Further Studies in the Chemistry of 2,3-Dihydro-1,2,3-triphenyl-1*H*-1,2,3-benzotriphosphole † and Related Compounds. Part I

By **Frederick G. Mann*** and **Anthony J. H. Mercer**, The University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The study of the probable mechanisms whereby certain *o*-dihalogenobenzenes react with the crude product of the interaction of lithium and phenylphosphonous dichloride to form 2,3-dihydro-1,2,3-triphenyl-1*H*-1,2,3-benzotriphosphole (I) and 5,10-dihydro-5,10-diphenylphosphanthren (II) has been extended. Lithium reacts with certain polyphenylcyclopolyphosphines in solution, giving a product (XIV) which similarly reacts with *o*-dihalogenobenzenes to form the benzotriphosphole (I). The latter can also be obtained by the interaction of phenylphosphonous dichloride and *o*-phenylenebis[lithio(phenyl)phosphine].

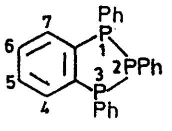
The syntheses of the 1,2,3-triethyl and 1,2,3-trimethyl analogues of compound (I) are described. The structures of their various *P*-sulphides have been elucidated by ^{31}P n.m.r. spectroscopy; in particular the disulphides have been shown to have the sulphur linked to P-1 and P-3.

The ^1H n.m.r. and mass spectra of various new compounds are discussed.

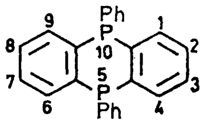
THE preparation of 2,3-dihydro-1,2,3-triphenyl-1*H*-1,2,3-benzotriphosphole[1] (I) and 5,10-dihydro-5,10-diphenylphosphanthren (II)[2] has been described previously. The triphosphole (I) readily forms *P*-sulphides. The heterocyclic ring in structure (I) is cleaved by permanganate or hydrogen peroxide to form *o*-phenylenebis(phenylphosphinic acid) (III) and by hot methyl iodide to form *o*-phenylenebis(dimethylphenylphosphonium iodide) (IV).

Structure (I) was subsequently confirmed by *X*-ray crystal analysis:[3] the two fused rings are coplanar, and the phenyl groups on P-1 and P-3 are *cis* to one another and both are *trans* to that on P-2. The intervalency angles within the ring at P-1, P-2, and P-3 are 99·7, 97·3, and 99·7°, respectively, and the ring should therefore be virtually unstrained.

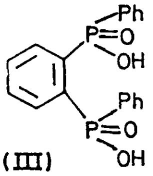
We now record further studies on this system, in particular an investigation of the mechanism of its formation by the reaction of certain *o*-halogenobenzenes with the product of the interaction of lithium and phenylphosphonous dichloride. A novel synthesis, in which *o*-bromochlorobenzene reacts with the product of the action of lithium on pentaphenylcyclopentaphosphine, is also described. The structures and configurations of the various *P*-sulphides both of the triphosphole (I) and of certain 1,2,3-trialkyl analogues have also been studied.



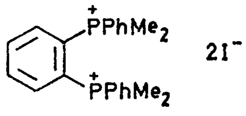
(I)



(II)



(III)



(IV)

Dilithio(phenyl)phosphine can be prepared in tetrahydrofuran solution by (*a*) treatment of phenylphosphine with butyl-lithium or (*b*) the addition of phenylphosphonous dichloride in tetrahydrofuran to a suspension of

---

† Previously referred to as 1,2,3-triphenyl-1,2,3-triphosphaindane.[1]

[1] F. G. Mann and M. J. Pragnell, *J. Chem. Soc.* (*C*), **1966**, **916**.

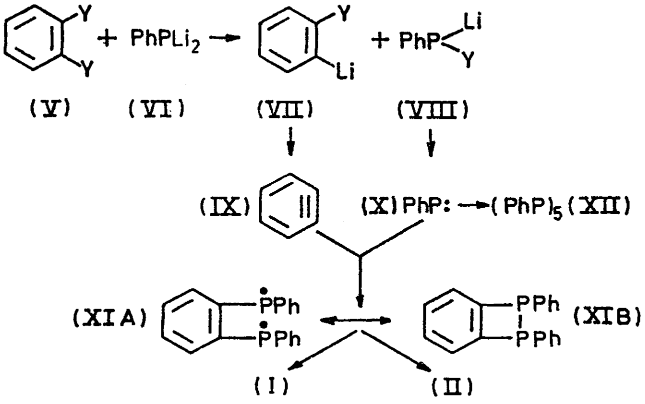
[2] M. Davis and F. G. Mann, *J. Chem. Soc.*, **1964**, **3770**.

[3] J. J. Daly, *J. Chem. Soc.* (*A*), **1966**, **1020**.

lithium foil, also in tetrahydrofuran at *ca.* 0°, with subsequent cooling to $-40°$.[4] The material obtained by method (*b*), however, contains various by-products (see later).

In the earlier work,[1] the conditions for the treatment of the dilithio(phenyl)phosphine, prepared by each of these methods, with the *o*-dihalogenobenzene, were varied widely. The particular dihalogenobenzene, the molar ratio between this compound and the dilithiophosphine, the time, temperature, and nature of the addition of the dihalogenobenzene solution to that of the dilithiophosphine, and the subsequent treatment were all varied, but although the yields of the triphosphole (I) and the phosphanthren (II) varied, the results gave little indication of the mechanism.

The mechanism suggested[1] involved halogen–lithium interchange between the *o*-halogenobenzene (V; Y = halogen) and the dilithiophosphine (VI) to give the highly reactive intermediates (VII) and (VIII). The compound (VII) will readily form benzyne (IX), provided that Y is a good leaving group.[5] The unstable arylhalogenolithiophosphines (VIII) readily lose lithium halide to give the crystalline pentaphenylcyclopentaphosphine (XII), by a process which probably involves the reactive intermediate phenylphosphinidene (X).[6] This radical might also react with benzyne (IX) to form a diphosphine, of which (XIA) and (XIB) are canonical forms. Further reaction of (X) with the diphosphine (XI) would give the 1,2,3-triphenyl-1*H*-1,2,3-benzotriphosphole (I), the process stopping at this stage because of the stability of the heterocyclic ring; the reaction of benzyne (IX) with the diphosphine (XI) would give 5,10-dihydro-5,10-diphenylphosphanthren (II) (Scheme 1).



SCHEME 1

We initially[1] suggested that the benzyne might cleave the P–P bonds in the cyclic polyphosphine product (XII) with direct formation of intermediates of type (XI) followed by generation of the compounds (I) and (II). We have now investigated the behaviour of benzyne generated *in situ* with compound (XII); no reaction was detected and the phosphine (XII) was recovered in high yield. This suggestion has therefore now been abandoned.

