726. *The Synthesis and Stereochemistry of* 5,10-*Disubstituted* 5,10-*Dihydrophosphanthrens and their Derivatives.*

By M. Davis and Frederick G. Mann.

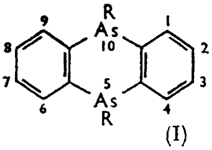
The synthesis of 5,10-diethyl(and diphenyl)-5,10-dihydrophosphanthren is described, with a brief discussion of some of the by-products in the syntheses. The diethyl member has been isolated in two isomeric forms, the stereochemistry of which is discussed; the diphenyl member was obtained in only one form.

Two isomeric forms of the quaternised dibenzyl dihalides have been obtained from the diethylphosphanthren, and also two forms of the dioxides from the diethyl- and the diphenyl-phosphanthren. The tricyclic system must be effectively planar in both these types of derivative, the isomers being the *cis*- and the *trans*-forms. The configurational identity of the dioxides has been determined by dipole-moment measurements, and the isomeric relationships between the various types of derivative are discussed. The structures of the palladobromides of these phosphanthrens and of the oxidation product of composition $C_{16}H_{18}O_2P,H_2O_2,2H_2O$, which the diethylphosphanthren gives with hydrogen peroxide, are discussed.

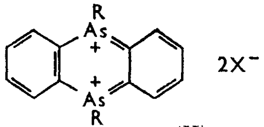
Certain chemical differences between the above phosphanthrens and analogous arsanthrens are demonstrated.

5,10-Diphenyl(and 10-ethyl-5-phenyl)-5,10-dihydro-5-phospha-10-arsa-anthracene have been synthesised, and their general chemistry more briefly investigated.

The chemistry of derivatives of 5,10-dihydroarsanthren (I; R = H) is now reasonably elucidated. The 5,10-dichloro-compound (I; R = Cl) was first synthesised by Kalb,[1] the 5,10-di-*p*-tolyl compound (I; R = C_6H_4·Me-*p*) was obtained in two isomeric forms by Chatt and Mann,[2] and the general chemistry of the 5,10-dimethyl compound (I; R = Me) and its many derivatives was studied in detail by Jones and Mann.[3] It was shown that



(I)



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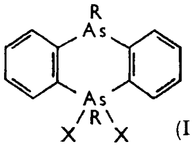

(III)

the dibromo-derivatives of the ditertiary arsines (I; R = Me or C_6H_4·Me-*p*) formed salts of type (II; X = Br) in solution,[2,3] and the compounds (II; R = Me, X = Br or I) existed in the crystalline state as isomeric covalent compounds (III; X = Br or I);[4] the di-iodide (III; R = Me, X = I) in organic solvents formed a tautomeric mixture of the forms (II; R = Me, X = I) and (III; R = Me, X = I).[3,5]

Derivatives of the 5,10-dihydrophosphanthren system (IV; R = H) have now been

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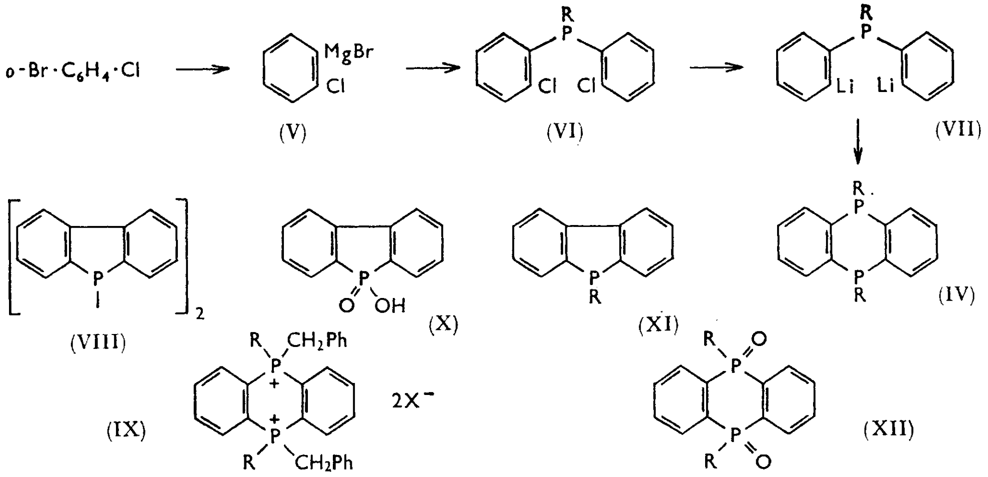
[1] Kalb, *Annalen*, 1921, **423**, 39.
[2] Chatt and Mann, *J.*, 1940, 1184.
[3] Emrys R. H. Jones and Mann, *J.*, 1955, 411.
[4] Sutor and Harper, *Acta Cryst.*, 1959, **12**, 585.
[5] Mann, *J.*, 1963, 4266.

synthesised for studies of the stereochemistry of this novel heterocyclic system and comparison of its properties with those of analogous arsanthren derivatives. The synthetic method is largely based on that earlier employed to prepare *o*-arsinophenylphosphines[6] and *o*-phenylenediphosphines.[7]

o-Bromochlorobenzene, treated in ether with magnesium (1·05 equiv.), gave the Grignard reagent (V) which with ethylphosphonous dichloride, $EtPCl_2$ (0·5 equiv.), gave the crystalline phosphine (VI; R = Et) in 39% yield. This phosphine in tetrahydrofuran at −35° was stirred with lithium (4 equiv.) until formation of the dilithio-compound (VII; R = Et) was apparently complete, and the black solution was cooled to *ca.* −65° while the phosphonous dichloride (1 equiv.) was again added. The mixture was hydrolysed at room temperature, and the dried organic layer gave an unbroken fraction, b. p. 100—200°/0·4 mm., collected as three intermediate fractions. The first fraction contained ethyldiphenylphosphine, produced by the hydrolysis of some unchanged dilithio-compound (VII; R = Et), and identified as the methiodide and ethiodide. All three fractions contained the required 5,10-diethyl-5,10-dihydrophosphanthren (IV; R = Et) and (unexpectedly) the highly crystalline yellow 9,9′-bi-(9-phosphafluorenyl) (VIII), with other unidentified products. The compounds (IV; R = Et) and (VIII), which apparently codistil, could be separated by the addition of ethanol to the fractions, when the insoluble diphosphine (VIII) separated almost quantitatively; the ethanolic filtrates, when warmed with benzyl iodide, then deposited the quaternary di-iodide (IX; R = Et, X = I). A marked characteristic of phosphanthrens of type (IV) is the almost complete insolubility of most of their di-quaternary bromides and iodides in common organic solvents.



(V) (VI) (VII) (VIII) (X) (XI) (IV) (IX) (XII)

The identification of the diphosphine (VIII) is based on analysis and molecular weight (Rast), and the following. (a) Aerial oxidation of a boiling suspension of the diphosphine in chloroform gave the acid (X), identified also as its sodium and benzylthiouronium salts. (b) An excess of hot benzyl bromide gave the crystalline quaternary bromide of 9-benzyl-9-phosphafluorene (XI; $R = CH_2Ph$), which in turn gave the corresponding picrate. (c) The diphosphine (VIII) when treated in ether with iodine (1 mol. equiv.) gave a clear solution of 9-iodophosphafluorene (XI; R = I), which with phenylmagnesium iodide gave crystalline 9-phenyl-9-phosphafluorene (XI; R = Ph), further identified by conversion by hydrogen peroxide into the oxide.

The diphosphine (VIII) is a comparatively stable compound, presumably because the

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[6] Emrys R. H. Jones and Mann, *J.*, 1955, 4472.
[7] Hart, *J.*, 1960, 3324.

phosphorus atoms are sterically protected. Its origin remains uncertain. The 2-chloro-2′-lithio-phosphine, which must be an intermediate in the stage (VI) ⟶ (VII), could readily cyclise to give 9-ethyl-9-phosphafluorene (XI; R = Et); this would then require ejection of the ethyl group by the lithium (a reaction which occurs more readily with aryl groups),[8] followed by hydrolysis to the secondary cyclic phosphine, and then atmospheric oxidation to the diphosphine. We have, however, failed to detect any of the phosphine (XI; R = Et) as an intermediate; the operations were all conducted under nitrogen; secondary phosphines on atmospheric oxidation usually give secondary phosphine oxides and not diphosphines.

The tricyclic system in the cation of a salt such as the di-iodide (IX; R = Et, X = I) must be almost flat, in view of the tetrahedral angle at the phosphorus atoms; this is confirmed by models, which, although not completely flat, " flex " readily about the planar position. Consequently, the salt should exist in a *cis*- and a *trans*-form. The crude di-iodide, prepared from the above ethanolic solutions after removal of the diphosphine (VIII), was separated into two forms, one (m. p. 326°) being insoluble in boiling water, and the other (m. p. 320—321°) (formed in very small amount) moderately soluble; these gave dipicrates, m. p. 300 and 241—244°, respectively. The quaternary dibromides were separated, by ethanolic extraction, into two forms, m. p. 346 and 319°, which gave the same respective picrates.

The di-iodide (IX; R = Et, X = I), m. p. 326°, when treated with warm aqueous sodium hydroxide, gave toluene and the dioxide (XII; R = Et), m. p. 235°; the isomeric iodide, m. p. 320—321°, gave the isomeric dioxide, m. p. 257°. The dipole moment of the symmetric *trans*-dioxide (XII; R = Et) must be zero, whereas that of the *cis*-dioxide will have a finite value. Insufficient material prevented the determination of the dipole moment of the dioxide of m. p. 257°, but that with m. p. 235° had a moment of 4·0 D, and must therefore be the *cis*-isomer. This is not, however, decisive evidence that the di-iodide of m. p. 326° is also the *cis*-form (cf. p. 3775).

