

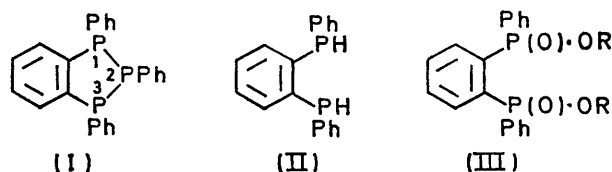
Further Studies in the Chemistry of 2,3-Dihydro-1,2,3-triphenyl-1*H*-1,2,3-benzotriphosphole and Related Compounds. Part II¹

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o-Phenylenebis(phenylphosphine) (II), now readily available, is a valuable precursor in the synthesis of several new heterocyclic systems having a benzene ring fused to a five- or six-membered ring containing at least two phosphorus atoms. The following heterocyclic systems (with phenyl substituents) have been prepared: the 1,2,3-benzotriphospholes (V; R = Me or Et); the 1,3,2-benzodiphospharsoles (VIII; R = Ph or Me); the 1,3-benzodiphosphole (X); the 1,4-benzodiphosphorins (XI) and (XXVII); and the dibenzo[*c,g*][1,2,5,6]-tetraphosphocin (XXIII). The chemistry and spectroscopic properties of these compounds have been investigated.

The mechanism of the alkaline hydrolysis of the 1,4-benzodiphosphorinium salt (XVI) to give the bis(phosphine oxide) (XVII) is discussed.

DURING an investigation of the mechanism of the formation of 2,3-dihydro-1,2,3-triphenyl-1*H*-1,2,3-benzotriphosphole (I) by the interaction of *o*-dihalogenobenzenes with the crude product from the action of lithium on phenylphosphonous dichloride,¹ it was found that compound (I) was readily reduced by lithium aluminium



hydride to give the valuable intermediate *o*-phenylenebis(phenylphosphine) (II) in 86–95% yield.

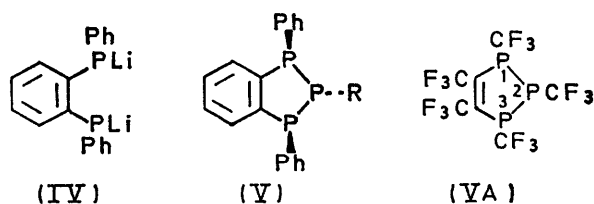
It had been noted earlier that oxidation of compound (I) by potassium permanganate² or by hydrogen peroxide¹ gave *o*-phenylenebis(phenylphosphinic acid) (III; R = H); treatment of this acid with diazomethane gave dimethyl *o*-phenylenebis(phenylphosphinite) (III; R = Me), but reduction of this ester with lithium aluminium hydride gave the diphosphine (II) in only 16% yield.

Crystallographic analysis of the compound (I) has shown that the fused bicyclic system is flat, and that the

1- and 3-phenyl groups are *cis* to one another and *trans* to the 2-phenyl group.^{2,3}

The ready accessibility of the diphosphine (II) has enabled a wide range of new heterocyclic compounds to be prepared.

The diphosphine (II), when treated with 2 equiv. of butyl-lithium in hexane is converted into the dilithiodiphosphine (IV), which reacts with alkylphosphonous dichlorides to give the corresponding 2-alkyl-2,3-dihydro-1,3-diphenyl-1*H*-1,2,3-benzotriphospholes (V). Thus prepared, the 2-methyl and 2-ethyl compounds (V; R = Me or Et) can be readily purified. In contrast, if either methyl- or ethyl-phosphonous dichloride is treated in boiling tetrahydrofuran solution with lithium,



and the product in turn is treated with *o*-dibromobenzene, the corresponding 1,2,3-trialkyl-2,3-dihydro-1*H*-1,2,3-benzotriphosphole is obtained in low yield and cannot be

¹ Part I, F. G. Mann and A. J. H. Mercer, *J.C.S. Perkin I*, 1972, 1631.

² F. G. Mann and M. J. Pragnell, *J. Chem. Soc. (C)*, 1966, 916.

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

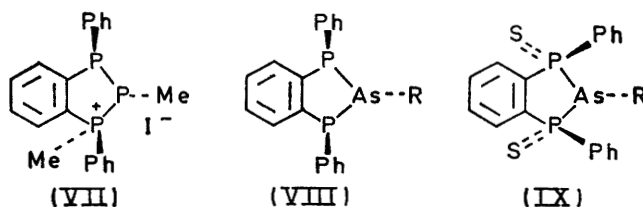
readily purified: this applies particularly to the 1,2,3-trimethyl member.¹ On the other hand, phenylphosphonous dichloride gives a high yield of the pure 1,2,3-triphenyl compound (I) by either method.^{1,2}

The structures of compounds (V; R = Me or Et) were confirmed by analysis, i.r. and n.m.r. spectroscopy, and mass spectrometry. The ³¹P n.m.r. spectra showed a low-field doublet (P-1 and P-3) with respect to 85% phosphoric acid as external standard and a high field triplet (P-2). Similar spectra have been observed for 2,3-dihydro-1,2,3-triphenyl-1*H*-1,2,3-benzotriphosphole (I)¹ and for 2,3-dihydro-1,2,3,4,5-pentakis(trifluoromethyl)-1,2,3-triphosphole (VA).^{1,4}

Both the 2-alkylbenzotriphospholes (V; R = Me or Et) react with sulphur to give disulphides. The ³¹P n.m.r. spectra indicate that these are the symmetrical 1,3-disulphides: both spectra are simple, showing a low-field doublet corresponding to two phosphorus atoms in identical magnetic environments, and a triplet at higher field.

As the methyl group on P-2 (V; R = Me) is electron-donating, nucleophilic attack by P-2 on sulphur would be more favoured on electronic grounds than attack by

A monomethiodide of the 2-methylbenzotriphosphole (V; R = Me) was isolated from the reaction with methyl iodide in toluene at room temperature. This compound was even more unstable than the methiodide of the 2-phenyl analogue,¹ and it was particularly susceptible to hydrolysis; consequently poor analytical figures were obtained and the ³¹P n.m.r. spectrum could not be recorded as an inert solvent was not available. However, on the basis of the evidence for the sulphide structures,¹ and as a similar nucleophilic mechanism is expected to operate, the methiodide probably has the structure (VII).



