

Phosphorus–Nitrogen Compounds. Part XXXVIII.¹ Reactions of Phenylphosphonic Dichloride and Phenylphosphonothioic Dichloride with Dibenzylamine

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PhP(O)Cl₂ (1) reacts with dibenzylamine in organic solvents at room temperature to give PhP(O)[N(CH₂Ph)₂](OEt) (3), PhP(O)(OEt)₂ (4), PhP(O)Cl[N(CH₂Ph)₂] (5), and {PhP(O)[N(CH₂Ph)₂]}₂O (6). The chloride (5) was not isolated but was characterised by preparation of the derivatives PhP(O)[N(CH₂Ph)₂](NH₂Et) (11) and PhP(O)[N(CH₂Ph)₂](NHCH₂Ph) (12). PhP(S)Cl₂ (2) reacts with dibenzylamine in organic solvents to give PhP(S)Cl[N(CH₂Ph)₂] (7), PhP(S)[N(CH₂Ph)₂](OEt) (8), PhP(S)[N(CH₂Ph)₂](NHCH₂Ph) (9), and {PhP(S)[N(CH₂Ph)₂]}₂O (two isomers, 10a and b); and with dibenzylamine in wet benzene to give [NH₂(CH₂Ph)₂]⁺{PhPS[N(CH₂Ph)₂]O}⁻ (14). The ethoxide derivatives (3, 4, 8) were obtained only in stabilised chloroform. Possible reaction mechanisms are discussed. ¹H N.m.r. spectra of the products provide numerous examples of intrinsically asymmetric methylene groups.

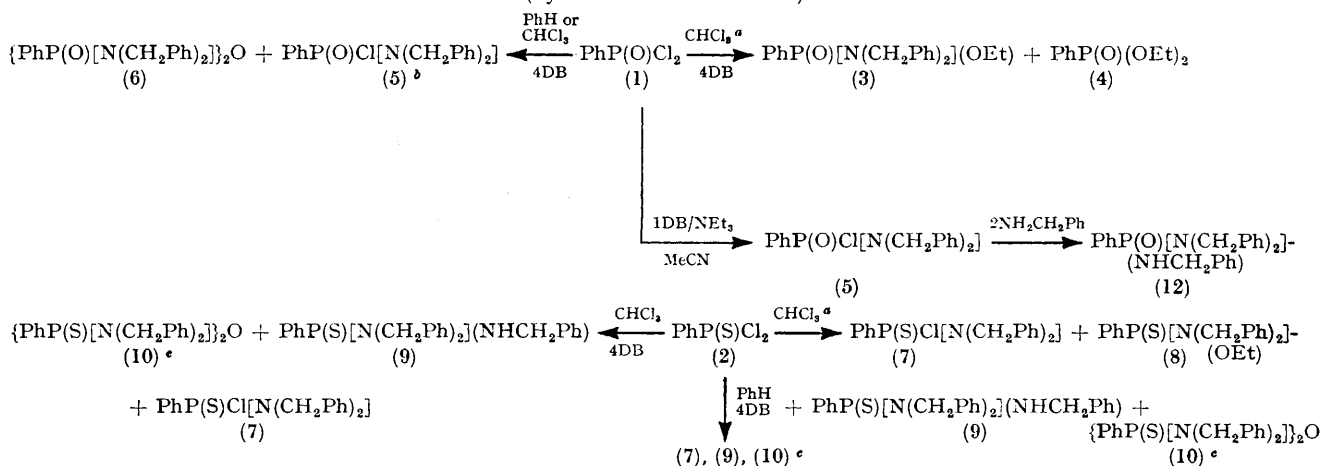
PART XXXIII of this series² reports the preparation of *NN'*-diethyl phenylphosphonothioic diamide, PhP(S)(NH₂Et)₂, and its thermolysis to give the *cis*- and *trans*-cyclodiphosphazanes, [PhP(S)NEt]₂. As part of a more extensive survey of the behaviour of phosphorus–nitrogen compounds at elevated temperatures (150–350 °C) we have attempted to prepare diamides containing secondary amino-groups. This paper describes some reactions of phenylphosphonic dichloride, PhP(O)Cl₂ (1), and phenylphosphonothioic dichloride, PhP(S)Cl₂ (2), with dibenzylamine in organic solvents at room temperature.

monochloride, PhP(O)Cl[N(CH₂Ph)₂] (5) (not isolated), and the anhydride, {PhP(O)[N(CH₂Ph)₂]}₂O (6), but the ethoxides (3) and (4) are not detected.