'Tetraphenylcyclotetraphosphine', $(PhP)_4$, was long considered to exist in two forms, m.p. 150 and 190°; however, Daly[7] has now shown by *X*-ray analysis that the crystalline product of m.p. 150° is actually the pentaphosphine $(PhP)_5$, having a planar ring of five phosphorus atoms, and the product of m.p. 190° is the hexaphosphine $(PhP)_6$, in which the ring of six phosphorus atoms has the 'chair' conformation.[8,9] There is at present only indecisive evidence for the condition of these cyclic polyphosphines in solution. Henderson *et al.*,[10] using cryoscopic, ebullioscopic, and isopiestic methods, have shown that both products in various solvents have virtually the same apparent molecular weights, which accord with the formula $(PhP)_4$; both products have the same i.r. spectra in carbon disulphide, but not in Nujol mull; the ^1H n.m.r. spectra of solutions in carbon disulphide, however, show distinct differences; the ^{31}P n.m.r. spectrum of the product of m.p. 150° shows that all the P atoms are identical, but the low solubility of the second product prevented measurement. Further evidence that the compound of m.p. 150° in solution in various solvents shows a molecular weight corresponding to the tetramer has been adduced by various workers,[11-13] but Reeson and Wright[14] record that the molecular weight of the compound of m.p. 154°, determined isopiestically in carbon disulphide, shows that it is a dimer, $(PhP)_2$, and that the compound of m.p. 193° is a tetramer. Fluck and Issleib[15] claim that the ^{31}P n.m.r. spectrum of the compound of m.p. 150°, when molten, shows the presence of both PhP and $(PhP)_2$, and that an identical spectrum is obtained when this molten material is dissolved in benzene or tetrahydrofuran: in these solutions the monomer and dimer are present in appreciable concentration and have considerable stability.

Thus any discussion of the mechanisms of reactions of these cyclopolyphosphines in solution must rest on an uncertain basis.

It has been observed[1,4,16] that when phenylphosphonous dichloride in tetrahydrofuran is treated with the 4 equiv. of lithium theoretically necessary for complete conversion into dilithio(phenyl)phosphine, *ca.* 20% of the lithium does not react, even when the final reaction mixture is boiled. Hence complete conversion into dilithio(phenyl)phosphine is not achieved.

---

[4] P. R. Bloomfield and K. Parvin, *Chem. and Ind.*, 1959, 541.

[5] R. W. Hoffmann, 'Dehydrobenzene and Cycloalkynes,' Academic Press, New York, 1969, p. 43.

[6] U. Schmidt and C. Osterroht, *Angew. Chem. Internat. Edn.*, 1965, **4**, 437.

[7] J. J. Daly, *J. Chem. Soc.*, 1964, 6147.

[8] J. J. Daly and L. Maier, *Nature*, 1965, **208**, 383.

[9] J. J. Daly, *J. Chem. Soc.*, 1965, 4789.

[10] W. A. Henderson, jun., M. Epstein, and F. S. Seichter, *J. Amer. Chem. Soc.*, 1963, **85**, 2462.

[11] F. Pass and H. Schindlbauer, *Monatsh.*, 1959, **90**, 148.

[12] W. Kuchen and H. Buchwald, *Chem. Ber.*, 1958, **91**, 2296.

[13] J. J. Daly and L. Maier, *Nature*, 1964, **203**, 1167.

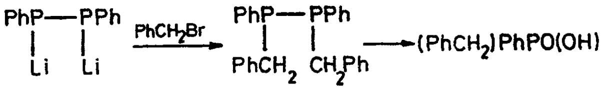
[14] J. W. B. Reeson and G. F. Wright, *J. Org. Chem.*, 1957, **22**, 386.

[15] E. Fluck and K. Issleib, *Z. Naturforsch.*, 1966, **21*b***, 736.

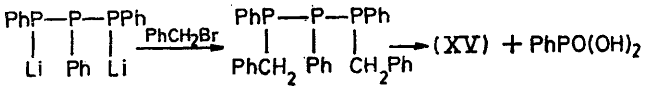
[16] A. M. Aguiar, personal communication.

However, Bloomfield and Parvin[4] report that although dilithio(phenyl)phosphine was not isolated in their preparation, it was characterised by reactions with methyl iodide and bromobenzene, which furnished dimethylphenylphosphine and triphenylphosphine, respectively (yields are not quoted). They also report that the addition of an excess of phenylphosphonous dichloride to their reaction mixture gave an intermediate compound 'identified as phosphobenzene, $(PhP)_4$, m.p. 150—151°.'

Aguiar[16] has adduced evidence that the foregoing reaction mixture contains also some linear lithiopolyphosphines, *e.g.* (XIII) and (XIV), for treatment with



(XIII) (XV)



(XIV)

benzyl bromide followed by oxidation affords benzylphenylphosphinic acid (XV), [40% yield if compound (XIII) alone is present].

Issleib has shown that the cyclopentaphosphine reacts with lithium phosphides[17] and with phenyl-lithium[18] to give mixtures of linear lithiopolyphosphines, according

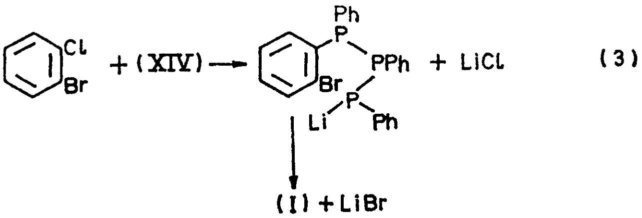
$$\frac{x}{5}(PhP)_5 + PhPLi_2 \longrightarrow Li(PhP)_{x+1}Li \qquad (1)$$

to the stoicheiometry of equation (1) where $x = 1$, 2, or 3. It appeared probable therefore that the cyclopentaphosphine, if treated in tetrahydrofuran with the appropriate stoicheiometric amount of lithium, would be converted largely into 1,3-dilithio-1,2,3-triphenyltriphosphine (XIV) [equation (2)]. To investigate this

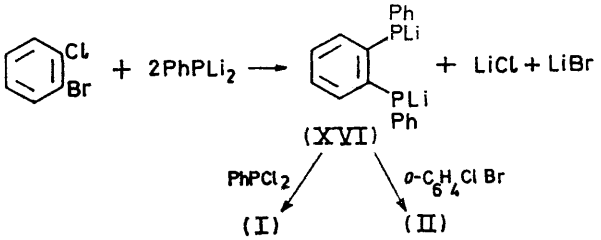
$$3(PhP)_5 + 10Li \longrightarrow \underset{\text{(XIV)}}{5LiPPh{\cdot}PPh{\cdot}PPhLi} \qquad (2)$$

possibility, the pentaphenylcyclopentaphosphine of m.p. 150° was dissolved in tetrahydrofuran and treated with lithium (3·5 equiv.). After stirring and a short boiling under reflux, the lithium had dissolved completely. Addition of *o*-bromochlorobenzene followed by treatment under the usual reaction conditions and work-up resulted in a yield (34%) of the benzotriphosphole (I) almost identical with that (35%) for the method using phenylphosphonous dichloride and lithium (see Experimental section). This reaction represents a novel and rapid synthesis of the benzotriphosphole (I).

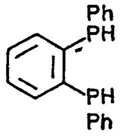
These results imply that the major pathway in the formation of the benzotriphosphole system is nucleophilic attack by the dilithiotriphosphine (XIV) on an *o*-dihalogenobenzene, probably in a two-step process [equation (3)]. This intramolecular reaction would be favoured by the formation of the almost unstrained five-membered triphosphine ring.



