*Tetrahedron* Vol. 27, pp. 5523 to 5537. Pergamon Press 1971. Printed in Great Britain

# ALKALI AZA-, PHOSPHA- AND ARSACYCLOPENTADIENIDES AND THEIR CHEMICAL PROPERTIES

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(*Received in the UK* 12 *May* 1971; *Accepted for publication* 15 *June* 1971)

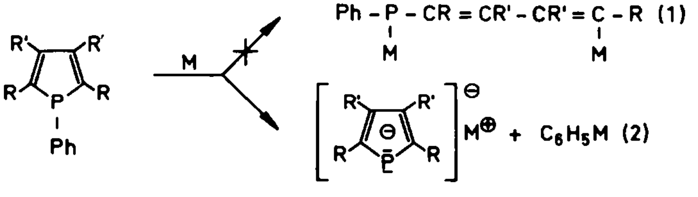
**Abstract**—When a 1-phenyl substituted pyrrole, phosphole or arsole, is reacted with an alkali metal in an inert solvent, the phenyl group is split off yielding the corresponding alkali heterocyclopentadienide. Hydrolysis of the alkali phosphacyclopentadienides gave the first P-unsubstituted phospholes (**7a**, **7b**, **10**). Similarly, this method allows the dephenylation of N-phenyl substituted pyrroles. Reaction of the alkali phospholides with alkyl halides offers a convenient way to synthesise phospholes which bear, on the P atom, an alkyl chain with functional groups. Thus, P-haloalkylphospholes have been prepared which upon heating gave by self-quarternisation either the novel spiro (**43**, **44**) or bispiro (**45**) heterocyclic systems or polyphosphonium salts having the P atom in the backbone (**46**, **47**).

## INTRODUCTION

IN A PREVIOUS publication,[1] some reactions of pentaphenylphospholes were reported in connection with the possible aromatic character of the phosphole system (phosphacyclopentadiene). In the meantime lack of aromacity has been confirmed by the X-ray structure determination of P-benzylphosphole.[2] The present paper[3] deals with the reaction of phospholes, arsoles and pyrroles with an alkali metal in an inert solvent.

It is known that a Ph group is split off in triphenylphosphine, -arsine and -stibine by an alkali metal in liquid ammonia[4] or in tetrahydrofuran (THF)[5] yielding the alkali diphenylphosphide, -arsenide or antimonide besides $C_6H_5M$ (M = alkali metal). Issleib and Völker[6] showed that in alkylarylphosphines it is generally the most electronegative group which is cleaved off leading to the combination of products which has the highest stabilization. The reaction between triphenylphosphine and alkali metals in THF has been studied[7] in more detail by using the ESR technique: the ESR signals do not result from the radical anion $Ph_3P^{\overline{\cdot}}$ as stated by Hanna[8] but from the reaction of the initially formed phosphide $Ph_2PM$ with a second metal atom, yielding the free radical anion $[Ph_2PM^{\overline{\cdot}}]M^+$.

In the case of a phosphole, reaction with an alkali metal may proceed by two routes, one involving ring opening (reaction 1), the other involving the splitting off of the substituent on the phosphorus (reaction 2):



1 M: alkali metal
**1a**, **2a** R=R'=Ph
**1b**, **2b** R=Ph, R'=H

2

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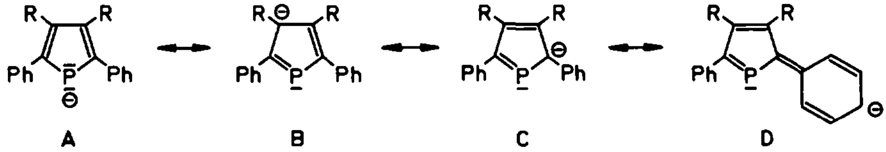
The absence of any product which would have resulted from reaction route 1 indicates that ring opening by an alkali metal does not occur, except in the case of pentaphenylarsole when Li or K is used. Reaction path 2 is apparently favoured because of the expected resonance stabilisation of the cyclic anion, as pictured below. Extra stabilisation by quinoid structures (D) should not be overlooked and their contributions can explain the intense violet colour of **2a** and **2b**.



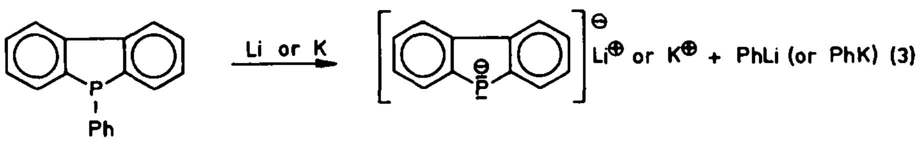
P-phenyldibenzophosphole (**3**) also reacts with K or Li with retention of the ring system, yielding **4**. The latter reaction has also been reported recently and has been used to prepare P-benzyldibenzophosphole.[9]

In the case of compound **4**, where the contributions of structures D do not exist, absorption of its solutions is limited to the yellow-orange region.

The canonical structures B, C and D involve an unusual bonding situation: the trivalent P atom is only dicoordinated. This rare electronic arrangement has only been encountered in phosphabenzene, elegantly synthesized by Märkl *et al.*,[10] and in phosphacyanines.[11] In the case of arsacyclopentadienide, one may also admit that electromeric structures similar to B, C and D contribute to the ground state, in which case the dicoordinated tervalent arsenic =As— would represent, to our knowledge, the first example of a dicoordinated tervalent arsenic. The electronic situation of the heterocyclopentadienides is closely related to that of cyclopentadienide, $C_5H_5^-$, with the important difference that in alkylation reactions, the alkyl group enters exclusively at the heteroatom due to the very high nucleophilic character of this site as in phosphides of type $R_2P^-$.

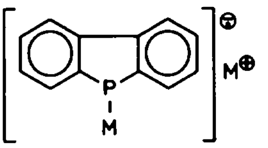
## PHOSPHOLES

As in the case of tertiary phosphines, the P-phenyl substituted phospholes react readily with Li or K in inert solvents, such as THF, dioxane, toluene, but very sluggishly with Na. Thus, pentaphenylphosphole **1a**, 1,2,5-triphenylphosphole **1b** and 1-phenyldibenzophosphole **3** have been converted into the corresponding Li or K phosphacyclopentadienides **2a**, **2b** and **4**, respectively. As with the $Ph_3P$ system,[7] Britt and



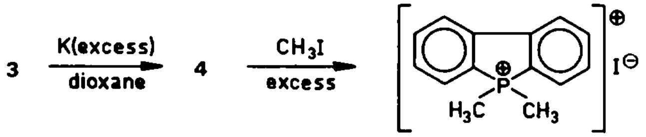
3 4

Kaiser[12] found that the reaction of **3** with alkali metals occurs in two distinct steps, the first being the Ph cleavage (reaction 3) and radical formation in a subsequent step by further attack of alkali metal on **4** producing the radical anion **5**. The latter species