The 5,10-diethyl-5,10-dihydrophosphanthren (IV; R = Et) was regenerated from the quaternary di-iodide (m. p. 326°) by reduction with lithium aluminium hydride,[9] and, after distillation and recrystallisation from ethanol and methanol, had m. p. 52—53°; the methanolic mother-liquors slowly deposited a second form, m. p. 96—97°. The two forms had the same composition and molecular weight, and a mixture had m. p. 43—50°. Our study of the reactions of this compound was largely limited to the form with m. p. 52—53°, for the second form was obtained in very small amount. Moreover, later preparations often gave a product, m. p. 46—51°, which resisted fractional crystallisation. Chatt and Mann,[2] when separating 5,10-dihydro-5,10-di-*p*-tolylarsanthren (I; R = C_6H_4·Me-*p*) into two forms, m. p. 178—179 and 179—181°, respectively, having a mixed m. p. 144—158°, occasionally encountered a product, m. p. 130—136°, which similarly did not readily lend itself to the fractional crystallisation by which the two isomers had been separated.

The diethylphosphanthren (IV; R = Et), m. p. 52—53°, has moderate basic properties. It dissolves in cold 5N- but not in 2N-hydrochloric acid; in ethanolic solution it deposits a deep reddish-purple picrate, which decomposes on exposure to air and cannot be recrystallised without dissociation.

Chatt and Mann noted that in simple symmetric arsines, AsR_3, where R is halogen or alkyl, the average intervalency angle is *ca.* 98°, and that, if in arsanthrens of type (I) the arsenic atoms retained this angle, the tricyclic system must be folded about the As---As axis, and such molecules should exist in a *cis*-form (as A1) and a *trans*-form (as B1). It was on this basis that the arsanthren (I; R = C_6H_4·Me-*p*) was synthesised and studied.[2] In a preliminary Note,[10] published after completion of the present work, we attributed the same basis for the two forms of our phosphanthren, namely the *cis*-form (A1) and the

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[8] Wittenberg and Gilman, *J. Org. Chem.*, 1958, **23**, 1063; Chatt and Hart, *J.*, 1960, 1378.

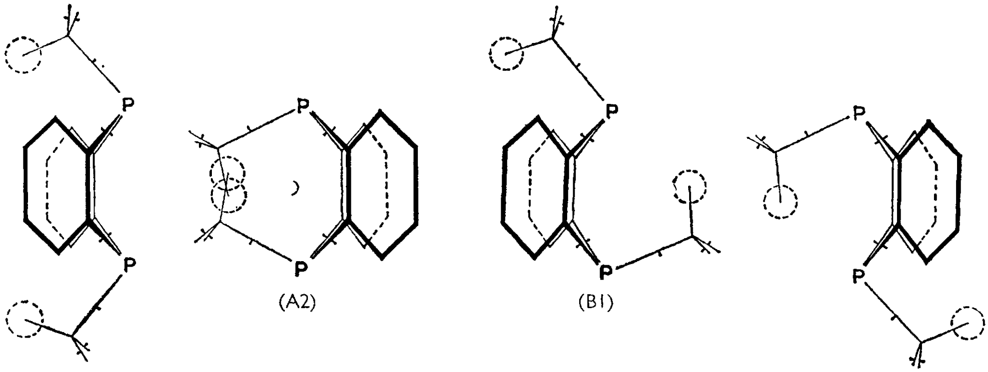
[9] Bailey and Buckler, *J. Amer. Chem. Soc.*, 1957, **79**, 3567.

[10] Davis and Mann, *Chem. and Ind.*, 1962, 1539.

trans-form (B1), for in symmetric compounds PR_3 the average intervalency angle at the phosphorus atom is also *ca.* 98°.

Mislow *et al.*[11] recently adduced theoretical evidence that the *cis*- and *trans*-forms of arsanthrens (I) and phosphanthrens (IV) can each " flex " readily about the planar conformation of the tricyclic system, and they consider that each form in solution can be regarded as having this conformation, with the pyramidal As or P atoms providing the configurational difference.

Mrs. Olga Kennard has prepared accurate Dreiding models of 5,10-dihydro-5,10-dimethylphosphanthren (IV; R = Me), having an intervalency angle of 98° around each phosphorus atom, and hence having the folded or " butterfly " conformation of the tricyclic ring; methyl groups were chosen to ensure minimum steric obstruction. These models, constructed to allow rotation of the P–aryl bonds without change of intervalency angles, show that the flexing about the planar tricyclic conformation does occur moderately easily, although the models slip readily from the planar back to the less strained " folded " conformation. The models illustrate the following factors. (a) When the *trans*-form (B1) is flexed completely over (to B2), it still has this form, and therefore no configurational change (*cis* $\rightleftharpoons$ *trans*) occurs in the flexing process. (b) Similar complete flexing of the *cis*-form (A1) produces the form (A2) in which there is insufficient space for even the two methyl groups if allowance is made for the effective size of the hydrogen atoms; consequently the flexing process over to the *cis*-conformation (A2) must remain incomplete to accommodate these groups. With larger groups R the flexing would obviously be even less complete. Mislow *et al.*[11] note this in their statement regarding the arsanthrens: " though we grant that special factors (such as very large 5,10-substituents) may lead to a situation where one of the two diastereomeric * ' exo ' and ' endo ' isomers of the *cis*-form exists as by far the most populous component in the mobile configurational equilibrium."



(A1) (A2) (B1) (B2)

5,10-Dihydro-5,10-dimethylphosphanthren (IV; R = Me). Diagrams based on photographs of the scale models. The phosphorus atoms, the carbon atoms of the methyl groups, and one C–H bond of each methyl group are depicted in the plane of the paper, the size of the hydrogen atom in these C–H groups being indicated by dotted circles. The molecule is folded about the P---P axis, one *o*-phenylene group (shown in thick lines) projecting towards, and the other away from, the observer. The boundary of the phosphorus atoms along the P–C bonds, and that of the carbon atoms along the C–H bonds of the methyl groups, are indicated by a notch in each bond. The C–H bonds of the central methyl groups in (A2) are (exceptionally) not in the plane of the paper because of mutual obstruction; in the model of (A2) these crossed bonds are in contact, but the hydrogen atoms would force them further apart.

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* This term reveals some confusion of thought. The arsanthrens of type (I), to which the statement refers, have no asymmetric atoms or molecular dissymmetry, irrespective of any folding about the As---As axis, and they cannot be diastereoisomers.

[11] Mislow, Zimmerman, and Melillo, *J. Amer. Chem. Soc.*, 1963, **85**, 594.

The " crowded " *cis*-form (A2) will be less stable than the *cis*-form (A1), and the *cis*- and *trans*-isomers will almost certainly crystallise in the most stable conformations, (A1) and (B1), respectively. Clearly, this flexing process of (A1) or (B1) does not involve any interconversion of the *cis*–*trans* forms.

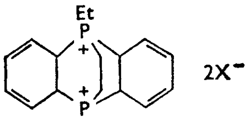
The available experimental evidence strongly supports the " folded " conformation in the solid state. The calculated angle subtended at the As—As axis by the *o*-phenylene groups in arsanthrens of type (I) is 121° if the intervalency angle of the arsenic atom is 98°. The *X*-ray structure evidence of the compounds (III; R = Me, X = Br or I) shows that the 5-covalent arsenic atom is approaching a trigonal bipyramid configuration, which by increasing the intervalency angle within the ring at this atom would tend to flatten the tricyclic system. The tervalent arsenic atom, however, retains its pyramidal configuration; consequently, the angle subtended at the As- - -As axis adopts an intermediate value of *ca.* 157°.[12,13] *X*-Ray investigations on the crystalline arsanthrens (I) and phosphanthrens (IV) are now proceeding, to determine the shape of the tricyclic system in these parent compounds.

It is noteworthy that the two forms of the phosphanthren (IV; R = Et) have reasonably high thermal stability; a sample of each form, when heated at 4° above its melting point and then cooled, crystallised without change of melting point.

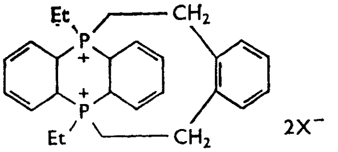
The configurations of our phosphanthrens (IV; R = Et) have not been decisively established, but the following evidence indicates that the form with m. p. 52—53° has very probably the *cis*-configuration (A1). The experiments (A)—(C) were made solely with this form.

(A) The phosphanthren, when oxidised in acetone–hydrogen peroxide, gave a compound of composition $C_{16}H_{18}O_2P_2,H_2O_2,2H_2O$, whose structure is discussed below (p. 3777). This compound, when warmed with aqueous sodium hydroxide, gave the dioxide (XII; R = Et), m. p. 234—235°, which has the *cis*-configuration.

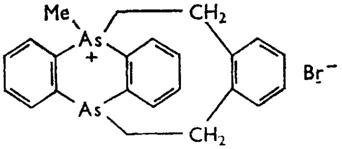
(B) The phosphanthren united very vigorously with 1,2-dibromoethane by cyclic diquaternisation, to give the dibromide (XIII; X = Br), which in turn gave a dipicrate (XIII; X = $C_6H_2N_3O_7$). Models show that the ethano bridge forms an almost strainless cyclic system about the two tetrahedral phosphorus atoms in the cation (XIII), but this system could only be formed initially from the *cis*-form (A1).



