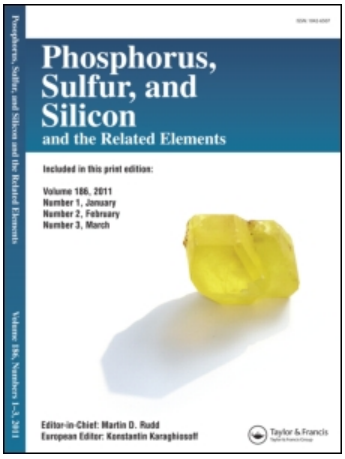

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PHOSPHORUS-NITROGEN COMPOUNDS. PART 52.[1] THE SYNTHESIS OF SOME 1,3,2-BENZODIAZAPHOSPHORINE 2-OXIDES AND 2-SULPHIDES

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PHOSPHORUS–NITROGEN COMPOUNDS. PART 52.[1] THE SYNTHESIS OF SOME 1,3,2-BENZODIAZAPHOSPHORINE 2-OXIDES AND 2-SULPHIDES

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(Received September 20, 1986)

The reactions of 4-methyl-2-[*N*-(*p*-toluidinyl)methyl]aniline with phosphorus oxychloride, thiophosphoryl chloride, and their derivatives yield 1,3,2-benzodiazaphosphorine 2-oxides and 2-sulphides. Their ^{1}H NMR and infrared spectra are discussed. Related 1,3,2-benzodiazophosphorine and 1,3,2-dibenzodiazaphosphocine 2-oxides and 2-sulphides are compared.

In part 48[2] we reported isolation and characterisation of the eight-membered heterocycles 1,3,2-dibenzodiazaphosphocine 6-oxide (**4**, $X = O$) and 6-sulphide (**4**, $X = S$) from the reaction of *N,N*-dimethyl-*p*-toluidine and phosphoryl (**5**, $X = O$, $Y = Cl$), respectively thiophosphoryl (**5**, $X = S$, $Y = Cl$) chloride. Recently[3] we studied the mechanism of this unusual reaction and developed a rational synthesis for the above phosphocine 6-oxide and 6-sulphide based on 4,4′,*N,N′*-tetramethyl-2,2′-methylenedianiline (**3**, $R = Me$) (Scheme 1).

The methylenedianiline (**3**, $R = Me$) was derived from 4-methyl-2-[*N*-(*p*-toluidinyl)methyl]aniline (**2**, $R = Me$) by acid catalysed rearrangement at approximately 130°C. We utilised this precursor, (**2**, $R = H$) and now report our studies on the six-membered ring analogues, the 1,3,2-benzodiazaphosphorine 2-oxides (**6**, $X = O$) and 2-sulphides (**6**, $X = S$). Our synthetic route is outlined in Scheme 2.

In the present study the diamine (**2**, $R = H$) (containing primary and secondary amino functions) was employed and allowed to react with phosphoryl chloride, thiophosphoryl chloride or their derivatives (**5**). Various 1,3,2-benzodiazaphosphorine 2-oxides (**6**, $X = O$) and 2-sulphides (**6**, $X = S$) were thus obtained (Scheme 2).

Earlier[4] the synthesis, spectroscopy and X-ray crystal structure of 2-chloro-6-methyl-3-*p*-tolyl-1,2,3,4-tetrahydro-1,3,2-benzodiazaphosphorine 2-oxide (**6**, $X = O$, $Y = Cl$) was reported. It was also noted[4] that in the reaction of the diamine (**2**, $R = H$) with thiophosphoryl chloride (**5**, $X = S$, $Y = Cl$), the expected 2-chloro-compound, (**6**, $X = S$, $Y = Cl$) was not obtained, but depending on reaction conditions, the further aminolysis product, (**8**), or the dimer, (**9**) (which has been crystallographically studied[5]), both probably derived from a common monomeric