The dilithiodiphosphine (IV) reacted with methyl- and phenyl-arsonous dichlorides to form (respectively) 2,3-dihydro-2-methyl-1,3-diphenyl-1*H*-1,3,2-benzodiphospharsole (VIII; R = Me) and its 2-phenyl analogue (VIII; R = Ph). Each reacted with sulphur to yield a 1,3-disulphide (IX; R = Me or Ph). Insufficient material was available for ³¹P n.m.r. spectroscopy to confirm the positions of the sulphur atoms, but the aromatic region in the ¹H n.m.r. spectrum was closely similar to that of analogous 1,3-disulphides prepared in this laboratory.¹

2,3-Dihydro-1,3-diphenyl-1,3-benzodiphosphole (X) was prepared by the reaction of the dilithiodiphosphine (IV) with dichloromethane at room temperature. The complex proton n.m.r. spectrum, consisting of an aromatic region (δ 7.6–6.8) and a high-field region (δ 2.9–2.0 p.p.m.) having at least 16 lines, suggests that the product may be a mixture of *cis*- and *trans*-isomers. Neither a crystalline disulphide nor a methiodide could be prepared.

1,2,3,4-Tetrahydro-1,4-diphenyl-1,4-benzodiphosphorin (XI) was prepared by addition of the dilithiodiphosphine (IV) to a solution of 1,2-dichloroethane in tetrahydrofuran. The manner of this addition was the reverse of normal practice but was based on the experience of Issleib and his collaborators,^{5,6} who found that addition of ethyl- or phenyl-dilithiophosphine to 1,2-dichloroethane gave the 1,4-disubstituted 1,4-diphosphorinans (XII; R = Et or Ph), whereas if the addition was reversed only polymeric materials could be isolated. The 1,4-benzodiphosphorin (XI) gave a proton n.m.r. spectrum in which the methylene protons gave a deceptively simple spectrum for an XAA'X' system similar to an example described by Harris.^{7,8} An

TABLE I

³¹P N.m.r. spectra

Compound	Chemical shift (p.p.m.) *	Multiplicity (integration)	¹ J _{PP} /Hz
(V; R = Me)	–32.8	d(2)	252
	+67.5	t(1)	
(VI; R = Me)	–60.6	d(2)	250
	+77.5	t(1)	
(V; R = Et) †	–24.8	d	255
(VI; R = Et) †	–59.8	d	260
(VIII; R = Me)	–35.4	s	
(VIII; R = Ph)	–35.1	s	
(XI)	–22.2	s	
(XV)	–33.6	s	

* From external 85% H₃PO₄. † High field side of H₃PO₄ not scanned.

tertiary phosphines with retention of configuration, the disulphides (VI; R = Me or Et) presumably have the same configuration as their 1,2,3-triphenyl analogue.¹

⁴ W. Mahler, *J. Amer. Chem. Soc.*, 1964, **86**, 2306.

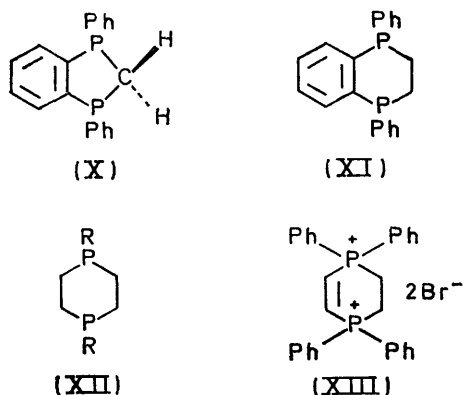
⁵ K. Issleib and K. Standtke, *Chem. Ber.*, 1963, **96**, 279.

⁶ K. Issleib and G. Döll, *Chem. Ber.*, 1963, **96**, 1544.

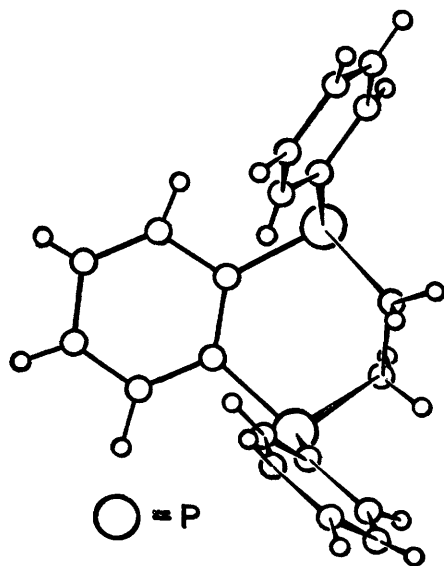
⁷ R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

⁸ R. K. Harris and R. G. Hayter, *Canad. J. Chem.*, 1964, **42**, 2282.

analogous spectrum for 1,2,3,4-tetrahydro-1,1,4,4-tetraphenyl-1,4-diphosphorindi-um dibromide (XIII) has been reported.⁹



A preliminary crystallographic analysis of the 1,4-benzodiphosphorin (XI) by Daly and Sanz has shown that the two phenyl groups lie *cis* to one another. These workers report: 'The phosphorus-carbon bond lengths show no significant differences from their average value of 1.837 Å. The average C-P-C angle is 101.3°, close to the normal value found in pyramidal organophosphorus compounds. The novel heterocyclic ring,

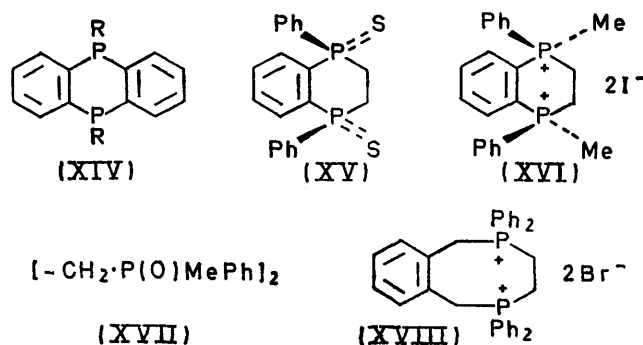


The configuration of 1,2,3,4-tetrahydro-1,4-diphenyl-1,4-benzodiphosphorin (XI) (diagram supplied by Dr. J. J. Daly)

which is formally analogous to cyclohexene¹⁰ in that it contains two sp^2 -hybridised carbon atoms, is in the half-chair form with one methylene group above and one below the plane of the other four atoms. The torsion angle $P-C(H_2)-C(H_2)-P$ is 73°. The phenyl groups both

lie on the same side of the $C_6H_4P_2$ plane and there seems to be no steric reason why there should not be another isomer of the molecule with the phenyl groups on opposite sides of this plane; this molecule would then have an approximate two-fold symmetry axis.'¹¹ The structure of the molecule is depicted in the Figure.