(XIII)



(XIV)



(XV)

o-Xylylene dibromide also united with the phosphanthren, to give the dibromide (XIV; X = Br); in this case there is a possibility that, in order to relieve strain, two molecules of *o*-xylylene dibromide united with two molecules of the phosphanthren. The formation of each type of salt, however, requires the phosphanthren to have the *cis*-configuration. Some evidence by analogy is available for the " monomer " (XIV). 5,10-Dihydro-5,10-dimethylarsanthren (I; R = Me) combines with *o*-xylylene dibromide to form at least two compounds; one of these, formed with the loss of one equivalent of methyl bromide, is the monobromide (XV), whose structure has been determined by *X*-ray crystal analysis.[3] The di-arsine (XVI) unites with *o*-xylylene dibromide to give a bridged monomer of type (XIII), whose structure has been similarly determined.[14]

(C) The phosphanthren co-ordinates with palladium dibromide to give a microcrystalline insoluble compound of composition $C_{16}H_{18}P_2,PdBr_2$. The structure of this compound,

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[12] Sutor and Harper, *Acta Cryst.*, 1959, **12**, 585.
[13] Mann, *J.*, 1963, 4266.
[14] Emrys R. H. Jones and Mann, *J.*, 1955, 405.

particularly as a monomer or dimer, is discussed later, but again each form requires the phosphanthren to be initially in the *cis*-form (A1).

It is noteworthy that the monoethiodide of the phosphanthren (IV; R = Et), m. p. 52—53°, when treated in aqueous ethanol with sodium picrate gave the crystalline double quaternary picrate—sodium picrate, $C_{24}H_{25}N_3O_7P_2,C_6H_2N_3NaO_7$, and with picric acid gave a similar picrate—hydrogen picrate; both salts could be recrystallised unchanged. (The diethiodide when similarly treated with each reagent gave solely the normal diethopicrate.) The formation of such double picrates occurs with many methyl-quaternised heterocyclic amines,[15] but this is apparently the first recorded example in derivatives of the other Group V elements.

We have similarly synthesised 5,10-dihydro-5,10-diphenylphosphanthren (IV; R = Ph) by the interaction of the Grignard reagent (V) (2 equiv.) and phenylphosphonous dichloride, which gave di-(*o*-chlorophenyl)phenylphosphine (VI; R = Ph) and some lower-boiling *o*-chlorophenylphenylphosphine, (o-Cl·C_6H_4)PPhH, identified both by oxidation to the phosphinic acid and conversion with benzyl bromide into the dibenzyl-*o*-chlorophenylphenylphosphonium bromide. The phosphine (VI; R = Ph) was converted into the dilithio-derivative (VII; R = Ph), which with an equivalent of the phosphonous dichloride gave the diphenylphosphanthren (IV; R = Ph), with some diphenylphosphine and a small proportion of the diphosphine (VIII).

The diphenylphosphine may arise in this second stage by some of the lithium splitting one of the o-Li·C_6H_4–P bonds of the compound (VII; R = Ph) to form LiPPh(C_6H_4·Li-*o*), or similarly splitting the Ph–P bond, so that later hydrolysis would give diphenylphosphine. The origin of the *o*-chlorophenylphenylphosphine during the earlier Grignard stage is obscure.

The phosphanthren (IV; R = Ph) was isolated as the insoluble quaternary dibromide (IX; R = Ph, X = Br); the sharp melting point of this salt and of the dipicrate indicated that they were probably isomerically pure. The dibromide, on reduction with lithium aluminium hydride, gave the pure phosphanthren, m. p. 184—187°, and on treatment with hot aqueous sodium hydroxide gave the dioxide (XII; R = Ph), m. p. >400°, and the monoxide, m. p. 231—232·5°. The phosphanthren, on oxidation with hydrogen peroxide, gave the isomeric dioxide (XII; R = Ph), m. p. 276—278°; the infrared spectra of the two isomeric dioxides were almost identical. The dioxide with m. p. >400° was too slightly soluble in benzene for dipole moment determinations, but the isomer of m. p. 276—278° had a dipole moment of 3·4 D in benzene solution and therefore is almost certainly the *cis*-form.

The formation of the monoxide in addition to the dioxide in the above reaction of sodium hydroxide on the pure dibromide (IX; R = Ph, X = Br) is remarkable. It shows that the hydroxide, in addition to the normal reaction with a benzylphosphonium salt to give toluene and the tertiary phosphine oxide, can give the hitherto unrecorded conversion into the tertiary phosphine, by loss of the benzyl group.

The configurational relationships of our phosphanthren derivatives cannot at present be fully elucidated. It is known that there is no configurational inversion when a dissymmetric tertiary phosphine is converted by hydrogen peroxide into the phosphine oxide, or by benzyl iodide into the quaternary benzylphosphonium salt, or when such salts undergo cathodic reduction to the tertiary phosphine, but that the conversion of the benzylphosphonium salts by aqueous sodium hydroxide into the phosphine oxides is accompanied by inversion.[16,17] These results have been obtained, however, with compounds in which the phosphorus atom has not been restricted as a member of a ring system.

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[15] Mann and Baker, *J.*, 1961, 3845.

[16] Kumli, McEwen, and VanderWerf, *J. Amer. Chem. Soc.*, 1959, **81**, 248; Kumli, VanderWerf, and McEwen, *ibid.*, p. 3805.

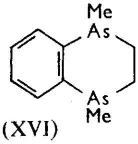
[17] Horner, Winkler, Rapp, Mentrup, Hoffmann, and Beck, *Tetrahedron Letters*, 1961, 161; Horner, Fuchs, Winkler, and Rapp, *ibid.*, 1963, 965.

In our diphenylphosphanthren series, the following relationships hold: the quaternary dibromide (m. p. 387°) gives the *trans*-dioxide (m. p. >400°) on treatment with sodium hydroxide; with lithium aluminium hydride it gives the phosphanthren (m. p. 184—187°) which is converted by hydrogen peroxide into the *cis*-dioxide (m. p. 276—278°). The configuration of the *cis*-dioxide is shown by its dipole moment (3·4 D); therefore, the phosphanthren of m. p. 184—187° is also *cis*. If the reduction of the dibromide is unaccompanied by inversion, this salt also has the *cis*-configuration. This would mean, however, that the action of sodium hydroxide on the dibromide has caused inversion at only one phosphorus atom, since inversion at both would leave the configuration unchanged. Alternatively, the dibromide may have the *trans*-configuration, and the inversion at one phosphorus atom may have occurred during the reduction stage or the subsequent distillation of the free phosphanthren. There is some indecisive evidence that the quaternisation of the phosphanthren with methyl iodide may give rise to isomeric dimethiodides (p. 3783), a process which would have some analogy to the racemisation which 10-methylphenoxarsine-2-carboxylic acid (5,10-dihydro-10-methyl-5-oxa-10-arsa-anthracene-2-carboxylic acid) undergoes during quaternisation with ethyl iodide.[18]

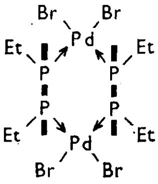
In the diethylphosphanthren series, it is similarly uncertain whether the mixture of the *cis*-phosphanthren (m. p. 52—53°) with the trace of the *trans*-isomer (m. p. 96—97°) arose from inversion at one phosphorus atom during reduction of the di-iodide or during the subsequent distillation of the phosphanthren, or whether the iodide was not quite isomerically pure. It should be emphasised that in this series no evidence of direct interconversion (*cis* $\rightleftharpoons$ *trans*) of the phosphanthrens was obtained.

The *cis*-configuration of the phosphanthren (IV; R = Ph) is supported by the formation of a deep red palladobromide complex of composition $C_{24}H_{18}P_2,PdBr_2$. This compound, like its orange diethyl analogue, was insoluble in all solvents investigated, but careful adjustment of the conditions (temperature and concentration) of preparation gave deposition of the compound in minute crystals.

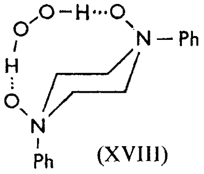
The constitution of this compound is of interest. The co-ordinated phosphorus atoms would undoubtedly be tetrahedral, a factor which would almost certainly prevent formation of a monomer by co-ordination of one palladium atom to the two phosphorus atoms of the phosphanthren, either by extreme flexing of the *cis*-form (A2) or by adoption of the normal planar configuration of the tricyclic system, as in the di-quaternary salts (IX) and the dioxides (XII).



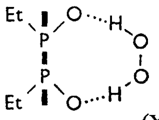
(XVI)



(XVII)



(XVIII)



(XIX)

A completely strainless structure would be provided by a dimer (XVII), in which all the molecule is shown in the plane of the paper except the two planar tricyclic systems, which are each represented by a broken line and are at right angles to this plane.

The crystals of the diphenylphosphanthren compound were too minute for *X*-ray structure determination, and a detailed investigation of the minimum molecular weight by *X*-ray powder photographs, kindly undertaken by Mrs. O. Kennard and Professor P. M. de Wolff, gave an inconclusive result (p. 3785), owing partly to the monoclinic nature of the crystals. The composition of the crystals, however, almost certainly requires a *cis*-arrangement of each pair of phenyl groups.

The nature of the compound of composition $C_{16}H_{18}O_2P_2,H_2O_2,2H_2O$, prepared by the

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[18] Lesslie and Turner, *J.*, 1934, 1170.

action of hydrogen peroxide on the diethylphosphanthren (IV; R = Et), is of great interest, but insufficient material precluded a detailed study of its structure. This compound forms colourless crystals, m. p. 128° (effervescence) from toluene–petroleum, and has a camphor-like odour. It is surprisingly volatile; a sample rapidly disappeared from a watch-glass kept at 100°, and the compound sublimed at 100°/15 mm. without change in melting point. Its infrared spectrum showed strong OH absorption at about 3250 $cm.^{-1}$, but only a very weak P–O band at 1260 $cm.^{-1}$. Warm aqueous sodium hydroxide converted it into the dioxide (XII; R = Et), which could not be reconverted into the compound by hydrogen peroxide.