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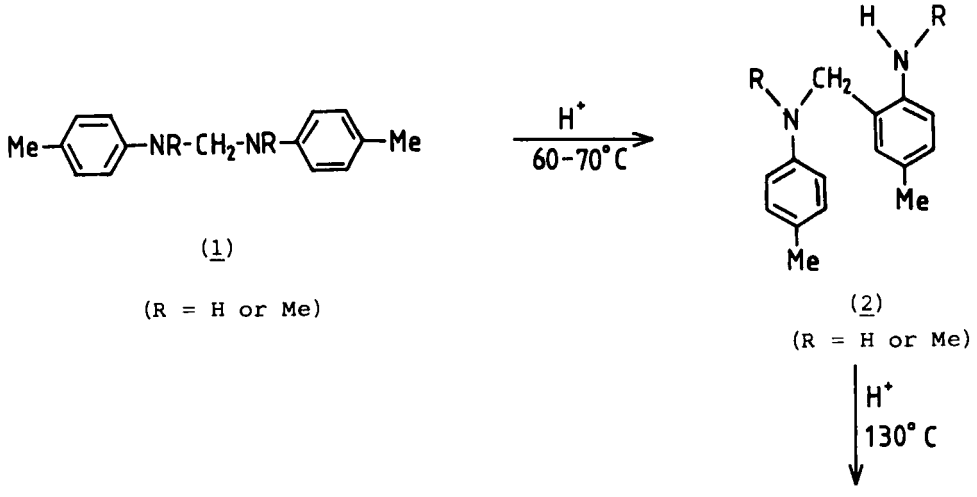
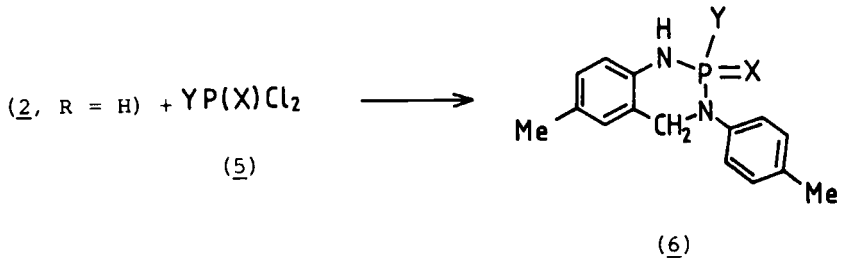
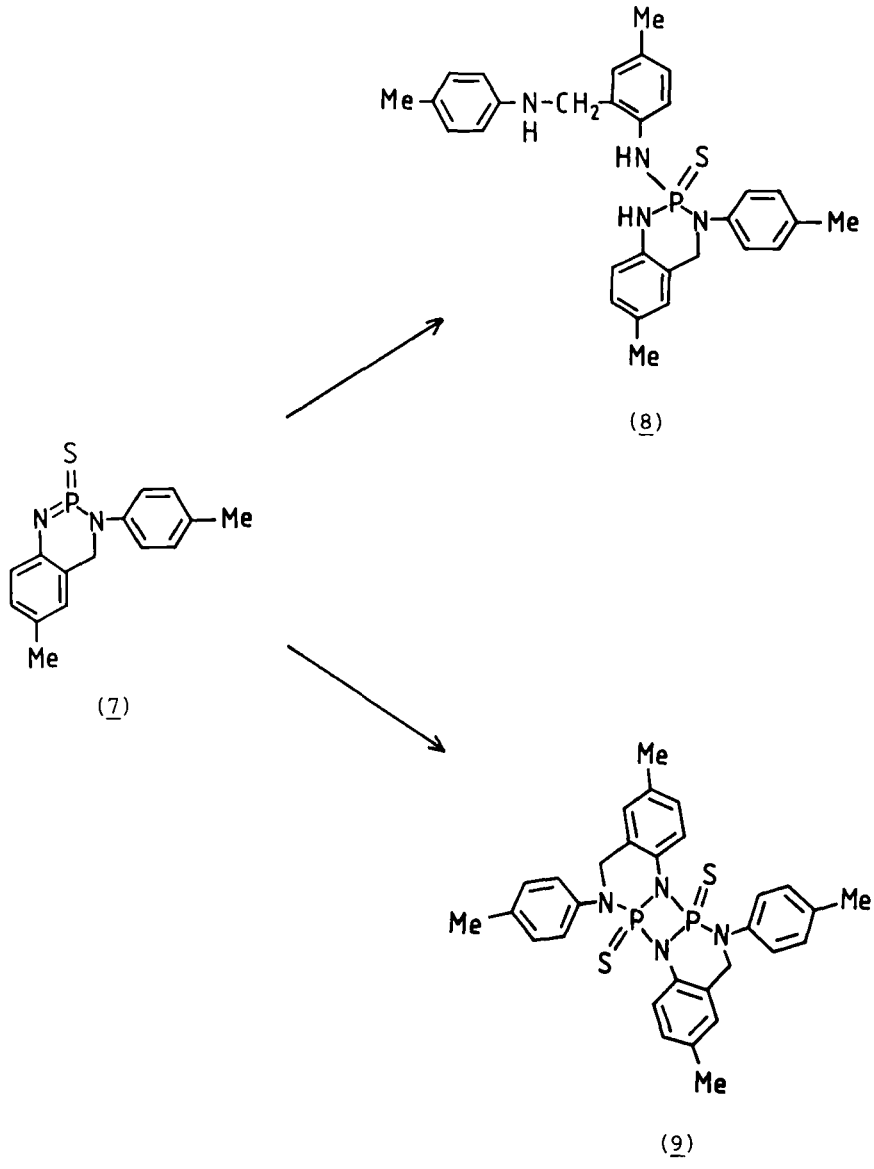


