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2-PHOSPHANAPHTHALENES

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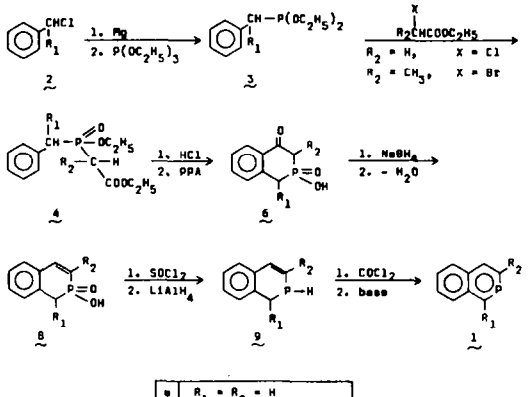
Abstract—The synthesis and physical properties of 2-phosphanaphthalene and of three methyl substituted derivatives are reported together with some observations concerning the reactivity of this system. It is concluded that these compounds possess aromatic character.

INTRODUCTION

In the last decade a lively interest has grown in the chemistry of phosphorus compounds with delocalized $p\pi$-$p\pi$ bonds.[1] First of all phosphamethincyanines were synthesized. In the years to follow phosphorin (phosphorus analogue of pyridine) and dibenzophosphorin systems were prepared. Quite recently Märkl and Heier published the synthesis of a benzo[b]phosphorin, 2 - phenyl - 1 phosphanaphthalene.[2] From physical and other data it is clear that these phosphorins have aromatic character.

In a preliminary communication[3] we reported the preparation of a benzo[c]phosphorin, 3 - methyl - 2 - phosphanaphthalene (**1c**). We now want to give a full account of our investigations concerning the 2-phosphanaphthalene system. The objective of this research was to synthesize unsubstituted 2-phosphanaphthalene (**1a**) and to study the stability and the reactivity of this system, because phosphabenzene is stable in nitrogen atmosphere, but phosphaanthracene cannot be isolated even in vacuum.[1] Moreover, the reactivity of phosphorin systems had only been tested with heavily substituted phosphabenzenes.[1] As we encountered initial difficulties in preparing **1a**, methyl substituted 2-phosphanaphthalenes were also prepared. The synthesis and physical properties of **1a**, 1-methyl-, 3-methyl- and 1,3 - dimethyl - 2 - phosphanaphthalene (**1b**, **1c** and **1d**, respectively) will be discussed together with some observations about the reactivity of the 2-phosphanaphthalene system.



a	$R_1 = R_2 = H$
b	$R_1 = CH_3$, $R_2 = H$
c	$R_1 = H$, $R_2 = CH_3$
d	$R_1 = R_2 = CH_3$

Scheme 1

Synthesis

The synthesis of 2 - hydroxy - 2 - phosphatetral - 4 - one - 2 - oxide (**6a**) has been published by Henning.[4] We found that his procedure could be improved by reacting the Grignard reagent from **2a** directly with triethyl phosphite,[5] instead of preparing the zincorganic derivative and treating it with phosphorus trichloride and then with isopropanol. **6b**, **6c** and **6d** were synthesized analogously from the appropriate starting materials.

The reduction of the keto group of **6** with $NaBH_4$ in H_2O yielded the corresponding alcohol **7**. **8a** and **8b** were obtained by heating **7a** and **7b** with 10% H_2SO_4. As this method was not reproducible with **7c** and **7d**, Lucas reagent was used to obtain **8c** and **8d**.

From **7** to **1** we followed the route which de Koe *et al.* had worked out in the phenanthrene series:[6] reduction of **8** to a 1,2 - dihydro - 2 - phosphanaphthalene **9** and reaction of the latter with phosgene to the corresponding chlorophosphine **10** followed by dehydrohalogenation with the aid of a nitrogen base.

Reduction of **8a** with silanes[6] did not yield **9a** but an unidentified polymer. Reaction of the phosphinic acid chloride (prepared from **8** and $SOCl_2$ in chloroform) with LAH_4 in ether at − 15° yielded **9**. In the ^1H NMR spectrum the coupling constants between the olefinic protons and phosphorus are in accordance with those reported by Quin for phospholenes[7a] and phospholes.[7b] Contrary to the normal observation ($^1J_{PH}$ *ca.* 180–220 Hz[8]) only one peak can be detected in this spectrum for the proton directly attached to phosphorus. Because inversion of configuration at phosphorus is usually slow in phosphines,[9,10] we feel that this phenomenon is caused by an intermolecular exchange of the proton directly attached to

phosphorus. The following observations support this explanation:

(1) In a ^{31}P NMR spectrum of **9c** recorded at a temperature below $-40°$ in CH_2Cl_2 the broad singlet present at room temperature is replaced by a doublet each of which is further split into two multiplets.

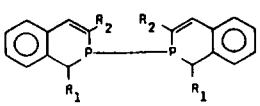
(2) On shaking a solution of **9c** in $CDCl_3$ with D_2O the peak at $\delta = 4{\cdot}26$ in the ^1H NMR spectrum, ascribed to the proton directly attached to phosphorus, disappears. This is not observed for diphenylosphine which has a pK_a of 21·7.[11]

(3) The mass spectrum of **9c** treated with CH_3OD shows, besides $m/e = 162$ $(C_{10}H_{11}P)^+$ also $m/e = 163$ $(C_9H_{10}DP)^+$. It is possible that the presence of both $m/e = 162$ and $m/e = 163$ is caused by an exchange reaction with proton sources in the mass spectrometer.

9a is extremely unstable. It decomposes to a large extent on standing at room temperature overnight. **9c, 9d** and also **9b** can be distilled undecomposed and seem to be quite stable at room temperature. We have no convincing explanation for these effects, which all point to instability connected with surprisingly easy deprotonation. One of the reasons may be polarisation of the P–H bond, because the negative charge on phosphorus can be delocalized effectively into the styrene system. Possibly the fact, that unsubstituted phosphole has not yet been prepared (only heavily substituted derivatives are known so far[12]), must also be attributed to this phenomenon.