**5**

would be responsible for the red brown colour observed by the authors. Furthermore, the anion radical **5** is said to be thermally unstable, decomposition into black materials having been observed at room temperature. These observations are in striking contrast with ours. Indeed, in most of the experiments, **3** was treated with a large excess of the alkali metal, even at the reflux temperature of the solvent and alkylation of the reaction mixture quite often gave high yields of the alkylation product. These results are not consistent with a possible further reaction of **4** with Li or K leading to a thermally labile species such as **5**. Thus by treating with excess $CH_3I$ the reaction product of **3** with a four molar ratio of K in boiling dioxane, the phosphonium iodide **6** was obtained with a 76·5% yield. Furthermore, the high thermal stability was also observed for the alkali metal derivatives of 2,5-diphenylphosphole and 2,3,4,5-tetraphenylphosphole in the presence of excess of metal. Recently, an ESR study has also appeared[13] on the reaction between 1,2,5-triphenylphosphole and K (*vide infra*); the observed signals were ascribed to radical polymerisation of the cleaved Ph group.

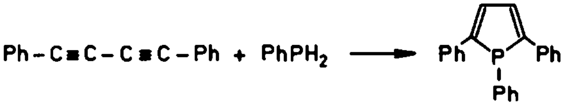


6, m.p. 271-276°

The isolation of **2** and **4** in the solid state was not attempted. Their solutions or suspensions were used as such for further reaction (see below). In certain cases, PhLi or PhK, also formed in the reaction, was destroyed selectively by adding an equimolar amount of t-BuCl according to Aguiar *et al.*[14]

### 1,2,5-*Triphenylphosphole*

1,2,5-Triphenylphosphole was prepared by addition of phenylphosphine to diphenyldiacetylene by analogy with the preparation of pyrroles by the addition of aromatic amines to diacetylenes.[15] Our compound shows the same physical properties as that obtained by Campbell *et al.*[16] from 1,4-diphenylbutadiene and $PhPCl_2$. Recently, Märkl *et al.*[17] prepared a number of phospholes using the same reaction with PhLi as a catalyst; they found only traces of phospholes in the thermal or free



**1b**

TABLE 1. FORMATION OF 1,2,5-TRIPHENYLPHOSPHOLE FROM DIPHENYLDIACETYLENE AND PHENYLPHOSPHINE

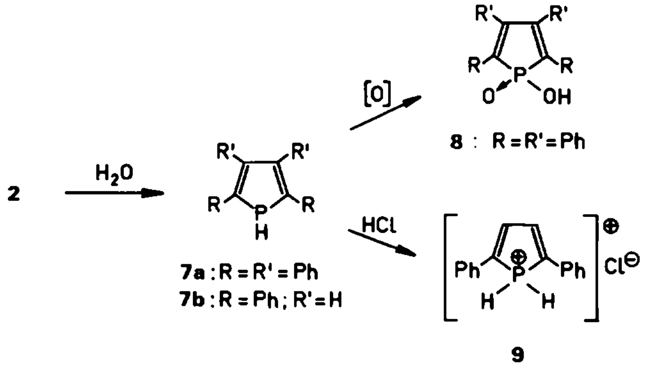
| No. | mmoles of $PhC_4Ph$ | mmoles of $PhPH_2$ | Catalyst in mmoles | | Solvent | Temp | Time hr | % Conversion of $PhC_4Ph$ | Yield of **1b**[d] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 4·95 | 3·63 | — | | dioxane | 175 | 7 | 50 | 23 |
| 2 | 4·95 | 4·55 | $Cu_2Cl_2$ | 0·5 | dioxane | 100 | 31 | 40 | 16·5 |
| 3 | 4·95 | 3·63 | $Cu_2Cl_2$ | 0·1 | dioxane | 120 | 16½ | 23 | 76 |
| 4 | 4·95 | 3·63 | $Cu_2Cl_2$ | 0·1 | dioxane | 140 | 17 | 43 | 25·6 |
| 5 | 4·95 | 4·55 | $Cu_2Cl_2$ | 0·1 | dioxane | 150 | 18 | 100 | 31·4 |
| 6 | 4·95 | 3·63 | $Cu_2Cl_2$ | 0·1 | dioxane | 160 | 17 | 40 | 36 |
| 7 | 4·95 | 6·35 | $HgSO_4$ | 0·17 | dioxane | 120 | 63 | 100 | 36·8 |
| 8 | 4·95 | 3·63 | $FeSO_4 \cdot 7H_2O$ | 0·072 | dioxane | 160 | 17 | 27 | 12 |
| 9 | 4·95 | 6·35 | AIBN[a] | 0·142 | benzene | 80 | 7 | 43 | 48 |
| 10 | 74·3 | 100 | AIBN | 1·4 | benzene | 80 | 48 | 64 | 25 |
| 11 | 4·95 | 6·35 | $H_2PtCl_6$ | 0·244 | dioxane | 100 | 4 | 3 | traces |
| 12 | 4·95 | 6·35 | $CH_3C_6H_4SO_3H$ | 0·7 | EtOH | 80 | 17 | 0 | 0 |
| 13 | 4·95 | 6·35 | KOH[b] | 50 | $CH_3CN$ | 25 | 19 | 23 | 11 |
| 14 | 4·95 | 6·35 | KOH[b] | 50 | $(CH_3OCH_2)_2$ | 85 | 8 | 32 | 44 |
| 15 | 4·95 | 6·35 | KOH[c] | 75 | $(CH_3OCH_2)_2$ | 85 | 7 | 74 | 28·3 |
| 16 | 4·95 | 12·70 | KOH[b] | 50 | $(CH_3OCH_2)_2$ | 85 | 7 | 47 | 37·6 |
| 17 | 4·95 | 6·35 | KOH[b] | 20 | $(CH_3OCH_2)_2$ | 140 | 5½ | 50 | 40 |
| 18 | 4·95 | 6·35 | $CH_3ONa$ | 50 | $CH_3OH$ | 25<br>65 | 60<br>7 | 18 | traces |
| 19 | 4·95 | 6·35 | *t*-BuOK | 0·9 | *t*-BuOH | 82 | 5 | 65 | 12 |
| 20 | 4·95 | 9 | $NaNH_2$ | 8·7 | $NH_3$/THF | −30 | 5 | 100 | traces |

[a] AIBN: azobisisobutyronitrile; [b] 5 ml of a 10N aqueous KOH; [c] 5 ml of a 15 N aq. KOH; [d] calc. on converted $PhC_4Ph$

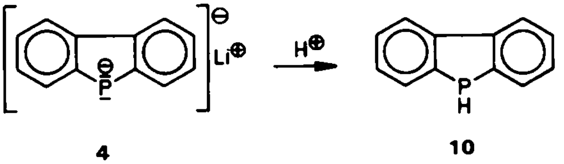
radical reactions. This is in contrast with our experience. From Table I it can be seen that beside the nucleophilic addition of phenylphosphine to diphenyldiacetylene best catalysed by concentrated KOH, the coordination synthesis by means of cuprous and mercury salts (exp. 2–7) is quite effective if not superior. Exp. 9 and 10 show that the cyclising addition can also proceed *via* a free radical mechanism in yields comparable with those of the nucleophilic additions. Strong acids (exp. 12) are completely ineffective. The cyclisation in exp. 9–10 (free radical type) and in exp. 13–17 (nucleophilic type) are not due to thermal reactions as is proven by exp. 1 which shows that even at 175° (7 hr) **1b** is only obtained in a low yield.