Phenylphosphonothioic dichloride (2) reacts with four mole equivalents of dibenzylamine in stabilised chloroform to give the chlorodibenzylamino-derivative, PhP(S)Cl[N(CH₂Ph)₂] (7); the ethoxy-derivative, PhP(S)[N(CH₂Ph)₂](OEt) (8); the mixed benzylaminodibenzylamino-derivative, PhP(S)[N(CH₂Ph)₂](NHCH₂Ph) (9); and two anhydrides, {PhP(S)[N(CH₂Ph)₂]}₂O (10a), m.p. 133° and (10b), m.p. 155° (ca. 4 : 1 mole ratio). These anhydrides have different

SCHEME

Some reactions of phenylphosphonic and phenylphosphonothioic dichloride with dibenzylamine (DB) at room temperature (hydrochlorides are omitted)



* Stabilised chloroform (containing EtOH). ^b Not isolated. ^c Two forms isolated.

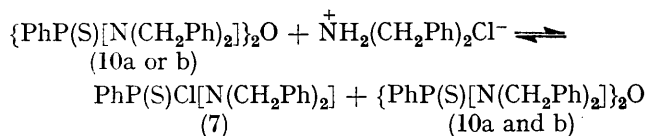
Phenylphosphonic dichloride (1) reacts with four mole equivalents of dibenzylamine in stabilised chloroform to give the dibenzylaminoethoxy-derivative, PhP(O)[N(CH₂Ph)₂](OEt) (3), and diethyl phenylphosphonate, PhP(O)(OEt)₂ (4). Stabilised chloroform contains ethanol and formation of the ethoxides (3) and (4) by competitive solvolysis is readily explained. Reactions in purified (ethanol-free) chloroform or benzene give the

¹ Part XXXVII, M. Biddlestone and R. A. Shaw, *J.C.S. Dalton*, 1973, 2740.

R_F values and recrystallise unchanged. They appear to be diastereoisomers but it is uncertain which is the *meso* form and which the *dl* racemate. Overall yields are increased by filtration of the precipitated dibenzylamine hydrochloride from time to time. Separate experiments show that either anhydride (10a or b) in the presence of dibenzylamine hydrochloride in chloroform at room temperature gives the monochloride (7)

² C. D. Flint, E. H. M. Ibrahim, R. A. Shaw, B. C. Smith, and C. P. Thakur, *J. Chem. Soc. (A)*, 1971, 3513.

and both anhydrides (10a and b) in approximately equal amounts. A similar experiment with the sole anhydride $\{\text{PhP}(\text{O})[\text{N}(\text{CH}_2\text{Ph})_2]\}_2\text{O}$ (6) gave no evidence of a second isomer.



The reaction of $\text{PhP}(\text{S})\text{Cl}_2$ (2) with dibenzylamine (4 mol) in alcohol-free chloroform or benzene gives the monochloride (7), the mixed amide (9), and the anhydrides (10a and b).

The bisdibenzylamino-derivatives $\text{PhP}(\text{X})\text{-}[\text{N}(\text{CH}_2\text{Ph})_2]_2$ ($\text{X} = \text{O}$ or S) were not obtained in any of our experiments. Their absence is presumably due to steric effects as the bisbenzylamino-derivatives, $\text{PhP}(\text{X})\text{-}(\text{NHCH}_2\text{Ph})_2$ (15, $\text{X} = \text{O}$; 16, $\text{X} = \text{S}$), and the benzylaminodibenzylamino-derivatives (9, 12), can be prepared without difficulty.