Because of the instability of **9a** and because Quin stated that 2-chlorophospholene is very unstable,[7a] we did not isolate the chlorophosphines, **10**, but reacted them with base without purification. The reaction with both triethyl amine (TEA) and 1,5 - diazabicyclo - [5.4.0]undec - 5 - ene (DBU) in high vacuum sealed glass vessels was rapid, maximum UV absorption being obtained immediately on mixing the reagents. The 2-phosphanaphthalenes were isolated and purified by extraction from the reaction mixture and sublimation. As described in detail in the experimental part, **1b** was the only member of the series which could not be obtained in pure state. The yield of purified **1** varied from 20% for **1a** to 64% for **1c** (based on **9**). The residue of the sublimation of **1c** and **1d** contained dimers **11c** and **11d**, respectively; this was suggested by:

(a) The mass spectra of these residues [$m/e = 322$, 30% $(C_{20}H_{20}P_2)^+$; $m/e = 162$, 100% $(C_{10}H_{11}P)^+$; $m/e = 161$, 66% $(C_{10}H_{10}P)^+$; $m/e = 160$, 74% $(C_{10}H_9P)^+$ for **1c** and $m/e = 350$, 4% $(C_{22}H_{24}P_2)^+$; $m/e = 176$, 7% $(C_{11}H_{13}P)^+$; $m/e = 175$, 20% $(C_{11}H_{12}P)^+$; $m/e = 174$, 100% $(C_{11}H_{11}P)^+$ for **1d**]; (b) The IR spectrum (no P–H stretch band); and (c). Oxidation of the residues with warm dilute HNO_3, which yielded **8c** and **8d**, respectively.



11c $R_1 = H$, $R_2 = CH_3$

11d $R_1 = R_2 = CH_3$

Properties of **1**. **1a** and **1c** are colourless crystalline compounds, **1d** is a pale yellow liquid at room temperature. The m.ps and b.ps show similar trends as those of the corresponding naphthalenes. All four compounds react immediately with atmospheric oxygen, as evidenced by the disappearence of the characteristic UV spectrum. In nitrogen atmosphere they are stable.

NMR spectra. In the ^1H NMR spectra of **1** the protons at C-1, C-3 and C-4 appear between $\delta = 8$ and $\delta = 10$ ppm. This low field chemical shift is an indication for the aromatic character of these compounds. The assignments of these protons in **1a** (Fig. 1) has been confirmed by spectrum simulation and are in accordance with those reported for phosphabenzene.[1]

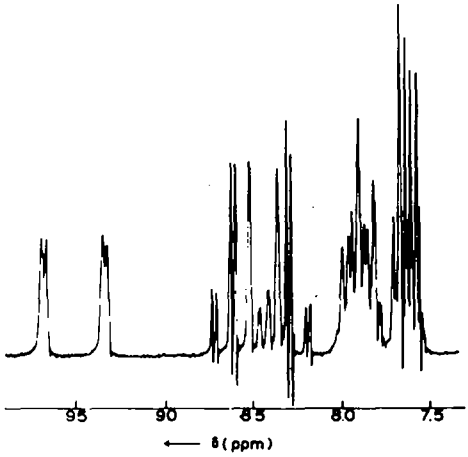


Fig. 1. ^1H NMR spectrum of 2-phosphanaphthalene (100 Mc) in $CDCl_3$ with TMS as internal standard.

The coupling constants found in the ^{31}P NMR spectrum of **1a** and **1c** are in agreement with those found in the ^1H NMR spectrum of these compounds. The center of the signals is -192 and -200 ppm relative to external H_3PO_4, respectively. These low chemical shifts are in agreement with the values found for other phosphorins.[1]

The ^{13}C NMR spectrum of **1c** (Fig. 2) shows besides an

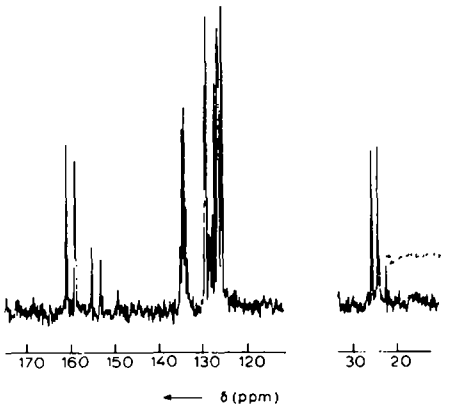


Fig. 2. ^{13}C NMR spectrum of 3-methyl-2-phosphanaphthalene (25·2 Mc) in $CDCl_3$ with TMS as internal standard.

aromatic multiplet and a doublet of the methyl carbon atom, two doublets at $\delta = 160{\cdot}2$ ppm and $\delta = 154{\cdot}5$ ppm relative to internal TMS which are ascribed to C-1 and C-3. For isoquinoline the same pattern is found.[13]

The reason why the C atoms and the protons next to phosphorus show a down-field shift, is not clear at this moment. Possibly it can be ascribed to magnetic anisotropy induced by the phosphorus atom.

UV spectra. The UV spectra of **1** (Fig. 3) show a bathochromic shift of *ca.* 3000–5000 cm^{-1} with regard to the corresponding naphthalenes. Compared with other phosphorins these are reasonable values.[1] Qualitatively the spectra of **1** resemble their carbon analogues more than their nitrogen analogues (Fig. 4).

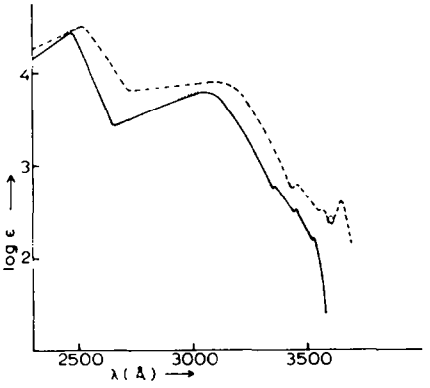


Fig. 3. UV spectra of **1a** (——), **1c** (. . . .) and **1d** (----) in diethyl ether.