*Reactions of the alkali phosphacyclopentadienides*

*Hydrolysis.* Hydrolysis of **2a** and **2b** gave **7a** and **7b** respectively which represent the first P unsubstituted phospholes. Compound **7a** formed yellow crystals, m.p.



147–150°. In contrast to P-phenyl and P-alkyl substituted phospholes[1, 18] it does not show fluorescence. The P-H stretching frequency of **7a** in tetrachloroethylene is observed at 2309 $cm^{-1}$ (4·33$\mu$) and falls almost to the region of 2270–2300 $cm^{-1}$ assigned to the P-H stretching frequency in compounds of the type R-PH-R'.[19] As expected for secondary phosphines, both **7a** and **b** are very sensitive to oxidation. Thus **7a** was readily converted into the corresponding orange phosphonic acid **8** by exposure to air. Treatment of **2b** with aqueous AcOH gave 2,5-diphenylphosphole **7b**, not characterised as such but isolated as its chlorohydrate **9**, pale yellow crystals of m.p. 170–190° (dec.).



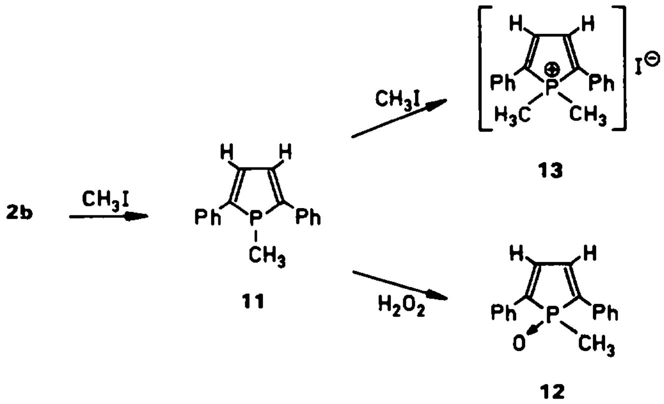
Hydrolysis of **4** with $H_2O$/AcOH gave dibenzophosphole **10** (76%). Compound **10** formed colourless needles m.p. 47–48°, b.p. ≈65°/0·3 mmHg) and is the phosphorus analogue of carbazole. A striking difference, however, is observed in their m.ps (47–48° versus 246°) in spite of the very similar shapes of both compounds. This can only be understood by the much more polar character of the NH function compared with that of P–H*. The NMR spectrum of **10** in DMF shows the expected doublet at 5·23τ for PH (1H) with a coupling constant of $J_{P-H} = 204$ cps. The aromatic protons form two complex multiplets (4H + 4H) centered at 2·6 and 2·1τ (TMS as internal reference).

### *Alkylation reactions*

The most interesting properties of alkali phosphacyclopentadienides are perhaps their easy alkylation which leads to phospholes having various substituents on the P atom which would be very difficult to synthesize by known methods, mainly due to the unavailability of the required dihalophosphines $RPCl_2$ or primary phosphines $RPH_2$. The reaction with dihaloalkanes is of particular interest: some of their reaction products lead to new cyclic systems or to polyelectrolyte type polymers (*vide infra*).

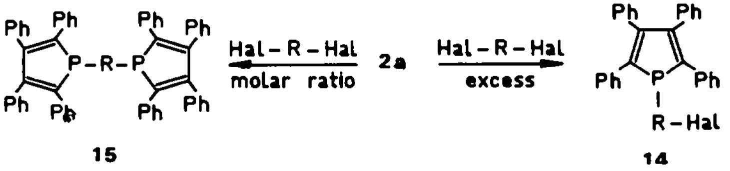
### *Alkylation of alkali* 2,5-*diphenylphosphacyclopentadienide* (**2b**)

Treatment of potassium 2,5-diphenylphosphacyclopentadienide (**2b**) with MeI gave 1-methyl-2,5-diphenylphosphole (**11**), which upon oxidation with $H_2O_2$ in acetone gave the oxide **12**. When **2b** was treated with an excess of MeI, the methiodide **13** was obtained directly.



### *Alkylations of alkali* 2,3,4,5-*tetraphenylphosphacyclopentadienide* (**2a**)

As expected from the known high nucleophilicity of phosphides, **2a** reacted readily with alkyl or arylalkyl halides, yielding thus P-alkyl-tetraphenylphospholes. When a dihalide is used it is possible to obtain either the P-haloalkylphospholes **14** or the P,P-diphospholylalkanes **15** depending on the conditions. The former are obtained readily when **2a** is added slowly to a great excess of the dihalide, Hal-R-Hal, whereas the diphosphines are formed when approximately molar ratios are used. Thus com-



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* N-acetylcarbazole and N-ethylcarbazole melt at 69 and 68°, respectively; on the other hand N-phenylcarbazole and P-phenyl-dibenzophosphole melt almost at the same temperature, 95° and 94·5–95°, respectively.

Table 2. P-alkyl-2,3,4,5-tetraphenylphospholes (**14**) from **2a** and RHal.

| **2a** | R-Hal | Solvent | 1-R-2,3,4,5-tetraphenylphosphole R = | | m.p. (cryst. solv.) | Yield % |
|---|---|---|---|---|---|---|
| K | $CH_3I$ | dioxane | $-CH_3$ | **16** | 195–196°<br>($CH_2Cl_2$/P.E.) | 53 |
| Li | $CH_2Cl_2$ | THF | $-CH_2Cl^b$ | **17** | 194–196°<br>(MeOH) | $35^b$ |
| K | $Br(CH_2)_2Br$ | dioxane | $-CH_2CH_2Br$ | **18** | 220°<br>($CH_2Cl_2$/MeOH) | 73 |
| Li | $Br(CH_2)_3Br$ | THF | $-(CH_2)_3Br$ | **19** | 205–206°<br>($CH_2Cl_2$/EtOH) | 56·5 |
| Li | $Br(CH_2)_4Br$ | THF | $-(CH_2)_4Br$ | **20** | *ca.* 150° (dec)<br>($C_6H_6$/n-octane) | 19 |
| Li | $Br(CH_2)_5Br$ | THF | $-(CH_2)_5Br$ | **21** | 132–135°<br>(MeOH or n-octane)$^c$ | 51 |
| Li | $Br(CH_2)_6Br$ | THF | $-(CH_2)_6Br$ | **22** | 160–163°<br>($Et_2O$)$^d$ | 43·5 |
| Li | *p*-$ClCH_2C_6H_4CH_2CH_2Cl$ | THF | *p*-$CH_2C_6H_4CH_2CH_2Cl^e$ | | 200–204°<br>($C_6H_6$/P.E.) | 11 |
| | | | P-oxide | **23** | | |
| K | $BrCH_2CO_2Et$ | dioxane | $-CH_2COOEt$ | **24** | 157–158°<br>(MeOH) | 60 |

