Dimethylamino-derivatives of Bis(dichlorophosphinyl)methylamine, $[Cl_2P(:O)]_2NMe$

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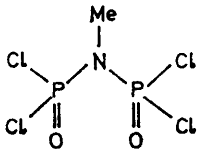
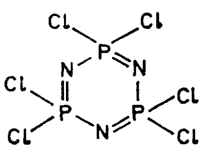
The reactions of bis(dichlorophosphinyl)methylamine, $[Cl_2P(:O)]_2NMe$, with dimethylamine and with *NN*-dimethyl(trimethylsilyl)amine have been studied. Mono, non-geminal bis-, tris-, and tetrakis-dimethylamino-derivatives have been identified; the bis-derivative has been separated into diastereomeric forms which interconverted either when heated, or in the presence of tetraethylammonium chloride. The mono-derivative was also obtained from the reactions of phosphoryl halides with heptamethyldisilazane, $(Me_3Si)_2NMe$, and the geminal bis- and the tris-derivatives were obtained from the condensation reactions of $(Me_2N)_2P(:O)\cdot NHMe$ with phosphoryl chloride and $Cl_2P(:O)\cdot NMe_2$, respectively. Structures were established by ^1H and ^{31}P n.m.r. spectroscopy and the results compared with those obtained for the dimethylaminolysis of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$.

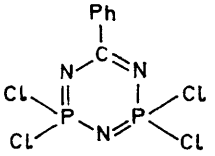
THE chemistry of the recently reported[1] compound, bis(dichlorophosphinyl)methylamine, (I), and of its derivatives is of interest in that it can provide comparisons of the way in which the formally saturated P–N–P system can relay electronic effects, relative to those in the phosphazenes,[2] which contain formally unsaturated P–N=P units. Differences in these effects, and in the reactivity of the individual phosphorus atoms may be expected to show in the nature and stereochemistry of the products obtained by reactions with nucleophiles. For example, it is well established that the chlorine atoms in hexachlorocyclotriphosphazatriene,[3] $N_3P_3Cl_6$, and in *C*-phenyltetrachlorocyclodiphosphazatriene,[4] $N_3CPhP_2Cl_4$, are replaced in a predominantly non-geminal manner by dimethylamine and piperidine. The relative reactivity of the phosphorus atoms to ammonolysis and aminolysis [by Me_3SiNMe_2 and $(Me_3Si)_2NH$] has been compared in only one group of linear phosphazenes [$XX'P(:S)-N=PF_3$ ($X = X' = F$; $X = F$, $X' = Cl$; $X = X' = Cl$)]. In all cases, preferential ammonolysis[5] or aminolysis[6] occurred at the $=PF_3$ group.



(I)



$N_3P_3Cl_6$



$N_3CPhP_2Cl_4$

The reactions of compound (I) with both dimethylamine and *NN*-dimethyl(trimethylsilyl)amine were, initially, strongly exothermic. A monodimethylamino-derivative (II), $Cl_2P(:O)\cdot NMe\cdot P(:O)Cl\cdot NMe_2$, and a bisdimethylamino-derivative (III), $[Cl(Me_2N)P(:O)]_2NMe$, were readily identified by ^1H and ^{31}P n.m.r. spectroscopy and obtained by the following reactions:

$$(I) + 2NHMe_2 \longrightarrow (II) + Me_2NH_2Cl$$
$$(I) + 2Me_3Si\cdot NMe_2 \longrightarrow (III) + 2Me_3SiCl$$

However, a pure sample of (II) could only be obtained by the route:

$$Cl_2P(:O)\cdot NMe_2 + (Me_3Si)_2NMe \longrightarrow Cl(Me_2N)P(:O)\cdot NMe\cdot SiMe_3 + Me_3SiCl$$
$$Cl(Me_2N)P(:O)\cdot NMe\cdot SiMe_3 + POCl_3 \longrightarrow (II) + Me_3SiCl$$