SCHEME 1



(**6a**, $X = O$, $Y = Cl$
6b, $X = O$, $Y = Ph$
6c, $X = S$, $Y = Ph$
6d, $X = S$, $Y = Me$
6e, $X = S$, $Y = Et$)

SCHEME 2

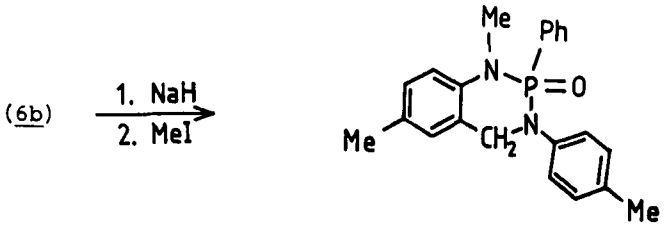


(9)

SCHEME 3

metathiophosphoramidate intermediate, (**7**) (Scheme 3). Such three-coordinate five-valent species are now amply documented and have recently been reviewed.[6] We have invoked them on several occasions in the past[7–9] to rationalise our experimental findings.

This work was extended using the diamine (**2**, $R = H$) and phenylphosphonic dichloride, $PhP(O)Cl_2$ (**5**, $X = O$, $Y = Ph$) and the corresponding 2-phenyl-derivative (**6b**) was obtained. This compound was then utilised to obtain a

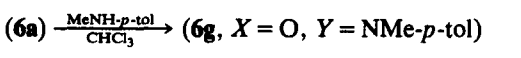


(10)

SCHEME 4

di-secondary amide derivative by methylating its primary amide centre (Scheme 4). Whilst the other 2-oxides are hydrogen-bonded dimers, this derivative, (**10**), is monomeric.

Earlier[2] the great reluctance of the 6-chloro-derivative of the 1,3,2-dibenzodiazaphosphocine 6-oxide to undergo nucleophilic reactions was noted. Reaction with sodium methoxide and ethoxide was slow, and no reaction was observed with *N*-methyl-*p*-toluidine. The corresponding 1,3,2-benzodiazaphosphorine 2-oxide is very much more reactive. Reaction with sodium methoxide is complete in one hour at room temperature to give the methoxide, (**6f**), whilst prolonged refluxing with *N*-methyl-*p*-toluidine in chloroform gave the amino-derivative, (**6g**) (Scheme 5).



SCHEME 5

This work was also extended to the 1,3,2-benzodiazaphosphorine 2-sulphide system. The diamine (**2**, $R = H$) was allowed to react with phenyl-, methyl-, and ethyl-phosphonothioc dichloride (**5**, $X = S$, $Y = Ph$, Me, Et), to give the corresponding 1,3,2-benzodiazaphosphorine 2-sulphides (**6**, $X = S$, $Y = Ph$, Me, Et) (Scheme 2).