[a] all compounds are yellow; they are fluorescent with the exception of **24**

[b] beside bis(tetraphenylphospholyl-1)methane (**27**)

[c] crystallized with one mole of benzene

[d] was also obtained with one mole of benzene, m.p. 153–157°

[e] only isolated as the oxide

pounds **20**–**22** were prepared with a three- to fourfold excess of the dihalide. Compounds **14** are listed in Table II together with some other alkylated phospholes.

Compound **17** (R = —$CH_2Cl$) was unexpectedly formed in addition to a few percent of the diphospholylmethane **27** when 2,3,4,5-tetraphenylphosphole (**7a**) was dissolved in $CH_2Cl_2$. Oxidation of **16** (R = —$CH_3$) gave the corresponding P-oxide which was identical with our earlier reported phosphole formed from 1,4-dilithiotetraphenylbutadiene and $CH_3PI_2$, followed by oxidation with air.[1]

Compound **18** (R = —$CH_2CH_2Br$) gave upon treatment with t-BuOK an 88% yield of 1-vinyl-2,3,4,5-tetraphenylphosphole (**25**). Attempts to polymerise **25** by means of azobisisobutyronitrile (0·1 mole %) in benzene at 70° failed. Hydrolysis of **24** afforded 2,3,4,5-tetraphenylphospholylacetic acid (**26**), pale yellow needles of m.p. 210–212° which showed no fluorescence. The diphospholylalkanes **15** are listed in Table III.

TABLE 3. BIS(TETRAPHENYLPHOSPHOLYL-1)ALKANES (**15**)

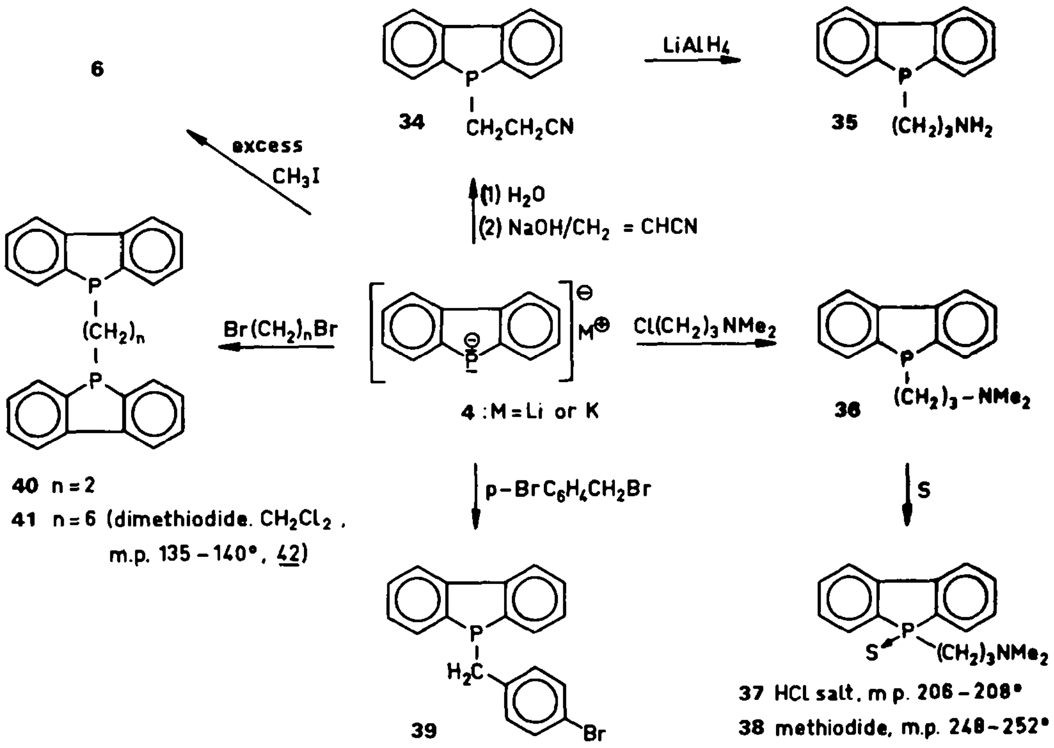
| 2a | Hal-R-Hal | Solvent | R in **15**[a] | | m.p. | Yield[b] % |
|---|---|---|---|---|---|---|
| Li | $CH_2Cl_2$ | dioxane | —$CH_2$— | **27** | 328–329 | 12·7[c] |
| Li | $CH_2Br_2$ | THF | —$CH_2$— | **27** | 328–329 | — |
| | | | P,P-dioxide | **28** | 334–338 | — |
| K | $BrCH_2CH_2Br$ | dioxane | —$CH_2CH_2$— | **29** | 325–330 | 23 |
| Li | $(ClCH{=}CH)_2$ *trans-trans* | THF | —CH=CH—CH=CH— | **30** | 280/335–355 | 11 |
| | | | P,P-dioxide | **31** | 350–357 | — |
| Li | p-$C_6H_4(CH_2Cl)_2$ | THF | p-$CH_2$—$C_6H_4$—$CH_2$— | **32** | 280 | 52 |
| | | | P,P-dioxide | **33** | >375 | — |

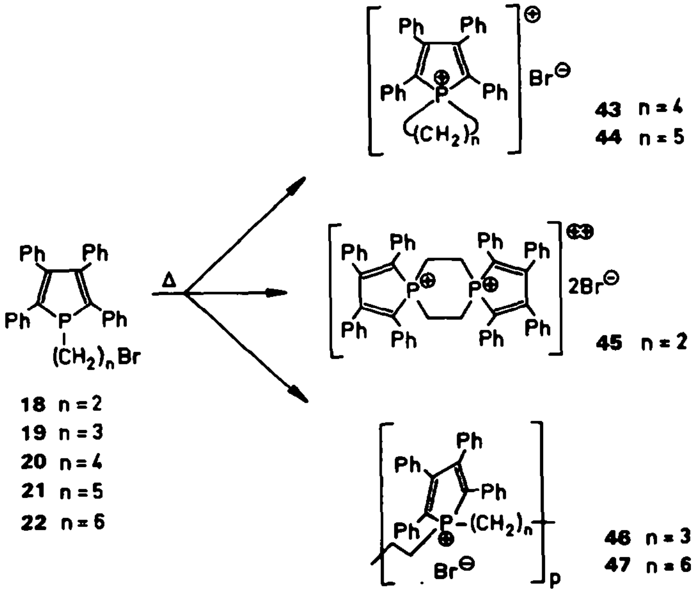
[a] all compounds **15** are yellow and fluorescent
[b] calc. on pentaphenylphosphole
[c] beside 35% of **17**

The structure of **30** is assumed to have the *trans-trans* configuration. The low yields of compounds **27**–**30** were obtained with an excess of the dihalide, which reaction conditions do not favour optimum yields. Where stoichiometric ratios were used (**32**) the yield is fair. The dioxides mentioned in Table III were obtained unintentionally by air oxidation during the work-up; they were readily separated from the parent compound by column chromatography.