The shifts of the maxima of **1b**, **1c** and **1d** relative to **1a** (Table 1) vary in the same way as those of the corresponding naphthalenes relative to unsubstituted naphthalene. This implies that it is probable, that the 2-phosphanaphthalenes and the naphthalenes have a similar electronic structure also in the excited state.

Mass spectra. The mass spectra (Experimental) are

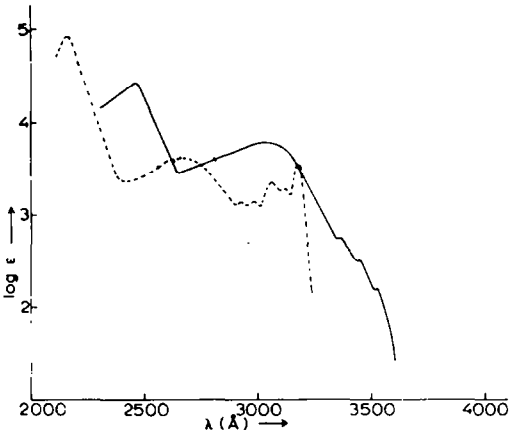


Fig. 4. UV spectra of naphthalene (····) (in hexane), isoquinoline (----) (in hexane) and **1a** (——) (in diethyl ether).

quite simple. The molecular ion is the base peak. The doubly charged molecular ions cause peaks of *ca.* 10%. These facts confirm that 2-phosphanaphthalenes are compounds of considerable stability.

Photoelectron spectra. The PE spectra of **1a** and **1c** were measured by Schweig *et al.* and are discussed elsewhere.[14a] As found for other phosphorins[14b] the energies of the orbitals of the naphthalenes and the phosphanaphthalenes are closer to each other than are those of the isoquinolines and the phosphanaphthalenes.

Fluorescence and phosphorescence spectra. The investigation of these spectra is under way.[15] Preliminary results confirm the structural analogy between **1** and the corresponding naphthalenes.

Reactions of **1.** Because of the high yields in the preparation of **1c** this compound was most readily available and was therefore chosen for a preliminary investigation of the reactivity of the 2-phosphanaphthalene system.

The reaction of **1c** with mercuric acetate in

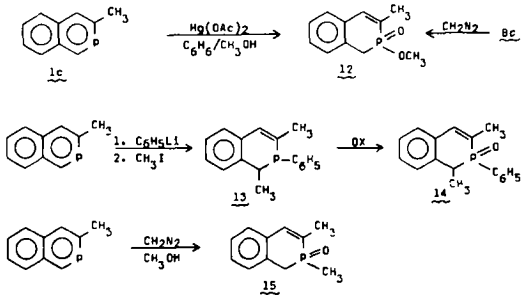
Table 1.

1a	**1b**		**1c**		**1d**	
λ_{max}(nm)	λ_{max}(nm)	$\Delta\bar{\nu}(cm^{-1})$	λ_{max}(nm)	$\Delta\bar{\nu}(cm^{-1})$	λ_{max}(nm)	$\Delta\bar{\nu}(cm^{-1})$
247			250	500	251	700
303	308	500	305	200	310	700
353	358	400	361	600	364	800
Naphthalene	1-Me-Naphthalene		2-Me-Naphthalene		1,3-diMe-Naphthalene	
λ_{max}(nm)	λ_{max}(nm)	$\Delta\bar{\nu}(cm^{-1})$	λ_{max}(nm)	$\Delta\bar{\nu}(cm^{-1})$	λ_{max}(nm)	$\Delta\bar{\nu}(cm^{-1})$
220	224	900	225	1000	228	1600
275	281	800	276.5	200	282	900
311	317	500	319.5	900	322	1100

UV maxima of methylsubstituted 2-phosphanaphthalenes and naphthalenes and their shifts relative to the respective parent compounds

benzene/methanol does not yield the λ^5-phosphorin as is the case for many monocyclic phosphorins,[1] but the phosphinic ester **12** which was also obtained from **8c** with diazomethane.

Although the products of the reactions of **1c** with phenyllithium followed by addition of methyl iodide and with diazomethane in methanol were not fully characterized, it is evident from NMR and mass spectroscopy (Experimental), that no λ^5-phosphorins were formed,[1,16] but 1,2-dihydro compounds:



Present investigations in our laboratory are aimed at settling the mechanism of these and other reactions of 2-phosphanaphthalenes, especially the striking preference for 1,2-addition as compared to monocyclic phosphorins. In a certain sense, the 2-phosphanaphthalene system seems to resemble the isoquinoline system which also has a pronounced preference for 1,2-addition; however, the polarity of the addition is reversed.

CONCLUSION

2-Phosphanaphthalenes are stable compounds under N_2 atmosphere. Their UV and PE spectra show a strong resemblance to the corresponding naphthalenes. These facts, together with the results of NMR spectroscopy, suggest that these compounds have an aromatic character. Their reactivity differs from that of monocyclic phosphorins.

EXPERIMENTAL

M.ps and b.ps are uncorrected. The IR spectra were measured with a Perkin Elmer Model 237 spectrophotometer, the ^{1}H NMR spectra with a Varian A-60 or a Varian XL-100 spectrometer, the ^{13}C NMR spectrum with a Varian XL-100 spectrometer at 25·2 Mc, the ^{31}P spectra with a Jeol C-60 spectrometer at 24·3 Mc or with a Varian XL-100 spectrometer at 40·5 Mc, the UV spectra with a Perkin-Elmer Model 137 spectrophotometer and the mass spectra with a Varian Mat CH5 spectrometer at 70 eV. In the NMR spectra (δ, ppm) TMS was used as internal standard unless otherwise stated. Elemental analyses were performed under supervision of Mr. W. J. Buis at the Microanalytical Department of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands.

All experiments with tervalent phosphorus were carried out under a blanket of N_2 unless otherwise stated.