^1H n.m.r. spectra

The data are given in Table I. The phenyl protons gave complex spectra, which were not analysed. The different *p*-CH_3 chemical environments were generally resolved. The CH_2 protons exhibited different environments, both coupling to phosphorus, This difference in chemical shift is most pronounced (1.3 p.p.m.) in the complex polycyclic compound, (**9**), and is also rather greater (0.5 p.p.m.) in compound (**10**), than in the others. Neither compound (**9**) or (**10**) contain an N—H bond. In the remaining ones, those containing a P=S group show marginally larger differences (~0.4 p.p.m.) than those containing a P=O group (~0.35 p.p.m.). The P(S)N*H* protons are somewhat more shielded than their P(O)N*H* counterparts.

TABLE I

The ^{1}H m.m.r. spectra of the 1,3,2-benzodiazaphosphorine 2-oxides and 2-sulphides[a,b]

Compound	CH_2	N*H*	*p*-CH_3	Other groups
(**2**, *R* = H)	4.03	3.61	2.21	
(**6a**)	H_A 4.57 $^2J(H_AH_B)$ 15.0	7.73	2.26	
	H_B 4.92 $^3J(PNCH_A)$ 23.5	^2J(PNH) 6.0	2.33	
	$^3J(PNCH_B)$ 13.0			
(**6b**)	H_A 4.33 $^2J(H_AH_B)$ 15.0	[c]	2.15	
	H_B 4.70 $^3J(PNCH_A)$ 15.0		2.28	
	$^3J(PNCH_B)$ 12.0			
(**6f**)	H_A 4.45 $^2J(H_AH_B)$ 16.0	[c]	2.25	3.66 (OCH_3)
	H_B 4.81 $^3J(PNCH_A)$ 16.0		2.28	^3J(POCH) 12.0
	$^3J(PNCH_B)$ 10.5			
(**6g**)	H_A 4.33 $^2J(H_AH_B)$ 15.0	[c]	2.20	2.92 (NCH_3)
	H_B 4.70 $^3J(PNCH_A)$ 15.0		2.27	^3J(PNCH) 9.0
	$^3J(PNCH_B)$ 13.0		2.31	
(**10**)	H_A 4.30 $^2J(H_AH_B)$ 15.0		2.12	2.90 (NCH_3)
	H_B 4.81 $^3J(PNCH_A)$ 17.0		2.30	^3J(PNCH) 9.0
	$^3J(PNCH_B)$ 11.0			
(**6d**)	H_A 4.29 $^2J(H_AH_B)$ 14.5	5.42	2.28	1.91 (PCH_3)
	H_B 4.72 $^3J(PNCH_A)$ 14.5	^2J(PNCH) 12.0	2.30	^2J(PCH) 14.0
	$^3J(PNCH_B)$ 14.5			
(**6e**)	H_A 4.28 $^2J(H_AH_B)$ 15.0	5.61	2.13	1.03 (PCH_2CH_3)
	H_B 4.70 $^3J(PNCH_A)$ 15.0	^2J(PNH) 12.0		^3J(PCCH) 22.0
	$^3J(PNCH_B)$ 13.0			^3J(HCCH) 7.5 PCH_2[d]
(**6c**)	H_A 4.29 $^2J(H_AH_B)$ 14.5	5.37	2.20	
	H_B 4.69 $^3J(H_AH_B)$ 14.5	^2J(PNH) 11.5	2.28	
	$^3J(PNCH_B)$ 14.5			
(**8**)	H_A 4.13 $^2J(H_AH_B)$15.0	5.80	2.21	
	H_B 4.50 $^3J(PNCH_A)$ 19.0	^2J(PNH) 10.0	2.26	
	$^3J(PNCH_B)$ 13.0	3.36		
	3.76 (acyclic)	[c]		
(**9**)	H_A 4.16 $^2J'(H_AH_B)$ 15.0[e]		2.32	
	H_B 5.46 $^3J'(PNCH_A)$ 27.5[e]		2.34	
	$^3J'(PNCH_B)$ 8.0[e]			

[a] Values in $CDCl_3$ solution, TMS internal standard. Coupling constants in Hz.
[b] The spectra of compounds 1, 2, 10 and 11 have been previously reported.[4]
[c] Obscured by phenyl protons.
[d] Complex spectrum in region δ 1.8–2.6.
[e] Apparent spin-spin coupling constants.