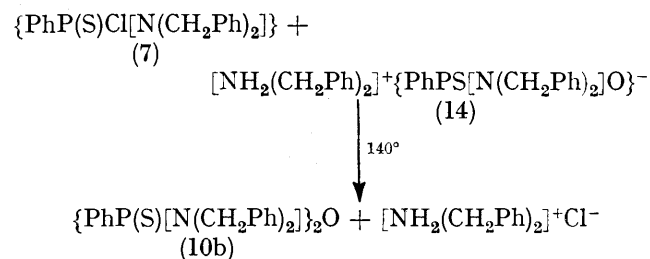
The mechanism of formation of the mixed amide, $\text{PhP}(\text{S})[\text{N}(\text{CH}_2\text{Ph})_2](\text{NHCH}_2\text{Ph})$ (9) is not clear. Although dibenzylamine undergoes disproportionation and decomposition reactions at high temperatures,³ there is no indication that it does so at room temperature. Independent experiments show that the mixed amide (9) is formed slowly from the chloride (7) in chloroform at room temperature in the presence of dibenzylamine and dibenzylamine hydrochloride. The presence of the hydrochloride is essential, which suggests that one of the mechanistic steps involves the participation of chloride ion. We envisage the possibility of a 'soft-soft' interaction⁴ between the sulphur atom and the benzyl group of the monochloride (7) followed by a chloride ion induced cleavage of the newly formed -S-CH_2 linkage to give (in the presence of dibenzylamine) tribenzylamine hydrochloride and possibly a reactive intermediate of the metaphosphate type; reaction of the latter with dibenzylamine would give compound (9). Alkaline extraction of the amine hydrochlorides formed during the reaction of $\text{PhP}(\text{S})\text{Cl}_2$ (2) with dibenzylamine confirms the presence of tribenzylamine.

The monochloride, $\text{PhP}(\text{O})\text{Cl}[\text{N}(\text{CH}_2\text{Ph})_2]$ (5), appears to be hydrolytically less stable than its thio-analogue (9). It is prepared *in situ* from the reaction of $\text{PhP}(\text{O})\text{Cl}_2$ (1) with dibenzylamine (1 mol) and triethylamine (1 mol) in acetonitrile but attempts to isolate a pure sample were unsuccessful. Further reaction with ethylamine gives $\text{PhP}(\text{O})[\text{N}(\text{CH}_2\text{Ph})_2](\text{NH}_2\text{Et})$ (11) and with benzylamine gives $\text{PhP}(\text{O})[\text{N}(\text{CH}_2\text{Ph})_2](\text{NHCH}_2\text{Ph})$ (12). The mixed amides $\text{PhP}(\text{S})[\text{N}(\text{CH}_2\text{Ph})_2](\text{NH}_2\text{Et})$ (13) and $\text{PhP}(\text{S})[\text{N}(\text{CH}_2\text{Ph})_2](\text{NHCH}_2\text{Ph})$ (9) can be prepared in a similar manner. The absence of $\text{PhP}(\text{O})\text{-}[\text{N}(\text{CH}_2\text{Ph})_2](\text{NHCH}_2\text{Ph})$ in reactions of $\text{PhP}(\text{O})\text{Cl}_2$ (1) with dibenzylamine may support the ideas suggested for the formation of the thio-analogue (9): a 'hard-

soft' interaction³ between the oxygen and the methylene group of the monochloride (5) would be much less favoured.