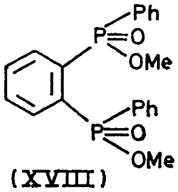
The formation of the 5,10-dihydro-5,10-diphenylphosphanthren (II) cannot be readily explained by this mechanism. In addition, however, to the dilithiotriphosphine (XIV), the solution derived from the interaction of phenylphosphonous dichloride and lithium contains some dilithio(phenyl)phosphine.[4] This compound may attack an *o*-dihalogenobenzene to form *o*-phenylenebis(lithiophenylphosphine) (XVI), which can react with unchanged phenylphosphonous dichloride to give the benzotriphosphole (I) or with *o*-dihalogenobenzene to give the phosphanthren (II). To test this hypothesis, *o*-phenylenebis(phenylphosphine) (XVII) was prepared by two methods:



(*A*) Initially the benzotriphosphole (I) was oxidised by hydrogen peroxide to *o*-phenylenebis(phenylphosphinic) acid (III),[1] which was converted by diazomethane into its dimethyl ester (XVIII). This ester showed i.r. absorptions corresponding to non-hydrogen bonded P=O (1235 cm^{-1}) and POMe (1185 cm^{-1}), and the n.m.r. spectrum showed signals for fourteen aromatic protons and two doublets (J_{PH} 11 Hz) at δ 3·61 and 3·56 p.p.m. due to the (±)- and *meso*-isomers. Reduction with lithium aluminium hydride[19] furnished *o*-phenylenebis(phenylphosphine) (XVII) in 16% yield based on compound (I) and 29% on the ester (XVIII).



(XVII)



(XVIII)

(*B*) Alternatively, direct reduction of the benzotriphosphole (I) in tetrahydrofuran solution with the hydride furnished the liquid diphosphine (XVII), in 86—95% yield.

The i.r. spectrum of the bis(phenylphosphine) (XVII)

---

[17] K. Issleib and F. Krech, *J. prakt. Chem.*, 1969, **311**, 463.
[18] K. Issleib and F. Krech, *Z. anorg. Chem.*, 1970, **372**, 65.
[19] K. B. Mallion and F. G. Mann, *J. Chem. Soc.*, 1964, 6121.

showed a PH band at 2295 cm^{-1}, and the n.m.r. spectrum showed signals for fourteen aromatic protons and two doublets (J_{PH} 210 Hz) at δ 5·15 and 5·36 p.p.m., corresponding to the (±)- and *meso*-forms of the diphosphine.

The bis(phenylphosphine) (XVII) in hexane was converted quantitatively by butyl-lithium into the bis(lithiophenylphosphine) (XVI). Addition of phenylphosphonous dichloride to the solution gave the benzotriphosphole (I) (43%). Alternatively, addition of *o*-bromochlorobenzene to the solution gave the phosphanthren (II). The phosphanthren could not be isolated directly from the reaction mixture, but was converted into its insoluble dibenzobromide (14%), which was then reduced back by lithium aluminium hydride to the pure phosphanthren (II).[2]

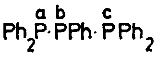
This ready preparation of *o*-phenylenebis(lithiophenylphosphine) (XVI) thus facilitates the synthesis of other benzotriphospholes in which P-2 is linked to various alkyl groups, and also of novel heterocyclic compounds similar to (I) but in which P-2 is itself replaced by other atoms (*cf.* Part II).[20]

Derivatives of 2,3-*Dihydro*-1,2,3-*triphenyl*-1H-1,2,3-*benzotriphosphole* (I).—Compound (I) forms a mono- and a di-sulphide,[1] whose structures have now been elucidated by analysis of their ^{31}P n.m.r. spectra.

The ^{31}P spectrum of the benzotriphosphole (I) itself shows a doublet at −32·5 p.p.m. (P-1 and P-3) from 85% phosphoric acid and a triplet at +39·4 p.p.m. (P-2, $^{1}J_{PP}$ 265 Hz; Table 1). This contrasts with that of the linear analogue 1,1,2,3,3-pentaphenyltriphosphine (XIX), which shows two signals at 3·9 (P_b) and 15·9 p.p.m. (P_a).[21] Thus in the former spectrum the resonances of the terminal phosphorus atoms are shifted downfield by 48 p.p.m. and that of the central phosphorus atom upfield by 36 p.p.m. A similar phenomenon has been observed in the case of the triphosphole (XX),[22] which shows resonances at −55 (P_a) and +41 p.p.m. (P_b). This has been explained on the basis that the formally non-bonding electron pair on each phosphorus atom is delocalised in π-type orbitals[23] which in a planar ring may overlap with the C–C π-orbitals of the fused benzene ring.

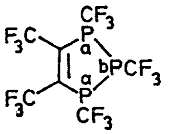
The 2,3-dihydro-1,2,3-triphenyl-1*H*-1,2,3-benzotriphosphole monosulphide could have structure (XXI) or (XXII).[1] The ^{31}P n.m.r. spectrum shows two doublets and a triplet, which can be accounted for only by the existence of three phosphorus atoms in different environments, as in structure (XXI). The simplicity of the spectrum of the disulphide indicates that it must be the symmetrical 1,3-disulphide (XXIII).

As the reaction of a tertiary phosphine with sulphur involves nucleophilic attack of the lone pair of the phosphorus atom,[24] and as phosphorus is less electron-withdrawing than a phenyl group, P-2 of the benzotriphosphole will be more nucleophilic than P-1 and P-3, and a P-2 sulphide might be expected. The formation of the 1-sulphide indicates that steric factors determine the course of the reaction: the incoming sulphur molecule approaches P-1 *cis* to only one phenyl group on the adjacent phosphorus atom, whereas attack at P-2 would result in the sulphur being *cis* to both phenyl groups on the adjacent P-1 and P-3. As sulphur reacts with tertiary phosphines with retention of configuration at phosphorus,[25] the stereochemistry of the mono- and di-sulphides must be as shown in (XXI) and (XXIII), respectively.

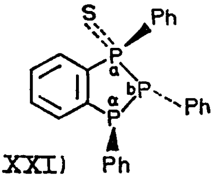


$\overset{a}{Ph_2P}\cdot\overset{b}{PPh}\cdot\overset{c}{PPh_2}$

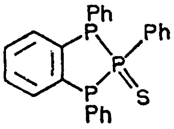
(XIX)



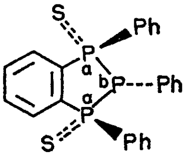
(XX)



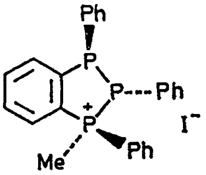
(XXI)



(XXII)



(XXIII)



(XXIV)

The ' low-melting ' disulphide reported previously[1] has been found by t.l.c. to be predominantly the 1,3-disulphide (XXIII), contaminated with *ca.* 10—15% of the 1-sulphide (XXI), which is difficult to eliminate by fractional crystallisation on the small scale previously employed.[1]

The monomethiodide[1] of the benzotriphosphole was too unstable to be examined by n.m.r. to confirm its structure, but on the basis of the evidence for the sulphide structures, and as a similar nucleophilic mechanism would be expected to operate, the methiodide is considered to have structure (XXIV). Hot methyl iodide and oxidising and reducing agents all readily cause the same type of splitting of the heterocyclic ring of compound (I).[1]

1,2,3-*Triethyl- and -Trimethyl*-2,3-*dihydro*-1H-1,2,3-*benzotriphospholes*.—The 1,2,3-triethyl compound has been prepared by the action of lithium on ethylphosphonous dichloride followed by addition of *o*-dibromobenzene. The liquid benzotriphosphole can be purified by careful distillation under vacuum and obtained in moderate yield (33% based on $EtPCl_2$). A crystalline disulphide (XXV) and a trisulphide (XXVI) have been isolated; the latter is prepared by heating an excess of sulphur with the benzotriphosphole in toluene for 8 h, whereas the disulphide is prepared by use of three atom equiv. of sulphur and also boiling for 8 h. The symmetrical structure (XXV) of the disulphide as opposed

---

[20] F. G. Mann and A. J. H. Mercer, *J.C.S. Perkin I*, in the press.