Infrared Spectra

Selected frequencies are presented in Table II. The N—H bands appear at frequencies postulated by Bellamy[10] for the hydrogen bonded *cis*-N—H stretching band for secondary amides. The broad P=O bands are also within the range for hydrogen bonded phosphoryl frequencies.[10–12] Both these features have been observed in the X-ray crystal structure of (**6a**).[4] The P=S bands occur in the region described by other authors.[13–16] The same pertains to P—N bonds without much multiple bond character.[17] The P—Cl bond at 522 cm^{-1} falls within the region specified by Bellamy.[10]

TABLE II

Selected infrared frequencies (cm^{-1})[a]

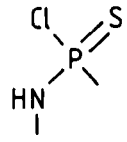
	νN—H	νP=O	νP=S	νP—Cl	νP—N
	3330 (m) 3260 (s)				
(2, *R* = H)	Primary N—H	—	—	—	—
	3440 (m)				
	Secondary N—H	—	—	—	—
(6a)	3180 (s)	1250 (s)	—	522 (s)	715 (w)
(6b)	3120 (s)	1200 (s)	—	—	690 (m) 710 d (w) 720
(6f)	3180 (s)	1240 (s)	—	—	640 d (m) 660
(6g)	3130 (s)	1200 (s)	—	—	695 (w)
(10)	—	1220 (s)	—	—	700 (s)
(6d)	3160 (s)	—	760 (m)	—	680 (s)
(6e)	3190 (s)	—	755 d (w) 700	—	700 d (s) 720
(6c)	3280 (s)	—	740 d (w) 760	—	690 d (s) 715
	3410 (w)				
(8)	3360 (w)	—	745 d (w)	—	
	3200 (s)		765		690 (s)
(9)	—	—	770 (s)	—	710 d (s) 730

[a] d = doublet, w = weak, m = medium, s = strong

Comparisons

It remains to consider similarities and contrasts between the related six-membered ring 1,3,2-benzodiazaphosphorine and the eight-membered ring 1,3,2-dibenzodiazaphosphocine systems. The former is a good deal more reactive towards nucleophilic reagents than the latter. X-ray crystallographic studies show that the phosphorine has a semi-chair-conformation;[4] the phosphocines have a distorted boat-form.[18,19] Access to the phosphorus atom at the side opposite to the P—Cl bond is unhindered in the former, and very hindered in the latter. In the phosphorine structure P—Cl, P—N and P=O (in spite of hydrogen-bonding) bond lengths are all shorter than in the corresponding phosphocine.[4] This may well imply greater electron-density on the phosphorus atom of the phosphorine compared with that of the phosphocine. In spite of this, we note the greater reactivity towards nucleophilic reagents of the phosphorine system. Hence, the probable reason for the relative inertness of the phosphocine derivatives is probably steric in origin.

In both systems, we failed to isolate compounds containing the structural moieties (**12**). Instead either further aminolysis with the diamine or dimerisation