The yields of precipitated salts in reactions of the dichlorides (1) and (2) with dibenzylamine are invariably greater than calculated for dibenzylamine hydrochloride. A more detailed investigation of the reaction of $\text{PhP}(\text{S})\text{Cl}_2$ (2) with dibenzylamine in wet benzene led to the precipitation of a compound of composition $\text{C}_{34}\text{H}_{35}\text{N}_2\text{OPS}$ (14). The ^1H n.m.r. spectrum consists of: (a) a doublet characteristic of $\equiv\text{P}[\text{N}(\text{CH}_2\text{Ph})_2]$ protons, $^3J(\text{PH})$ 12.0 Hz; (b) a singlet characteristic of $\text{-N}(\text{CH}_2\text{Ph})_2$ methylene protons; (c) a multiplet [aromatic protons ($\text{Ph-P}\equiv$)]; (d) a singlet ($=\text{N-CH}_2\text{Ph}$ aromatic protons); and (e) a broad signal (δ 9.37) (NH protons) which disappears on shaking with deuterium oxide. The relative intensities of the signals $a:b:c:d:e$ are 4:4:5:20:2, consistent with the structure $[\text{NH}_2(\text{CH}_2\text{Ph})_2]^+\{\text{PhP}(\text{S})[\text{N}(\text{CH}_2\text{Ph})_2]\text{O}\}^-$ (14). Compounds of this type containing bulky cations and anions have been reported in phosphorus chemistry, *e.g.*, ref. 5.

The monochloride (7) and the salt (14) react in boiling xylene to give moderate quantities of the anhydride (10b) m.p. 155°, and dibenzylamine hydrochloride. Although we did not observe any reaction at



room temperature, it is still possible that formation of the salt (14) *in situ* may be a contributing factor during the reactions of dibenzylamine with $\text{PhP}(\text{S})\text{Cl}_2$ (2). When extensive precautions are taken to exclude moisture from the reactants and solvent (*e.g.*, xylene, which can be rigorously dried more easily than benzene), the anhydrides (10) are not formed and only compounds (7) and (9) are isolated.

Many of the compounds prepared in this work possess one or two asymmetric centres. A feature of such molecules is the non-equivalence of protons adjacent to the chiral centre (phosphorus in these examples). This non-equivalence can often be discerned by a study of the n.m.r. spectrum of the compound. Table I summarises the n.m.r. data.

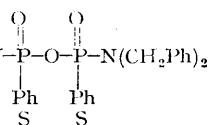
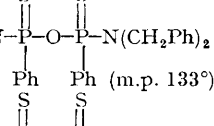
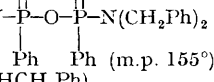
The methylene-proton spectra are of two main types: (a) non-equivalence is not observed and the resonance of the methylene protons of the benzylamino- or dibenzylamino-groups appears as a doublet (coupling to phosphorus); (b) non-equivalence is observed and eight lines are seen (AB pattern with coupling to phosphorus).

³ L. B. Howard, G. E. Hildert, R. Wiebe, and V. L. Gaddy, *J. Amer. Chem. Soc.*, 1932, **54**, 3628.

⁴ R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533.

⁵ M. Mikolajczyk and J. Łuczak, *Tetrahedron*, 1972, **28**, 5411.

TABLE 1
¹H N.m.r. data (100 MHz, CDCl₃ solution)