Bennett and Glynn[19] found that 1,4-diphenylpiperazine with aqueous hydrogen peroxide in acetic acid gave a crystalline product of composition $C_{16}H_{18}N_2O_2,H_2O_2,2H_2O$. They suggested that " the hydrogen peroxide unit formed a bridge, with hydrogen bonds between the two oxygen atoms of the dioxide, which must therefore have the *cis*-configuration," and have the structure as (XVIII). Mann and Millar[20] showed that 1,4-diphenyl-1-aza-4-phosphacyclohexane when heated in acetic acid with hydrogen peroxide at 70—80° gave an apparently similar hydrogen peroxide adduct, of composition $C_{16}H_{18}NO_2P,H_2O_2,H_2O$ (although in acetone under similar conditions it gave solely the monoxide). The phosphanthren compound would on this basis have the structure (XIX), in which all the molecule is shown in the plane of the paper, except the planar tricyclic system which is at right angles to this plane and indicated by the broken line.

Although this large peroxide ring might be stabilised by the puckering enforced by the structure of the hydrogen peroxide molecule,[21, 22] this formulation does not explain the very weak P–O band for this compound, or the function (and true condition) of the water molecules that are present in the three known compounds of this class. Its structure therefore remains uncertain.

It is noteworthy that triphenylphosphine (or its oxide) with hydrogen peroxide gives a crystalline adduct, $[Ph_3PO]_2,H_2O_2$, whose infrared spectrum suggests a hydrogen-bonded structure.[23] Furthermore, a spirocyclic compound having two phosphoryl groups, and giving an adduct with butane-1,4-diol, has also been recently reported; a similar hydrogen-bonding of the diol to the P–O groups is suggested.[24]

To investigate the possible formation of phosphanthren salts analogous to the arsenic compounds (II), iodine (one mol. equiv.) was added in ethereal solution to the diethyl- and the diphenyl-phosphanthrens, producing, respectively, a yellow and an orange precipitate, undoubtedly the analogues of the covalent dihalides (III). The yellow diethyl product was very deliquescent, and hydroxylic solvents gave colourless solutions from which no salt-like compound could be isolated. The orange diphenyl compound had rather greater stability, but gave a colourless solution in ethanol, from which the addition of water deposited the monoxide. This result was not unexpected, for the 5-covalent phosphine dihalides of type R_3PBr_2, as in (III), are far more readily hydrolysed than their arsine analogues, as in (III).

We have investigated more briefly the synthesis of the analogous 5-phospha-10-arsa-anthracene system (XX). The 2,2′-dilithiotriphenylphosphine (VII; R = Ph), prepared as before, was treated with phenylarsonous dichloride (1 equiv.). The product, worked up as before and distilled at 0·009 mm., yielded two main fractions and a small intermediate fraction. The lowest fraction contained triphenylarsine and 9-phosphafluorene (XI; R = H), identified, after treatment with methyl iodide and then sodium picrate, by the isolation of methyltriphenylarsonium picrate and 9,9-dimethyl-9-phosphoniafluorene picrate, respectively. The highest fraction, when rubbed with acetone, gave the crystalline

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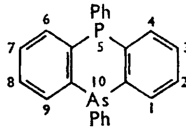
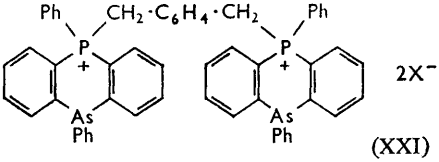
[19] Bennett and Glynn, *J.*, 1950, 211.
[20] Mann and Millar, *J.*, 1952, 3039.
[21] Penney and Sutherland, *Trans. Faraday Soc.*, 1934, **30**, 898.
[22] Lu, Hughes, and Giguère, *J. Amer. Chem. Soc.*, 1941, **63**, 1507.
[23] Temple, Tsuno, and Leffler, *J. Org. Chem.*, 1963, **28**, 2495.
[24] Rätz and Sweeting, *J. Org. Chem.*, 1963, **28**, 1608.

5,10-dihydro-5,10-diphenyl-5-phospha-10-arsa-anthracene (XX); this was isolated in only one form, and no other crystalline compound could be isolated from this fraction.

The compound (XX) when heated with methyl iodide, or even with methyl toluene-*p*-sulphonate at 180° for 4 hours and then treated with sodium iodide, gave only a mono-methiodide, in which, undoubtedly, the more reactive phosphine group had been quaternised, with considerable deactivation of the arsine group. Vigorous treatment of the compound (XX) with benzyl bromide similarly gave a mono(quaternary bromide); the structure of this salt was shown conclusively by its conversion with aqueous sodium hydroxide into the monoxide, whose infrared spectrum showed a strong P–O band. A very small quantity of a dibromide was obtained as a very insoluble powder which gave a crystalline dipicrate.



(XX)



(XXI)

The monoxide, when treated in acetone with hydrogen peroxide, gave the dioxide without intermediate formation of a peroxide addition product.

The phospha-arsa-anthracene (XX) showed the following reactions. (a) With palladium dibromide it gave insoluble orange crystals of composition $C_{24}H_{18}AsP,PdBr_2$. (b) With bromine (1 equiv.) in carbon tetrachloride it gave a yellow precipitate, which on treatment with ethanol gave the dioxide in low yield, neither the monoxide nor a salt of type (II) being detected. (c) It gave no crystalline derivatives with 1,2-dibromoethane or 1,3-dibromopropane, but with *o*-xylylene dibromide it gave the " double " compound (XXI; X = Br), again illustrating the marked deactivation of the tertiary arsine atoms by the positive charges on the phosphonium atoms.

When the dilithio-derivative (VII; R = Ph) was similarly treated with ethylarsonous dichloride, the crude product on distillation underwent considerable decomposition with deposition of arsenic, but the small amount of distillate contained 10-ethyl-5,10-dihydro-5-phenyl-5-phospha-10-arsa-anthracene which on treatment with benzyl bromide gave the quaternary mono- and the di-bromides, identified as their crystalline picrates. The ethylarsine group in the parent compound would have greater activity than that of the phenylarsine group in compound (XX), and hence could more successfully resist the deactivating influence of the quaternary phosphonium group.

EXPERIMENTAL

All compounds were colourless, except the yellow diphosphine (VIII), the yellow picrates, and the orange-red palladobromides. Molecular weights were determined in dichloromethane by the vapour-pressure thermistor technique. The term " petroleum " is used throughout for light petroleum of b. p. 60—80°.

Ethylphosphonous Dichloride.—The original preparation,[25] although subsequently improved,[26] still gave a product requiring careful fractionation; the following conditions give the product in high yield. Tetraethyl-lead (356 g.) was added to phosphorus trichloride (454 g., 3 mol.), and the stirred mixture was heated under reflux in nitrogen at 110—115° for 36 hr. Distillation gave the almost pure dichloride (380 g., 87%), b. p. 110—112°; redistillation gave the pure dichloride, b. p. 111°.

*Di-(*o*-chlorophenyl)ethylphosphine* (VI; R = Et).—A solution of *o*-bromochlorobenzene (383 g.) in ether (800 ml.) was slowly added to magnesium turnings (51 g., 1·05 atom) containing an iodine crystal, the first 50 ml. of the solution being diluted with ethyl bromide (5·45 g., 0·025 mol.). The reaction started readily, and the addition of the solution was adjusted to maintain boiling (*ca.* 2 hr.). The mixture was then boiled for 1 hr., cooled, treated during 1¼ hr. with a solution

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[25] Kharasch, Jensen, and Weinhouse, *J. Org. Chem.*, 1949, **14**, 429.
[26] Beeby and Mann, *J.*, 1951, 411.

of ethylphosphonous dichloride (134 g., 0·51 mol.) in ether (150 ml.), stirred for 1 hr. more, and then hydrolysed with dilute sulphuric acid. The residue, after removal of the solvent from the ethereal layer, on rapid distillation gave a total fraction (146 g.), b. p. 100—184°/0·4 mm., which gave *the phosphine* (VI) (110 g., 39%), m. p. 85 (from ethanol, 150 ml.) (Found: C, 59·5; H, 4·7. $C_{14}H_{13}Cl_2P$ requires C, 59·4; H, 4·6%). It gave a syrupy ethiodide, which was converted into the *di-(*o*-chlorophenyl)diethylphosphonium picrate*, m. p. 104—105° (Found: C, 49·1; H, 3·8; N, 7·8. $C_{22}H_{20}Cl_2N_3O_7P$ requires C, 48·8; H, 3·7; N, 7·8%).

5,10-*Diethyl*-5,10-*dihydrophosphanthren Dibenzyl Quaternary Salts* (IX; R = Et).—Fine clean strips of lithium foil (7·2 g., 4 atoms) were added to a stirred solution of the phosphine (VI) (73·1 g.) in pure tetrahydrofuran (700 ml.) cooled to *ca.* −35°. After 2½ hr., the almost black solution was cooled to *ca.* −65° and treated dropwise with ethylphosphonous dichloride (33·8 g., 1 mol.) in tetrahydrofuran (60 ml.), the colour of the mixture fading considerably. The stirred mixture was allowed to reach room temperature (3 hr.) and then treated with water (100 ml.) and benzene (200 ml.). The organic layer was separated, the aqueous layer re-extracted with benzene (50 ml.), and the united dried extracts distilled, giving finally three fractions at 0·4 mm.: (A) b. p. 100—129° (mostly 117—118°), 6·5 g.; (B) b. p. 130—152°, 21·4 g.; (C) b. p. 153—200°, 14·1 g.