Diethyl benzylphosphonite (**3a**). This compound was prepared by the method of Sander.[5]

Diethyl 1-phenylethylphosphonite (**3b**). This compound was prepared in analogy to **3a**. The yield was 29·3%, b.p. 78°/5·10^{-1} mm. ^{1}H NMR spectrum (60 Mc in $CDCl_3$): δ = 7·28 (s, 5H, aryl H); δ = 4·2 – 3·5 (m, 4H, $-CH_2-$); δ = 2·94 (d of q, $^2J_{PH}$ = 2·5, $^3J_{HH}$ = 7·5, 1H, R_3CH); δ = 1·39 (d of d, $^3J_{PH}$ = 13·5, $^3J_{HH}$ = 7·5, $R_2CH\underline{CH_3}$); δ = 1·25 and 1·00 (2t, $^3J_{HH}$ = 7, 6H, $-OCH_2\underline{CH_3}$).

Ethyl benzylcarbethoxymethylphosphinate (**4a**). A mixture of 1 eq. of **3a** and 2 eq. of ethyl chloroacetate was heated to 120°. At this temp the exothermic reaction started. After the evolution of EtCl had stopped the temp was raised to 150° for 45 min. The excess of ethyl chloroacetate was removed and the residue was vacuum distilled, yielding 89% of **4a**, b.p. 123°/0·1 mm. ^{1}H NMR spectrum (60 Mc in CCl_4): δ = 7·5 – 7·1 (m, 5H, aryl H); δ = 4·4 – 3·8 (m, 4H, $-OCH_2\underline{CH_3}$); δ = 3·27 (d, $^2J_{PH}$ = 18, 2H, $-CH_2-$); δ = 2·81 (d, $^2J_{PH}$ = 17, 2H, $-CH_2-$); δ = 1·25 (t, $^3J_{HH}$ = 7, 3H, $-CH_3$); δ = 1·20 (t, $^3J_{HH}$ = 7, 3H, $-CH_3$).

Ethyl 1-phenylethylcarbethoxymethylphosphinate (**4b**). 1 eq. of **3b** was added to 2 eq. of ethyl chloroacetate heated at 130°. Otherwise the same procedure was followed as for **4a**, yielding 78·5% of **4b**, b.p. 130°/1 mm. ^{1}H NMR spectrum (60 Mc in CCl_4): δ = 7·6 – 7·1 (m, 5H, aryl H); δ = 4·35 – 2·45 (m, 7H, $-OC\underline{H_2}CH_3$, $-CH_2-$ and R_3CH); δ = 1·8 – 0·9 (m, 9H, $-CH_3$).

Ethyl benzyl - 1 - carbethoxyethylphosphinate (**4c**). This compound was prepared in the same way as **4b**, starting from **3a** and ethyl α-bromopropionate. The yield was 76·5%, b.p. 138°/1 mm. ^{1}H NMR spectrum (60 Mc in CCl_4): δ = 7·4 – 7·1 (m, 5H, aryl H); δ = 4·3 – 3·6 (m, 4H, $OC\underline{H_2}CH_3$); δ = 3·4 – 2·5 (m, 3H, R_3CH and $ArCH_2R$); δ = 1·5 – 1·0 (m, 9H, $-CH_3$).

Ethyl 1 - phenylethyl - 1 - carbethoxyethylphosphinate (**4d**). This compound was prepared in the same way as **4b**, starting from **3b** and ethyl α-bromopropionate. The yield was 86%, b.p. 136 – 142°/0·1 mm. ^{1}H NMR spectrum (60 Mc in CCl_4): δ = 7·6 – 7·1 (m, 5H, aryl H); δ = 4·4 – 2·2 (m, 6H, $-OC\underline{H_2}CH_3$ and R_3CH); δ = 1·8 – 0·8 (m, 12H, $-CH_3$).

Benzylcarboxymethylphosphinic acid (**5a**). This compound was prepared from **4a** according to Henning.[4]

1-Phenylethylcarboxymethylphosphinic acid (**5b**). Except for the reflux time (20 hr) this compound was prepared in the same way as **5a**. The yield was 90%, m.p. 118·5 – 120°. ^{1}H NMR spectrum (60 Mc in D_6-DMSO): δ = 10·7 (s, 2H, –OH); δ = 7·33 (s, 5H, aryl H); δ = 3·42 (d of q, $^2J_{PH}$ = 16, $^3J_{HH}$ = 7, 1H, R_3CH); δ = 2·85 (d, $^2J_{PH}$ = 16, 2H, $-CH_2-$); δ = 1·54 (d of d, $^3J_{PH}$ = 18, $^3J_{HH}$ = 7, 3H, $-CH_3$).

Benzyl - 1 - carboxyethylphosphinic acid (**5c**). This compound was prepared in the same way as **5b**, starting from **4c**. The yield was 91%, m.p. 151·5 – 153·5°. ^{1}H NMR spectrum (60 Mc in D_6-DMSO): δ = 11·6 (s, 2H, –OH); δ = 7·33 (s, 5H, aryl H); δ = 3·23 (d, $^2J_{PH}$ = 17, $-CH_2-$); δ = 3·05 – *ca.* 2·5 (obscured by D_6-DMSO), (m, 1H, R_3CH); δ = 1·20 (d of d, $^3J_{PH}$ = 15·5, $^2J_{HH}$ = 7, 3H, $-CH_3$).

1 - Phenylethyl - 1 - carboxyethylphosphinic acid (**5d**). This compound was prepared in the same way as **5b** starting from 8·3 g **4d**. The yield was 94%, m.p. 174°. ^{1}H NMR spectrum (60 Mc in D_6DMSO): δ = 11·1 (s, 2H, –OH): δ = 7·33 (s, 5H, aryl H); δ = 3·6 – *ca.* 2·5 (obscured by D_6-DMSO) (m, 2H, R_3CH); δ = 1·75 – 0·9 (m, 6H, $-CH_3$).