The 1,4-benzodiphosphorin (XI) reacted with an aqueous ethanolic solution of potassium tetrabromopalladate(II) to give a palladodibromide adduct in which the bis-tertiary phosphine appeared to act as a bidentate ligand to form a 1:1 complex; Davis and Mann have reported a similar complex from the analogous phosphanthren (XIV; $R = Ph$ or Et).¹² The diphosphorin (XI) gave a 1,4-disulphide (XV) when treated with an excess of sulphur in toluene solution.



Treatment of the 1,4-benzodiphosphorin (XI) with an excess of methyl iodide gave 1,2,3,4-tetrahydro-1,4-dimethyl-1,4-diphenyl-1,4-benzodiphosphorindi-um diiodide (XVI) having the configuration shown. Hydrolysis of this salt with aqueous sodium hydroxide gave ethylenebis(methylphenylphosphine oxide) (XVII). As this molecule has two asymmetric phosphorus atoms, a racemate and a *meso*-isomer were expected; these isomers, m.p. 190.5–191 and 246–247°, were separated by fractional crystallisation from diethyl carbonate. We were unable to determine which of the two isomers was the *meso*-form and which the racemate.

The mechanism of this hydrolysis is postulated to be similar to that of Aguiar's 1,2,3,4,5,6-hexahydro-2,2,5,5-tetraphenyl-2,5-benzodiphosphocindi-um dibromide (XVIII).¹³ Molecular models suggest that the least hindered direction of approach of the hydroxide ion is collinear with the *P*-phenylene bond, and a pentacovalent phosphorus intermediate (XIX) is formed in which the hydroxy- and *o*-phenylene groups occupy the apical positions of the trigonal bipyramid. Furthermore the *o*-phenylene group will be stabilised (compared with the phenyl group) as the anion in the subsequent rate-determining elimination step because of inductive electron withdrawal by the phosphonium group. A second hydroxide ion then abstracts a proton from the

⁹ A. M. Aguiar and H. J. Aguiar, *J. Amer. Chem. Soc.*, 1966, **88**, 4090.

¹⁰ J. F. Chiang and S. H. Bauer, *J. Amer. Chem. Soc.*, 1969, **91**, 1898.

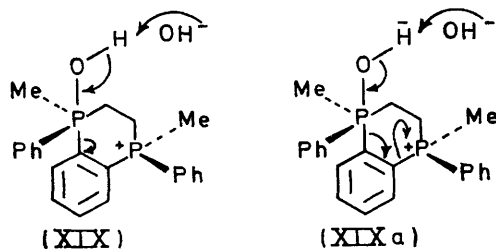
¹¹ J. J. Daly and F. Sanz, personal communication.

¹² M. Davis and F. G. Mann, *J. Chem. Soc.*, 1964, 3770.

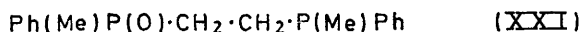
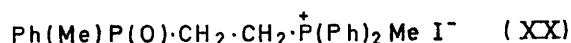
¹³ A. M. Aguiar and M. G. R. Nair, *J. Org. Chem.*, 1968, **33**, 579.

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hydroxy-group in the intermediate (XIX) with simultaneous formation of a phosphine oxide group and elimination of the phenylene group as an anion which will be rapidly protonated by the solvent in the normal

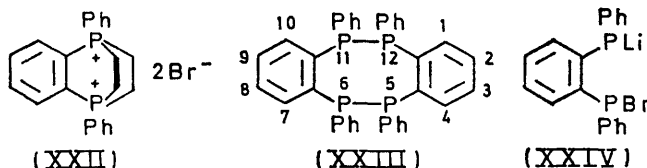


manner.¹⁴ The resultant mixed phosphine oxide-phosphonium salt (XX), which was not isolated, is hydrolysed further to give the bis(phosphine oxide) (XVII). An alternative breakdown of the pentacovalent phosphorus intermediate (XIXa) to give the



diphosphine mono-oxide (XXI) in a manner analogous to the alkaline hydrolysis of certain 1,4-diphosphorindium salts^{9,15} was discounted as a result of repeating the hydrolysis under conditions in which oxygen was rigorously excluded. In this experiment the bis(phosphine oxide) (XVII) was still formed and no evidence of the diphosphine mono-oxide (XXI) was detected. Furthermore this concerted mechanism would be expected to give ultimately only the *meso*-bis(phosphine oxide) (XVII), whereas in practice a mixture of the (\pm)- and *meso*-isomers was isolated.

Attempts to prepare 1,2,3,4-tetrahydro-1,4-diphenyl-1,4-ethano-1,4-benzodiphosphorindium dibromide (XXII) by heating the 1,4-benzodiphosphorin (XI) with 1,2-dibromoethane under various conditions were unsuccessful, although this type of reaction has been achieved with the analogous phosphanthrens (XIV)¹² and with 1,2,3,4-tetrahydro-1,4-dimethyl-1,4-benz-arsenin.¹⁶