A portion of fraction (A), boiled with ethanolic ethyl iodide, afforded diethyldiphenylphosphonium iodide, m. p. 210° (lit.,[27] 207—208°) after four recrystallisations from ether–ethanol (Found: C, 52·3; H, 5·4. Calc. for $C_{16}H_{20}IP$: C, 51·9; H, 5·4%). The methiodide, similarly prepared, had m. p. and mixed m. p. 186—188° (lit.,[28] 182—183°).

The fractions (A), (B), and (C), when each diluted with air-free ethanol, deposited 9,9′-*bi*-(9-*phosphafluorenyl*) (VIII) (total, 1·5 g.), yellow prisms, m. p. 242—243° (from pyridine) [Found: C, 78·5; H, 4·6%; *M* (Rast), 388. $C_{24}H_{16}P_2$ requires C, 78·7; H, 4·4%; *M*, 366].

Air was passed for 10 min. through a boiling suspension of this compound (0·362 g.) in chloroform (10 ml.), and the clear solution, cooled and diluted with ether, deposited the phosphinic acid (X) (0·2 g.), m. p. 252° (decomp.) (lit.,[29] 253—257°) (from aqueous ethanol) (Found: C, 66·6; H, 3·8. Calc. for $C_{12}H_9O_2P$: C, 66·6; H, 4·2%). The acid formed a *benzylthiouronium salt*, m. p. 214—215° (decomp.) [from ethanol–light petroleum (b. p. 40—60°)] (Found: C, 62·6; H, 5·0; N, 7·3. $C_{20}H_{19}N_2O_2PS$ requires C, 62·8; H, 5·0; N, 7·3%). The *sodium salt trihydrate*, recrystallised from aqueous ethanol, was unmelted at 360° (Found: C, 49·8; H, 5·2. $C_{12}H_8NaO_2P,3H_2O$ requires C, 49·7; H, 4·9%).

A suspension of the diphosphine (VIII) in ethanol (5 ml.), dimethylformamide (5 ml.), and benzyl bromide (1·0 g.), when boiled under reflux, gave a vigorous reaction. The clear solution, when cooled and diluted with ether, deposited 9,9-*dibenzyl*-9-*phosphoniafluorene bromide monoethanolate*, m. p. 263—264°, from ethanol–ether, unaffected by heating at 120°/0·2 mm. for 15 hr. (Found: C, 68·7; H, 5·6. $C_{26}H_{22}BrP,C_2H_6O$ requires C, 68·5; H, 5·7%); this gave the *picrate*, m. p. 188—189° (from aqueous ethanol) (Found: C, 64·9; H, 4·0; N, 7·1. $C_{32}H_{24}N_3O_7P$ requires C, 64·7; H, 4·0; N, 7·1%).

A solution of iodine (0·254 g., 1 mol.) in ether (5 ml.) was added to a suspension of the diphosphine (0·366 g.) in ether (5 ml.), which was shaken for 1 hr. The clear yellow solution, when decanted from some black sludge and added to ethereal phenylmagnesium bromide, on working up gave 9-phenyl-9-phosphafluorene (XI; R = Ph), m. p. 91° (lit.,[30] 93—94°) (from methanol) (Found: C, 82·5; H, 4·9. Calc. for $C_{18}H_{13}P$: C, 83·0; H, 5·0%); its infrared spectrum was identical with that recorded. Oxidation with hydrogen peroxide gave the phosphine oxide, m. p. 164—165° (lit.,[30] 165°) (from toluene–petroleum).

The combined ethanolic mother-liquors from fractions (B) and (C), when treated with benzyl iodide (50 g.), became hot; next day the deposited mixture of the di-iodides (IX; R = Et, X = I) were collected, and washed with ethanol, acetone, and ether. The dry product (11·0 g.) was thoroughly extracted with boiling water. The united extracts deposited one form of the *di-iodide* as a *hemihydrate*, leaflets, m. p. 320—321°, after five recrystallisations from water (Found: C, 50·1; H, 4·5. $C_{30}H_{32}I_2P_2,\frac{1}{2}H_2O$ requires C, 50·2; H, 4·6%). The undissolved residue, recrystallised from aqueous dimethylformamide, gave the *hydrated form*, prisms, m. p. 326° (Found: C, 49·7; H, 4·8. $C_{30}H_{32}I_2P_2,H_2O$ requires C, 49·6; H, 4·8%).

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[27] Arbuzov, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 549.

[28] Gough and Trippett, *J.*, 1961, 4263.

[29] Freedman and Doak, *J. Org. Chem.*, 1956, **21**, 238.

[30] Wittig and Geisler, *Annalen*, 1953, **580**, 44.

The form with m. p. 320—321°, in hot aqueous solution, gave with sodium picrate the *dipicrate* (IX; R = Et, X = $C_6H_2N_3O_7$), m. p. 241—244° (from aqueous acetone) (Found: C, 54·8; H, 4·4; N, 9·4. $C_{42}H_{36}N_6O_{14}P_2$ requires C, 55·4; H, 4·0; N, 9·2%). The form with m. p. 326°, when boiled under reflux with aqueous sodium picrate, gave the *dipicrate*, m. p. 299—300° (from aqueous dimethyl sulphoxide) (Found: C, 55·8; H, 3·9; N, 9·4%).

In a second preparation, the combined ethanolic mother-liquors were similarly treated with benzyl bromide. The mixture of isomeric dibromides was recrystallised from much aqueous ethanol (1 : 9, v/v), giving needles, m. p. 345—346°, of the *dihydrated isomer* (Found: C, 55·1; H, 5·8. $C_{30}H_{32}Br_2P_2,2H_2O$ requires C, 55·3; H, 5·6%), which when heated at 210°/0·2 mm. gave the *anhydrous form* of unchanged m. p. (Found: C, 58·2; H, 5·6. $C_{30}H_{32}Br_2P_2$ requires C, 58·6; H, 5·3%). The mother-liquor from this recrystallisation, when diluted with acetone, very slowly deposited the second isomer, m. p. 318—320°, after several recrystallisations from absolute ethanol (Found: C, 58·2; H, 5·1%). The isomer with m. p. 345—346° is insoluble in absolute ethanol.

The dibromide of m. p. 318—320° gave the dipicrate, m. p. 241—244°, alone and mixed with the corresponding dipicrate (above), and gave a *diperchlorate*, m. p. 320—322° (from water) (Found: C, 54·8; H, 4·9. $C_{30}H_{32}Cl_2O_8P_2$ requires C, 55·0; H, 4·9%). The second isomer gave a dipicrate, m. p. 299—300°, alone and mixed with the above isomer.

The Dioxides (XII; R = Et).—Sodium hydroxide (0·2 g.) in water (2 ml.) was added to a suspension of the di-iodide hemihydrate, m. p. 320—321° (1·0 g.) in water (2 ml.), which was boiled gently for 10 min., the odour of toluene becoming apparent. The cold solution was extracted with chloroform (2 × 10 ml.), and the united dried extracts concentrated and then diluted with petroleum. The deposited *dioxide* had m. p. 234—235° (from ethyl methyl ketone–petroleum), unchanged by sublimation at 240°/15 mm. (Found: C, 63·2; H, 5·6%; *M*, 306. $C_{16}H_{18}O_2P_2$ requires C, 63·1; H, 5·9%; *M*, 304).

The di-iodide of m. p. 326°, similarly treated, gave the isomeric *dioxide*, m. p. 257°, unchanged by sublimation as before (Found: C, 63·2; H, 6·1%; *M*, 292).

The Diethyldihydrophosphanthrens (IV; R = Et).—Lithium aluminium hydride (1·0 g.) was added portionwise to a suspension of the di-iodide hemihydrate, m. p. 320—321° (7·3 g.) in tetrahydrofuran (60 ml.), the vigorous reaction entailing cooling in ice-water. The complete mixture was boiled under reflux for 3½ hr., concentrated by distillation, and the chilled stirred residue treated first with " wet " ether (50 ml.) and then with potassium sodium tartrate (15 g). in water (40 ml.). The ethereal layer was removed and the residue extracted with ether (2 × 25 ml.). The dried united extracts, after removal of the solvent and distillation at 0·4 mm., gave two fractions: (*a*) b. p. 108—155° (0·37 g.); (*b*) b. p. 155—160° (1·3 g., 50%).

A solution of fraction (*b*) in ethanol (2 ml.), when cooled, with scratching, rapidly deposited crystals (0·66 g., 25%) having m. p. 46—48°, with a portion remaining solid until *ca.* 60°. Three recrystallisations from methanol gave the *phosphanthren* (IV; R = Et), needles, m. p. 52—53° (Found: C, 70·1; H, 6·8; P, 22·5%; *M*, 278. $C_{16}H_{18}P_2$ requires C, 70·5; H, 6·7; P, 22·8%; *M*, 272).

The methanolic mother-liquor from the first recrystallisation, when set aside for 15 hr., deposited the *phosphanthren* isomer, prisms (*ca.* 15 mg.), m. p. 96—97°, after collection and washing with a drop of methanol (Found: C, 70·0; H, 6·4; P, 22·1%; *M*, 264).

The fraction (*a*) gave no definite constituents.

Supplies of the isomeric di-iodide hydrate, m. p. 326°, and of the dibromide, m. p. 346°, were insufficient for similar reduction.