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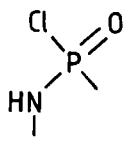
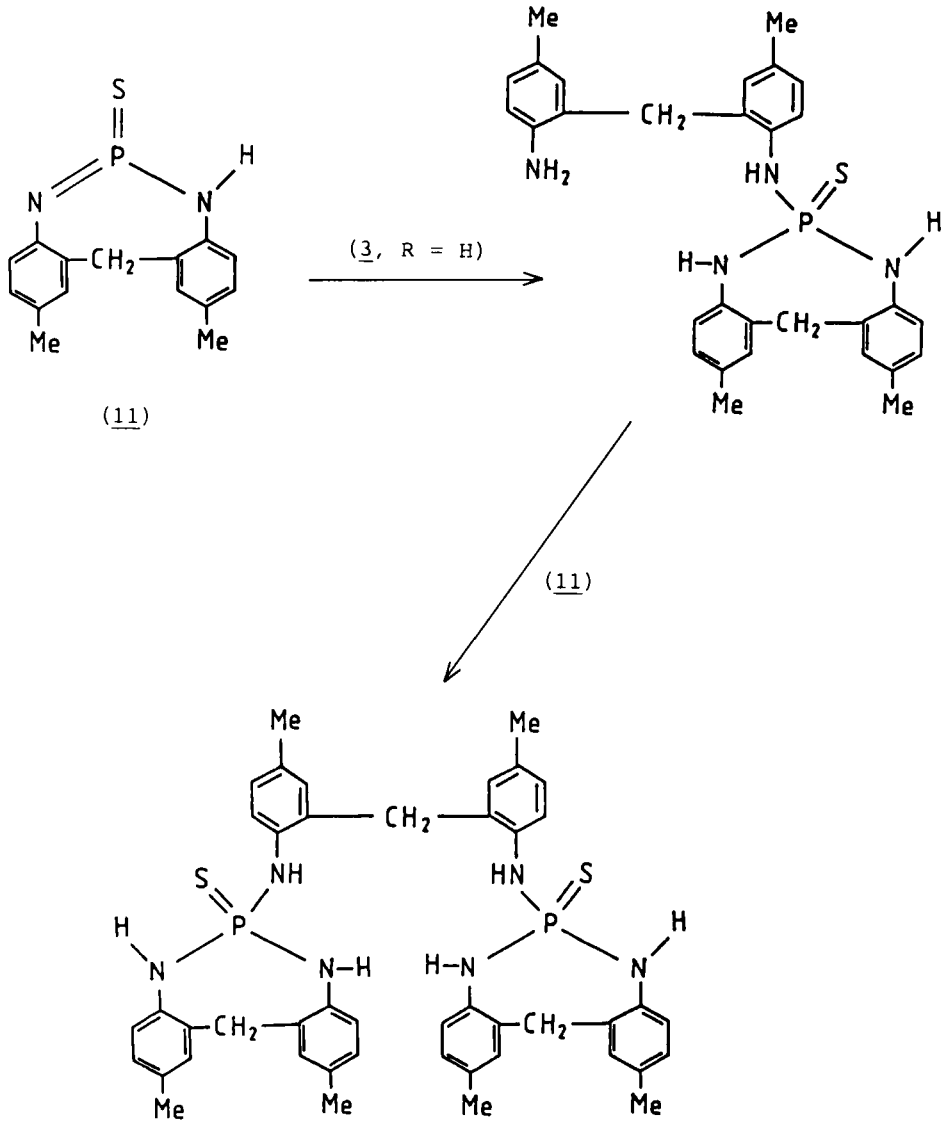


(13)

to a complex cyclodiphosphazane in the phosphorine system occurred, probably *via* a monomeric metathiophosphoramidate (cf. **7**) (Schemes 3 and 6).



SCHEME 6

Whilst a compound with the structural moiety (**13**) was isolated without difficulty in the phosphorine system, in our hands the phosphocine gave only intractable, probably polymeric, material. A conceivable cause of this could be that whilst the sole P—NH bond in the phosphorine is involved in hydrogen-bonding to the phosphoryl group, in the phosphocine there are two P—NH groups *per* P=O moiety.

EXPERIMENTAL

Chemicals and Spectroscopic Techniques. Phosphorus oxychloride (May and Baker Ltd), thiophosphoryl chloride (Alfa Inorganics Inc.), triethylamine, and *p*-toluidine (Koch-Light Ltd.) were purified by conventional methods. *N*-Methyl-*p*-toluidine was obtained from Eastman Kodak Ltd., phenylphosphonic dichloride and phenylphosphonothioic dichloride from Aldrich Chemical Co. Ltd., methyl- and ethyl- phosphonic dichloride from Farbenfabriken Bayer A.G. ^{1}H N.m.r. spectra were obtained from Varian Associates Model A60 and JEOL Model JNM-MH-100 spectrometers ($SiMe_4$ as internal standard). I.r. spectra were recorded (KBr disc) on a Perkin–Elmer Model 457 grating i.r. spectrometer. Mass spectra were obtained from an A.E.I. MS9 spectrometer, P.C.M.U., Harwell. Microanalyses were carried out by Dr. Kolbe Laboratories, Mülheim, Ruhr, Germany. Compounds (**2**, R = H), (**6a**), (**8**) and (**9**) have been previously described.[4]