Attempts to obtain compound (II) by the following condensation reaction were unsuccessful:

$$Cl_2P(:O)\cdot NMe_2 + Cl_2P(:O)\cdot NHMe \xrightarrow{Et_3N} (II) + HCl$$

Pure samples of the bisdimethylamino-derivative (III) were easily obtained from the reactions of (I) with four and two molar equivalents of dimethylamine and trimethylsilyldimethylamine respectively. The oily distillates from these reactions gave colourless crystals, mixed with an oil, which were shown to be isomeric (nongeminal) forms of (III). A third isomer (IV), $Cl_2P(:O)\cdot NMe\cdot P(:O)(NMe_2)_2$, was synthesised by the condensation reaction:

$$(Me_2N)_2P(:O)\cdot NHMe + POCl_3 \xrightarrow{Et_3N} Cl_2P(:O)\cdot NMe\cdot P(:O)(NMe_2)_2 + HCl$$

Attempts to rearrange compound (IV), $Cl_2P(:O)\cdot NMe\cdot P(:O)(NMe_2)_2$ by heating it at 120° were unsuccessful, so it was unlikely that (IV) had formed in the refluxing toluene solution, and had undergone subsequent rearrangement to give (III).

NN-Dimethyl(trimethylsilyl)amine could not be induced to replace the chlorine atoms in (III), an observation which parallels that of Abel *et al.*,[7] who found that only two of the chlorine atoms in phosphoryl chloride

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[1] R. Keat, *J. Chem. Soc.* (*A*), 1970, 2732.

[2] R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, 1962, **62**, 247.

[3] R. Keat and R. A. Shaw, *J. Chem. Soc.* (*A*), 1966, 908.

[4] A. Schmidpeter and N. Schindler, *Chem. Ber.*, 1969, **102**, 856.

[5] H. W. Roesky and L. F. Grimm, *Chem. Ber.*, 1970, **103**, 3114.

[6] H. W. Roesky and L. F. Grimm, *Chem. Ber.*, 1970, **103**, 1664.

[7] E. W. Abel, D. A. Armitage, and G. R. Willey, *J. Chem. Soc.*, 1965, 57.

could be aminolysed by *NN*-diethyl(trimethylsilyl)amine. However, (I) and six molar equivalents of dimethylamine gave a *ca.* 5 : 5 : 1 mixture of (III), the tetrakisdimethylamino-derivative (VI), $[(Me_2N)_2{\cdot}P(:O)]_2$-NMe, and the trisdimethylamino-derivative (V), $(Me_2N)_2$-$P(:O){\cdot}NMe{\cdot}P(:O)ClNMe_2$. Exchange of dimethylamino-groups in this mixture readily occurred on heating and distillation gave a *ca.* 1 : 1 : 1 mixture of the same components. Compound (V) was best obtained from the condensation reaction:

$$(Me_2N)_2P(:O){\cdot}NHMe + Cl_2P(:O){\cdot}NMe_2 \xrightarrow{Et_3N} (V) + HCl$$

The hygroscopic solid tetrakisdimethylamino-derivative (VI) was readily obtained from (I) and an excess of dimethylamine in ether solution at room temperature. Compound (VI) has previously been reported in the patent literature,[8] and obtained by the reaction:

$$ClP(:O)(NMe_2)_2 + (Me_2N)_2P(:O){\cdot}NHMe \xrightarrow{C_5H_5N} (VI) + HCl$$

It seems likely that the reaction of dimethylamine and of *NN*-dimethyl(trimethylsilyl)amine with phosphoryl halides is initiated by nucleophilic attack of the nitrogen lone pair of these amines at the electrophilic phosphorus atoms. The importance of subsequent steps involving dehydrohalogenation in the case of dimethylamine and loss of trimethylchlorosilane in the case of the silylamine is very difficult to estimate. Qualitative observations show that one of the most important effects determining the rate of reaction for a given phosphoryl halide is the base strength of the amine. Indeed, it is tempting to compare the ease with which full aminolysis of (I) occurs with dimethylamine compared to the less basic *NN*-dimethyl(trimethylsilyl)amine, but other factors, such as the relatively bulky nature of the latter amine need consideration. A more convincing demonstration of the importance of base strength is provided by the observations that, towards phosphoryl chloride, the following order of reactivity is apparent: $(Me_3Si)_2NMe > Cl(Me_2N)P(:O){\cdot}NMe{\cdot}SiMe_3 > Cl_2P(:O){\cdot}NMe{\cdot}SiMe_3$. The base strength of the bridging nitrogen atom can reasonably be expected to decrease in the same order. Changes in reactivity, following the same trend, have also been observed [9] in reactions with P^{III} halides.