2 - Hydroxy - 2 - phosphatetral - 4 - one - 2 - oxide (**6a**). This compound was prepared from **5a** according to Henning.[4]

1 - Methyl - 2 - hydroxy - 2 - phosphatetral - 4 - one - 2 - oxide (**6b**). This compound was prepared in the same way as **6a**. The yield was 50%, m.p. 192–194°. ^{1}H NMR spectrum (60 Mc in D_6-DMSO): δ = 9·3 (s, –OH); δ = 8·1–7·8 (m, 1H, aryl H); δ = 7·7 – 7·2 (m, 3H, aryl H); δ = 3·7 – 2·7 (m, 3H, $-CH_2-$ and R_3CH); δ = 1·5 (d of d, $^3J_{PH}$ = 16, $^3J_{HH}$ = 7·5, 3H, $-CH_3$) (Found: C, 57·24; H, 5·46; P, 14·07. Calc. for $C_{10}H_{11}O_3P$ (210·158): C, 57·15; H, 5·28; P, 14·71%).

3 - Methyl - 2 - hydroxy - 2 - phosphatetral - 4 - one - 2 - oxide (**6c**). This compound was prepared in the same way as **6b** starting from 5 g **5c**. The yield was 69%, m.p. 204 – 205°. IR spectrum (in

KBr): C=O 1690 cm^{-1}. ^1H NMR spectrum (60 Mc in D_6-DMSO): $\delta = 9{\cdot}1$ (s, –OH); $\delta = 8{\cdot}15 - 7{\cdot}85$ (m, 1H, aryl H); $\delta = 7{\cdot}6 - 7{\cdot}3$ (m, 3H, aryl H); $\delta = 3{\cdot}8 - 3{\cdot}0$ (m, 3H, $-CH_2-$ and R_3CH); $\delta = 1{\cdot}31$ (d of d, $^3J_{PH} = 14$, $^3J_{HH} = 7$, 3H, $-CH_3$) (Found: C, 56·71; H, 5·07; P, 14·82. Calc. for $C_{10}H_{11}O_3P$ (210·158): C, 57·15, H, 5·28; P, 14·71%).

1,3 - *Dimethyl* - 2 - *hydroxy* - 2 - *phosphatetral* - 4 - *one* - 2 - *oxide* (**6d**). This compound was prepared in the same way as **6b** starting from 5 g **5d**. The yield was 57%, m.p. 191 – 193°. ^1H NMR spectrum 100 Mc in D_6-DMSO): $\delta = 8{\cdot}7$ (s, –OH); $\delta = 8{\cdot}05 - 7{\cdot}85$ (m, 1H, aryl H); $\delta = 7{\cdot}75 - 7{\cdot}25$ (m, 3H, aryl H); $\delta = 3{\cdot}75 - 3{\cdot}05$ (m, 2H, R_3CH); $\delta = 1{\cdot}57$ and $1{\cdot}53$ (two d of d, $^3J_{PH} = 14$, $^3J_{HH} = 7$ and $^3J_{PH} = 15$, $^3J_{HH} = 7$, respectively, $-CH_3$ at C–1, diastereomers) $\delta = 1{\cdot}32$ (d of d, $^3J_{PH} = 14$, $^3J_{HH} = 7$, $-CH_3$ at C-3).

2 - *Hydroxy* - 1,2 - *dihydro* - 2 - *phosphanaphthalene* - 2 - *oxide* (**8a**). To a stirred soln of 1·2 g (32 mmole) of $NaBH_4$ in 7 ml of H_2O a solution of 1·7 g (8·7 mmole) of **6a** in 25 ml of H_2O neutralized by 2 N NaOH was added during 15 min. After the addition the solution was stirred for 1 hr. The mixture was evaporated to dryness and 8 ml of MeOH and 4 ml of conc. HCl were added to destroy the excess of $NaBH_4$. After evaporation the residue was extracted with $CHCl_3$ yielding 1·4 g (8.2 mmole, 94%) of crude **7a**. Without purification this product was refluxed with 14 ml of 10% H_2SO_4 for 1 hr. This mixture was extracted with $CHCl_3$ and the residue after evaporating $CHCl_3$ was recrystallized from THF, yielding 0·9 g (5 mmole, 61%) of **8a**, m.p. 148 – 150°. ^1H NMR spectrum (60 Mc in D_6-DMSO) $\delta = 8{\cdot}7$ (s, –OH); $\delta = 7{\cdot}33$ (s, 4H, aryl H); $\delta = 7{\cdot}30$ (d of d, $^3J_{PH} = 38$, $^3J_{HH} = 13$, 1H, H at C-4); $\delta = 6{\cdot}23$ (d of d, $^2J_{PH} = 10$, $^3J_{HH} = 13$, 1H, H at C-3); $\delta = 3{\cdot}22$ (d, $^2J_{PH} = 18{\cdot}5$, 2H, $-CH_2-$) (Found: C, 59·57; H, 5·06; P, 16·38. Calc. for $C_9H_9O_2P$ (180·132): C, 60·00; H, 5·04; P, 17·19%).

1 - *Methyl* - 2 - *hydroxy* - 1,2 - *dihydro* - 2 - *phosphanaphthalene* - 2 - *oxide* (**8b**). This compound was prepared in the same way as **8a**. The yield was 16% (based on **6b**), m.p. 127·5 – 131°. ^1H NMR spectrum (60 Mc in D_6-DMSO): $\delta = 10{\cdot}1$ (s, 1H, –OH); $\delta = 7{\cdot}40$ (s, 4H, aryl H); $\delta = 7{\cdot}20$ (d of d, $^3J_{PH} = 38$, $^3J_{HH} = 13$, 1H, H at C-4); $\delta = 6{\cdot}21$ (d of d, $^2J_{PH} = 10$, $^3J_{HH} = 13$, 1H, H at C-3); $\delta = 3{\cdot}1$ (d of q, $^3J_{PH} = 20$, $^3J_{HH} = 7{\cdot}5$, 1H, R_3CH); $\delta = 1{\cdot}35$ (d of d, $^3J_{PH} = 16$, $^3J_{HH} = 7{\cdot}5$, 3H, $-CH_3$) (Found: C, 61·83; H, 4·87; P, 15·35. Calc. for $C_{10}H_{11}O_2P$ (194·158): C, 61·86; H, 5·71; P, 15·95%).