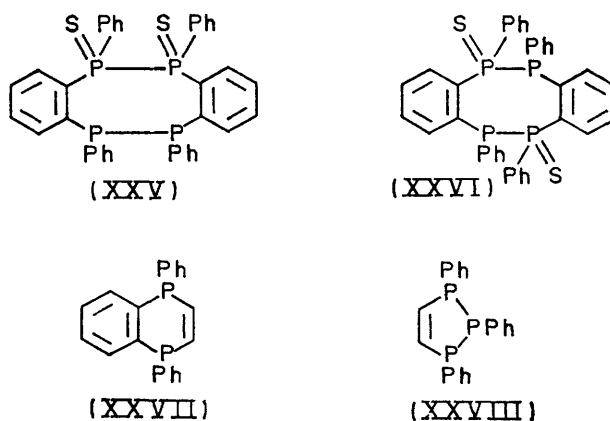


The dilithiodiphosphine (IV) reacted with 1,2-dibromoethane to give, not the expected 1,4-benzodiphosphorin (XI), but 5,6,11,12-tetrahydro-5,6,11,12-tetraphenylidibenzo[*c,g*][1,2,5,6]tetraphosphocin (XXIII) in 0.3% yield. The structure of this compound was confirmed mainly by mass spectrometry. High resolution measurements indicated that the molecular ion

had the formula $\text{C}_{36}\text{H}_{28}\text{P}_4$; furthermore the base peak of the spectrum was at $M/2$, as expected of a molecule containing two easily broken P-P bonds. The i.r. spectrum and results of elemental analysis supported the suggested structure. X-Ray crystallographic investigation was precluded by the small size of the crystals and their twinned nature. The mechanism of formation probably involves initial halogen exchange between 1,2-dibromoethane and the dilithiodiphosphine (IV) to give a bromolithiodiphosphine (XXIV), two molecules of which may react to give the tetraphosphocin (XXIII) and lithium bromide. An alternative synthesis of the tetraphosphocin involved the addition of 1 mol. equiv. of bromine to *o*-phenylenebis(lithiophenylphosphine) (IV), but an even lower yield (0.2%) was obtained.

The tetraphosphocin (XXIII), when treated with 4 atom equiv. of sulphur in toluene, gave a disulphide, the structure of which was investigated by mass spectrometry. High resolution measurements of the molecular ion gave an exact mass of 648.0459 corresponding to a molecular formula of $\text{C}_{36}\text{H}_{28}\text{P}_4\text{S}_2$. The most intense peak of the spectrum corresponded to $M/2$, and so indicated that the disulphide must have the symmetrical structure (XXV) or (XXVI). It was not possible to differentiate between these two structures, but (XXVI) is preferred for steric reasons.

1,4-Dihydro-1,4-diphenyl-1,4-benzodiphosphorin (XXVII) was prepared by addition of the dilithiodiphosphine (IV) to *cis*-dichloroethylene; the product was obtained in 3% yield after column chromatography on silica to remove polymeric material. The chemistry of this compound is under further investigation, in particular the hydrolysis of its dimethiodide.



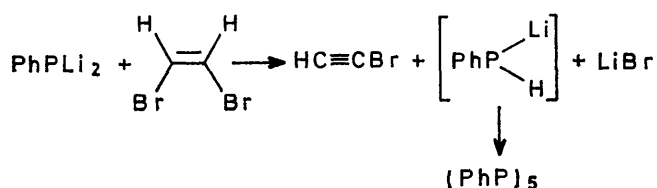
An attempt to prepare the triphospholen (XXVIII) by the reaction of *cis*-1,2-dibromoethylene with the product of the interaction of lithium and phenylphosphonous dichloride¹ was unsuccessful. Instead of nucleophilic attack by the phenylphosphide ion, basic attack apparently occurred with elimination of hydrogen

¹⁴ H. Hoffmann, *Annalen*, 1960, **634**, 1.

¹⁵ A. M. Aguiar, H. Aguiar, and D. Daigle, *J. Amer. Chem. Soc.*, 1965, **87**, 671.

¹⁶ F. G. Mann and F. C. Baker, *J. Chem. Soc.*, 1952, 4142.

bromide to give bromoacetylene (not isolated) and pentaphenylcyclopentaphosphine.^{1,17}



Mass Spectra (Table 2).—The main fragmentation pathway of the benzotriphospholes (V) and -diphos-

TABLE 2

Mass spectra *

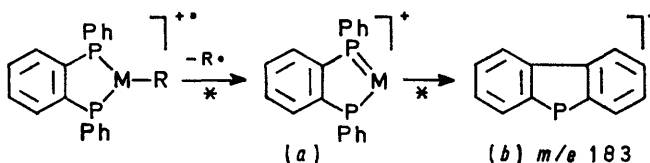
(V; R = Me)	<i>m/e</i> 338 (88), 323 (100), 214 (5), 183 (63), 107 (17)
(V; R = Et)	<i>m/e</i> 352 (60), 323 (100), 262 (9), 183 (58), 157 (42), 154 (24), 152 (10), 141 (28), 110 (30), 107 (12)
(VI; R = Me)	<i>m/e</i> 402 (10), 370 (15), 356 (10), 355 (8), 338 (31), 324 (66), 292 (20), 262 (11), 260 (9), 256 (14), 247 (26), 214 (9), 200 (25), 183 (100), 154 (24), 152 (18), 139 (11), 120 (70), 107 (37)
(VI; R = Et)	<i>m/e</i> 416 (19), 384 (5), 355 (24), 324 (100), 292 (10), 247 (26), 214 (10), 183 (81), 152 (7), 139 (6), 107 (24)
(VIII; R = Me)	<i>m/e</i> 382 (47), 367 (100), 289 (5), 227 (9), 214 (7), 213 (8), 191 (15), 185 (7), 183 (44), 152 (16), 107 (54)
(VIII; R = Ph)	<i>m/e</i> 444 (100), 367 (84), 292 (13), 227 (7), 214 (9), 183 (94), 152 (11), 107 (31)
(IX; R = Me)	<i>m/e</i> 446 (6), 324 (100), 292 (9), 247 (15), 183 (22), 107 (6)
(IX; R = Ph)	<i>m/e</i> 508 (32), 476 (39), 444 (19), 399 (14), 367 (28), 356 (14), 336 (11), 327 (26), 324 (100), 292 (36), 247 (47), 229 (14), 227 (10), 214 (11), 183 (100), 107 (69)
(X)	<i>m/e</i> 306 (100), 305 (27), 262 (9), 183 (13), 107 (12)
(XI)	<i>m/e</i> 320 (100), 319 (5), 305 (23), 185 (27), 183 (34), 152 (5), 131 (5), 107 (16)
(XV)	<i>m/e</i> 384 (82), 351 (100), 324 (22), 320 (30), 319 (20), 305 (14), 275 (16), 247 (22), 183 (80), 170 (11), 152 (9), 107 (100)
(XVII) †	<i>m/e</i> 306 (0.1), 291 (60), 263 (17), 229 (62), 213 (10), 167 (100), 139 (24), 107 (4)
(XXIII)	<i>m/e</i> 584 (14), 507 (36), 369 (21), 340 (7), 324 (21), 308 (25), 292 (100), 214 (27), 199 (13), 183 (100), 152 (12), 107 (41)
(XXV) or (XXVI)	<i>m/e</i> 648 (1), 647 (1), 646 (2), 645 (1), 644 (2), 388 (23), 356 (18), 324 (100), 293 (9), 292 (8), 279 (21), 247 (88), 215 (9), 183 (84), 170 (15), 152 (9), 107 (41)
(XXVII)	<i>m/e</i> 318 (100), 317 (5), 305 (5), 209 (9), 196 (5), 185 (26), 183 (42), 178 (14), 152 (5), 133 (5), 107 (16)

* Relative intensities (%) in parentheses. Generally peaks with intensities >5% are included. † High-melting isomer; the spectrum of the low-melting isomer is the same except for minor differences in intensity.