The following experiments were all performed with the diethylphosphanthren (IV; R = Et), m. p. 52—53°.

(1) An excess of benzyl iodide was added to an ethanolic solution of this isomer. The precipitated di-iodide was converted into the dipicrate, m. p. 299—300° (from aqueous dimethyl sulphoxide), unchanged on admixture with that prepared earlier. The ethanolic solution continued to precipitate the di-iodide, but this apparently was not isomerically pure, for samples collected in turn gave dipicrates melting below 299—300°.

(2) The similar addition of methyl iodide to the ethanolic phosphanthren gave the *dimethiodide*, m. p. 400° (decomp.) (from water)(Found: C, 39·1; H, 4·8. $C_{18}H_{24}I_2P_2$ requires C, 38·9; H, 4·4%); it was insoluble in common organic solvents. It gave a yellow *dimethopicrate*, m. p. 250° (decomp.) (from ethanolic dimethylformamide) (Found: C, 47·9; H, 3·7; N, 11·4. $C_{30}H_{28}N_6O_{14}P_2$ requires C, 47·5; H, 3·7; N, 11·1%).

Ethyl iodide (0·080 g., 1 mol.) was added to a solution of the phosphanthren (0·115 g.) in ethanol (10 ml.), which when briefly heated, cooled, filtered to remove a trace of diethiodide, and diluted with ether until turbid, deposited the crystalline *monoethiodide* (0·094 g., 52%), m. p. 159—160° (effervescence) (from ethanol–ether) (Found: C, 50·0; H, 5·7. $C_{18}H_{23}IP_2$ requires C, 50·3; H, 5·4%). This salt, treated with aqueous sodium picrate, gave the *ethopicrate-sodium picrate* salt, m. p. 209—210° (decomp.) (Found: C, 46·0; H, 3·6; N, 10·9. $C_{24}H_{25}N_3O_7P_2,C_6H_2N_3NaO_7$ requires C, 46·1; H, 3·5; N, 10·8%), and with aqueous picric acid gave the *ethopicrate-hydrogen picrate,* m. p. 120—121° (Found: C, 47·5; H, 3·8; N, 10·9. $C_{24}H_{25}N_3O_7P_2,C_6H_3N_3O_7$ requires C, 47·5; H, 3·7; N, 11·1%). The two salts were recrystallised from aqueous ethanol containing a trace of sodium picrate and picric acid, respectively.

A solution of the ethiodide and ethyl iodide in ethanol, when boiled under reflux for several hours, deposited the insoluble *di-ethiodide*, m. p. >400° (decomp.) (from water) (Found: C, 41·3; H, 5·0. $C_{20}H_{28}I_2P_2$ requires C, 41·1; H, 4·8%). It gave a *di-ethopicrate*, needles, m. p. 267° (from ethanolic dimethylformamide) (Found: C, 49·1; H, 4·0; N, 11·0. $C_{32}H_{32}N_6O_{14}P_2$ requires C, 48·8; H, 4·1; N, 10·7%).

(3) An ethanolic solution of the phosphanthren, when set aside in contact with air, slowly deposited the *monoxide*, m. p. 140°, after washing with methanol (Found: C, 66·6; H, 6·3. $C_{16}H_{18}OP_2$ requires C, 66·7; H, 6·3%).

An excess of 30% aqueous hydrogen peroxide was added to a solution of the phosphanthren (0·2 g.) in acetone (5 ml.), which was set aside overnight and then evaporated under reduced pressure. A solution of the solid residue in water (10 ml.), when chilled, deposited crystals, which when dried and recrystallised from toluene–petroleum gave the *dihydrated phosphanthren dioxide–(hydrogen peroxide)* addition product, leaflets, m. p. 128° (effervescence) (Found: C, 50·6, 50·4; H, 6·9, 6·2. $C_{16}H_{18}O_2P_2,H_2O_2,2H_2O$ requires C, 51·3; H, 6·5%). The presence of hydrogen peroxide in this compound was shown by the action of acidified potassium iodide, which liberated iodine, and that of an acidified solution of potassium dichromate, which gave a blue colour that could be extracted with ether.

After the compound had been gently warmed with aqueous sodium hydroxide, extraction with chloroform yielded the dioxide (XII; R = Et), m. p. and mixed m. p. 234—235°. Attempts to convert this dioxide back into the addition product, m. p. 128°, by the action of aqueous hydrogen peroxide were unsuccessful.

(4) A mixture of the phosphanthren (0·138 g.) and an excess of 1,2-dibromoethane (1 g.), when cautiously warmed, combined vigorously with partial solidification. Propan-1-ol (10 ml.) was added, and the solution boiled under reflux for 5 hr. and cooled. The deposited 5,10-*diethyl*-5,10-*dihydro*-5,10-*ethanophosphanthronium dibromide* (XIII; X = Br) had m. p. 325—326° (decomp.) (Found: C, 46·6; H, 5·2. $C_{18}H_{22}Br_2P_2$ requires C, 47·0; H, 4·8%), and gave a *dipicrate* (XIII; X = $C_6H_2N_3O_7$), m. p. 272° (decomp.) (Found: C, 47·4; H, 3·4; N, 11·0. $C_{30}H_{26}N_6O_{14}P_2$ requires C, 47·6; H, 3·5; N, 11·1%); both salts were recrystallised from ethanolic dimethyl sulphoxide.

Several attempts were made to combine the phosphanthren similarly with 1,3-dibromopropane (1 mol. or an excess), with or without a solvent, but no crystalline dibromide or dipicrate could be isolated.

A solution of the phosphanthren (0·172 g.) and *o*-xylylene dibromide (0·178 g., 1 mol.) in ethanol (5 ml.), when boiled under reflux, rapidly deposited crystals. It was then heated at 80° for 2 hr., cooled, and the crystalline 5,10-diethyl-5,10-dihydro-5,10-*o*-xylylenephosphanthronium dibromide (XIV; X = Br) (0·294 g., 87%), m. p. *ca.* 305° (decomp.), collected. This salt could not be satisfactorily recrystallised, being insoluble in organic solvents and readily soluble in water; it was converted by aqueous sodium iodide into the *di-iodide* (XIV; X = I), m. p. 305—306° (from water) (Found: C, 45·6; H, 4·1. $C_{24}H_{26}I_2P_2$ requires C, 45·7; H, 4·2%). It gave a yellow-orange *dipicrate* (XIV; X = $C_6H_2N_3O_7$), m. p. 278° (preliminary darkening) (from ethanolic dimethyl sulphoxide) (Found: C, 52·2; H, 3·7; N, 10·0. $C_{36}H_{30}N_6O_{14}P_2$ requires C, 51·9; H, 3·6; N, 10·1%).

The di-iodide was heated under reflux with an excess of aqueous 10% sodium hydroxide for 30 min., producing an odour of *o*-xylene, and was then cooled, neutralised, and extracted with chloroform. The residue from evaporation of the chloroform extracts, when thrice recrystallised from ethyl methyl ketone–petroleum, gave the dioxide (XII; R = Et), m. p. 252—253°, a mixture with the authentic dioxide, m. p. 257°, having an intermediate m. p.

(5) A solution of potassium palladobromide (26 mg., 1 mol.) in dimethylformamide (2 ml.)

was added dropwise to the phosphanthren (14 mg.) also dissolved in the amide (1 ml.), giving an immediate deep yellow precipitate. This *palladobromide*, when collected and washed in turn with hot ethanol, acetone, water, acetone, and ether, had m. p. 375° (decomp., preliminary shrinking) (Found: C, 36·0; H, 3·1. $C_{16}H_{18}Br_2P_2Pd$ requires C, 35·7; H, 3·3%).

(6) Iodine (0·061 g., 1 mol.) was added to the phosphanthren (0·066 g.), each dissolved in dry ether (5 ml.), giving an immediate bright yellow very deliquescent precipitate. It gave colourless solutions in water or ethanol, which gave no crystalline picrate or perchlorate, and by analogy with the diphenyl analogue undoubtedly contained the phosphanthren monoxide.

Di-(o-*chlorophenyl*)*phenylphosphine* (VI; R = Ph).—This was prepared as for the ethyl analogue, *o*-bromochlorobenzene (183 g.) in ether (400 ml.) being brought into reaction with activated magnesium (25 g., 1·08 equiv.). A solution of phenylphosphonous dichloride (88 g., 0·49 mol.) in ether (100 ml.) was then added at such a rate that the solvent boiled steadily. (The dichloride solution should drop directly into the stirred reaction mixture; if it runs down the side of the flask it forms a hard cake which later undergoes very slow hydrolysis.) The complete mixture was stirred for 1½ hr. and then hydrolysed by a solution of ammonium chloride (100 g.) in water (500 ml.). The dried ethereal layer, after removal of the ether and distillation at 0·4 mm., gave the fractions: (A) b. p. 40—135° (6·0 g.); (B) b. p. 135—176° (11·7 g.); (C) b. p. 177—212° (almost all at 203—204°) (77 g.).

Fraction (C) when dissolved in hot propan-1-ol (80 ml.) and cooled, deposited the *phosphine* (VI; R = Ph) (47 g., 30%), m. p. 133—134° (Found: C, 65·4; H, 4·2. $C_{18}H_{13}Cl_2P$ requires C, 65·1; H, 4·2%).

