis of certain of the cyclic phosphonium salts discussed has been investigated. Several workers[23] have investigated the hydrolysis of simple quaternary phosphonium compounds: in general the reaction of hydroxide ions with alkyl or aryl phosphonium compounds gives principally phosphine oxides and hydrocarbons. The group eliminated as the hydrocarbon is usually that which is able to form the most stable anion, and the following order of preference for group cleavage has been established:

p-nitrobenzyl > benzyl > aryl > phenylethyl > alkyl

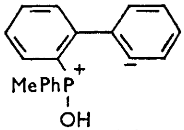
Alkaline hydrolysis of the *o*-xylylene-bridged dibromide (IV) gave *o*-xylene and 2,2′-biphenylylenebisdiethylphosphine dioxide, with the expected preferential cleavage of benzyl groups. Hydrolysis of the methiodides of 9-phenyl-9-phosphafluorene (VI; R^1 = Ph, R^2 = Me, X = I) and of 9-methyl-9-phosphafluorene (VI; $R^1 = R^2$ = Me, X = I) proceeded exclusively with opening of the five-membered phosphafluorene ring to give 2-biphenylylmethylphenylphosphine oxide (XVI) and 2-biphenylyldimethylphosphine oxide (XVII),



(XVI)



(XVII)



(XVIII)

respectively. No ring-preserved products were observed. In the case of the methiodide (VI; $R^1 = R^2$ = Me, X = I) this is not surprising in view of the established preference for $\overset{+}{P}$-aryl cleavage under alkaline conditions. In the case of (VI; R^1 = Ph, R^2 = Me, X = I), the absence of $\overset{+}{P}$-phenyl cleavage to give a ring-preserved product indicates considerable stabilisation of an intermediate of the type (XVIII), with negative charge on the 2′-position of the biphenyl system, which leads to the observed preferential direction of cleavage. The structures of (XVI) and (XVII) were determined by (*a*) analysis, (*b*) their infrared spectra, which exhibited strong peaks at 1175 and 1160 cm.$^{-1}$, respectively, in accord with the presence of a P=O group, (*c*) their ultraviolet spectra, which were typical of hindered biphenyl systems, and very different from the characteristic spectra of 9-phosphafluorene derivatives, and (*d*) their nuclear magnetic resonance spectra.

Our studies on the alkaline hydrolysis of salts of type (IV) and (VI) recall the observations of Bergeson[24] on the alkaline hydrolysis of the methiodides of 1,2,5-triphenylphosphole and 1,2,3,4,5-pentaphenylphosphole, which gave the corresponding substituted butadienylphosphine oxides.

EXPERIMENTAL

Operations involving phosphines or arsines were performed under nitrogen. M. p.s were determined on a Kofler hot-stage apparatus. The v.p.c. analyses were carried out with a 10 ft. spiral glass column packed with 'Gaschrome P' coated with 1% S.E.30 silicone oil. An argon ionisation detector was used. For some compounds, the name corresponding to that used previously in the *Journal* in cognate work is given first, followed by the name of the same compound using the Revised Ring Index system.

2,2′-*Biphenylylenebisdiethylphosphine* (I).—A solution of 2,2′-dibromobiphenyl (12 g.) in ether (150 ml.) was added dropwise to thin lithium foil (1·08 g.) during 1½—2 hr.; the mixture was stirred at room temperature for a further 2 hr. Diethylphosphinous chloride (9·1 g.) in benzene (50 ml.) was added dropwise during 30 min. and the mixture was refluxed for 1 hr., cooled, and hydrolysed with cold air-free water. The organic layer was separated and dried (Na_2SO_4), the solvents were evaporated off, and the residue was distilled under reduced pressure in nitrogen to give 2,2′-*biphenylylenebisdiethylphosphine*, b. p. 152°/0·25 mm. (8·07 g., 70%) (Found: C, 72·95; H, 8·7. $C_{20}H_{28}P_2$ requires C, 72·7; H, 8·5%). When set aside in the refrigerator, the

---

[23] G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 1929, 2342; L. Hey and C. K. Ingold, *ibid.*, 1933, 531; M. Zanger, C. A. VanderWerf, and W. F. McEwen, *J. Amer. Chem. Soc.*, 1959, **81**, 3806; G. Aksnes and L. J. Brudvick, *Acta Chem. Scand.*, 1963, **17**, 1616.