[21] L. Maier, personal communication to the eds., *Topics Phosphorus Chem.*, 1970, **5**, 247.

[22] W. Mahler, *J. Amer. Chem. Soc.*, 1964, **86**, 2306.

[23] W. Mahler and A. B. Bury, *J. Amer. Chem. Soc.*, 1958, **80**, 6161.

[24] P. D. Bartlett and G. Meguerian, *J. Amer. Chem. Soc.*, 1956, **78**, 3710.

[25] D. P. Young, W. E. McEwen, D. C. Velez, J. W. Johns, and C. A. VanderWerf, *Tetrahedron Letters*, 1964, 359.

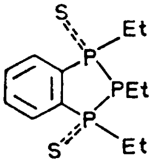
to the alternative unsymmetrical structure with two sulphur atoms linked to adjacent phosphorus atoms is proved by the simplicity of the ^{31}P n.m.r. spectrum, which shows a low-field doublet and a higher-field triplet (Table 1). The ^{31}P n.m.r. spectrum of the trisulphide (XXVI) is complex as a result of non-zero long-range coupling between P-1 and P-3 [compare a similar situation, discussed later, in the case of the trisulphide (XXVII)].

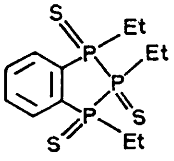
TABLE 1

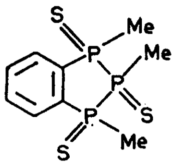
^{31}P N.m.r. spectra of benzotriphosphole derivatives

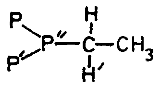
Compd.	Chemical shift (p.p.m.) *	Multiplicity (integration)	Assignment	$^1J_{PP}$/ Hz
(I)	-32.5	d (2)	P-1 and P-3	265 ± 4
	$+39.4$	t (1)	P-2	
(XXI)	-56.6	d (1)	P_a	270 ± 4
	-50.0	d (1)	P_a	
	$+37.6$	t (1)	P_b	
(XXIII)	-53	d (2)	P_a	265 ± 5
	$+37$	t (1)	P_b	
(XXV)	-68.2	d (2)	P_a	265 ± 10
	$+89.0$	t (1)	P_b	
(XXVI)	-43.0	m (2)	P_a	
	-24.9	m (1)	P_b	

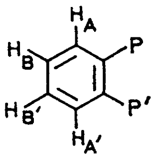
* Relative to 85% H_3PO_4.


(XXV)


(XXVI)

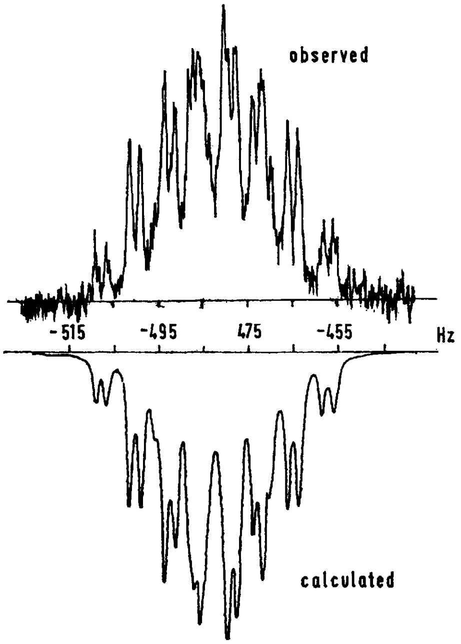

(XXVII)

(XXVIII)



(XXIX)

The 100 MHz ^{1}H n.m.r. spectrum of the disulphide (XXV) in deuteriochloroform was extremely complex. However if hexadeuteriobenzene was used as solvent and the spectrum was run at 220 MHz, the multiplets were well separated. The multiplet at δ 2·16 p.p.m. [P(2)·CH_2] was complex but was susceptible to a least-squares method of line-shape analysis (program devised by Sheldrick [26]). The model used was an $AA'B_3XX'Y$ spin system (XXVIII); 105 data points were taken from the observed spectrum and the six parameters derived from the calculations are presented in Table 2. The observed and calculated spectra are shown for comparison in the Figure. As seen (Table 2), the estimated standard deviations are $\leqslant 0.08$ and the R factor is 0·10. The R factor is defined as $[\Sigma(I_{obs} - I_{calc})^2/\Sigma(I_{obs})^2]^{\frac{1}{2}}$, where I_{obs} and I_{calc} are the observed and calculated intensities.

In such a complex system of six groups of magnetically non-equivalent nuclei, the calculated spectrum was not sensitive to refinement of all parameters and so those obtainable unequivocally by observation of other parts of the spectrum and from the ^{31}P n.m.r. data by first-order analysis were given fixed values. Furthermore, although the chemical shifts of the three phosphorus nuclei are correct relative to one another, they have not been calculated relative to hydrogen but have been given an arbitrary large positive value (*ca.* 10^6 Hz).



Observed and calculated n.m.r. spectra for the low field methylene multiplet of 1,2,3-triethyl-2,3-dihydro-1*H*-1,2,3-benzotriphosphole 1,3-disulphide

TABLE 2

N.m.r. parameters (δ and J in Hz) for low-field methylene group of 1,2,3-triethyl-2,3-dihydro-1*H*-1,2,3-benzotriphosphole [a]

	(a)	(b)	(c)
Half-width	1·36 (05)	1·32 (05)	
δ[P]*	85000·00	85000·00	
δ[P″]*	119570·00	119570·00	
δ[H]	−482·39 (02)	−482·39 (02)	−482·39
δ[H_3]*	−277·00	−277·00	
J[PP′]*	0·00	0·00	
J[PP″]*	265·00	265·00	
J[PH]	11·19 (08)	11·59 (07)	11·2—11·6
J[PH′]	16·39 (07)	15·99 (07)	16·4—16·0
J[PH_3]*	0·00	0·00	
J[P″H]	2·49 (04)	2·48 (04)	2·49—2·48
J[P″H_3]*	21·40	21·40	
J[HH′]*	−14·00	−10·00	
J[HH_3]	7·76 (03)	7·75 (03)	7·76—7·75
R factor	0·10	0·10	

Negative δ values are downfield from tetramethylsilane; to convert chemical shifts to p.p.m. divide by 220; estimated standard deviations are given in parentheses.

Parameters marked by an asterisk have fixed values.