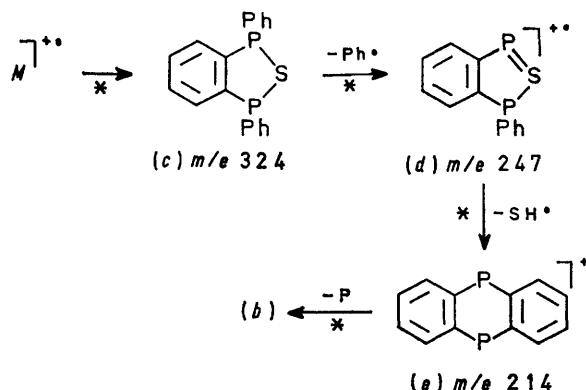
pharsoles (VIII) appears to involve the initial loss of the 2-substituent to give a stable quasiaromatic species

¹⁷ W. A. Henderson, jun., M. Epstein, and F. S. Seichter, *J. Amer. Chem. Soc.*, 1963, **85**, 2462.

(a) (M = P, *m/e* 323; M = As, *m/e* 367) which is normally observed as the base peak. This ion breaks down further to give a species (b) familiar in the mass spectra of organophosphorus compounds. Further breakdown of fragment (b) is well known. An analogous fragmentation scheme can be postulated for the 1,3-benzodiphosphole (X) where M = CH and R = H.



The fragmentation of the disulphides [(VI) and (IX)] of the benzotriphospholes and benzodiphospharsoles provides further evidence for the fragmentation pathway suggested in an earlier paper.¹ Electron impact-induced fragmentation of the molecular ion gives an ion (c), which subsequently loses a phenyl group to give (d). A further favourable pathway involves expulsion of SH• to give the stable phosphanthren ion (e), which can



lose a phosphorus atom to yield the species (b) (see before), the breakdown of which is described by Williams *et al.*¹⁸

All electron impact-induced fragmentations supported by the observation of metastable peaks are indicated by an asterisk.

The molecular ions of the 1,4-benzodiphosphorin disulphide (XV) and the dibenzotetraphosphocin disulphide, (XXV) or (XXVI), undergo similar fragmentations to yield initially ion (c).

EXPERIMENTAL

¹H N.m.r. spectra were recorded for solutions in deuteriochloroform with tetramethylsilane as internal standard by use of Perkin-Elmer R10 or Varian HA100 spectrometers; ³¹P n.m.r. spectra were recorded at 40.5 MHz for solutions in chloroform (85% phosphoric acid as external standard) with a Varian HA100 spectrometer. I.r. spectra were recorded (Nujol mulls) with a Perkin-Elmer 257 spectro-

¹⁸ D. H. Williams, R. S. Ward, and R. G. Cooks, *J. Amer. Chem. Soc.*, 1968, **90**, 966.

meter, and mass spectra with an A.E.I. MS9 spectrometer. New compounds reported (with the exception of salts) ran as single spots on t.l.c. (silica GF 254 plates).

All ethereal extracts were dried with anhydrous sodium sulphate.

o-Phenylenebis(phenylphosphine) (II) was obtained by reduction¹ of the triphosphole (I).

2-Alkyl-2,3-dihydro-1,3-diphenyl-1H-1,2,3-benzotriphospholes (V).—A solution of butyl-lithium in hexane (1.40M; 15.0 ml) was added dropwise to a solution of *o*-phenylenebis(phenylphosphine) (II) (3.0 g) in dry tetrahydrofuran (300 ml) at -40° under nitrogen. The solution was boiled under reflux to ensure complete conversion into the dilithiodiphosphine (IV), then cooled to -40° , and a solution of methylphosphonous dichloride (1.2 g, 1 equiv.) in tetrahydrofuran was added dropwise. The solution initially darkened and the colour was completely discharged as the addition was finished. The solution was evaporated to a paste to which were added wet ether (150 ml) and dilute hydrochloric acid (50 ml). The ethereal layer was separated, dried, and evaporated to give an oil which slowly crystallised. The waxy solid was sublimed at 150° and 0.01 mmHg to give *2,3-dihydro-2-methyl-1,3-diphenyl-1H-1,2,3-benzotriphosphole* (V; R = Me) (3.0 g, 87%), m.p. $80-81^\circ$ (Found: C, 67.5; H, 5.2; P, 27.2. $C_{19}H_{17}P_3$ requires C, 67.5; H, 5.1; P, 27.4%). ν_{\max} , 1439, 1429, 1422, 1030, 1002 (PPh), 1290, and 890 cm^{-1} (PMe), δ 7.97 (2H, m), 7.54 (3H, m), 2.98 (9H, m), and 1.45 p.p.m. (3H, dt, $^2J_{\text{PH}}$ 7, $^3J_{\text{PH}}$ 16.0 Hz).

A similar experiment with butyl-lithium in hexane (1.55M; 13.6 ml), the diphosphine (II) (3.0 g), and ethylphosphonous dichloride (1.34 g) gave *2-ethyl-2,3-dihydro-1,3-diphenyl-1H-1,2,3-benzotriphosphole* (V; R = Et) (3.0 g, 85%), sublimed at 154° and 0.1 mmHg, m.p. $54-57^\circ$ (Found: C, 67.95; H, 5.5; P, 26.3. $C_{20}H_{19}P_3$ requires C, 68.2; H, 5.4; P, 26.4%). ν_{\max} , 1444, 1430, and 1420 cm^{-1} (PPh), δ 7.9 (2H, m), 7.45 (2H, m), 7.04br (10H, s), 1.88 (2H, ten lines), and 1.34 p.p.m. (3H, five lines, $^3J_{\text{PH}}$ 16.0, J_{HH} 7.0 Hz).