[24] K. Bergeson, *Acta Chem. Scand.*, 1966, **20**, 899 (see also ref. 25).

diphosphine slowly crystallised, m. p. 28—30°. A sample (200 mg.) in acetone (5 ml.) was treated with hydrogen peroxide solution (100 vol.; 1 ml.) and the solution was set aside for 24 hr. Evaporation of the solvents left an oil which was dissolved in chloroform (10 ml.), and shaken with aqueous sodium hydrogen sulphite. The chloroform solution was then dried (Na_2SO_4) and evaporated to give crystals of *2,2'-biphenylylenebisdiethylphosphine dioxide*, m. p. 193—195° [sealed evacuated tube (s.e.t.)] (Found: C, 65·9; H, 7·75. $C_{20}H_{28}O_2P_2$ requires C, 66·3; H, 7·75%), $\nu_{max.}$ (mull) 1180 cm.$^{-1}$.

Quaternary Salts of 2,2'-*Biphenylylenebisdiethylphosphine*.—(a) 2,2'-*Biphenylylenebisdiethylmethylphosphonium di-iodide* (II). To the diphosphine (0·1 g.) was added an excess of methyl iodide; a vigorous reaction ensued. Removal of the excess of methyl iodide left the *dimethiodide*, m. p. 255—256° (from ethanol) (Found: C, 42·7; H, 5·4. $C_{22}H_{34}I_2P_2$ requires C, 43·05; H, 5·6%). The *dipicrate* formed yellow crystals, m. p. 137—138° (from aqueous ethanol) (Found: C, 50·0; H, 4·85; N, 9·7. $C_{34}H_{38}N_6O_{14}P_2$ requires C, 50·0; H, 4·65; N, 10·2%).

(b) 5,5,7,7-*Tetraethyl*-5,7-*diphosphonia*-1,2:3,4-*dibenzocycloheptadiene dibromide* (*i.e.*, 5,5,7,7-tetraethyl-6,7-dihydro-5*H*-dibenzo[*d,f*][1,3]diphosphepinium dibromide) (III; *n* = 1). The diphosphine (1·0 g.) was heated with dibromomethane (0·53 g.) in a sealed tube at 100° for 15 hr. The product when washed with dry ether gave the extremely hygroscopic dibromide, m. p. 228—230°. Satisfactory analytical data could not be obtained for this salt, but the *dipicrate* formed yellow crystals, m. p. 221—222° (from aqueous ethanol) (Found: C, 49·3; H, 4·55; N, 11·0. $C_{33}H_{34}N_6O_{14}P_2$ requires C, 49·5; H, 4·25; N, 10·5%).

(c) 5,5,8,8-*Tetraethyl*-5,8-*diphosphonia*-1,2:3,4-*dibenzocyclo-octadiene dibromide* (*i.e.*, 5,5,8,8-tetraethyl-5,6,7,8-tetrahydrodibenzo[*e,g*][1,4]diphosphocinium dibromide) (III; *n* = 2). The diphosphine (1·35 g.) was heated with 1,2-dibromoethane (0·77 g., 1 mol.) in a sealed tube containing a trace of methanol at 100° for 12 hr. The product was washed with dry ether and purified by precipitation from a chloroform solution with acetone, to give the hygroscopic *dibromide*, m. p. 268—272° (Found: C, 51·7; H, 6·15. $C_{22}H_{32}Br_2P_2$ requires C, 51·0; H, 6·2%). The yellow *dipicrate monoethanolate* had m. p. 142° (followed by solidification and remelting at 164—165°) (from aqueous ethanol) (Found: C, 50·3; H, 4·6; N, 10·25. $C_{34}H_{36}N_6O_{14}P_2,C_2H_5OH$ requires C, 50·2; H, 4·9; N, 9·8%).