### *Alkylations of alkali dibenzophosphacyclopentadienide* (**4**)

The alkali derivatives **4** were obtained either by reaction with an excess of Li shavings in dry THF at room temperature or with an excess of K in boiling dioxane. Compounds were not isolated although the K derivative was sometimes observed to crystallise out as yellow crystals. The yields of **4** were determined indirectly from their alkylation products. Thus, compound **41** was obtained from the Li salt in 83% yield (calc. on **3**) and the phospholonium iodide **6** was prepared in 76·5% yield through the K derivative. The reaction scheme below shows some examples of the functionalisation of dibenzophosphole.


6
34
CH2CH2CN
LiAlH4
35
(CH2)3NH2
excess CH3I
(1) H2O
(2) NaOH/CH2 = CHCN
Br(CH2)nBr
M⊕
Cl(CH2)3NMe2
4 : M = Li or K
36
(CH2)3-NMe2
40 n = 2
41 n = 6 (dimethiodide. CH2Cl2, m.p. 135 - 140°, 42)
p-BrC6H4CH2Br
S
39
Br
37 HCl salt, m.p. 206 - 208°
38 methiodide, m.p. 248-252°

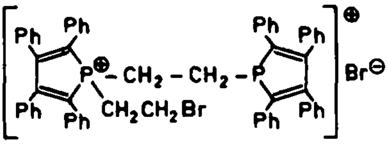

Ph
(CH2)nBr
18 n = 2
19 n = 3
20 n = 4
21 n = 5
22 n = 6
Δ
Br⊖
43 n = 4
44 n = 5
2Br⊖
45 n = 2
Br⊖
46 n = 3
47 n = 6
p

*Self-quaternisation of haloalkylphospholes* (**14**)

Tertiary phosphines are known to have excellent nucleophilic properties and are thus more easily quaternised than the corresponding amines. Since compounds of the type **14** bear both the alkylating function, -R-Hal, and the tertiary phosphine function, they will undergo autoquaternisation either in an inter- or in an intramolecular way. Depending on the chain length of -R-, three types of quaternisation products have been obtained upon thermal treatment, as shown by the reaction scheme below. The most striking result is the formation of 5- and 6-membered rings to the exclusion of any other ring size, even if cyclic dimerisation is necessary to achieve this (dispiro compound **45**). When a 5- or 6-membered ring cannot be formed, the product is a linear polyphosphonium salt; this is namely the case when n = 3 or 6.

The reaction rate strongly depends upon the polarity of the solvent as is known for the quaternisation of amines.[20] Thus, when **18** (n = 2) was heated for 20 hr at 207° in tetralin, over 90% of the starting material was recovered, but in benzonitrile **45** was obtained in a 61% yield at 175° after only 3 hr.

Molecular weight determination of **45** was not possible for solubility reasons. Elemental analysis would also fit with an open structure (**48**). However, potentiometric titration of bromide ion with $AgNO_3$ gave a figure corresponding to 89% of the theory calculated for structure **45**. The compound is not polymeric because it is highly crystalline, in contrast to the amorphous state of the polyphosphonium halides. Furthermore, its high melting point (320–325°) reflects the high symmetry of the dispiro-compound.* Compound **45** was also prepared by quaternisation of the diphospholylethane **29** with dibromoethane in benzonitrile at 160–175°.



**48**

When **20** was heated at 175° for 2 hr, an almost quantitative yield of spirocompound **43** was obtained. However, the same thermal treatment of **21** (n = 5) gave partial resinification; the yield of spirocompound **44** was only 31%. Both bicyclic systems form pale yellow non-fluorescent crystals of m.p. 333–335° and 338–339°, respectively. The polymerisation of **19** (n = 3) was carried out at 210° for 1½ hr without solvent.

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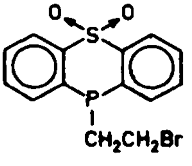
* A similar dispiro compound was obtained upon heating P-(2 bromoethyl) phenothiaphosphine-S-dioxide **49** and melted at 298°.[21]

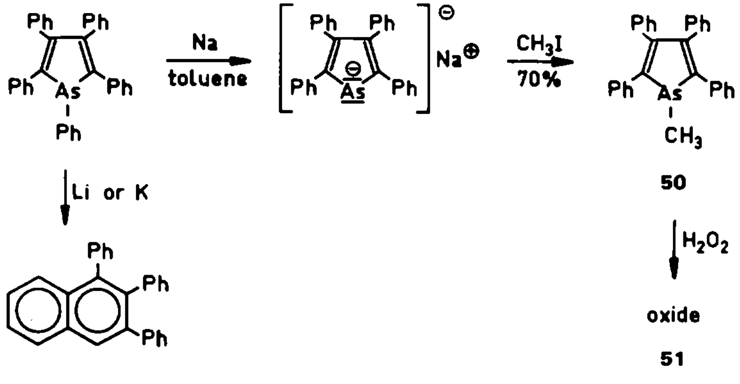


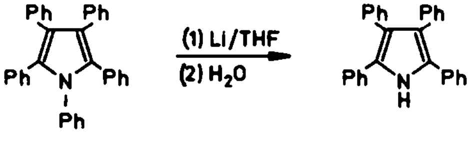
**49**

An amorphous yellowish product was obtained which softened at about 190°. The polymer was separated into four fractions by adding benzene to the $CH_2Cl_2$ solution. They melted at 245, 210, 200 and 180°, respectively. Similarly, when **22** was heated at 160°, the fluid melt gradually became more viscous. Heat treatment was continued for 2 hr at 200°. The polymer left after extraction with hot benzene melted at 190°, yielding a very viscous liquid which at 300–310° showed no visible signs of decomposition. Polymer **47** was very soluble in polar solvents such as MeCN, $CH_2Cl_2$, $CHCl_3$, EtOH, but almost insoluble in pure water. However, addition of 20% of EtOH to an aqueous suspension gave immediately a clear solution which was strongly fluorescent (solutions in other solvents showed no fluorescence). Hot AcOH solutions became turbid upon cooling. The polymer was almost insoluble in tetrachloroethylene, THF, dioxane and acetone. Fractionation was carried out as above. When deposited on silicagel, the polymer showed anion exchange properties: the column could be converted into its sulfate and hydroxide forms. An exchanging capacity of 25–30% of the theoretical value was measured.