3 - *Methyl* - 2 - *hydroxy* - 1,2 - *dihydro* - 2 - *phosphanaphthalene* - 2 - *oxide* (**8c**). The reduction step was performed in the same way as for **6a**. 12·2 g (0·058 mole) of **7c** was refluxed with 130 ml of benzene, 130 ml of conc. HCl and 115 g of $ZnCl_2$ for 2 hr. On pouring the mixture into 800 ml of H_2O a ppt was formed, which was isolated by filtration. The filtrate was extracted three times with $CHCl_3$. The residue from the $CHCl_3$-extract was combined with the ppt. Recrystallisation from THF yielded 9·1 g (0·047 mole, 76% based on **6c**) of **8c**, m.p. 200 – 202°. ^1H NMR spectrum (60 Mc in D_6-DMSO); $\delta = 9{\cdot}0$ (s, –OH); $\delta = 7{\cdot}35 - 7{\cdot}10$ (m, 4·5H, aryl H and 0·5H at C-4); $\delta = 6{\cdot}63$ (q, $^4J_{HH} = 1{\cdot}5$, 0·5H, 0·5H at C-4); $\delta = 3{\cdot}12$ (d, $^2J_{PH} = 18{\cdot}5$, 2H, $-CH_2-$); $\delta = 1{\cdot}95$ (d of d, $^3J_{PH} = 12$, $^4J_{HH} = 1{\cdot}5$, 3H, $-CH_3$) (Found: C, 61·55; H, 5·66; P, 15·80. Calc. for $C_{10}H_{11}O_2P$ (194·158): C, 61·86; H, 5·71; P, 15·95%).

1,3 - *Dimethyl* - 2 - *hydroxy* - 1,2 - *dihydro* - 2 - *phosphanaphthalene* - 2 - *oxide* (**8d**). This compound was prepared in the same way as **8c**. The yield was 55%, m.p. 171 – 173°. ^1H NMR spectrum (60 Mc in D_6-DMSO): $\delta = 9{\cdot}23$ (s, –OH); $\delta = 7{\cdot}26$ (s, 4H, aryl H); $\delta = 7{\cdot}02$ (d of q, $^3J_{PH} = 34$, $^4J_{HH} = 1{\cdot}5$, 1H, H at C-4); $\delta = 3{\cdot}04$ (d of q, $^2J_{PH} = 20$, $^3J_{HH} = 7{\cdot}5$, 1H, H at C-1); $\delta = 2{\cdot}02$ (d of d, $^3J_{PH} = 12{\cdot}4$, $^4J_{HH} = 1{\cdot}5$, 3H, $-CH_3$ at C-3); $\delta = 1{\cdot}35$ (d of d, $^3J_{PH} = 15{\cdot}5$, $^3J_{HH} = 7{\cdot}5$, 3H, $-CH_3$ at C-1) (Found: C, 61·86; H, 6·58; P, 15·04. Calc. for $C_{11}H_{12}O_2P$ (207·176): C, 63·76; H, 5·84; P, 14·95%).

1,2 - *Dihydro* - 2 - *phosphanaphthalene* (**9a**). 1·5 g (8·33 mmole) of **8a**, 4·95 g (41·5 mmole) of $SOCl_2$ and 7·5 ml of $CHCl_3$ were refluxed for 0·5 hr. The soln was evaporated to dryness and the residue was dissolved in 15 ml of THF. This soln was added during 5 min to 0·6 g (15·7 mmole) of LAH_4 in 10 ml of diethyl ether at – 15°. The solution was stirred for another 10 min and 3 ml of air-free H_2O was added. At room temp. the soln was filtered under N_2 and the residue was extracted twice with diethyl ether. The combined solns were dried on $MgSO_4$, filtered and evaporated to dryness. The yield was 1·0 g (6·7 mmole, 81%) of **9a**, a colourless liquid with unknown b.p. ^1H NMR spectrum (60 Mc in $CDCl_3$): $\delta = 7{\cdot}03$ (s, 4H, aryl H); $\delta = 7{\cdot}00$ (pseudotriplet, $^3J_{PH} = {}^3J_{HH} = 11$, 1H, H at C-4); $\delta = 6{\cdot}03$ (d of d, $^2J_{PH} = 45$, $^3J_{HH} = 11$, 1H, H at C-3); $\delta = 3{\cdot}7$ (very broad s, 1H, P-H); $\delta = 2{\cdot}75$ (d, $^2J_{PH} = 7{\cdot}5$, 2H, $-CH_2-$). IR spectrum ($CHCl_3$): P-H 2250 cm^{-1}. Mass spectrum, *m/e* (%): 148 (*ca.* 1), 146 (100), 120 (10), 115 (30), 102 (10).

1 - *Methyl* - 1,2 - *dihydro* - 2 - *phosphanaphthalene* (**9b**). This compound was prepared in the same way as **9a**. The yield after distillation was 66%, b.p. 70°/*ca.* 0·1 mm. ^1H NMR spectrum (60 Mc in $CDCl_3$): $\delta = 7{\cdot}5 - 6{\cdot}9$ (m, 5H, aryl H and H at C-4); $\delta = 6{\cdot}17$ (d of d, $^2J_{PH} = 41$, $^3J_{HH} = 12$, 1H, H at C-3); $\delta = 3{\cdot}8 - 1{\cdot}0$ (m, 6·5H, other H and impurity). We have not checked the purity of this material.