(d) 5,5,9,9-*Tetraethyl*-5,9-*diphosphonia*-1,2:3,4-*dibenzocyclononadiene dibromide* (*i.e.*, 5,5,9,9-tetraethyl-6,7,8,9-tetrahydro-5*H*-dibenzo[*f,h*][1,5]diphosphoninium dibromide) (III; *n* = 3). The diphosphine (1·65 g.) was heated with 1,3-dibromopropane (1·01 g., 1 mol.) and methanol (1 ml.) in a sealed tube at 100° for 16 hr. The methanol was evaporated, and the product washed with dry ether, to give the *dibromide sesquihydrate*, m. p. 335—336° (decomp.) (from ethanol) (Found: C, 49·1; H, 6·7. $C_{23}H_{34}Br_2P_2,1{\cdot}5H_2O$ requires C, 49·4; H, 6·6%). The yellow *dipicrate* had m. p. 185—186° (from aqueous ethanol) (Found: C, 50·8; H, 4·45; N, 9·8. $C_{35}H_{38}N_6O_{14}P_2$ requires C, 50·7; H, 4·6; N, 10·15%).

(e) 5,5,10,10-*Tetraethyl*-5,10-*diphosphonia*-1,2:3,4-*dibenzocyclodecadiene dibromide* (*i.e.*, 5,5,10,10-tetraethyl-5,6,7,8,9,10-hexahydrodibenzo[*b,d*][1,6]diphosphecinium dibromide) (III; *n* = 4). The diphosphine (1·65 g.) was heated with 1,4-dibromobutane (1·08 g., 1 mol.) and methanol (1 ml.) in a sealed tube at 100° for 20 hr. The product was triturated with ether to give the *dibromide tetrahydrate*, m. p. 152—155° (Found: C, 46·45; H, 7·6. $C_{24}H_{36}Br_2P_2,4H_2O$ requires C, 46·6; H, 7·1%). On treatment with aqueous sodium picrate, the salt gave an uncrystallisable picrate.

(f) 5,5,10,10-*Tetraethyl*-5,10-*diphosphonia*-1,2:3,4:7,8-*tribenzodecatriene dibromide* (*i.e.*, 9,9,16,16-tetraethyl-9,10,15,16-tetrahydrotribenzo[*b,d,h*][1,6]diphosphecinium dibromide) (IV). The diphosphine (1·51 g.) was heated with *o*-xylylene dibromide (1·32 g., 1 mol.) and methanol (1 ml.) in a sealed tube at 100° for 20 hr. The product was triturated with ether and purified by boiling in ethanol, to give a solid, m. p. 360° (decomp.). The salt was too insoluble in organic solvents for satisfactory recrystallisation (Found: C, 57·2; H, 6·45. $C_{28}H_{36}Br_2P_2$ requires C, 56·5; H, 6·05%). The *dipicrate* formed yellow crystals, m. p. 77—78° (from water) (Found: C, 54·4; H, 4·55; N, 9·4. $C_{40}H_{40}N_6O_{14}P_2$ requires C, 53·95; H, 4·5; N, 9·45%).

9-*Ethyl*-9-*phosphafluorene* (*i.e.*, 5-ethyl-5*H*-dibenzophosphole) (V; R = Et).—A solution of 2,2'-dibromobiphenyl (10 g.) in ether (150 ml.) was added dropwise to fine lithium foil (0·9 g.) during 1·5—2 hr. The mixture was stirred at room temperature for a further 2 hr. Ethylphosphonous dichloride (3·77 g.) in benzene (50 ml.) was added dropwise during 30 min. and the resulting mixture was refluxed for 1 hr., cooled and hydrolysed with cold air-free water. The organic layer was separated and dried (Na_2SO_4), the solvents were evaporated off, and the residue was distilled to give 9-*ethyl*-9-*phosphafluorene*, b. p. 106°/0·15 mm. (3·91 g., 58%) (Found: C, 79·1; H, 6·4. $C_{14}H_{13}P$ requires C, 79·25; H, 6·15%). The phosphine slowly crystallised in the refrigerator, m. p. 42—44°.