## ARSOLES AND PYRROLES

In contrast to the phospholes, pentaphenylarsole[1,22] lost the As-moiety when reacted with Li or K, yielding mainly 1,2,3-triphenylnaphthalene. However, when the less electropositive Na was used in boiling toluene, a 70% yield of 1-methyl-2,3,4,5-tetraphenylarsole (**50**) was obtained by reaction of the *in situ* formed sodium tetraphenylarsacyclopentadienide with MeI. Although triphenylamine is known[5a,23] to be cleaved by Li in THF yielding lithium diphenylamide, this method has apparently not been used to dephenylate N-phenyl substituted pyrroles. Thus pentaphenylpyrrole reacted similarly with an excess of Li in THF at room temp. and gave a 76% yield of 2,3,4,5-tetraphenylpyrrole upon hydrolysis of the lithium tetraphenylpyrrolide.





## EXPERIMENTAL

Pentaphenylphosphole,[1, 22] P-phenyl-dibenzophosphole,[24] 4(2'-chloroethyl)benzyl chloride[25] and 2,3,4,5-tetraphenylpyrrole[26] were prepared according to the literature. 1,4-Dichloro-*trans, trans*-1,3-butadiene[27] was obtained by repeated freezing out of a mixture of 1,4-dichlorobutadiene isomers.

*Alkali 2,3,4,5-tetraphenylphosphacyclopentadienide* (**2a**). *Lithium derivative.* The lithium phospholide **2a** was always prepared in THF, either under reflux or at room temp.

(a) Thus 1 g (2·15 mmoles) of pentaphenylphosphole was refluxed for 2 hr with freshly cut Li shavings in large excess in anhydrous THF under $N_2$. The surface of the Li became clean after 10 min at which time a wine-red colour developed, turning to brownish-red after 20 min. The cooled soln thus obtained was either reacted further as such, or treated under reflux with one mole of t-BuCl for 10–20 min in order to destroy PhLi.[14]

(b) 1-*Methyl-2,3,4,5-tetraphenylphosphole* (**16**). Pentaphenylphosphole (1 g = 2·15 mmoles) and 0·3 g of a 30% Li dispersion in mineral oil (13 mmoles) were stirred for 25 hr at room temp. in 75 ml dry THF. After 5 min a blue colour was observed which rapidly turned violet and finally wine-red. 1 ml of MeI was added and after 6 min the mixture evaporated *in vacuo* at room temp. Addition of $AcOH/H_2O$ and evaporation of the $CH_2Cl_2$ extracts left a pale yellow powder which was recrystallised from EtOH, yielding 63% of the title compound, m.p. 195–196°. IR spectrum: ref. 28. $\lambda_{max}$ (cyclohexane) 378 nm (log ε 3,777). (Found: C, 86·52; H, 5·79. Calc. for $C_{29}H_{23}P$: C, 86·50; H, 5·76%). Oxidation of **16** gave the P-oxide which was found identical (m.p., IR spectrum[29]) with the product obtained by reacting 1,4-dilithiotetraphenylbutadiene with $CH_3PI_2$ followed by oxidation.[1]

*Potassium derivative.* (a) In dioxane: 10 g (21·5 mmoles) of pentaphenylphosphole and 1·82 g (46·5 mmoles) of K were refluxed for 4 hr. Alkylation with dibromoethane indicated that the yield of **2a** (K) was over 73%.

(b) In toluene: 1-*Methyl-2,3,4,5-tetraphenylphosphole methiodide.* 5·5 g (11·85 mmoles) of pentaphenylphosphole and 0·92 g (23·5 mmoles) of K were refluxed for 3 hr in toluene (50 ml). A red colour was formed immediately at reflux. After alkylation with excess $CH_3I$ (½ hr reflux), and addition of water, the $CH_2Cl_2$ extracts were chromatographed on silicagel, yielding 0·1 g of starting phosphole ($C_6H_6$ as eluent) and 4·6 g (73%) ($CH_2Cl_2/Et_2O$ as eluent) of 1-methyl-2,3,4,5-tetraphenylphosphole methiodide, yellow crystals of m.p. 289–297° (from $CH_2Cl_2/CH_3OH$). $\lambda_{max}$($THF/H_2O$) 363 nm (log ε 3·35). (Found: C, 65·99; H, 4·62; I, 22·72. Calc. for $C_{30}H_{20}IP$: C, 66·18; H, 4·82; I, 23·31%).

(c) In THF: 2,3,4,5-*Tetraphenylphosphole* (**7a**). Pentaphenylphosphole (5 g, 10·8 mmoles) and 0·85 g (21·7 mmoles) of K were refluxed for 3 hr in THF (80 ml). On addition of $AcOH/H_2O$ (1:1) the red soln became pale yellow. After evaporation of solvents, the benzene extracts were chromatographed on silicagel. Freeze-drying of the benzene fraction gave 3·85 g (92·5%) of crude **7a**, the IR spectrum of which was almost identical with that of a pure sample. Crystallisation from benzene/petroleum ether gave yellow crystals of m.p. 147–150° (Thiele, sealed cap). All operations were carried out in an inert atmosphere. $\nu_{P-H}$: 4.33μ. (Found: C, 86·08; H, 5·66. Calc. for $C_{28}H_{21}P$: C, 86·52; H, 5·44%).

1-*Hydroxy*-1 *oxy-tetraphenylphosphole* (**8**). When air was not carefully excluded, oxidation of **7a** to the phosphonic acid **8** readily took place. Compound **8** was easily obtained pure by chromatography on silicagel (elution with benzene/ether) and formed orange crystals, m.p. 287–289°. The O—H stretching band is very diffuse; the broad bands observed at 8·53 and 10·20μ are ascribed to P=O and P—OH stretching vibrations respectively.[30] (Found: C, 80·78; H, 5·37. Calc. for $C_{28}H_{21}O_2P$: C, 79·99; H, 5·03%).

*Reaction of pentaphenylphosphole* (**1a**) *with sodium.* Compound **1a**, after having been refluxed with Na in dioxane for 8 hr was recovered in over 85% yield.

1,2,5-*Triphenylphosphole* (**1b**). Diphenyldiacetylene (1 g, 4·95 mmoles), 0·7 ml of phenylphosphine, 0·05 g of $HgSO_4$ and 10 ml of dioxane were heated in a sealed tube at 120° for 63 hr (run 7, Table I). Evaporation of solvent and chromatography on alumina of the benzene soln of the residue yielded 0·55 g (36·8% based on diphenyldiacetylene) of **1b**, eluted with benzene and with $CH_2Cl_2$. The phosphole **1b** formed yellow fluorescent needles, m.p. 186–187°; the product was identical with a sample prepared according to Campbell *et al.*[16] The work up of the other runs (Table I) was similar to the above procedure.