3 - *Methyl* - 1,2 - *dihydro* - 2 - *phosphanaphthalene* (**9c**). This compound was prepared in the same way as **9b**. The yield was 75%, b.p. *ca* 80°/0·1 mm. ^1H NMR spectrum (60 Mc in $CDCl_3$ with TMS as external standard): $\delta = 7{\cdot}7 - 7{\cdot}4$ (m, 4H, aryl H); $\delta = 7{\cdot}22$ (d of q, $^3J_{PH} = 9$, $^4J_{HH} = 1{\cdot}5$, 1H, H at C-4); $\delta = 4{\cdot}26$ (broad s, 1H, P-H); $\delta = 3{\cdot}32$ (d, $^2J_{PH} = 7{\cdot}5$, 2H, $-CH_2-$); $\delta = 2{\cdot}54$ (d of d, $^3J_{PH} = 12$, $^4J_{HH} = 1{\cdot}5$, 3H, $-CH_3$). IR spectrum ($CHCl_3$): P-H 2250 cm^{-1}. *m/e* = 162·0598; calc. for $C_{10}H_{11}P$: 162·0599.

1,3 - *Dimethyl* - 1,2 - *dihydro* - 2 - *phosphanaphthalene* (**9d**). This compound was prepared in the same way as **9b**. The yield was 70%, b.p. *ca* 70°/0·1 mm. ^1H NMR spectrum (60 Mc in $CDCl_3$): $\delta = 7{\cdot}4 - 7{\cdot}0$ (m, 4H, aryl H); $\delta = 6{\cdot}73$ (d of q, $^3J_{PH} = 9{\cdot}5$, $^4J_{HH} = 1{\cdot}5$, 1H, H at C-4); $\delta = ca$ 3·75 (very broad s, 1H, P-H); $\delta = 3{\cdot}3 - 2{\cdot}7$ (m, 1H, H at C-1); $\delta = 2{\cdot}05$ (d of d, $^3J_{PH} = 11$, $^4J_{HH} = 1{\cdot}5$, 3H, $-CH_3$ at C-3); $\delta = 1{\cdot}35$ (d of d, $^3J_{PH} = 14$, $^3J_{HH} = 7$, 3H, $-CH_3$ at C-1).

2-*Phosphanaphthalene* (**1a**). The reaction with $COCl_2$ was carried out under N_2 but the further procedure leading to **1a** and the purification of the material was carried out in vacuum using the glass apparatus described by de Koe[17] and Vermeer.[18] Two hr after its preparation 900 mg (6·15 mmole) of **9a** was dissolved in 15 ml of toluene, frozen in liquid N_2 and 12 ml of a toluene soln containing 6·0 mmoles of $COCl_2$ was added. The liquid N_2 was replaced by a cooling bath at – 70°. The material melted and a ppt was present. The structure of this ppt (*ca* 40%) has not been elucidated. It may be caused by already decomposed phosphine **9a** or by instability of the chlorophosphine **10a**. During $\frac{1}{2}$ hr the temp. was raised to – 20°. After some min at room temp the vessel was evacuated and sealed. Another vessel was added via a side arm by glass blowing techniques. The soln was filtered through a glass filter and 606 mg (6·0 mmole) of TEA in 20 ml of toluene was added. A ppt of TEA/HCl (74% as determined by titration of Cl^- according to Mohr) was formed. After 1 hr the liquid was evaporated to dryness and the residue was extracted with cyclohexane. The cyclohexane soln was filtered through a glass filter and again evaporated to dryness. Sublimation at 50 – 55°/10^{-4} mm yielded 180 mg (1·23 mmole, 20%) of **1a**, m.p. 82 – 84°. ^1H NMR spectrum (Fig. 1) (100 Mc in $CDCl_3$): see Table 2. ^{31}P NMR spectrum (24·3 Mc in $CDCl_3$ with H_3PO_4 as external standard): $\delta = -192$. UV spectrum: see Table 1. Mass spectrum, *m/e* (%): 146 (100), 120 (16·2), 115 (27·6), 102 (15·0), 73 (11·7).

1 - *Methyl* - 2 - *phosphanaphthalene* (**1b**). This compound was prepared largely in the same way as **1a**. Because **9b** is more stable than **9a**, it was not necessary to perform the reaction of **9b** with $COCl_2$ immediately after its formation. In the reaction of **9b** with $COCl_2$ no precipitate was formed. However, distillation at

Table 2. Chemical shifts of the protons of **1a**, **1c** and **1d** (δ ppm, 100 Mc in $CDCl_3$)

	H at C-1	H at C-3	H at C-4	other aromatic protons	$-CH_3$ at C-1	$-CH_3$ at C-3
1a	9.50, d of d $^2J_{PH}$ = 35.5 $^4J_{HH}$ = 2.5	8.43, d of d of d $^2J_{PH}$ = 39.6 $^4J_{HH}$ = 2.5 $^3J_{HH}$ = 11	8.42, d of d $^3J_{PH}$ = 9.3 $^3J_{HH}$ = 11	8.08 - 7.53 multiplet		
1b[M]	9.84, d $^2J_{PH}$ = 35		8.47, d $^3J_{PH}$ = 7.5	8.35 - 7.85 m		3.30, d $^3J_{PH}$ = 13.5
1c	see column 5			8.35 - 7.5 m	3.17, d $^3J_{PH}$ = 19	2.92, d of d $^3J_{PH}$ = 12 $^4J_{HH}$ = 1

[M] External TMS

70°/10^{-4} mm yielded two compounds, a crystalline one and a liquid one. The ^1H NMR spectrum of this mixture showed signals at $\delta = 8{\cdot}4 - 6{\cdot}7$ (m), $\delta = 6{\cdot}2$ (d of d), $\delta = 3{\cdot}0$ (d) and $\delta = 2{\cdot}4$ (d). The ^{31}P NMR spectrum showed two signals $\delta = -190$ ppm (a region characteristic for phosphorins) and $\delta = -20$ (external H_3PO_4). The mass spectrum only showed $m/e = 160$ ($C_{10}H_9P$) and the pattern described for **1c**. From these facts we conclude that **1b** was formed, although we could not obtain it in pure form. The UV spectrum (Table 1) was also taken from this mixture.