9-*Ethyl*-9-*methyl*-9-*phosphoniafluorene Iodide* (VI; R^1 = Me, R^2 = Et, X = I).—9-Ethyl-9-phosphafluorene (0·1 g.) was dissolved in an excess of methyl iodide and the mixture was set aside overnight. The excess of methyl iodide was then distilled off under reduced pressure. The residue was triturated with ether and recrystallised from acetone with the addition of ethanol to yield the *iodide*, m. p. 195° (Found: C, 51·0; H, 4·7. $C_{15}H_{16}IP$ requires C, 50·8; H, 4·5%). The yellow *picrate* had m. p. 190—191° (from aqueous ethanol) (Found: C, 54·9; H, 4·0; N, 9·45. $C_{21}H_{18}N_3O_7P$ requires C, 55·3; H, 3·95; N, 9·25%).

9-*Methyl*-9-*phosphafluorene* (*i.e.*, 5-methyl-5*H*-dibenzophosphole) (V; R = Me).—A solution of 2,2'-dibromobiphenyl (10 g.) in ether (150 ml.) was added dropwise to fine lithium foil (0·9 g.) during 1·5—2 hr. The mixture was stirred at room temperature for a further 2 hr. Methylphosphonous dichloride (3·75 g.) in benzene (50 ml.) was added dropwise during 30 min., and the mixture was refluxed for 1 hr., cooled, and hydrolysed with cold air-free water. The organic layer was separated and dried (Na_2SO_4), the solvents were evaporated off, and the residue was distilled to give 9-*methyl*-9-*phosphafluorene*, b. p. 103°/0·2 mm. (2·37 g., 37%) (Found: C, 78·2; H, 5·8. $C_{13}H_{11}P$ requires C, 78·8; H, 5·5%).

9,9-*Dimethyl*-9-*phosphoniafluorene Iodide* (VI; R^1 = R^2 = Me, X = I).—9-Methyl-9-phosphafluorene (0·1 g.) was dissolved in an excess of methyl iodide and the mixture set aside overnight. The excess of methyl iodide was then evaporated off. The residue was triturated with ether and purified by crystallisation from ethanol, to yield the *iodide*, m. p. 280—280·5° (Found: C, 49·9; H, 4·25. $C_{14}H_{14}IP$ requires C, 49·4; H, 4·15%). The yellow *picrate* had m. p. 217° (from aqueous ethanol) (Found: C, 54·9;

H, 3·65; N, 9·4. $C_{20}H_{16}N_3O_7P$ requires C, 54·45; H, 3·7; N, 9·5%).

Thermal Decompositions.—(a) 2,2′-*Biphenylylenebis*-(*diethylmethylphosphonium*) *di-iodide* (II). The di-iodide (0·5 g.), in a bulb-tube distillation apparatus evacuated to 0·15 mm., was heated to 250° to give a viscous semi-crystalline distillate, which was treated with aqueous sodium hydrogen carbonate solution, and the liberated phosphines were extracted with ether. The dried extract, examined by v.p.c. at 130°, contained 9-methyl-9-phosphafluorene (V; R = Me), retention time (*t*) 10·0 min., and 9-ethyl-9-phosphafluorene (V; R = Et), *t* 14·4 min. (1 : 4·8). Examination (v.p.c.) of the dried ether extract at 176° indicated the absence of any diphosphines, which might have arisen from pyrolysis of the salt with simple loss of alkyl halide. At this temperature, authentic 2,2′-biphenylylenebisdiethylphosphine had *t* = 11·4 min.

(b) 9-*Ethyl*-9-*methyl*-9-*phosphoniafluorene iodide* (VI; R^1 = Me, R^2 = Et, X = I). The iodide (1·0 g.) was decomposed in a bulb-tube apparatus and the distillate treated as described in (a). The dried ether extract contained 9-methyl-9-phosphafluorene (V; R = Me), *t* 10·0 min., and 9-ethyl-9-phosphafluorene (V; R = Et), *t* 14·4 min. (1 : 1·3).