Column (a) gives values when $J_{HH'} = -14$ Hz; column (b) gives values when $J_{HH'} = -10$ Hz; column (c) gives the range of values within which each parameter must lie.

[a] The symbolism used is the same as that used by Glidewell, Rankin, and Sheldrick [26] in their paper on a similar n.m.r. problem, and is based on the way the computer prints out the data.

---

[26] C. Glidewell, D. W. H. Rankin, and G. M. Sheldrick, *Trans. Faraday Soc.*, 1969, **65**, 2801.

Refinement of the geminal HH coupling constant could not be achieved, so values were fixed at −10 and −14 Hz (ref. 27 gives extreme values of −9·6 and −15·5 Hz) and the other parameters were found to vary by only a small amount. Column (c) of Table 2 gives the range within which the parameters must lie.

The 'aromatic' part of the n.m.r. spectrum was analysed in a similar way using an AA′BB′XX′ model (XXIX) with 139 data points from the observed spectrum; the results are shown in Table 3. In this case the standard deviations range up to 0·14 and the R factor is 0·15. It cannot therefore be asserted with certainty that the values represent a unique solution to the problem, but they nevertheless are reasonable values based on coupling constants derived from similar compounds.[28]

TABLE 3

N.m.r. parameters (δ and J in Hz) for aromatic region of 1,2,3-triethyl-2,3-dihydro-1*H*-1,2,3-benzotriphosphole [a]

Half-width	1·67 (08)
δ[P]*	10,000·00
δ[H_A]	−1706·33 (05)
δ[H_B]	−1559·68 (03)
J[PH_A]	10·44 (09)
J[PH_B]	3·58 (10)
J[$PH_{B'}$]	2·81 (12)
J[$PH_{A'}$]	3·45 (12)
J[PP′]*	0·00
J[H_A–H_B]	7·85 (09)
J[H_A–$H_{B'}$]	0·86 (14)
J[H_A–$H_{A'}$]*	0·30
J[H_B–$H_{B'}$]*	7·50
R factor	0·15

[a] See footnote *a* in Table 2

The computed parameters for the aryl and alkyl parts of the molecule are consistent with the proposed structure (XXV).

Lithium reacted vigorously with methylphosphonous dichloride to give an orange solution, the colour of which was discharged when the mixture was boiled with *o*-dibromobenzene. After the usual work-up, an oil was obtained which when distilled under reduced pressure gave a mixture. The mass spectrum of this mixture showed that the major constituents were 2,3-dihydro-1,2,3-trimethyl-1*H*-1,2,3-benzotriphosphole and pentamethylcyclopentaphosphine, together with a small amount of *o*-dibromobenzene. The b.p. of the mixture was identical with that of the polymethylcyclopolyphosphine,[10] and it was impossible to obtain pure dihydrotrimethylbenzotriphosphole. After addition of an excess of sulphur to the mixture a crystalline solid was isolated and identified as the trisulphide (XXVII) from its i.r., mass, and n.m.r. spectra; the last provided unequivocal support for the structure (XXVII).

The ^{1}H n.m.r. spectrum of this compound in the aliphatic region consists of a double triplet (3H, $P_2P{\cdot}CH_3$) and four lines of equal intensity at higher field [6H, $C_6H_4{\cdot}P(CH_3){\cdot}P$]. Harris[29] has shown that in a system $X_3AA'X'_3$ in the special case where $J_{AA'} \gg |J_{AX} - J_{AX'}|$ a deceptively simple spectrum is obtained. This has three lines of which the central one is broad and approximately the same height as the outer ones. Under these circumstances the only parameter which can be derived independently is $|J_{AX} + J_{AX'}|$, which is the distance between the sharp outer lines. Such a case is that of tetramethyldiphosphine, Me_2PPMe_2.[30] In 2,3-dihydro-1,2,3-trimethylbenzotriphosphole trisulphide (XXVII), the P-1 and P-3 methyl groups have an intervening *o*-phenylene group but still act as an $X_3AA'X'_3$ system, further split by the central phosphorus atom. Thus the four high-field lines at δ 1·63 are actually two overlapping systems of a broad central line and two sharp outer lines. Full analysis of the system may be possible by examination of the ^{31}P and ^{13}C spectra[30] and work is continuing on this subject.

Mass Spectra.—The mass spectra of various benzotriphosphole derivatives are presented (Table 4). A number of features are common to all the sulphides. The major pathway involves fragmentation of the molecular ion (of a mono-, di-, or tri-sulphide) to give an ion (*a*) (R = Ph, *m*/*e* 324; R = Et, *m*/*e* 228; R = Me, *m*/*e* 200) which subsequently loses the group R to give (*b*) (R = Ph, *m*/*e* 247; R = Et, *m*/*e* 199; R = Me, *m*/*e* 185).

TABLE 4

Mass spectra * of some benzotriphosphole derivatives

(I)	*m*/*e*	400(100), 323(54), 183(52) †
(XXI)	*m*/*e*	432(38), 400(91), 369(10), 356(4), 324(32), 323(59), 292(76), 247(20), 214(18), 183(100) †
(XXIII)	*m*/*e*	464(22), 432(26), 400(9), 369(7), 356(11), 324(100), 292(48), 247(37), 214(18), 183(85) †
(XXV)	*m*/*e*	320(87), 292(17), 291(21), 264(9), 263(11), 259(12), 231(33), 228(78), 199(100), 171(31), 139(21)
(XXVI)	*m*/*e*	352(15), 292(24), 258(35), 256(69), 243(25), 228(21), 199(38), 192(24), 171(36), 160(41), 139(10), 128(58), 118(26), 106(100)
(XXVII)	*m*/*e*	310(20), 258(31), 256(86), 200(35), 192(22), 185(41), 171(14), 160(43), 139(8), 128(100), 96(39)

* Relative intensities (%) in parentheses. Generally values of *m*/*e* greater than 5% of the base peak are given. † In (I), (XXI), and (XXIII), the peaks below *m*/*e* 183 are not given but are similar to those in ref. 31.

The further breakdown of this ion depends on the nature of R. If R is Ph then a favourable pathway involves expulsion of sulphur and hydrogen to give the stable phosphanthren ion (*c*), which can lose a phosphorus atom to yield another quasiaromatic species (*d*), the breakdown of which has been described by Williams *et al.*[31] If R is alkyl, an anthracene analogue cannot be formed and an alternative pathway is followed. Loss of the group R − H from ion (*b*) (R = Me or Et) gives ion (*e*), which further loses sulphur to form (*f*).

---

[27] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' vol. 1, Pergamon, London, 1965, p. 172.

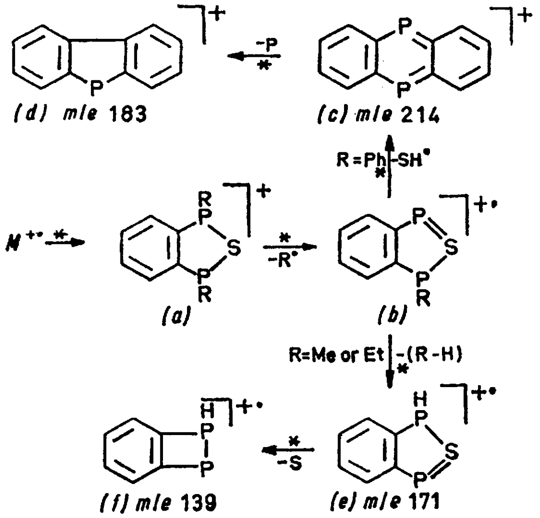
[28] F. G. Mann and A. J. H. Mercer, unpublished results.