Derivatives of the Benzotriphospholes.—*2,3-Dihydro-2-methyl-1,3-diphenyl-1H-1,2,3-benzotriphosphole* (628 mg), sulphur (165 mg, 3 atom equiv.), and toluene (20 ml) were boiled under reflux under nitrogen for 12 h. The solution was cooled and evaporated under reduced pressure to give an oil which when stirred with ether gave *2,3-dihydro-2-methyl-1,3-diphenyl-1H-1,2,3-benzotriphosphole 1,3-disulphide* (VI; R = Me) (360 mg, 48%), needles, m.p. $154-155^\circ$ (from aqueous acetone) (Found: C, 56.95; H, 4.3; P, 23.3. $C_{19}H_{17}P_3S_2$ requires C, 56.7; H, 4.2; P, 23.1%). ν_{\max} (KBr) 1446, 1432, 1420, 998 (PPh), and 716 cm^{-1} (P=S), δ 8.2—7.1 (14H, m), and 1.72 p.p.m. (3H, dt, $^2J_{\text{PH}}$ 6.75, $^3J_{\text{PH}}$ 15.75 Hz).

A similar reaction with the 2-ethylbenzotriphosphole (V; R = Et) (118 mg), sulphur (22 mg), and toluene (40 ml) gave *2-ethyl-2,3-dihydro-1,3-diphenyl-1H-1,2,3-benzotriphosphole 1,3-disulphide* (VI; R = Et) (94 mg, 67%), m.p. $189-190^\circ$ (Found: C, 57.7; H, 4.5; P, 21.8. $C_{20}H_{19}P_3S_2$ requires C, 57.7; H, 4.55; P, 22.4%). ν_{\max} , 1440, 1430, 1002 (PPh), and 730 cm^{-1} (P=S), δ 8.0—7.2 (14H, m), 2.26 (2H, eight lines, $^2J_{\text{PH}}$ 0, $^3J_{\text{PH}}$ 15.0 Hz), and 1.36 p.p.m. (3H, dt, $^3J_{\text{PH}}$ 20.8, J_{HH} 7.50 Hz).

Methyl iodide (2 ml) was added to a solution of the 2-methylbenzotriphosphole (V; R = Me) (700 mg) in dry toluene (25 ml) under nitrogen. The mixture was set aside at room temperature in the dark for 48 h to yield a pale yellow hygroscopic solid. This was washed rapidly with

dry ether to give *2,3-dihydro-1,2-dimethyl-1,3-diphenyl-1H-1,2,3-benzotriphospholium iodide* (VII) (1.0 g, 100%), m.p. $148-151^\circ$ (decomp.) (Found: C, 47.9; H, 4.3; P, 16.6. $C_{20}H_{20}IP_3$ requires C, 50.0; H, 4.2; P, 19.4%).

2,3-Dihydro-2-methyl-1,3-diphenyl-1H-1,3,2-benzodiphospharsole (VIII; R = Me).—Disodium methylarsonate¹⁹ was converted into methylarsonous dichloride by the usual method.

o-Phenylenebis(lithiophenylphosphine) (IV) was prepared as described previously from butyl-lithium in hexane (1.51M; 9.3 ml) and *o*-phenylenebis(phenylphosphine) (2.0 g) in tetrahydrofuran (35 ml) under nitrogen. Methylarsonous dichloride (1.1 g) in tetrahydrofuran (10 ml) was added dropwise to the red solution at -45° and the solution became colourless. The mixture was set aside overnight and then evaporated to give a paste, to which ether (50 ml) and deoxygenated dilute hydrochloric acid (20 ml) were added. The ethereal layer was separated, dried, and evaporated to give the benzodiphospharsole (VIII; R = Me) (1.8 g, 69%), needles, m.p. $83.5-84^\circ$ (from aqueous acetone) (Found: C, 59.7; H, 4.6. $C_{19}H_{17}AsP_2$ requires C, 59.7; H, 4.45%). ν_{\max} , 1440, 1425, 1030, and 1000 cm^{-1} (PPh), δ 8.1—7.1 (14H, m) and 1.42 p.p.m. (3H, t, $^3J_{\text{PH}}$ 12.5 Hz).

A similar reaction with butyl-lithium in hexane (1.36M; 15.5 ml), the diphosphine (3.0 g), and phenylarsonous dichloride (2.3 g) gave *2,3-dihydro-1,2,3-triphenyl-1H-1,3,2-benzodiphospharsole* (3.2 g, 72%), needles, m.p. $175-176^\circ$ (from aqueous acetone) (Found: C, 65.15; H, 4.25; P, 13.9; As, 16.9. $C_{24}H_{19}AsP_2$ requires C, 64.9; H, 4.3; P, 13.95; As, 16.9%). ν_{\max} (KBr) 1452, 1440, 1430, 1035, 1030, and 1008 cm^{-1} (PPh and AsPh).

Derivatives of the Benzodiphospharsoles (VIII).—*2,3-Dihydro-2-methyl-1,3-diphenyl-1H-1,3,2-benzodiphospharsole* (205 mg), sulphur (35 mg, 2 atm equiv.), and toluene were boiled under reflux for 6 h. The mixture was cooled and evaporated to a paste, which was extracted with ether and stirred to induce crystallisation of *2,3-dihydro-2-methyl-1,3-diphenyl-1H-1,3,2-benzodiphospharsole 1,3-disulphide* (IX; R = Me) (95 mg, 40%), needles, m.p. $158-159^\circ$ (from aqueous acetone) (Found: C, 50.5; H, 3.7. $C_{19}H_{17}AsP_2S_2$ requires C, 51.1; H, 3.8%). ν_{\max} , 1444, 1440, 1430, 1004 (PPh), and 721 cm^{-1} (P=S), δ 8.1—7.2 (14H, m) and 1.75 p.p.m. (3H, t, $^3J_{\text{PH}}$ 14.5 Hz).