(c) 5,5,7,7-*Tetraethyl*-5,7-*diphosphonia*-1,2:3,4-*dibenzocycloheptadiene dibromide* (III; *n* = 1). The dibromide (1·0 g.) was decomposed in a bulb-tube apparatus and the distillate treated as described in (a). The dried ether extract contained 9-methyl-9-phosphafluorene (V; R = Me) *t* 10·0 min., and 9-ethyl-9-phosphafluorene (V; R = Et) *t* 14·4 min. (1 : 2). Examination of the extract at 170° indicated the absence of diphosphines.

(d) 5,5,8,8-*Tetraethyl*-5,8-*diphosphonia*-1,2:3,4-*dibenzocyclo-octadiene dibromide* (III; *n* = 2). The dibromide (0·5 g.) was decomposed in a bulb-tube apparatus and the distillate treated as described in (a). The dried ether extract contained 9-ethyl-9-phosphafluorene (V; R = Et), *t* 14·4 min. Examination of the extract at 180° indicated the absence of diphosphines. It was evaporated in a stream of nitrogen, and the oily residue was treated with methyl iodide. The mixture was refluxed for 30 min., and the excess of methyl iodide was removed by distillation. The crude methiodide resisted crystallisation and was converted into the corresponding methopicrate of 9-ethyl-9-phosphafluorene, m. p. 188—190° (from aqueous ethanol).

(e) 5,5,9,9-*Tetraethyl*-5,9-*diphosphonia*-1,2:3,4-*dibenzocyclononadiene dibromide* (III; *n* = 3). The dibromide (1·0 g.) was decomposed in a bulb-tube apparatus and the distillate treated as described in (a). The dried ether extract contained 9-ethyl-9-phosphafluorene (V; R = Et), *t* 14·4 min. Examination (v.p.c.) of the extract at 180° indicated the absence of diphosphines. It was evaporated and the oily residue converted into the corresponding methopicrate of 9-ethyl-9-phosphafluorene, m. p. and mixed m. p. 189—190° (from aqueous ethanol).

(f) 5,5,10,10-*Tetraethyl*-5,10-*diphosphonia*-1,2:3,4-*dibenzocyclodecadiene dibromide* (III; *n* = 4). The dibromide (0·7 g.) was decomposed in a bulb-tube apparatus and the distillate treated as described in (a). The product was 9-ethyl-9-phosphafluorene, methopicrate, m. p. 189—190° (from aqueous ethanol), identical with the authentic methopicrate. As before, v.p.c. indicated the absence of diphosphines.

(g) 5,5,10,10-*Tetraethyl*-5,10-*diphosphonia*-1,2:3,4:7,8-*tribenzocyclodecatriene dibromide* (IV). The dibromide (2·0 g.) was decomposed at 300° and the distillate treated as in (a). The dried extract was examined by v.p.c. at 130 and 182°, and contained 9-ethyl-9-phosphafluorene (V; R = Et), *t* 14·4 min. (130°) with a small quantity of 2,2′-biphenylylenebisdiethylphosphine (I), *t* 8·8 min. (182°). The extract was evaporated and the oily residue (0·7 g.) converted into the corresponding methiodides by treatment with an excess of methyl iodide. Attempted recrystallisation of the crude methiodides from ethanolic acetone yielded a small crop of crystals, m. p. 254—256°, of the dimethiodide of 2,2′-biphenylylenebisdiethylphosphine (m. p. 255—256°). The supernatant liquid was then poured into water and the solution treated with a saturated solution of sodium picrate. The picrate could not be purified by crystallisation owing to the presence of traces of the dimethopicrate of the diphosphine. The aqueous phase from the ether extraction of the distillation products was heated on a steam-bath for 1 hr. to decompose any phosphonium salts to phosphine oxides, and the resulting solution was evaporated to dryness. The inorganic residue was extracted with hot chloroform and the chloroform extract was evaporated to yield a gum (33 mg.). Examination of the gum by thin-layer chromatography (t.l.c.) (silica-gel, 95% ethanol) showed it to consist of a number of components, which were incompletely separated. The cold-traps of the oil-pump used for the distillation contained little material, but when this was exposed to the air a foul smell was noticeable and considerable fuming occurred.