No.	Compound	$\delta_{\text{CH}_2}^a$	$^2J(\text{CH})$	$^3J(\text{PH})$	$\delta_{\text{CH}_2}^b$	$^2J(\text{CH})$	$^3J(\text{PH})$
(7)	PhP(S)Cl[N(CH ₂ Ph) ₂]	4.44, 4.26	15.0	12.5, 16.5			
(3)	PhP(O)[N(CH ₂ Ph) ₂](OEt)	4.08		10.0			
		^{c,d} 4.19, 4.11	15.0	10.0, 10.0	3.95, 3.87	10.0	7.5, 7.5
(8)	PhP(S)[N(CH ₂ Ph) ₂](OEt)	4.22		12.0			
		^d 4.28, 4.23	15.0	12.0, 11.5			
(11)	PhP(O)[N(CH ₂ Ph) ₂](NH ₂ Et)	4.10		10.0, 10.0	2.97		9.0
		^c 4.32, 4.18	15.5	10.0, 10.0			
(13)	PhP(S)[N(CH ₂ Ph) ₂](NH ₂ Et)	4.10		12.0			9.5
		^c 4.09		12.0	2.97, 2.83	12.5	9.5, 9.5
(12)	PhP(O)[N(CH ₂ Ph) ₂](NHCH ₂ Ph)	4.31, 4.20	16.0	10.5, 10.0	4.18		9.0
		^c 4.35, 4.15	15.0	10.0, 10.0	4.08		9.0
(9)	PhP(S)[N(CH ₂ Ph) ₂](NHCH ₂ Ph)	4.38, 4.35	15.0	12.0, 12.0	4.22, 4.14	14.0	9.0, 9.0
		^d 4.46, 4.36	15.0	12.0, 12.0	4.28, 4.17	14.0	8.5, 8.0
(6)		4.35, 4.16	15.0	11.0, 11.0			
(10a)		4.83, 4.13	15.5	12.5, 12.0			
(10b)		4.82, 4.12	15.5	12.5, 12.0			
(15)	PhP(O)(NHCH ₂ Ph) ₂				4.15		8.5
(16)	PhP(S)(NHCH ₂ Ph) ₂				4.11		9.5
(14)	[NH ₂ (CH ₂ Ph) ₂] ⁺ [PhPS[N(CH ₂ Ph) ₂]O] ⁻	4.24, 3.90		12.0			

^a Dibenzylamino-methylene protons. ^b Benzylamino-, ethylamino-, or ethoxy-methylene protons. ^c Benzene solution. ^d At 220 MHz.

* Complex overlap of lines.

The latter type is illustrated in Figure 1 for the compound PhP(O)[N(CH₂Ph)₂](OEt) (3). The -OCH₂ resonance (also illustrated) is complex because in addition to

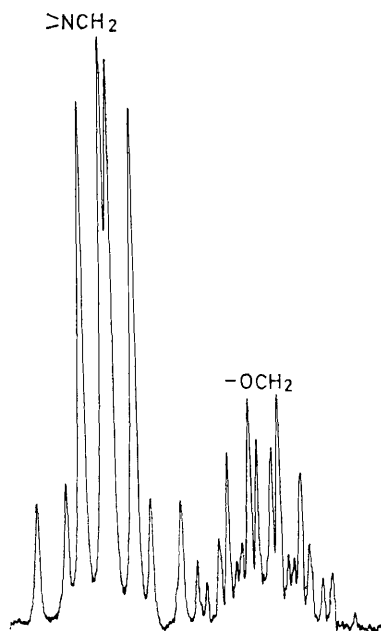


FIGURE 1 220 MHz Methylene ¹H n.m.r. spectrum of PhP(O)[N(CH₂Ph)₂](OEt) (3) in CDCl₃

the non-equivalence of the methylene protons, there is coupling to phosphorus and to the adjacent methyl

protons. Although 32 lines are predicted for this system, a numerical coincidence of coupling constants [$^3J(\text{PH}) = ^3J(\text{HH}) = 7.5$ Hz] simplifies the spectrum and permits a full analysis of the 20 visible lines. The spectrum shown in Figure 1 was measured at a frequency of 220 MHz. The non-equivalence of the ethoxy-methylene protons of compound (3) is not observed at 60 or 100 MHz. Data in Table 1 indicate that observation of the non-equivalence of these methylene protons often depends on the field strength of the instrument and on the choice of n.m.r. solvent (*e.g.*, compounds 3 and 11). The magnitude of the shift difference observed for non-equivalent methylene protons varies considerably and is presumably a feature of the anisotropy of neighbouring groups.