Fraction (B) contained a considerable proportion of *o*-chlorophenylphenylphosphine. A portion, treated with hot benzyl bromide, followed by sodium picrate solution, gave *dibenzyl-*o-*chlorophenylphenylphosphonium picrate*, prisms, m. p. 136—138° (from ethanol) (Found: C, 61·0; H, 4·1; N, 6·6. $C_{32}H_{25}ClN_3O_7P$ requires C, 61·0; H, 4·0; N, 6·7%). A second portion, warmed with acetone–hydrogen peroxide, gave *o*-chlorophenylphenylphosphinic acid, which after repeated crystallisation from aqueous ethanol had m. p. and mixed m. p. 186—187° (lit.,[31] 186—187°).

5,10-*Dihydro*-5,10-*diphenylphosphanthren* (IV; R = Ph).—The general preparative conditions followed those for the compound (IV; R = Et). Lithium foil (2·8 g., 4 atoms) was added to a solution of the phosphine (VI; R = Ph) (33·1 g.) in tetrahydrofuran (600 ml.) at *ca.* −35°, and, after stirring for 2 hr., the mixture was cooled to *ca.* −60° and phenylphosphonous dichloride (17·9 g., 1 mol.) in tetrahydrofuran (100 ml.) added slowly. The mixture was allowed to reach room temperature, and benzene (100 ml.) and water (100 ml.) were then added. The solvents were removed from the dried organic layer, and the residue, distilled at 0·2 mm., gave the fractions: (A) b. p. 98—147° (3·9 g.); (B) b. p. 148—180° (5·7 g.); (C) b. p. 180—250° (15·6 g.); undistilled residue (10 g.).

Fraction (A), diluted with ethanol (5 ml.), deposited the yellow diphosphine (VIII) (0·11 g.), m. p. and mixed m. p. 241—243°. The rest of the fraction was mainly diphenylphosphine; a portion with methyl iodide furnished dimethyldiphenylphosphonium iodide, m. p. 249—250° (lit.,[27] 241°), which gave a picrate, m. p. and mixed m. p. 116—118°; another portion, on oxidation, gave diphenylphosphinic acid, m. p. and mixed m. p. 192—194° (from ethanol).

The combined fractions (B) and (C) were dissolved in propan-1-ol (50 ml.) and heated under reflux with benzyl bromide (30 g.) for 10 min. The deposited powdery dibenzylphosphanthren *dibromide* (IX; R = Ph, X = Br) (9·8 g.), when collected, and washed thoroughly with ethanol, acetone, and ether, had m. p. 387° (Found: C, 64·4; H, 4·8. $C_{38}H_{32}Br_2P_2$ requires C, 64·3; H, 4·6%); it was almost insoluble in organic solvents and underwent slight decomposition on attempted crystallisation from water. A portion, when boiled with aqueous sodium picrate, gave the *dipicrate*, needles, m. p. 281° (decomp.) (from aqueous dimethylformamide) (Found: C, 59·7; H, 3·5; N, 8·3%. $C_{50}H_{36}N_6O_{14}P_2$ requires C, 59·6; H, 3·6; N, 8·3%).

The dibromide (8·0 g.), suspended in tetrahydrofuran (150 ml.), was reduced with lithium aluminium hydride (1·0 g.), the mixture being boiled for 4 hr. The mixture was hydrolysed and worked up as before, and after distillation of the organic solvent the semi-solid residue (4·7 g.) was dissolved in acetone. The solution deposited the *phosphanthren* (IV; R = Ph) (2·1 g., 51%), m. p. 184—187° after repeated recrystallisation from ethyl methyl ketone (Found: C, 77·9; H, 4·9; P, 16·8%; *M*, 372. $C_{24}H_{18}P_2$ requires C, 78·2; H, 4·9; P, 16·9%; *M*, 368).

5,10-*Dihydro*-5,10-*diphenylphosphanthren Dioxide and Monoxide*.—The dibromide (IX;

[31] Gallagher and Mann, *J.*, 1963, 4846.

R = Ph, X = Br) was treated with aqueous sodium hydroxide, followed by chloroform extraction, as previously described. The residue from the evaporation of the extract, when treated with acetone, deposited the *dioxide* (XII; R = Ph), needles, m. p. >400° (from aqueous ethanol) (Found: C, 71·9; H, 5·1. $C_{24}H_{18}O_2P_2$ requires C, 72·0; H, 4·5%; *M*, 400); a portion sublimed unchanged at 350°/15 mm. (Found: C, 71·7; H, 4·7%; *M*, 394). The acetone mother-liquor, when diluted with water, deposited the *monoxide*, m. p. 231—232·5° (from aqueous acetone) (Found: C, 74·6; H, 4·9. $C_{24}H_{18}OP_2$ requires C, 75·0; H, 4·7%).

The phosphanthren (IV; R = Ph) (0·1 g.), dissolved in acetone (20 ml.), was treated with 30% aqueous hydrogen peroxide. Next day, the acetone was removed under reduced pressure, and the residue afforded the isomeric hygroscopic *dioxide*, m. p. 276—278° (from aqueous ethanol), after drying at 150°/0·2 mm. (Found: C, 72·1; H, 5·3%); this m. p. was unaffected after a portion had been sublimed at 270°/15 mm. (Found: C, 72·7; H, 4·6%; *M*, 381). This dioxide had a dipole moment 3·4 D in benzene solution.

A solution of potassium palladobromide (0·484 g., 1 mol.) in water (1 mol.) and dimethylformamide (10 ml.) was added slowly to one of the phosphanthren (0·323 g.) in the hot amide (25 ml.). The mixture was heated gently, and the precipitated crystalline *palladobromide* (0·14 g.) was collected and washed with ethanol, water, and acetone; it did not melt below 400° (Found: C, 45·4; H, 2·8. $C_{24}H_{18}Br_2P_2Pd$ requires C, 45·4; H, 2·8%). Under other conditions, an almost amorphous product was obtained.

Quaternary Dimethiodides and Dimethopicrates.—The phosphanthren (IV; R = Ph) (0·32 g.), dissolved in toluene (15 ml.), when treated with methyl iodide (1·0 g.) and heated under reflux for 30 min., rapidly deposited the *dimethiodide* which, after thorough extraction with acetone, had m. p. *ca.* 385° (decomp.) (Found: C, 48·1; H, 4·0. $C_{26}H_{24}I_2P_2$ requires C, 47·8; H, 3·7%). It was insoluble in most solvents, and was converted into the *dimethopicrate*, which after one recrystallisation from ethanolic dimethylformamide had m. p. 238—242°, changed to 238—252° by repeated recrystallisation (Found: C, 53·6; H, 3·6; N, 10·0. $C_{38}H_{28}N_6O_{14}P_2$ requires C, 53·4; H, 3·3; N, 9·9%). When a portion of the original fraction (C) was boiled with ethanolic methyl iodide, it gave the dimethiodide, m. p. *ca.* 330° (decomp.) (from methanolic dimethylformamide) (Found: C, 47·6; H, 3·8%), which gave the dimethopicrate, m. p. 263° (decomp.), after one recrystallisation from ethanolic dimethylformamide, rapidly increased to a constant m. p. 269—270° after further recrystallisation (Found: C, 52·9; H, 3·4; N, 9·8%).

The significance of these discordant m. p.s is uncertain. It is possible that the dimethiodide, m. p. *ca.* 330°, prepared from the crude fraction (C), was a mixture of difficultly-soluble *cis–trans* isomers, from which the isomerically pure dimethopicrate, m. p. 269—270°, was obtained by recrystallisation. The dimethiodide, m. p. *ca.* 385°, prepared from the apparently pure phosphanthren, may have been mainly the other isomer, whose pure dipicrate may have a m. p. in the 238—240° region, but slight contamination with the less soluble isomeric dipicrate caused the proportion of the latter to increase with recrystallisation and thus to widen the range of m. p.

5,10-*Dihydro*-5,10-*diphenyl*-5-*phospha*-10-*arsa-anthracene* (XX).—This was prepared similarly to the phosphanthren (IV; R = Ph), the phosphine (VI; R = Ph) (33·1 g.) being converted as before into the dilithio-derivative, the mixture being then treated with phenylarsonous dichloride (22·3 g., 1 mol.) in tetrahydrofuran. After working up as before, the crude residue was distilled at 0·009 mm. and gave the fractions: (A) b. p. 95—148° (mainly 143—148°) (5·8 g.); (B) b. p. 148—195° (2·8 g.); (C) b. p. 196—228° (mainly 216°) (19·2 g.); undistilled residue (12 g.). Slight deposition of arsenic occurred during the distillation.

Fraction (A) was mixed with methyl iodide, boiled for 1 hr., cooled, and treated with ethanol (10 ml.) and an excess of aqueous sodium picrate. The two precipitated picrates were readily separated, one being very soluble and the second only moderately soluble in methanol. The first, after several recrystallisations from aqueous ethanol, gave methyltriphenylarsonium picrate, m. p. 146—147°, unchanged when mixed with an authentic sample, m. p. 145·5—146·5°. The second was readily recrystallised from ethanol, and gave 9,9-dimethyl-9-phosphoniafluorene picrate, m. p. and mixed m. p. 217—218°. These picrates indicated that fraction (A) contained triphenylarsine (*ca.* 3·5 g.) and 9-phosphafluorene (XI; R = H) (*ca.* 1 g.).

Fraction (B), which also contained the phosphafluorene, was not investigated in detail.

Fraction (C) was heated with acetone (60 ml.) until the glassy solid dissolved, when the *phospha-arsa-anthracene* (XX) (5·7 g.) rapidly separated; it formed prisms, m. p. 189—190° after three recrystallisations from ethyl methyl ketone (charcoal) (Found: C, 69·9; H, 4·5. $C_{24}H_{18}AsP$ requires C, 69·9; H, 4·4%).