2,5-*Diphenylphosphole chlorohydrate* (**9**). A mixture of 2·5 g (80 mmoles) of 1,2,5-triphenylphosphole and about 1·5 g of K pieces was stirred in 100 ml of abs. THF for 2 hr at reflux. The cooled mixture was filtered (using a Schlenk tube) and the violet filtrate acidified with $H_2O/AcOH$. After evaporation to dryness, the benzene extracts were chromatographed on silicagel and the yellow fluorescent band eluted with benzene. The residue, taken up in dioxane was treated with gaseous HCl; addition of ether precipitated the chlorohydrate **9**, recrystallised from $THF/Et_2O$: yellow crystals m.p. 170–190°. All operations have to be carried out under strictly anaerobic conditions. (Found: C, 70·08; H, 5·34. Calc. for $C_{16}H_{14}ClP$: C, 70·48; H, 5·18%).

1-*Methyl-2,5-diphenylphosphole* (**11**). A stoichiometric ratio of **1b** and K was refluxed for 3 hr in dioxane. A slight excess of MeI was slowly added to the cooled soln of **2b**. Column chromatography gave with $CCl_4$ as eluent **9** in 40% yield, yellow crystals of m.p. 110–111° (from MeOH). (Found: C, 80·98; H, 5·86. Calc. for $C_{17}H_{15}P$: C, 81·60; H, 6·04%).

1,1-*Dimethyl-2,5-diphenylphospholonium iodide* (**13**). Refluxing for 30 min of **11** with excess MeI in benzene precipitated the methiodide **13** in 51% yield. Recrystallisation from $CH_2Cl_2/C_6H_6$ gave pure **13**, m.p. 249–252°. (Found: C, 55·51; H, 4·84. Calc. for $C_{18}H_{18}IP$: C, 55·12; H, 4·63%).

1-*Methyl-2,5-diphenylphosphole-*P*-oxide* (**12**). Compound **11** (0·1 g) and 0·2 ml of 30% $H_2O_2$ in 1 ml of acetone was refluxed for 5 min. Dilution with a few drops of water and cooling gave yellow-orange needles of **12**: transition point at 115°, m.p. 163–165°. The NMR spectrum is compatible with the proposed structure.

*Dibenzophosphole* (**10**). Compound **3** (10 g) was stirred for 3 hr with 3·5 g of Li shavings in 50 ml THF. After removal of unreacted Li, water and AcOH were added and the solvents evaporated. The residual oil was distilled in a molecular still at 65°/0·1 mm Hg yielding 5·4 g (76%) of **10**, which solidified to colourless crystals of m.p. 47–48°. Partial oxidation could not be avoided during the elemental analysis. (Found: C, 76·32; H, 4·81. Calc. for $C_{12}H_9P$: C, 78·25; H, 4·92%).

1(2′-*Cyanoethyl*)*dibenzophosphole* (**34**). A mixture of 10 g of **3** was stirred with excess of Li shavings in pure THF for 1½ hr. Water was added, yielding a yellow soln, which was concentrated to about 5 ml. MeCN (25 ml) aq KOH (5 ml, 10N) were added, followed by dropwise addition of 2·3 g of acrylonitrile in 10 ml of $CH_3CN$. After addition, the orange colour of **4** faded completely. The mixture was acidified with AcOH, giving a colourless ppt of **34**, m.p. 81–82° (MeOH) (7 g, 78% yield). $\nu_{C\equiv N}$: 4·45$\mu$. (Found: C, 75·76; H, 5·28. Calc. for $C_{15}H_{12}NP$: C, 75·95; H, 5·09%).

1-(3′-*Aminopropyl*)*dibenzophosphole* (**35**). A soln of 5 g of **34** in ether was added slowly to an ethereal suspension of 1·5 g of LAH at 0°. The mixture was allowed to warm and water added. The benzene extracts were treated with aq HCl, the aq phase made alkaline and extracted with benzene. The residue was distilled in a molecular still at 110°/$10^{-2}$ mm, yielding 1·5 g of **35**. (Found: C, 73·92; H, 6·59; N, 5·82. Calc. for $C_{15}H_{16}NP$: C, 74·69; H, 6·68; N, 5·80%).

1-(3′-*Dimethylaminopropyl*)*dibenzophosphole* (**36**). The Li derivative **4** was made from 10 g (38·5 mmoles) of **3** in THF at room temp. A stoichiometric amount of t-BuCl was added and after 15 min reflux, 34·6 mmoles of $(CH_3)_2NCH_2CH_2CH_2Cl$, dissolved in THF, was added dropwise at 15° and then refluxed for ½ hr. Water and benzene were added, the benzene layer treated with aq HCl and the free amine liberated by base. Its ethereal extract was distilled in a molecular still at 90°/0·03 mm, yielding 4·4 g (42%) of the title compound. (Found: C, 75·19; H, 7·43. Calc. for $C_{17}H_{20}NP$: C, 75·81; H, 7·48%).

1-(3′-*Dimethylaminopropyl*)*dibenzophosphole* P-*sulfide chlorohydrate* (**37**). Compound **36** was refluxed for 2 hr in benzene with a fourfold amount of sulphur. Its excess was removed by boiling the residue of the mixture with aq $Na_2S$ in dioxane, for 1 hr. The mixture was shaken with water and ether, and gaseous HCl was introduced into the dried ether layer. The colourless crystals (93% yield) of **37** had m.p. 206–208°. (Found: C, 60·17; H, 6·60. Calc. for $C_{17}H_{21}ClNPS$: C, 60·48; H, 6·27%).

1-(3′-*Dimethylaminopropyl*)*dibenzophosphole* P-*sulphide methiodide* (**38**). The free amine was refluxed for 90 min with excess $CH_3I$ in benzene, yielding (70%) upon cooling the title compound, m.p. 248–252° (from EtOH/acetone). (Found: C, 48·88; H, 5·18. Calc. for $C_{18}H_{23}INPS$: C, 48·77; H, 5·23%).

1(p-*Bromobenzyl*)*dibenzophosphole* (**39**). Compound **3** (3 g, 11·5 mmoles) was reacted with excess of Li pieces in 50 ml absolute THF for 2½ hr and the mixture refluxed for 10 min with 11·5 mmoles of t-BuCl. After cooling, 11·6 mmoles of *p*-bromobenzyl bromide were added and the solvent evaporated. The residue was extracted with benzene which gave upon concentration 4 g (86·5%) of **39**, m.p. 123·5–123·6° (from EtOH). (Found: C, 64·99; H, 4·02; Br, 22·73. Calc. for $C_{19}H_{14}BrP$: C, 64·60; H, 3·99; Br, 22·62%).