A similar reaction with *2,3-dihydro-1,2,3-triphenyl-1H-1,3,2-benzodiphospharsole* (333 mg), sulphur (72 mg, 3 equiv.), and toluene (40 ml) gave *2,3-dihydro-1,2,3-triphenyl-1H-1,3,2-benzodiphospharsole 1,3-disulphide* (205 mg, 71%), needles, m.p. $219-220^\circ$ (from acetone) (Found: C, 56.2; H, 3.5; S, 12.6. $C_{24}H_{19}AsP_2S_2$ requires C, 56.7; H, 3.7; S, 12.2%). ν_{\max} , 1450, 1440, 1430, 1004 (PPh and AsPh), and 730 cm^{-1} (P=S).

2,3-Dihydro-1,3-diphenyl-1,3-benzodiphosphole (X).—A solution of the dilithiodiphosphine (IV) [from *o*-phenylenebis(phenylphosphine) (II) (2.0 g), butyl-lithium in hexane (1.51M; 9.3 ml), and tetrahydrofuran (35 ml)] was cooled to -50° and redistilled dichloromethane (0.6 g) in tetrahydrofuran (5 ml) was added dropwise. There was no discharge of colour and the solution was allowed to warm to room temperature, during which time the colour was discharged. The mixture was set aside overnight, and evaporated to give an oil which was distilled at 150° and 0.1 mmHg to yield the solid *benzodiphosphole* (X) (1.6 g, 76%), crystals,

¹⁹ A. J. Quick and R. Adams, *J. Amer. Chem. Soc.*, 1922, **44**, 805.

m.p. 79–81° (from aqueous acetone) (Found: C, 74.8; H, 5.4; P, 20.2. $C_{19}H_{16}P_2$ requires C, 74.5; H, 5.2; P, 20.25%), ν_{\max} 1448, 1440, 1031, and 1006 cm^{-1} (PPh), δ (C_6H_6) 7.6–6.8 (14H, m), and 2.9–2.0 p.p.m. (2H, m).

Attempts to prepare a crystalline sulphide or methiodide were unsuccessful.

1,2,3,4-Tetrahydro-1,4-diphenyl-1,4-benzodiphosphorin (XI).—The dilithiodiphosphine (IV) [from the bis(phenylphosphine) (3.0 g), butyl-lithium in hexane (1.59M; 13.3 ml), and tetrahydrofuran (40 ml)] was added dropwise at -20° to 1,2-dichloroethane (1.0 g) in tetrahydrofuran (5 ml). The mixture was then stirred at room temperature for 2 h, boiled under reflux for 15 min, cooled, and evaporated to a paste, to which were added ether (30 ml) and dilute hydrochloric acid (20 ml). The ethereal layer was separated, dried, and evaporated to give the *tetrahydrodiphosphorin* (XI) (3.1 g, 95%), needles, m.p. 114–115° (from aqueous acetone) (Found: C, 75.1; H, 5.8; P, 19.7. $C_{20}H_{18}P_2$ requires C, 75.0; H, 5.6; P, 19.4%), ν_{\max} 1439, 1432, 1420, 1412, 1032, 1029, 1010, 1005, and 996 cm^{-1} (PPh), δ (C_6D_6) 7.5–6.8 (14H, m) and 1.94 p.p.m. (4H, pseudo-quartet, $^2J_{PH} + ^3J_{PH} = 18.8$ Hz).

Potassium tetrabromopalladate(II) (170 mg) dissolved in water (1 ml) and ethanol (20 ml) was added to a solution of the diphosphorin (106 mg) in ethanol (20 ml) to precipitate the yellow amorphous *palladobromide* (150 mg, 80%), m.p. $>360^\circ$ after thorough washing with hot ethanol; it was insoluble in all common solvents (Found: C, 41.2; H, 3.2; P, 10.3. $C_{20}H_{18}Br_2P_2Pd$ requires C, 40.9; H, 3.1; P, 10.6%).

1,2,3,4-Tetrahydro-1,4-diphenyl-1,4-benzodiphosphorin 1,4-disulphide (XV).—The diphosphorin (XI) (403 mg), sulphur (80 mg), and toluene (25 ml) were boiled under reflux for 5 h. The mixture was evaporated to give an oil which crystallised when stirred with ether to yield the *disulphide* (420 mg, 88%), needles, m.p. 207–208° (from aqueous acetone) (Found: C, 62.8; H, 4.6; P, 16.4. $C_{20}H_{18}P_2S_2$ requires C, 62.5; H, 4.7; P, 16.15%), ν_{\max} 1450, 1442, 1432, 1004 (PPh), 738, and 724 cm^{-1} (P=S), δ 8.0–7.4 (14H, m) and 2.82 p.p.m. (4H, m).

1,2,3,4-Tetrahydro-1,4-dimethyl-1,4-diphenyl-1,4-benzodiphosphorindium Di-iodide (XVI).—A solution of the diphosphorin (XI) (457 mg) in methyl iodide (2 ml) and methanol (25 ml), when boiled under reflux for 3 h and then cooled and evaporated under reduced pressure, gave the *di-iodide* (726 mg, 84%), m.p. 348–349° (decomp.), rhombs (from methanol) (Found: C, 44.0; H, 4.2; P, 10.5. $C_{22}H_{24}I_2P_2$ requires C, 43.7; H, 4.0; P, 10.25%), ν_{\max} 1440, 1432, 1423, 1019, 1000 (PPh), and 871 cm^{-1} (PMe), δ [(CD_3)₂SO] 8.5–7.9 (14H, m), 3.55 (4H, s), and 3.18 p.p.m. (6H, d, J_{PH} 15 Hz).

Alkaline Hydrolysis of the Tetrahydro-1,4-benzodiphosphorindium Di-iodide (XVI).—The salt (726 mg) was added to aqueous sodium hydroxide (2N; 20 ml); the mixture was boiled under reflux for 10 min, cooled, and extracted with chloroform (2 \times 30 ml). The extracts were dried and evaporated under reduced pressure to give a solid phosphine oxide (300 mg, 82%), m.p. 181–215°, which showed two spots (R_F 0.42 and 0.31) of approximately equal intensity on t.l.c. [methanol-ethyl acetate (40:60) as eluant].