[29] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

[30] R. K. Harris and R. G. Hayter, *Canad. J. Chem.*, 1964, **42**, 2282.

[31] D. H. Williams, R. S. Ward, and R. G. Cooks, *J. Amer. Chem. Soc.*, 1968, **90**, 967.

The fragmentations are summarised in Scheme 2; the processes marked by an asterisk were supported by the observation of the appropriate metastable ions.



SCHEME 2

EXPERIMENTAL

^{31}P N.m.r. spectra were recorded for solutions in deuteriochloroform with tetramethylsilane as internal standard (Perkin-Elmer R10, Varian HA 100 or HA 220 spectrometers); ^{31}P n.m.r. spectra were recorded in chloroform with phosphoric oxide as external standard (JEOL JHN-4H-100 spectrometer). I.r. spectra were recorded (Nujol mulls) with a Perkin-Elmer 257 spectrometer, and mass spectra with an A.E.I. MS9 spectrometer. T.l.c. was carried out on silica GF 254 plates.

All ethereal extracts were dried with anhydrous sodium sulphate before evaporation.

2,3-*Dihydro*-1,2,3-*triphenyl*-1H-1,2,3-*benzotriphosphole* (I).—Highest yields of the benzotriphosphole were achieved with *o*-bromochlorobenzene by the following modification of the earlier method.[1]

Phenylphosphonous dichloride (50 g) in dry tetrahydrofuran (200 ml) was added dropwise during 30 min to a suspension of lithium foil (6·2 g) in dry tetrahydrofuran (200 ml) under nitrogen at *ca.* 0°. After a short induction period the colour of the mixture became red and the solution was then cooled to −20°; this temperature was maintained for the remainder of the addition. The mixture was stirred for a further 2 h at −20° and then filtered under nitrogen to remove the excess of lithium metal (0·7 g). The mixture was cooled to −40°, *o*-bromochlorobenzene (27 g) in tetrahydrofuran (100 ml) was added during 20 min, and the mixture was set aside overnight at room temperature. It was then boiled under reflux for 3 h; the solvent was distilled off at atmospheric pressure and the ice-cooled residue was treated with wet ether (500 ml) and deoxygenated water (200 ml). The two layers were contaminated with grey insoluble material, which was collected. The ethereal layer was separated, dried, and treated as described previously[1] to give the benzotriphosphole (5·6 g). The insoluble material was boiled with acetone (4 × 200 ml) until no more solid was extracted. After concentration of the extracts more benzotriphosphole crystallised out (7·3 g). A total of 12·9 g (35% with respect to $PhPCl_2$) of the benzotriphosphole, m.p. 184—186°, was isolated; $\nu_{max.}$ (KBr) 1450, 1440, 1430, 1040, and 1030 cm^{-1} (PAr).

The preparation was carried out from a number of *o*-dihalogenobenzenes; the results are summarised in Table 5.

TABLE 5

o-C_6H_4XY	$PhPCl_2$ (g)	Dihalogeno-benzene (g)	Tri-phosphole (g)	Yield % based on $PhPCl_2$
X = Y = Cl	50	22	7·4	22
X = Cl, Y = Br	50	27	12·9	35
X = Cl, Y = I	42	28	7·4	24
X = Y = Br	25	16	5·8	32
X = Br, Y = I	33	26	6·1	25
X = Y = I	33	31	4·8	20

Attempted Reaction of Benzyne with Pentaphenylcyclopentaphosphine.—A solution of anthranilic acid (3·0 g) and pentaphenylcyclopentaphosphine (7·0 g) (prepared by the method of Henderson using magnesium[10]) in acetone (15 ml) and dichloromethane (20 ml) was added dropwise under nitrogen during 1 h to a solution of 3-methylbutyl nitrite (2·8 g) in dichloromethane (40 ml). The mixture was boiled under reflux for 5 h, set aside overnight at room temperature, and then evaporated on a water-bath to small bulk, whereupon pentaphenylcyclopentaphosphine crystallised (5·8 g, 83% recovery), m.p. and mixed m.p. 149—151° (lit.,[10] 148—152°). The filtrate was evaporated, giving an oil which was sublimed at 0·1 mmHg and 140° (bath) to give biphenylene (20 mg), m.p. and mixed m.p. 110—111° (lit.,[32] 110—111°), identical (u.v. spectrum) with an authentic sample. 2,3-Dihydro-1,2,3-triphenyl-1*H*-1,2,3-benzotriphosphole (I) could not be sublimed from the residue.

A second experiment with the same amount of cyclopolyphosphine but twice as much anthranilic acid and 3-methylbutyl nitrite to generate benzyne also gave a high recovery (88%) of starting material and no triphosphole.

Interaction of Lithium and Pentaphenylcyclopentaphosphine followed by Addition of o-*Bromochlorobenzene.*—A solution of the cyclopentaphosphine (12·2 g) in dry tetrahydrofuran (50 ml) under nitrogen was treated with lithium foil (0·53 g; sufficient theoretically to give complete conversion into LiPPh·PPh·PPhLi), and the mixture was stirred for 2 h with external cooling to ensure that the temperature did not exceed 25°. The resultant red mixture was then boiled for 10 min to give complete dissolution of the lithium.

The solution was cooled to −40° and *o*-bromochlorobenzene (7·2 g) in tetrahydrofuran (10 ml) was added during 20 min. The mixture became brown in colour and was set aside at room temperature for 2 h. It was then boiled under reflux for 10 min, the tetrahydrofuran was distilled off, and ether (100 ml) was added, followed by dil. hydrochloric acid (50 ml). Two layers and some solid separated; the solid was collected and recrystallised from acetone to give 2,3-dihydro-1,2,3-triphenyl-1*H*-1,2,3-benzotriphosphole (4·4 g). The ethereal layer was separated, dried, and evaporated, giving an oil which on cooling and dilution with acetone (10 ml) yielded a further crop of the triphosphole (0·5 g; total yield 4·9 g, 34%).