1,2-*Bis*(*dibenzophospholyl*-1)*ethane* (**40**). Addition of a stoichiometric amount of t-BuCl (20 min reflux) followed by a stoichiometric amount of ethylene dibromide to **4** in THF gave a ppt of **40**, m.p. 250° (from $CH_2Cl_2$) with a transition point at 180°. (Found: C, 78·98; H, 4·45. Calc. for $C_{26}H_{20}P_2$: C, 79·17; H, 5·11%).

1,6-*Bis*(*dibenzophospholyl*-1)*hexane* (**41**). Compound **41** was prepared as above in a 83% yield and crystallised from MeOH as colourless crystals, m.p. 142–143°. (Found: C, 79·31; H, 6·24. Calc. for $C_{30}H_{28}P_2$: C, 79·98; H, 6·27%).

1,6-*Bis*(*dibenzophospholyl*-1)*hexane bismethiodide* (**42**). The compound was obtained from **41** and excess $CH_3I$ in boiling benzene, m.p. 135–140° ($CH_2Cl_2$) with gas evolution (loss of $CH_2Cl_2$). (Found: I, 30·70. Calc. for $C_{32}H_{34}I_2P_2 \cdot CH_2Cl_2$: I, 30·99%).

P-*Alkyl-2,3,4,5-tetraphenylphospholes* (**16–24**). These phospholes listed in Table II with the exception of

**17**, were prepared by slow addition of **2a** to a large excess of the required dihalide, using molar ratios of up to 15. All the products gave satisfactory analyses.

1-*Vinyl*-2,3,4,5-*tetraphenylphosphole* (**25**). Compound **18** was heated with a 100% excess of t-BuOK in benzene for 90 min yielding 88·5% of **25**, which was obtained in two different crystalline forms, the one melting at 153–156° (blocks from $C_6H_6/CH_3OH$), the other at 181–183° (needles also from $C_6H_6/CH_3OH$). They showed slightly different fluorescence and had different IR spectra in the solid state (KBr discs) but were identical in soln. UV (cyclohexane): broad flat maximum at 300–350 nm, log ε: 3·9. (Found: C, 86·84; H, 5·42. Calc. for $C_{30}H_{23}P$: C, 86·92; H, 5·60%).

2,3,4,5-*Tetraphenylphospholyl*-1-*acetic acid* (**24**). The ester **24** was saponified by heating with KOH in EtOH for 30 min. Addition of dilute HCl gave crude **24**, m.p. 207–210°. Crystallisation from $CH_2Cl_2$/light petroleum gave pure **24**, pale yellow crystals, m.p. 210–212°. $\nu_{C=O}$: 5·88μ. (Found: C, 80·29; H, 4·77. Calc. for $C_{30}H_{23}O_2P$: C, 80·69; H, 5·20%).

*Bis*(*tetraphenylphospholyl*-1)*alkanes and related compounds* (**27–33**) were essentially prepared as **40**, but for a number of them (see above) the yield might be improved by using more appropriate ratios of reagents. The elemental analyses gave satisfactory values.

1,2,3,4-*Tetraphenyl*-5-*phosphoniaspiro*[4,4]*nona*-1,3-*diene bromide* (**43**). Compound **20**, when heated at 175° for 2 hr without solvent underwent cyclisation to give cream coloured **43**, m.p. 333–335° in almost quantitative yield. Recrystallisation was best achieved by dissolving the product in $CH_2Cl_2$ and adding benzene. The test on bromide ion was positive. (Found: C, 73·59; H, 5·37. Calc. for $C_{32}H_{28}BrP$: C, 73·24; H, 5·39%).

1,2,3,4-*Tetraphenyl*-5-*phosphoniaspiro*[4,5]*deca*-1,3-*diene bromide* (**44**). Pure **21** was first molten at 175°, then the temperature was raised to 200° where the molten mass became black. After 10 min the mixture was cooled, dissolved in $CH_2Cl_2$ and treated with activated charcoal. The filtered soln was evaporated and the residue boiled with benzene giving 31% yield of yellow **44**, m.p. 357°. (Found: C, 73·43: H, 5·70. Calc. for $C_{33}H_{30}BrP$: C, 73·74; H, 5·62%).

1,2,3,4,9,10,11,12-*Octaphenyl*-5,8-*diphosphoniadispiro*[4,2,4,2]*tetradeca*-1,3,9,10-*tetraene dibromide* (**45**). (a) Four grams of **18** and 6 ml of benzonitrile were kept for 3 hr at 175° in an evacuated sealed tube. Upon cooling 2·45 g (61%) of **45** crystallised out (crude m.p. 305–320°). Recrystallisation from MeOH gave a m.p. of 320–325° (dec.). (Found: C, 72·46; H, 4·83; Br, 14·3. Calc. for $C_{60}H_{48}Br_2P_2$: C, 72·73; H, 4·89; Br, 16·14%).

(b) Compound **45** was also obtained by heating **29** with a stoichiometric amount of 1,2-dibromoethane in benzonitrile at 160–175° for 2½ hr. Upon cooling, **45** crystallised out with a 22·5% yield, m.p. 325–330°. Its IR spectrum was identical with that of a sample prepared as under (a).

1-*Methyl*-2,3,4,5-*tetraphenylarsole* (**50**). One gram of pentaphenylarsole[1] and 0·6 g of Na were refluxed for 19 hr in toluene. After cooling at about 40°, 1·5 ml of MeI was added and ½ hr later, EtOH and water were added cautiously in order to destroy unreacted Na. The benzene extracts were chromatographed on silicagel. Compound **50** was eluted with benzene with a yield of 68% after crystallisation from $CH_2Cl_2$/EtOH. The almost colourless prisms melted at 212–213°. (Found: C, 77·69; H, 5·10. Calc. for $C_{29}H_{23}As$: C, 78·01; H, 5·20%).

1-*Methyl*-2,3,4,5-*tetraphenylarsole As-oxide* (**51**). Treatment of **48** with $H_2O_2$ in boiling acetone for 1 hr gave the oxide **51**, pale yellow crystals, m.p. 222–223° (eluted from silica gel with $C_6H_6/CH_3OH$). $\nu_{As\to O}$ = 11·24 μ. (Found: C, 74·29; H, 4·75. Calc. for $C_{29}H_{23}AsO$: C, 75·32; H, 5·02%).

2,3,4,5-*Tetraphenylpyrrole*. Two grams of pentaphenylpyrrole and 1 g of Li pieces were stirred in 100 ml of freshly distilled THF (from LAH) for 3 hr. Hydrolysis and chromatography on $Al_2O_3$ gave a 76% yield of pure 2,3,4,5-tetraphenylpyrrole; m.p. 214°; m.m.p. with authentic sample: 214°. Good elemental analysis was obtained.

*Acknowledgement*—The authors are indebted to Mr. R. G. Merényi for the interpretation of the NMR spectra.

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