A prominent feature of the 100 MHz spectra of the three anhydrides (6, 10a, 10b) is the presence of broad humps between each set of doublets. In the spectrum of the phosphoryl compound (6), the eight line signal and complementary humps are only observed clearly at 220 MHz (Figure 2). This is because the chemical shift difference between each proton of the methylene groups is very much less in the anhydride containing the $\equiv\text{P}=\text{O}$ group. The appearance of humps (or unresolved lines) is also found in the n.m.r. spectra of many cyclic phosphorus-nitrogen compounds.⁶

Table I also records values of $^3J(\text{PH})$. The magnitude of this coupling constant varies with the nature of the

⁶ E. G. Finer, R. K. Harris, M. R. Bond, R. Keat, and R. A. Shaw, *J. Mol. Spectroscopy*, 1970, **33**, 72.

substituent groups, but is always greater for derivatives of PhP(S)Cl_2 (2) than for the corresponding derivatives

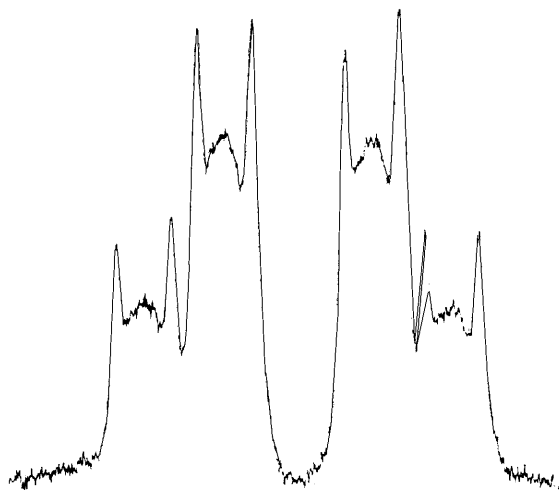


FIGURE 2 220 MHz Methylene ^1H n.m.r. spectrum of $\{\text{PhP(O)[N(CH}_2\text{Ph)}_2\}_2\text{O}$ (6) in CDCl_3

of PhP(O)Cl_2 (1). This observation is characteristic of many acyclic phosphorus compounds containing $\equiv\text{P=O}$

distilled *in vacuo*. Benzylamine and dibenzylamine were distilled from zinc dust under reduced pressure. Two typical experiments are described.

(a) *Reaction of Phenylphosphonothioic Dichloride with Dibenzylamine in Benzene*.—A solution of dibenzylamine (40.0 g, 0.21 mol) in benzene (200 ml) was added slowly to a stirred solution of phenylphosphonothioic dichloride (2) (10.5 g, 0.05 mol) in benzene (200 ml). The mixture was stirred (2 h) and left to stand overnight. The precipitate of amine hydrochlorides (23.0 g) was filtered. The following were isolated from the filtrate by column chromatography using activated silica and eluting with a 9:1 mixture of benzene and light petroleum (b.p. 60–80°): *P-phenyl-NN-dibenzylchlorophosphonothioic amide* (7) (4.2 g, 21%), m.p. 93°; *P-phenyl-N-benzyl-N'-N'-dibenzylphosphonothioic diamide* (9) (1.4 g, 7.0%), m.p. 102°; *P-phenyl-NN-dibenzylphosphonoamidothioic anhydride* (10a) (1.7 g, 6%), m.p. 133°; *P-phenyl-NN-dibenzylphosphonoamidothioic anhydride* (10b) (0.9 g, 3.0%), m.p. 155°.

(b) *Preparation of P-Phenyl-N-ethyl-N'-N'-dibenzylphosphonic Diamide*.—A solution of dibenzylamine (0.85 g, 0.05 mol) in acetonitrile (25 ml) was added dropwise to a stirred solution of phenylphosphonic dichloride (1) (9.75 g, 0.05 mol) and triethylamine (5.05 g, 0.05 mol) in acetonitrile (*ca.* 40 ml). The reaction mixture was stirred vigorously (1 h), and triethylamine hydrochloride (6.1 g) was removed.