Alkaline Hydrolyses of Phosphonium Salts.—(a) 9-*Methyl*-9-*phenyl*-9-*phosphoniafluorene iodide* (VI; R^1 = Me, R^2 = Ph, X = I). The iodide was prepared as by Wittig and Maercker,[25] m. p. 204—205° (lit.,[25] 204—206°) (Found: C, 57·4; H, 4·15. Calc. for $C_{19}H_{16}IP$: C, 57·4; H, 4·0%). To a solution of the iodide (250 mg.) in 50% aqueous acetone (10 ml.) was added sodium hydroxide solution (30%; 1 ml.), and the mixture was set aside at room temperature for 24 hr. The solution was then heated on a steam-bath for 5 min. and the excess of alkali was neutralised by dropwise addition of concentrated hydrochloric acid. The solution was poured into water (15 ml.) and extracted with chloroform (2 × 10 ml.). The dried chloroform extract was evaporated to a viscous residue (163 mg.) which contained (t.l.c.) one major component, $\nu_{max.}$ (mull), 1175 cm.$^{-1}$ (P=O), $\lambda_{max.}$ (95% EtOH) 208 and 274 mμ (ε 29,550 and 2496), τ ($CDCl_3$) 2·6 (multiplet, 14H) and 8·35 (doublet, *J* = 14 c./sec., 3H), as expected for 2-*biphenylylmethylphenylphosphine oxide* (XVI). The residue resisted crystallisation from a variety of solvents, and could not be purified satisfactorily by sublimation, or by column chromatography. It was therefore converted into the cobalt(II) chloride complex by the procedure due to Pickard and Kenyon.[26] The complex was purified by precipitation from benzene solution with light petroleum (b. p. 60—80°) to yield a blue solid, *dichlorobis*-(2-*biphenylylmethylphenylphosphine oxide*)*cobalt*, m. p. 68—70° (Found: C, 63·5; H, 4·5. $C_{38}H_{34}Cl_2CoO_2P_2$ requires C, 63·9; H, 4·75%).

(b) 9,9-*Dimethyl*-9-*phosphoniafluorene iodide* (VI; R^1 = R^2 = Me, X = I). The iodide (250 mg.) was hydrolysed and the product extracted with chloroform as described in (a). Evaporation of the dried chloroform extract gave an oil which crystallised to give the pure (t.l.c.), hygroscopic 2-*biphenylyldimethylphosphine oxide*, m. p. 92—93° (156 mg.) (Found: C, 72·7; H, 6·0. $C_{14}H_{15}OP$ requires C,

---

[25] G. Wittig and A. Maercker, *Chem. Ber.*, 1964, **97**, 747.

[26] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, 1906, **89**, 262.

73·05; H, 6·5%), $\nu_{max.}$ (mull) 1160 cm.$^{-1}$ (P=O), $\lambda_{max.}$ (95% ethanol) 210, 235sh, and 275 mμ (ε 22,320, 5860, and 1862), τ ($CDCl_3$) 1·75 (multiplet, 1H), 2·5 (multiplet, 8H), and 8·58 (doublet, J_{PH} = 14 c./sec., 6H).