Derivatives of 2,3-*Dihydro*-1,2,3-*triphenyl*-1H-1,2,3-*benzotriphosphole* (I).—The following derivatives were prepared

---

[32] W. Baker, M. P. V. Boarland, and J. F. W. McOmie, *J. Chem. Soc.*, 1954, 1476.

by the method described previously:[1] 2,3-dihydro-1-methyl-1,2,3-triphenyl-1*H*-1,2,3-benzotriphospholium iodide, m.p. *ca.* 175°, $\nu_{max.}$ 1440, 1430, 1420, 1020, 996 (PAr), 1280, and 875 cm^{-1} (PMe); the benzotriphosphole 1-sulphide (XXI), m.p. 123—124°, $\nu_{max.}$ 1440, 1430, 1420, 1022, 998 (PAr), and 708 cm^{-1} (P=S); the benzotriphosphole 1,3-disulphide (XXIII), m.p. 203—204°, $\nu_{max.}$ 1440, 1430, 1420, 1022, 996 (PAr), 748, 710, and 702 cm^{-1} (P=S) (the so-called 'high melting' disulphide[1]).

o-*Phenylenebis(phenylphosphinic Acid)* (III).—A solution of 2,3-dihydro-1,2,3-triphenyl-1*H*-1,2,3-benzotriphosphole (15·0 g) in acetone (400 ml) and aqueous hydrogen peroxide (100 vol; 25 ml) was set aside overnight, then gently evaporated to half-bulk, and finally boiled under reflux for 2 h. It was evaporated under reduced pressure, giving an oil which was dissolved in dilute sodium hydroxide (2N; 70 ml); the solution was extracted with chloroform (3 × 100 ml) and then neutralised with dil. sulphuric acid to precipitate the bis(phosphinic acid) (5·8 g, 43%) as needles, m.p. 207—208° (from aqueous ethanol) (Found: C, 60·4; H, 4·6; P, 16·5. Calc. for $C_{18}H_{16}O_4P_2$: C, 60·3; H, 4·5; P, 17·3%), $\nu_{max.}$ 2600 (OH), 1442 (PAr), and 1175 cm^{-1} (P=O).

Dimethyl o-*Phenylenebis(phenylphosphinate)* (XVIII).—A solution of *o*-phenylenebis(phenylphosphinic acid) (III) (7·0 g) in methanol (60 ml) was treated dropwise with ethereal diazomethane in ether[33] until the mixture remained permanently yellow. The solvent was evaporated off under reduced pressure to give an oil, which when distilled gave impure dimethyl *o*-phenylenebis(phenylphosphinate) (5·3 g, 57%), b.p. 260° at 0·5 mmHg, $\nu_{max.}$ (film) 1440 (PAr), 1235 (P=O), and 1185 cm^{-1} (POMe); δ 7·3—8·4 (14H, m), 3·61 (3H, d, J_{PH} 11 Hz), and 3·56 p.p.m. (3H, d, J_{PH} 11 Hz). The distillate solidified to a hygroscopic glass which could not be induced to crystallise and which did not give a satisfactory analysis (Found: C, 60·2; H, 5·0. Calc. for $C_{20}H_{20}O_4P_2$: C, 62·2; H, 5·2%).

o-*Phenylenebis(phenylphosphine)* (XVII).—*Method A*. Lithium aluminium hydride (1·3 g) was added in portions to a stirred solution of dimethyl *o*-phenylenebis(phenylphosphinate) (5·0 g) in dry tetrahydrofuran (70 ml) under nitrogen cooled in ice. Effervescence occurred during initial addition of the hydride, and after about half was added a red colour had developed. After addition was complete, the mixture was boiled under reflux for 10 h, and the solvent distilled off to give a paste to which ether (125 ml) and deoxygenated dil. hydrochloric acid (50 ml) were added; the two layers were filtered under nitrogen and separated, and the dried ethereal layer was evaporated to give an oil which on distillation gave o-*phenylenebis(phenylphosphine)* (1·1 g, 29%), b.p. 170—174° at 0·05 mmHg (Found: C, 73·4; H, 5·5; P, 20·9. $C_{18}H_{16}P_2$ requires C, 73·5; H, 5·4; P, 21·1%), $\nu_{max.}$ (film) 2295 (PH), 1442, and 1005 cm^{-1} (PAr); δ (C_6D_6) 7·0—7·6 (14H, m), 536 (1H, d, $^1J_{PH}$ 210 Hz), and 5·15 p.p.m. (1H, d, $^1J_{PH}$ 210 Hz).

Method B.—The hydride (11 g) was similarly added to a solution of the benzotriphosphole (I) (30 g) in tetrahydrofuran (350 ml) under nitrogen. The mixture was boiled for 10 h, set aside overnight, and then evaporated to give a paste. After addition of ether (350 ml) and dilute hydrochloric acid (3N; 300 ml), the product was worked up as in method A, giving the bis(phenylphosphine) (18·9 g, 86%), b.p. 175—176° at 0·01 mmHg, identical (i.r. spectrum) with the foregoing sample.

Reaction of o-*Phenylenebis(lithiophenylphosphine)* (XVI) *with Phenylphosphonous Dichloride*.—A solution of butyl-lithium in hexane (1·25M; 1·6 ml) was added dropwise to *o*-phenylenebis(phenylphosphine) (294 mg) in dry tetrahydrofuran (10 ml) under nitrogen at −40° to give a red solution, which was subsequently boiled under reflux for 10 min to ensure complete conversion into the dilithiobisphosphine. The solution was again cooled to −40° and a solution of phenylphosphonous dichloride (179 mg) in tetrahydrofuran (10 ml) was added dropwise. The red colour was discharged immediately. The solution was evaporated under reduced pressure to give a paste to which were added water (15 ml) and ether (40 ml). The ethereal layer was separated, dried, and evaporated to give 2,3-dihydro-1,2,3-triphenyl-1*H*-benzotriphosphole (I) (25 mg). Solid residues from the ether–water separation were extracted with boiling acetone to give more triphosphole (147 mg; total 172 mg, 43%), m.p. and mixed m.p. 186—187° (Found: P, 22·9. Calc. for $C_{24}H_{19}P_3$: P, 23·2%), identical (i.r. spectrum) with an authentic sample.

Reaction of o-*Phenylenebis(lithiophenylphosphine) with* o-*Chlorobromobenzene*.—Butyl-lithium in hexane (1·55M; 6·6 ml) was added dropwise to *o*-phenylenebis(phenylphosphine) (1·45 g) in tetrahydrofuran (35 ml) under nitrogen at −40° to give the bis(lithiophenylphosphine). The solution was cooled to −50° and a solution of *o*-chlorobromobenzene (1·0 g) in tetrahydrofuran (5 ml) was added dropwise, the colour of the mixture changing from red to black. The mixture was allowed to warm to room temperature and was evaporated to a paste to which were added ether (50 ml) and dil. hydrochloric acid (25 ml). The ethereal solution was separated, dried, and evaporated to give an oil which could not be induced to crystallise. It was dissolved in acetone (10 ml) and benzyl bromide (5 g) was added; the mixture was boiled under reflux to give a white precipitate of 5,10-dibenzyl-5,10-dihydro-5,10-diphenylphosphanthrenium dibromide (0·5 g, 14%), which was washed with boiling acetone and ethanol; m.p. 370° (decomp.), mixed m.p. 375—376° (lit.,[2] m.p. 387° dependent on rate of heating).

The dibromide (0·5 g) in tetrahydrofuran (10 ml) was reduced by boiling under reflux with lithium aluminium hydride (0·2 g) for 4 h.[2] The mixture was evaporated under reduced pressure and hydrolysed with dilute hydrochloric acid, and the hydrolysate was extracted with ether. The extracts were dried and evaporated under reduced pressure to give 5,10-dihydro-5,10-diphenylphosphanthren (II) (125 mg), crystals from ethyl methyl ketone, m.p. 183—185°, mixed m.p. 184—187°, identical (i.r. spectrum) with an authentic sample.