TABLE 2

Preparation ^a of some dibenzylamino- and benzylamino-derivatives of PhP(O)Cl_2 (1) and PhP(S)Cl_2 (2)

	Amount		Reactants	Amount		Solvent		Time /h	Products		
	g	mol		g	mol	ml			g	%	
(1)	7.7	0.039	$\text{NH(PhCH}_2)_2$	36.5	0.185	CHCl_3 ^b	400	3	{(3) (4)}	1.2 1.8	88 21
(1)	7.7	0.039	$\text{NH(PhCH}_2)_2$	39.4	0.2	CHCl_3	450	2	{(5) (6)}	trace ^c 2.0	21 16
(1)	9.75	0.05	$\text{NH(PhCH}_2)_2$	39.4	0.2	PhH	400	4	{(5) (6)}	trace ^c 2.6	16
(2)	21.1	0.1	$\text{NH(PhCH}_2)_2$	78.8	0.4	CHCl_3 ^b	400	12	{(7) (8) (9) (10) ^d	0.88 0.42 1.47 2.41	19 9 13 7
(2)	21.1	0.1	$\text{NH(PhCH}_2)_2$	78.8	0.4	CHCl_3	400	4	{(9) (10) ^a	2.60 2.30	15 4
(2)	21.1	0.1	$\text{NH(PhCH}_2)_2$	78.8	0.4	PhH	450	12	{(7) (9) (10) ^a	1.92 1.90 2.10	20 10 5
(2)	10.6	0.05	$\text{NH(PhCH}_2)_2$	19.7	0.1	MeCN	400	24	(7)	13.2	71
(1)	9.75	0.05	{(a) $\text{NH(PhCH}_2)_2$ (b) NH_2Et	19.7 4.5	0.1 0.1	MeCN	400	1	(11)	10.6	58
(1)	9.75	0.05	{(a) $\text{NH(PhCH}_2)_2$ (b) $\text{NH}_2\text{CH}_2\text{Ph}$	19.7 10.7	0.1 0.1	MeCN	400	1	(12)	14.2	67
(2)	10.6	0.05	{(a) $\text{NH(PhCH}_2)_2$ (b) NH_2Et	19.7 4.5	0.1 0.1	MeCN	450	1	(13)	8.4	44
(2)	10.6	0.05	{(a) $\text{NH(PhCH}_2)_2$ (b) $\text{NH}_2(\text{CH}_2\text{Ph})$	19.7 10.7	0.1 0.1	MeCN	450	1	(9)	14.3	65
(1)	20.0	0.102	$\text{NH}_2\text{CH}_2\text{Ph}$	44.0	0.46	PhH	500	3	(15)	29.0	84
(2)	16.5	0.078	$\text{NH}_2\text{CH}_2\text{Ph}$	42.8	0.4	PhH	250	3	(16)	18.4	65
(2)	21.1	0.1	$\text{NH(CH}_2\text{Ph)}_2$	78.8	0.4	{PhH H_2O	400 50	6	(14)	17.0	31

^a All reactions carried out at room temperature (*ca.* 25 °C). ^b Stabilised chloroform (containing EtOH). ^c Detected by t.l.c. and characterised by preparation of derivatives (11, 12). ^d Two forms isolated.

or $\equiv\text{P=S}$ groups.⁷ It is worth noting that two distinct phosphorus–hydrogen couplings (12.5 and 16.5 Hz) are observed in the spectrum of $\text{PhP(S)Cl[N(CH}_2\text{Ph)}_2]$ (7).

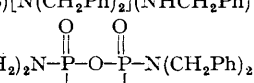
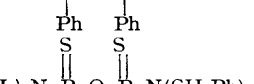
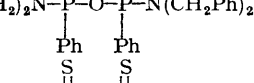
EXPERIMENTAL

Phenylphosphonic dichloride (1) and phenylphosphonothioic dichloride (2) from Eastman Organic Chemical were

T.l.c. of the filtrate indicated the single product (5). After evaporation of half the solvent, a solution of ethylamine (4.5 g, 0.1 mol) in acetonitrile (25 ml) was added dropwise to the stirred solution (24 h). Ethylamine hydrochloride (3.8 g) was filtered off and solvent was removed from the filtrate. The resulting oil was shaken vigorously with

⁷ R. A. Shaw and M. Woods, *Phosphorus*, 1971, 1, 191.