3 - *Methyl* - 2 - *phosphanaphthalene* (**1c**). This compound was prepared in the same way as **1b** starting from 1·9 g **9c**. The yield was 64%, m.p. 72 – 74°. ^1H NMR spectrum (100 Mc in $CDCl_3$ with TMS as external standard): see Table 2. ^{31}P NMR spectrum (40·5 Mc in $CDCl_3$ with H_3PO_4 as external standard): $\delta = -200$. ^{13}C NMR spectrum (25·2 Mc in $CDCl_3$): $\delta = 160{\cdot}2$ (d, $^1J_{PC} = 46{\cdot}9$, C-1); $\delta = 154{\cdot}5$ (d, $^1J_{PC} = 50{\cdot}1$, C-3); $\delta = 135 - 126$ (other aromatic carbon atoms); $\delta = 24{\cdot}6$ (d, $^2J_{PC} = 35{\cdot}3$, methyl C). UV spectrum: see Table 1. Mass spectrum m/e (%): 160 (100), 128 (94), 115 (58), 80 (12) (Found: C, 75·37; H, 6·04. Calc. for $C_{10}H_9P$ (160·142): C, 74·99; H, 5·67%).

1,3 - *Dimethyl* - 2 - *phosphanaphthalene* (**1d**). This compound was prepared in the same way as **1b** starting from 836 mg **9d**. The yield was 47%, b.p. *ca.* 70°/10^{-2} mm. ^1H NMR spectrum (100 Mc in $CDCl_3$): see table 2. UV spectrum: see Table 1. Mass spectrum: m/e (%): 174 (100), 159 (26), 142 (49), 141 (37), 133 (31), 129 (23), 128 (20), 115 (29), 87 (8). $m/e = 174{\cdot}0593$; calc. for $C_{11}H_{11}P$ 174·0598.

Reaction of **1c** *with* $Hg(OAc)_2$. 195 mg (0·61 mmole) of $Hg(OAc)_2$ in 20 ml of MeOH was added to a stirred soln of 98 mg (0·61 mmole) of **1c** in 20 ml of benzene during ½ hr. A ppt (Hg) was formed and a yellow colour could be detected. After stirring overnight the colour had disappeared. The soln was evaporated to dryness and the residue was dissolved in $CDCl_3$. After filtration a ^1H NMR spectrum was measured (60 Mc): $\delta = 7{\cdot}23$ (s, 4H, aryl H); $\delta = 7{\cdot}05$ (d of q, $^3J_{PH} = 40$, $^4J_{HH} = 1{\cdot}5$, 1H, H at C-4); $\delta = 3{\cdot}70$ (d, $^3J_{PH} = 11{\cdot}5$, 3H, $-OCH_3$); $\delta = 3{\cdot}28$ (d, $^2J_{PH} = 18{\cdot}5$, 2H, $-CH_2-$); $\delta = 2{\cdot}17$ (d of d, $^3J_{PH} = 12{\cdot}5$, $^4J_{HH} = 1{\cdot}5$, 3H, $-CH_3$). This NMR spectrum is identical with that of the reaction product of **8c** with diazomethane.

Reaction of **1c** *with phenyllithium.* 1·13 mmole of PhLi in 20 ml of diethyl ether was added to a stirred soln of 182 mg (1·13 mmole) of **1c** in 20 ml of diethyl ether at – 70° during 1 hr. After this time the soln was coloured red. After stirring for another ½ hr at – 70° 1 ml of MeI in 10 ml of diethyl ether was added; the colour was yellow. The soln was stirred for 1 hr at room temp and evaporated to dryness. A NMR spectrum of the residue ($\delta = 7{\cdot}7 - 6{\cdot}5$, m; $\delta = 3{\cdot}8 - 1{\cdot}1$, m) showed that it was a mixture of 2·3 H, but no low field aromatic signals (protons α and β to phosphorus in aromatic phosphorus compounds) were present. The UV spectrum of the residue did not show an absorption beyond 325 nm. The most intensive peaks in the mass spectrum were $m/e = 252$, 61% $(13)^+$, $m/e = 238$, 88% $(13\text{-}CH_2)^+$, $m/e = 237$, 100% $(13\text{-}CH_3)^+$. TLC (silicagel, acetone; hexane 1:2) showed four components. This procedure was not performed under N_2. The component with *Rf* *ca.* 0·7 was isolated (48 mg). The mass spectrum of this material showed one peak more than the previous one, i.e. $m/e = 268$, 13% $(13+0)^+$. The NMR spectrum affirmed that this material was a mixture of (13) and its oxide ($\delta = 8{\cdot}0 - 6{\cdot}7$, m, 10H, aryl H and H at C-4; $\delta = 3{\cdot}6 - 3{\cdot}0$, 1·5H, H at C-1 and impurity; $\delta = 2{\cdot}25 - 1{\cdot}95$, m, 3H, $-CH_3$ at C-3; $\delta = 1{\cdot}95 - 1{\cdot}1$, m, 3H, $-CH_3$ at C-1).

Reaction of **1c** *with diazomethane.* We followed the procedure described by Dimroth.[16] The reaction was performed with 195 mg (1·22 mmole) of **1c**, 3·2 ml of CH_2N_2/ether and 10 ml of benzene. After sublimation at 100°/10^{-1} mm the yield of **15** was 173 mg (0·9 mmole, 74%). ^1H NMR spectrum (60 Mc in $CDCl_3$): $\delta = 7{\cdot}3 - 7{\cdot}0$ (m, 4·5H, 4 aryl H and 0·5H at C-4); $\delta = 6{\cdot}58$ (q, $^4J_{HH} = 1{\cdot}5$, 0·5H, 0·5H at C-4); $\delta = 3{\cdot}8 - 2{\cdot}8$ (*m*, 2·3H, $-CH_2-$ and impurity); $\delta = 2{\cdot}15$ (d of d, $^3J_{PH} = 12$, $^4J_{HH} = 1{\cdot}5$, 3H, $-CH_3$ at C-3); $\delta = 1{\cdot}48$ (d, $^2J_{PH} = 13$, 3H, $-CH_3$ at P). Mass spectrum, m/e (%): 192 (100), 178 (17), 130 (72), 129 (69), 128 (48), 127 (17), 115 (27). $m/e = 192{\cdot}0700$; calc. for $C_{11}H_{13}OP$ 192·0703.

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