Quaternary salts. A solution of the compound (XX) (120 mg.) in toluene (5 ml.) and methyl iodide (0·5 g.), when boiled rapidly, deposited the *monomethiodide* (0·15 g., 95%), m. p. 300—302° (from ethanol) (Found: C, 54·2; H, 3·7. $C_{25}H_{21}AsIP$ requires C, 54·2; H, 3·8%); it gave a *picrate*, m. p. 171—172° (from aqueous ethanol) (Found: C, 57·3; H, 3·3; N, 6·4. $C_{31}H_{23}AsN_3O_7P$ requires C, 56·8; H, 3·5; N, 6·4%). A mixture of the compound (XX) and an excess of methyl toluene-*p*-sulphonate was heated at 180° for 4 hr., cooled, and stirred with ether; the insoluble syrup, when treated with aqueous sodium iodide, gave the monomethiodide, m. p. and mixed m. p. 300—302°.

When the compound (XX) in toluene was similarly boiled with an excess of benzyl bromide, the quaternary *monobromide* (83%) rapidly separated, and when recrystallised from water formed a *hydrate*, m. p. 318—322° (Found: C, 61·7; H, 4·3. $C_{31}H_{25}AsBrP,H_2O$ requires C, 61·9; H, 4·5%); it gave a *picrate*, needles, m. p. 170—171° (from ethanol) (Found: C, 61·1; H, 3·8; N, 5·6. $C_{37}H_{27}AsN_3O_7P$ requires C, 60·8; H, 3·7; N, 5·7%).

A solution of the compound (XX) in dimethylformamide was boiled with an excess of benzyl bromide for 5 hr. and then set aside for 1 week. The quaternary dibromide had then separated in small amount as a fine powder, m. p. >360° (decomp.), insoluble in all solvents. When boiled with an aqueous dimethylformamide solution of sodium picrate, it gave the *dipicrate*, needles, m. p. 212—213° (from ethanolic dimethylformamide) (Found: C, 58·8; H, 3·6; N, 8·2. $C_{50}H_{36}AsN_6O_{14}P$ requires C, 57·1; H, 3·5; N, 8·0%).

The P-*oxide.* A mixture of the monobromide (0·396 g.), water (4 ml.), and 10% aqueous sodium hydroxide (2 ml.) was boiled under reflux for 5 min. and cooled. The *monoxide* (0·267 g., 95%) had m. p. 214—216° (from aqueous ethanol) (Found: C, 67·4; H, 4·5. $C_{24}H_{18}AsOP$ requires C, 67·3; H, 4·2%).

The dioxide. The monoxide, when treated with acetone and hydrogen peroxide (as before), gave the *dioxide dihydrate*, prisms, m. p. 360° (from aqueous ethanol) (Found: C, 59·8; H, 4·5. $C_{24}H_{18}AsO_2P,2H_2O$ requires C, 60·0; H, 4·6%); drying at 120°/0·1 mm. gave the *dioxide*, m. p. 360° (Found: C, 64·7; H, 3·6. $C_{24}H_{18}AsO_2P$ requires C, 65·0; H, 4·1%). The same product was obtained by the peroxide oxidation of the parent compound (XX). The fact that the dihydrate was not a peroxide addition compound was shown by the negative tests for hydrogen peroxide, and by the unchanged m. p. on dehydration.

In an attempt to prepare a dibromide of type (II), a suspension of the compound (XX) (93·6 mg.) in carbon tetrachloride was treated with bromine (1 mol.) in the same solvent. The very deliquescent cream-coloured precipitate, with orange flecks, was dissolved in ethanol, giving a yellow solution which did not give a picrate or perchlorate. Dilution of the solution with water gave the crystalline dioxide (60 mg., 55%), m. p. and mixed m. p. 360°.

The palladobromide. A solution of potassium palladobromide (113 mg., 1 mol.) in water (0·25 ml.) and dimethylformamide (2 ml.) was added to a solution of the compound (XX) (91·2 mg.) in hot dimethylformamide; the mixture was heated for *ca.* 1 min. and cooled, when the *palladobromide* separated as orange crystals, m. p. 344° (decomp.), insoluble in all solvents (Found: C, 42·4; H, 2·4. $C_{24}H_{18}AsBr_2PPd$ requires C, 42·4; H, 2·7%). The molecular complexity of this compound is unknown.

5,10,5′,10′-*Tetrahydro*-5,10,5′,10′-*tetraphenyl*-5,5′-o-*xylylenebis*-(5-*phosphonia*-10-*arsa-anthracene*) *Dibromide.* (XXI; X = Br).—*o*-Xylylene dibromide (0·179 g., 1 mol.) was added to a solution of the compound (XX) (0·2564 g.) in hot dimethylformamide, which was boiled under reflux for 3 hr. On cooling, the dibromide (XXI; X = Br) separated as prisms, which were converted into the *dipicrate* (XXI; X = $C_6H_2N_3O_7$), needles, m. p. 239—240°, after five recrystallisations from ethanol (Found: C, 59·5; H, 2·9; N, 6·0. $C_{68}H_{48}As_2N_6O_{14}P_2$ requires C, 59·0; H, 3·5; N, 6·1%). The absence of bromine was confirmed.

10-*Ethyl*-5,10-*dihydro*-5-*phenyl*-5-*phospha*-10-*arsa-anthracene.*—This preparation was similar to that of compound (XX), starting with the phosphine (VI; R = Ph) (33·1 g.) and using ethylarsonous dichloride (17·5 g.). The final residue was distilled at 0·5 mm., but much arsenic was deposited. Arbitrary fractions were collected: (A) b. p. 70—165° (5·3 g.); (B) b. p. 165—190° (2·2 g.); (C) b. p. 190—240° (17·0 g.); undistilled residue, 12·0 g.

Fractions (A) and (B) contained 9-phosphafluorene identified as before. Fraction (C) was dissolved in hot propan-1-ol (35 ml.), filtered to remove arsenic, treated with benzyl bromide (30 g.), and heated at 100° for 5 hr. The crude quaternary dibromide (1·0 g.), m. p. 363—365° (decomp.), which separated could not be satisfactorily purified (Found: C, 61·7; H, 4·3. Calc. for $C_{34}H_{32}AsBr_2P$; C, 57·8; H, 4·5%). A sample, boiled with aqueous sodium picrate, gave the pure *dipicrate*, m. p. 206° (decomp.), after five recrystallisations from ethanolic dimethylformamide (Found: C, 55·5; H, 3·4; N, 8·6. $C_{46}H_{36}AsN_6O_{14}P$ requires C, 55·1; H, 3·6; N, 8·4%). The solution from which the dibromide had been collected, when diluted with acetone (100 ml.), deposited the *monobromide* (0·2 g.), needles, m. p. 295—296° (decomp.) after four recrystallisations from water (Found: C, 60·1; H, 5·1. $C_{27}H_{25}AsBrP$ requires C, 60·5; H, 4·7%); it gave a *picrate*, needles, m. p. 180—182° (from ethanol) (Found: C, 57·9; H, 4·1; N, 6·2. $C_{33}H_{27}AsN_3O_7P$ requires C, 58·0; H, 4·0; N, 6·1%). Ethanol dissolves the mono- but not the di-bromide.

The reduction of the crude dibromide gave no decisive result, partly owing to the small amount available, and the parent compound was not isolated.

5,10-*Diphenyl*-5,10-*dihydrophosphanthren Palladobromide*. (The following report was provided by Mrs. O. KENNARD.)—An *X*-ray crystallographic examination of this compound was undertaken to determine, if possible, the number of units of $C_{24}H_{18}P_2PdBr_2$ forming a single molecule. The unit cell of a crystal must contain an integral number (Z) of molecules of formula weight M which can be derived from the relationship $M \times Z = V \times D/1{\cdot}6604$ by measuring the cell volume V and the bulk density D of the crystal. The minimum value Z may in some cases be decided by the symmetry requirements of the unit cell.

As the material was available only in the form of extremely small crystals (<0·01 mm.), the cell dimensions were derived from powder photographs taken in a Guinier-type camera. Copper radiation was used with Hg_3TeO_6 as calibration standard. Although the appearance of the photograph was complex, indicating a cell of low symmetry, it was possible to derive the values of the cell constants, by courtesy of Professor P. M. de Wolff, of the Technische Hogeschool, Delft, who repeated our experimental measurements and used the values in the " zone detection " programme developed by him on a Zebra computer.[32] By means of this programme Professor de Wolff succeeded in assigning indices to all the powder lines, and derived the cell dimensions recorded below. The triclinic symmetry deduced from the powder photograph was further checked by us, taking a series of Laue photographs. The bulk density of the sample was determined by centrifuging in a calibrated continuous gradicut density column.[33]

Crystal data. $C_{24}H_{18}P_2PdBr_2$, Triclinic, $a = 18{\cdot}54$, $b = 10{\cdot}86$, $c = 12{\cdot}14$ Å, $\alpha = 112° \; 3'$, $\beta = 90° \; 47'$, $\gamma = 94° \; 11'$; $U = 2257$ Å^3, $D_m = 1{\cdot}83$, $D_x = 1{\cdot}87$. $Z \times M_x = 2487{\cdot}4$ or $M_x = 621{\cdot}8$, if $Z = 4$; $M_c = 634{\cdot}2$. Space Group $P1$ or $P\bar{1}$. Indexed powder data are available in the A.S.T.M. Powder Data File.

Discussion. On the basis of the above determination the unit cell contains four formula units of $C_{24}H_{18}P_2PdBr_2$, which may form a single tetramer, two dimers, or four monomers. Unfortunately, as the unit cell contains no symmetry elements with the possible exception of a centre (not detectable by the present measurements), no decision can be made between these possibilities.

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