TABLE 3
 Physical and analytical data

No.	Compound	M.p. (or b.p.) °C	Found (%)					Formula	Required (%)				
			C	H	N	P	S		C	H	N	P	S
(7)	PhP(S)Cl·N(CH ₂ Ph) ₂	93	63.8	5.8	4.1	8.7	8.6	C ₂₀ H ₁₆ ClNPS	64.2	5.1	3.7	8.3	8.6
(3)	PhP(O)[N(CH ₂ Ph) ₂](OEt)	172/0.05mmHg	72.2	6.7	3.8	8.3		C ₂₂ H ₂₄ NO ₂ P	72.3	6.6	3.8	8.5	0.0
(8)	PhP(S)[N(CH ₂ Ph) ₂](OEt)	54	69.1	6.4	3.5	7.9	8.8	C ₂₂ H ₂₄ NOPS	69.3	6.3	3.7	8.1	8.4
(12)	PhP(O)[N(CH ₂ Ph) ₂](NHCH ₂ Ph)	147	76.0	6.4	6.6	7.3		C ₂₇ H ₂₇ N ₂ OP	76.1	6.3	6.6	7.3	0.0
(9)	PhP(S)[N(CH ₂ Ph) ₂](NHCH ₂ Ph)	101	73.8	5.0	6.4	7.1	7.4	C ₂₇ H ₂₇ N ₂ PS	74.1	5.0	6.4	7.1	7.4
(6)		135	73.0	6.1	4.3	9.4		C ₄₀ H ₃₆ N ₂ O ₃ P ₂	73.2	5.8	4.3	9.4	0.0
(10a)		133	70.2	5.5	4.2	9.1	9.2	C ₄₀ H ₃₈ N ₂ OP ₂ S ₂	69.8	5.5	4.0	9.0	9.2
(10b)		155	70.0	5.5	4.2	9.3	9.6	C ₄₀ H ₃₈ N ₂ OP ₂ S ₂	69.8	5.5	4.0	9.0	9.2
(11)	PhP(O)[N(CH ₂ Ph) ₂](NH ₂ Et)	93	72.6	7.1	7.2	8.0		C ₂₂ H ₂₅ N ₂ OP	72.5	6.9	7.7	8.5	0.0
(13)	PhP(S)[N(CH ₂ Ph) ₂](NH ₂ Et)	81	69.3	6.8	7.3	8.1	8.4	C ₂₂ H ₂₅ NPS	69.5	6.6	7.4	8.1	8.4
(14)	[(PhCH ₂) ₂ NH ₂] ⁺ [PhPS[N(CH ₂ Ph) ₂]O] ⁻	124	74.2	6.4	5.1	5.6	5.8	C ₃₄ H ₃₆ N ₂ OPS	74.1	6.4	5.1	5.6	5.8
(15)	PhP(O)(NHCH ₂ Ph) ₂	99	71.5	6.2	8.5	9.2		C ₂₀ H ₂₁ N ₂ OP	71.4	6.2	8.3	9.5	0.0
(16)	PhP(S)(NHCH ₂ Ph) ₂	80 ^a	68.2	5.9	8.3	9.2	9.4	C ₂₀ H ₂₁ N ₂ PS	68.1	6.0	8.0	8.8	9.1

^a Lit. m.p. 80—81 °C (S. Trippett, *J. Chem. Soc.*, 1962, 4731).

diethyl ether and more ethylamine hydrochloride (0.5 g) was filtered off. Evaporation gave a sticky oil which was extracted with light petroleum (b.p. 60—80°) and allowed to crystallise (3 days). Recrystallisation from diethyl ether gave *P-phenyl-N-ethyl-N'-dibenzylphosphonic diamide* (11) (7.4 g, 40.7%), m.p. 93°.

Other experiments are summarised in Table 2. Yields

refer to pure products (*i.e.*, in some cases after column chromatography). Analytical and physical data are given in Table 3. N.m.r. spectra were obtained from JEOL MH 100 and Varian HA 100 spectrometers.

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⁸ S. Trippett, *J. Chem. Soc.*, 1962, 4731.