The solid was extracted with hot diethyl carbonate (12 ml); on cooling the extract a low-melting isomer of *ethylenebis(methylphenylphosphine oxide)* (XVII) was deposited, m.p. 190.5–191° after several recrystallisations

from diethyl carbonate (Found: C, 63.3; H, 6.6; P, 20.55. $C_{16}H_{20}O_2P_2$ requires C, 62.9; H, 6.5; P, 20.25%), ν_{\max} 1438 (PPh), 1291, 885, 855 (PMe), 1190, 1175, and 1170 cm^{-1} (P=O), δ 7.7–7.3 (10H, m), 2.1 (4H, m), and 1.7 p.p.m. (6H, broad s). This was the slower running isomer on t.l.c.

Extraction of the mixture with a second portion of diethyl carbonate (12 ml) gave the high-melting *isomer*, m.p. 246–247° (Found: C, 62.8; H, 6.5; P, 20.0), ν_{\max} 1448, 995 (PPh), 1298, 888, 875 (PMe), 1188, 1175, and 1165 cm^{-1} (P=O), δ 7.62br (4H, s), 7.55 (6H, s), 2.1 (4H, m), and 1.63br p.p.m. (6H, s).

A similar reaction carried out under nitrogen gave the same two isomers.

Reaction of *o*-Phenylenebis(lithiophenylphosphine) with 1,2-Dibromomethane.—The lithiophosphine (IV) [from *o*-phenylenebis(phenylphosphine) (2.77 g), butyl-lithium in hexane (1.59M; 12.3 ml), and tetrahydrofuran (40 ml)] was added dropwise at -20° under nitrogen to a solution of 1,2-dibromoethane (1.77 g, 1 mol. equiv.) in tetrahydrofuran (5 ml) at -20° . Effervescence occurred and the red solution became colourless. The mixture was then stirred at room temperature for 4 h and boiled for 15 min. The resulting solution was evaporated to a paste to which were added ether (30 ml) and dilute hydrochloric acid (30 ml). The ethereal layer was separated, dried, and evaporated to a paste to which were added a few drops of acetone to give a white solid, which was collected and washed with a little acetone. Recrystallisation gave 5,6,11,12-tetrahydro-5,6,11,12-tetraphenyldibenzo[c,g][1,2,5,6]tetraphosphocin (XXIII) (100 mg, 0.3%), needles (from acetone) (Found: C, 73.75; H, 4.8; P, 21.0%; M^+ , 584.1179. $C_{36}H_{28}P_4$ requires C, 74.0; H, 4.8; P, 21.2%; M , 584.1142), ν_{\max} 1435, 1430, 1020, and 993 cm^{-1} (PPh).

Reaction of *o*-Phenylenebis(lithiophenylphosphine) with Bromine.—To the dilithiodiphosphine (IV) [from the diphosphine (2.0 g), butyl-lithium in hexane (1.55M; 9.1 ml), and tetrahydrofuran (40 ml)] at -45° under nitrogen, bromine (1.1 g, 1 mol. equiv.) in benzene (5 ml) was added dropwise; the solution became colourless. The mixture was stirred at room temperature for 1 h and evaporated to a paste, ether (50 ml) and dilute hydrochloric acid (50 ml) were added, and the ethereal layer was separated, dried, and evaporated to an oil. This was dissolved in a few drops of acetone and the solution was cooled in ice and seeded to give the tetraphosphocin (XXIII) (41 mg, 0.2%), identical with that already prepared.

The tetraphosphocin (XXIII) (73 mg), sulphur (16 mg), and toluene (15 ml) were boiled under reflux for 15 h to give the tetraphosphocin disulphide [probably (XXV) or (XXVI)] (33 mg, 41%), needles, m.p. 247–248° (from acetone) (Found: C, 66.05; H, 4.2%; M^+ , 648.0459. Calc. for $C_{36}H_{28}P_4S_2$: C, 66.7; H, 4.3%; M , 648.0582), ν_{\max} 1432, 995 (PPh), and 716 cm^{-1} (P=S).

1,4-Dihydro-1,4-diphenyl-1,4-benzodiphosphorin (XXVII).—*o*-Phenylenebis(lithiophenylphosphine) [from the diphosphine (3.0 g), butyl-lithium in hexane (1.58M; 13.3 ml), and tetrahydrofuran] was added dropwise to a solution of *cis*-1,2-dichloroethylene (0.99 g) in tetrahydrofuran (10 ml) under nitrogen. The solution was then set aside for 1 h, boiled under reflux for 10 min, and evaporated to a black oil to which ether (150 ml) and dilute deoxygenated sulphuric acid (40 ml) were added. The ethereal layer was separated, dried, and evaporated to give an oil, which was chromatographed on a Silicar CC7 column (100 g). Elution with benzene-petroleum (b.p. 40–60°) (1:4; 200 ml) gave

the *dihydrodiphenylbenzodiphosphorin* (XXVII) (105 mg, 3%), needles, m.p. 108–109° (from ethanol) (Found: C, 75.2; H, 5.1; P, 19.2. $C_{20}H_{16}P_2$ requires C, 75.5; H, 5.0; P, 19.5%); ν_{\max} 3040, 698 (*cis*-C=C), 1444, 1439, 1424, 1025, and 1000 cm^{-1} (PPh); δ (C_6D_6) 7.62 (2H, m), 7.2–6.8 (12H, m), and 6.54 p.p.m. (2H, t, $^2J_{PH} = ^3J_{PH} = 21$ Hz).

Reaction of Dilithiophenylphosphine with cis-1,2-Dibromoethylene.—Phenylphosphonous dichloride (25 g) in tetrahydrofuran (100 ml) was added under nitrogen to a suspension of lithium foil (3.1 g) in tetrahydrofuran (100 ml) at -20° . The mixture was stirred for 3 h at -20° , the excess of lithium (0.2 g) was collected and the solution was cooled to -65° . A solution of *cis*-1,2-dibromoethylene (12.5 g) in tetrahydrofuran was added dropwise during 15 min. The mixture was set aside at room temperature overnight, and

then boiled under reflux for 2 h and evaporated to give an oil, to which ether (250 ml) and water (150 ml) were added. The ethereal layer was separated, dried, and evaporated, giving an oil from which crystallised pentaphenylcyclopentaphosphine (9.5 g, 63%), m.p. and mixed m.p. 148–152° (lit.,¹⁷ 148–152°).

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