2-Phenyl-6-methyl-3-p-tolyl-1,2,3,4-tetrahydro-1,3,2-benzodiazaphosphorine 2-oxide, (**6b**). (**2**, R = H) (4.52 g, 0.02 mol) and triethylamine (4.04 g, 5.54 ml, 0.04 mol) were dissolved in dry benzene (100 ml) and this mixture cooled in an ice bath. Then (**5**, X = O, Y = Ph) (3.88 g, 0.02 mol) in benzene (25 ml) were added and the mixture allowed to come to ambient temperature and to stand with occasional shaking for 3 days. A t.l.c. examination showed the presence of some starting material. After a further 6 days the triethylamine hydrochloride was filtered off, this precipitate washed with benzene and the combined benzene extracts reduced to 20 ml. More crystals were filtered off, and then the benzene removed to give an oil, which was dissolved in dichloromethane/light petroleum (b.p. 60–80°C) to give crystals of (**2**, R = H), m.p. 192°C, yield 4.9 g (71%). (Found: C, 72.3; H, 6.1; N, 8.1; P, 8.8%; M^+, 348.1400. $C_{21}H_{21}ON_2P$ requires C, 72.4; H, 6.1; N, 8.0; P, 8.9%; M, 348.1392).

2-Methoxy-6-methyl-3-p-tolyl-1,2,3,4-tetrahydro-1,3,2-benzodiazaphosphorin 2-oxide, (**6f**). Sodium hydride (0.078 g, 0.00326 mol) was dissolved in an excess of methanol. To this was added (**6a**) (1.0 g, 0.00326 mol) in dry benzene (90 ml). T.l.c. showed that the reaction was complete in 1 h. Solvents were removed on a rotary evaporator and the residue treated with dichloromethane. Sodium chloride was removed by filtration and to the clear solution was added dropwise light petroleum (b.p. 60–80°C) until crystallisation occurred. These crystals were redissolved in chloroform and again light petroleum added slowly to induce crystallisation of (**6f**), m.p. 155°C, yield 0.8 g (82%). (C, 63.6, H, 6.4; N, 9.3; P, 10.2%; M^+, 302.1182. $C_{16}H_{19}O_2N_2P$ requires C, 63.6; H, 6.3; N, 9.3; P, 10.2%; M, 302.1184).

6-Methyl-2(N-methyl-p-toluidinyl)-3-p-tolyl-1,2,3,4-tetrahydro-1,3,2-benzodiazaphosphorine 2-oxide, (**6g**). *N*-Methyl-*p*-toluidine (0.79 g, 0.00652) and (**6a**) (1.0 g, 0.00326 mole) were boiled for 30 h under reflux in dry chloroform (25 ml). On cooling the solvent was removed and the residue dissolved in benzene, to which light petroleum (b.p. 60–80°C) was added, to facilitate removal of amine hydrochloride. T.l.c. indicated that the oil obtained was a mixture. Treatment with benzene preferentially dissolved (**6g**). Removal of solvent gave an oil, which crystallised after 0.5 h on a shaker. It was recrystallised from ethyl acetate to give (**6g**), m.p. 198°C, yield 0.46 g (36%). (Found: C, 70.7; H, 6.6; N, 10.8; P, 7.9%, M^+ 391.1825. $C_{23}H_{26}ON_3P$ requires C, 70.6; H, 6.7; N, 10.7; P, 7.9% m, M, 391.1816).