1,2,3-*Triethyl*-2,3-*dihydro*-1H-1,2,3-*benzotriphosphole*.—Ethylphosphonous dichloride (16 g) in dry tetrahydrofuran (75 ml) was added dropwise to a suspension of lithium foil (2·5 g) in tetrahydrofuran (75 ml) at −40° under nitrogen. The mixture was stirred for 1 h to give a yellow-orange solution. *o*-Dibromobenzene (9·6 g) in tetrahydrofuran (20 ml) was added dropwise during 10 min to give a dark red solution, which was stirred for 1 h at −40 to −65° and then allowed to warm to room temperature and left overnight. The mixture was boiled under reflux for 3 h and then evaporated to small bulk. Ether (200 ml) and deoxygenated water (150 ml) were added. The ethereal layer was separated, dried, and evaporated to give an oil which was distilled to yield fractions (*a*) b.p. 80—125° at 1 mmHg (0·7 g); (*b*) b.p. 127—130° at 1 mmHg (2·0 g); and (*c*)

---

[33] T. J. de Boer and H. J. Backer, *Org. Synth.*, 1963, Coll. Vol. IV, p. 250.

b.p. 130—155° at 1 mmHg (1·5 g). Analysis indicated that a middle cut of fraction (*b*) was 1,2,3-*triethyl*-2,3-*dihydro*-1H-

130—155° at 1 mmHg (1·5 g). Analysis indicated that a middle cut of fraction (*b*) was 1,2,3-*triethyl*-2,3-*dihydro*-1H-

1,2,3-*benzotriphosphole* (Found: C, 55·3; H, 7·2. $C_{12}H_{19}P_3$ requires C, 56·3; H, 7·4%), $\nu_{max.}$ (film) 1420 and 1030 cm^{-1} (PAr); δ (C_6D_6) 7·54 (2H, m), 7·04 (2H, m), 2·61 (6H, m), and 1·08 p.p.m. (9H, 6 lines). Comparison of i.r. spectra indicated that fractions (*b*) and (*c*) were also the pure triethyldihydrobenzotriphosphole (3·5 g, 33%).

Sulphides of 1,2,3-*Triethyl*-2,3-*dihydro*-1H-1,2,3-*benzotriphosphole*.—The benzotriphosphole (500 mg), toluene (50 ml), and sulphur (1 g, 16 atom equiv.) were boiled under reflux for 8 h under nitrogen. The mixture was cooled and the solution was decanted from residual sulphur and evaporated under reduced pressure to give a viscous oil, which when stirred with ether deposited the crystalline 1,2,3-triethyl-2,3-dihydro-1*H*-1,2,3-benzotriphosphole 1,2,3-trisulphide (XXVI), prisms, m.p. 121·5—122° (lit.,[1] 120—122°) (from aqueous acetone) (400 mg, 58%) (Found: C, 41·1; H, 5·4. Calc. for $C_{12}H_{19}P_3S_3$: C, 41·2; H, 5·4%), $\nu_{max.}$ 1430, 1030, 996 (PAr), and 730 cm^{-1} (P=S); δ (220 MHz; C_6D_6) 7·60 (2H, m), 6·98 (2H, m), 2·52 (4H, m), 1·67 (2H, 9 lines), 1·32 (3H, dt, J_{HH} 7·5, $^3J_{PH}$ 22·5 Hz), and 1·13 p.p.m. (6H, dt, J_{HH} 7·5, $^3J_{PH}$ 21·8 Hz).

The benzotriphosphole (969 mg), dry toluene (15 ml), and sulphur (320 mg, 2·6 atom equiv.) were boiled under reflux for 8 h under nitrogen. The mixture, worked up as previously, yielded 1,2,3-*triethyl*-2,3-*dihydro*-1H-1,2,3-*benzotriphosphole* 1,3-*disulphide* (XXV) (320 mg, 29%), prisms, m.p. 141—142° (from acetone) (Found: C, 45·1; H, 5·9; P, 28·8. $C_{12}H_{19}P_3S_2$ requires C, 45·0; H, 5·9; P, 29·05%), $\nu_{max.}$ 1430, 1030, 998 (PAr), and 730 cm^{-1} (P=S); δ (220 MHz; C_6D_6) 7·72 (2H, m), 7·05 (2H, m), 2·16 (2H, m), 1·75 (4H, m), 1·24 (3H, dt, $^3J_{PH}$ 21·4, J_{HH} 7·75 Hz), and 1·05 p.p.m. (6H, dt, $^3J_{PH}$ 21·4, J_{HH} 7·75 Hz).

2,3-*Dihydro*-1,2,3-*trimethyl*-1H-1,2,3-*benzotriphosphole*.—This was prepared precisely as the 1,2,3-triethyl analogue, but from methylphosphonous dichloride (14·3 g) in place of ethylphosphonous dichloride (16 g), and lithium (2·5 g).

The final ethereal layer was separated, dried, and evaporated, giving an oil, b.p. 107—114° at 1 mmHg; this distillate (900 mg) appeared to be a mixture of 2,3-dihydro-1,2,3-trimethyl-1*H*-1,2,3-benzotriphosphole, *o*-dibromobenzene, and pentamethylcyclopentaphosphine (see Discussion section) [Found: C, 41·3; H, 4·5; P, 33·05, 33·6. Calc. for $C_9H_{13}P_3$: C, 50·5; H, 6·1; P, 43·5. Calc. for $(CH_3P)_5$: C, 26·1; H, 6·5; P, 67·4. Calc. for $C_6H_4Br_2$: C, 30·5; H, 1·7%].

A portion of the crude dihydrotrimethylbenzotriphosphole (659 mg) was boiled under reflux with sulphur (700 mg) in toluene (15 ml) under nitrogen for 6 h. The solution was evaporated under reduced pressure to give a solid which was extracted with ether (40 ml); the residue was recrystallised from acetone to give 2,3-*dihydro*-1,2,3-*trimethyl*-1H-1,2,3-*benzotriphosphole* 1,2,3-*trisulphide* (XXVII) (318 mg), needles, m.p. 184—185° (Found: C, 34·5; H, 4·3; P, 29·9. $C_9H_{13}P_3S_3$ requires C, 34·85; H, 4·2; P, 30·0%), $\nu_{max.}$ 1435 (PAr), 1280, 898, 872 (PMe), and 735 cm^{-1} (P=S); δ(C_6D_6 7·68 (2H, m), 6·92 (2H, m), 1·92 (3H, dt, $^2J_{PH}$ 11·8, $^3J_{PH}$ 7·2 Hz), 1·63 (6H, pseudo-dd, $^2J_{PH} + {}^4J_{PH} = 12·8$, $^3J_{PH}$ 6·4 Hz).

We thank Dr. G. M. Sheldrick for discussion of n.m.r. spectra and for the provision of the computer programs for line-shape analysis of these spectra. We are grateful to Dr. K. Morallee, Oxford University, for recording ^{31}P n.m.r. spectra, Mr. B. Crysell for 100 MHz spectra, and Imperial Chemical Industries, Runcorn, for 220 MHz spectra. We are indebted to Messrs. Albright and Wilson Ltd. for gifts of chemicals, to the S.R.C. for a post-doctoral grant, and to the University of Cambridge Computer Laboratory for provision of computing facilities. Calculations were made on the Titan Computer.

[2/066 *Received*, 13*th January*, 1972]