(c) 5,5,10,10-*Tetraethyl*-5,10-*diphosphonia*-1,2:3,4:7,8-*tribenzocyclodecatriene dibromide* (IV). The dibromide (0·5 g.) in water (15 ml.) was heated on a steam-bath for 4 hr. with potassium hydroxide solution (40%; 4 ml.). The solution was then cooled, and the excess of alkali was neutralised by the dropwise addition of concentrated hydrochloric acid. The solution was extracted with ether (10 ml.) and then with chloroform (2 × 10 ml.). The ether extract was dried (Na_2SO_4) and examined by v.p.c., which showed the presence of *o*-xylene, *t* 6·4 min. (19°). The chloroform extract was dried (Na_2SO_4) and evaporated to give 2,2′-biphenylylenebisdiethylphosphine dioxide, m. p. and mixed m. p. 193—195° (s.e.t.) (0·232 g.).

Quaternary Salts of 2,2′-*Biphenylylenebisdiethylarsine*.—The diarsine (VII; R = Et) was prepared as described [22] (61%) (Found: C, 57·3; H, 6·45. Calc. for $C_{20}H_{28}As_2$: C, 57·45; H, 6·7%).

(a) 2,2′-*Biphenylylenebis*(*diethylmethylarsonium*) *di-iodide*. To a solution of the diarsine (0·1 g.) in benzene was added an excess of methyl iodide; the mixture was heated to boiling and set aside for 24 hr. Removal of the solvent gave the *dimethiodide*, m. p. 199—200° (from absolute ethanol) (Found: C, 37·15; H, 4·55. $C_{22}H_{34}As_2I_2$ requires C, 37·6; H, 4·85%).

(b) 5,5,8,8-*Tetraethyl*-5,8-*diarsonia*-1,2:3,4-*dibenzocyclooctadiene dibromide* (*i.e.*, 5,5,8,8-tetraethyl-5,6,7,8-tetrahydrodibenzo[*e,g*][1,4]diarsocinium dibromide) (VIII; R = Et, *n* = 2). The diarsine (1·97 g.) was heated with 1,2-dibromoethane (0·87 g., 1 mol.) in a sealed tube containing a trace of ethanol at 100° for 300 hr. The product was washed several times with dry ether to give the extremely hygroscopic *dibromide*, which resisted purification by crystallisation or precipitation. It was characterised by conversion into the *dipicrate*, which formed yellow crystals, m. p. 153—155° (from aqueous ethanol) (Found: C, 45·3; H, 3·95; N, 9·0. $C_{34}H_{36}As_2N_6O_{14}$ requires C, 45·25; H, 4·0; N, 9·3%).

(c) 5,5,10,10-*Tetraethyl*-5,10-*diarsonia*-1,2:3,4:7,8-*tribenzocyclodecatriene dibromide* (*i.e.*, 9,9,16,16-tetraethyl-9,10,15,16-tetrahydrotribenzo[*b,d,h*][1,6]diarsecinium dibromide) (X; R = Et). The diarsine (1·89 g.) was heated with *o*-xylylene dibromide (1·18 g., 1 mol.) and methanol (1 ml.) in a sealed tube at 100° for 8 hr. The product was triturated with dry ether and purified by boiling in ethanol, to give the *dibromide*, m. p. 267—270° (decomp.) (Found: C, 49·4; H, 5·15; ionic Br, 23·0. $C_{28}H_{36}As_2Br_2$ requires C, 49·3; H, 5·3; ionic Br, 23·4%).

9-*Ethyl*-9-*arsafluorene* (*i.e.*, 5-ethyl-5*H*-dibenzoarsole) (IX; R = Et).—A solution of 2,2′-dibromobiphenyl (6·2 g.) in ether (100 ml.) was added dropwise to fine lithium foil (0·54 g.) during 1·5—2 hr.; the mixture was stirred at room temperature for a further 2 hr. Ethylarsonous di-iodide (7 g.) in benzene (50 ml.) was added dropwise during 30 min. and the mixture was then refluxed for 1 hr., cooled, and hydrolysed with cold air-free water. The organic layer was separated and dried (Na_2SO_4), the solvents were evaporated off, and the residue was distilled (under reduced pressure in nitrogen) to give 9-*ethyl*-9-*arsafluorene*, b. p. 120°/0·07 mm. (3·18 g., 64%) (Found: C, 65·5; H, 4·6. $C_{14}H_{13}As$ requires C, 65·65; H, 5·05%). This arsine (0·1 g.) was dissolved in an excess of methyl iodide and the mixture was heated under reflux for 2 hr. The excess of methyl iodide was distilled off, and the residue was recrystallised from light petroleum (b. p. 60—80°) with the addition of acetone to give 9-*ethyl*-9-*methyl*-9-*arsoniafluorene iodide*, m. p. 156·5—157° (decomp.) (Found C, 45·1; H, 3·6. $C_{15}H_{16}AsI$ requires C, 45·25; H, 4·0%). The *picrate* formed yellow crystals, m. p. 182—183° (from aqueous ethanol) (Found: C, 50·5; H, 3·6; N, 8·2. $C_{21}H_{18}AsN_3O_7$ requires C, 50·5; H, 3·6; N, 8·4%).