2-Phenyl-1,6-dimethyl-3-p-tolyl-1,2,3,4-tetrahydro-1,3,2-benzodiazaphosphorine 2-oxide, (**10**). (**6b**) (1.0 g, 0.0029 mol) was dissolved in dry benzene (200 ml). To this was added sodium hydride (0.138 g, 0.0029 mol) as a 50% suspension in paraffin and the mixture boiled under an atmosphere of nitrogen for 9 h. The slightly yellow solution was then cooled, and an excess of methyl iodide (2 ml) added. After standing overnight, a sediment was observed. To this mixture further methyl iodide was added. To the cold-water condenser was attached a solid CO_2-acetone condenser and the mixture refluxed for 6 h, filtered hot through a sintered glass crucible and the solvent removed. The resultant oil was

chromatographed on silica gel with light petroleum/acetone (3:1) as eluent. The product required at least four recrystallisations from light petroleum (b.p. 60–80°C) to give (**10**), m.p. 191°C (dec.), yield 0.43 g (41%). (Found: C, 73.0; H, 6.4; N, 7.8; P, 8.5; M$^+$, 362.1551. $C_{22}H_{23}ON_2P$ requires C, 72.9; H, 6.4; N, 7.7; P, 8.5; M, 362.1548).

2,6-Dimethyl-3-p-tolyl-1,2,3,4-tetrahydro-1,3,2-benzodiazaphosphorine 2-sulphide, (**6d**). (**2**, R = H) (2.26 g, 0.01 mol) and triethylamine (2.02 g, 2.75 ml, 0.02 mol) were dissolved in dry benzene (50 ml). To this solution was added dropwise (**5**, X = S, Y = Me) (1.49 g, 0.01 mol) and the mixture boiled under reflux for 16 h. It was then cooled, amine hydrochloride filtered off in a sintered glass crucible, the solvent removed and the resultant oil crystallised from light petroleum (b.p. 60–80°C) to give (**6d**), m.p. 129°C, yield 1.81 g (60%). (Found: C, 63.5, H, 6.5; N, 9.3; P, 10.3, S, 10.4%; M$^+$, 302.1010. $C_{16}H_{19}N_2PS$ requires C, 63.6; H, 6.3; N, 9.3; P, 10.2; S, 10.6%; M, 302.1007).

2-Ethyl-6-methyl-3-p-tolyl-1,2,3,4-tetrahydro-1,3,2-benzodiazaphosphorine 2-sulphide, (**6e**). (**2**, R = H) (2.26 g, 0.01 mol) and triethylamine (2.02 g, 2.77 ml, 0.02 mol) were dissolved in dry benzene (50 ml). To this, (**5**, X = S, Y = Et) (1.63 g, 0.01 mol) was added at room temperature. The mixture was then refluxed (9 h), amine hydrochloride removed in a sintered glass crucible, the solvent removed and the resultant oil crystallised with difficulty from light petroleum (b.p. 60–80°C) to give (**6e**), m.p. 137°C, yield 1.64 g (52%). (Found: C, 64.5; H, 6.6; N, 8.9; P, 9.8; S, 10.3%; M$^+$, 316.1174. $C_{17}H_{21}N_2PS$ requires C, 64.6; H, 6.7; N, 8.9; P, 9.8; S, 10.1%; M, 316.1164.

2-Phenyl-6-methyl-3-p-tolyl-1,2,3,4-tetrahydro-1,3,2-benzodiazaphosphorine 2-sulphide, (**6c**). (**2**, R = H) (2.26 g, 0.01 mol) and triethylamine (2.02 g, 2.77 ml, 0.02 mol) were dissolved in dry benzene (50 ml). To this (**5**, X = S, Y = Ph) (2.11 g, 0.01 mol) was added and the mixture boiled 4 days under reflux. Amine hydrochloride was filtered off in a sintered glass crucible, the solvent removed and the resultant oil recrystallised from a mixture of light petroleum/dichloromethane (2:1) to give (**6c**), m.p. 141°C, yield 1.56 g (43%). (Found: C, 69.3; H, 5.8; N, 7.7; P, 8.4; S, 8.8%; M$^+$, 364.1172. $C_{21}H_{21}N_2PS$ requires C, 69.2; H, 5.8; N, 7.7; P, 8.5; S, 8.8%; M, 364.1164).

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