Thermal Decompositions.—(a) 2,2′-*Biphenylylenebis*(*diethylmethylarsonium*) *di-iodide*. The di-iodide (100 mg.), in a bulb-tube distillation apparatus evacuated to 0·1 mm., was heated gently until decomposition occurred, to give a mobile distillate. The distillate, dissolved in ether (1 ml.) and examined by v.p.c. at 160°, contained 2,2′-biphenylylenebisdiethylarsine, *t* 20·0 min., with similar quantities of other products (unidentified), *t* 14·4, 12·5, and 10·1 min. 9-Ethyl-9-arsafluorene was not detected.

(b) 9-*Ethyl*-9-*methyl*-9-*arsoniafluorene iodide*. The iodide (100 mg.) was decomposed in a bulb-tube apparatus to give a mobile distillate. This was dissolved in ether (1 ml.) and the ether solution, examined by v.p.c. at 134°, contained 9-methyl-9-arsafluorene (IX; R = Me), *t* 7·8 min., identified with authentic material,[27] and 9-ethyl-9-arsafluorene (IX; R = Et) *t* 10·8 min. (1 : 2).

(c) 5,5,8,8-*Tetraethyl*-5,8-*diarsonia*-1,2:3,4-*dibenzocyclooctadiene dibromide* (VIII; R = Et, *n* = 2). The dibromide (0·8 g.), in a bulb-tube distillation apparatus evacuated to 0·05 mm., was heated gently until decomposition occurred to give a viscous distillate, which was treated with ether and aqueous sodium hydrogen carbonate solution as in the case of the corresponding phosphonium salt. The dried ether extract, examined by v.p.c. at 134 and 180°, contained 9-ethyl-9-arsafluorene, *t* 10·8 min. (134°). The ether extract was evaporated and the oily residue was mixed with methyl iodide and refluxed for 2 hr. The excess of methyl iodide was distilled off. The crude methiodide resisted crystallisation and was converted into the methopicrate, m. p. 181—183° (from aqueous ethanol), identical with that of the methopicrate of 9-ethyl-9-arsafluorene.

(d) 5,5,10,10-*Tetraethyl*-5,10-*diarsonia*-1,2:3,4:7,8-*tribenzocyclodecatriene dibromide* (X; R = Et). The dibromide (1·0 g.), in a bulb-tube distillation apparatus evacuated to 0·05 mm., was heated gently; the solid decomposed with considerable decrepitation to give a viscous distillate, which was treated with aqueous sodium hydrogen carbonate and ether as in (c). The ether extract, dried (Na_2SO_4) and examined by v.p.c. at 180 and 134°, contained 9-ethyl-9-arsafluorene, *t* 10·8 min. (134°), and 2,2′-biphenylylenebisdiethylarsine, *t* 9·8 min. (180°).

We thank Dr. H. Heaney (University of Technology, Loughborough) for discussion and the provision of materials, and Dr. H. Coates (Messrs. Albright & Wilson Ltd.) for gifts of materials.

[7/317 *Received, March* 16*th*, 1967]

---

[27] J. A. Aeschlimann, N. D. Lees, N. P. McCleland, and G. N. Nicklin, *J. Chem. Soc.*, 1925, **127**, 66.