The separation of bisdimethylamino-derivative (III) into two diastereomeric forms (which were present in a 1 : 1 ratio) provides good evidence that the dimethylamino-groups are bonded to different phosphorus atoms. Further, our ability to separate these *meso*- and (±)-forms (which were not identified) suggests that chloride ion exchange is slow at ambient temperatures. Interconversion of these diastereoisomers on heating, or with tetraethylammonium chloride in acetonitrile solution shows that chloride ion exchange proceeds, at least in part, with inversion of configuration at the phosphorus atoms (provided that exchange at the two phosphorus atoms takes place in a non-synchronous manner). This result is consistent with measurements on other nucleophilic displacement reactions at phosphorus(v),[10] which often proceed with inversion of configuration at phosphorus and follow second-order kinetics.

It is notable that neither compound (II) nor (IV) could be obtained from attempted condensation of $Cl_2P(:O){\cdot}$-NHMe with $Cl_2P(:O){\cdot}NMe_2$, or with $ClP(:O)(NMe_2)_2$, a result which suggests that self-condensation of the methylamino-derivative is preferable to condensation with the dimethylamino-derivatives with their reduced electrophilic nature. Condensations of the type:

$$Cl_2P(:O){\cdot}NHMe + RP(:O)Cl_2 \xrightarrow{Et_3N} Cl_2P(:O){\cdot}NMe{\cdot}P(:O)ClR + HCl$$

have been observed when R = Ph,[1] Me,[9] and CH_2Cl,[9] where, presumably, conjugative supply of electron density to phosphorus is reduced.

The results obtained for the dimethylaminolysis of compound (I) may usefully be compared with those well established [3,11,12] for hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$.

(*a*) The fact that the monodimethylamino-derivative (II) is always obtained together with unchanged compound (I) and with (III) in *ca.* 2 : 1 : 1 proportions respectively (n.m.r.) suggests that the deactivating effect of the first dimethylamino-group is not very effective at the $-P(:O)Cl_2$ group; it is only after the second dimethylamino-group is introduced that there is a noticeable decrease in the reactivity to the nucleophiles employed. With dimethylamine, $N_3P_3Cl_6$ gives a monodimethylamino-derivative with, relative to reactions with (I), much smaller proportions of unchanged $N_3P_3Cl_6$, and bisdimethylamino-derivatives, $N_3P_3Cl_4(NMe_2)_2$ (*ca.* 20% together).[11]

(*b*) The total absence (n.m.r.) of the geminal bisdimethylamino-derivative (IV) in the reaction products of (I) with four molar equivalents of dimethylamine at −78°, ambient temperatures, and +110° contrasts with related reactions with $N_3P_3Cl_6$, which show that the proportion of geminal isomers are increased (roughly to that expected on a statistical basis) as the temperature at which the reaction is carried out [11] is increased. One factor that may be important in accounting for the absence of compound (IV) is related to (*a*) above. Electron density conferred on the near phosphorus atom by the dimethylamino-group in (II) is possibly mainly localised on that phosphorus atom making it resistant to nucleophilic attack, whereas in the cyclophosphazenes electron density is more readily delocalised around the ring making aminolysis at the $\equiv PClNMe_2$ group more probable. Steric effects may also be important in favouring the formation of (III) relative to (IV).

(*c*) The fact that very small proportions of the trisdi-

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[8] U.S.P. 2,798,086 (*Chem. Abs.*, 1957, **51**, 16,535a).

[9] R. Keat and L. Stobbs, unpublished results.

[10] M. J. Gallagher and I. D. Jenkins, *Topics in Stereochemistry*, 1968, **3**, 1.

[11] R. Keat and R. A. Shaw, *J. Chem. Soc.*, 1965, 2215.

[12] H. Koopman, F. J. Spruit, F. van Deursen, and J. Bakker, *Rec. Trav. chim.*, 1965, **84**, 341.

methylamino-derivative (V), were obtained from (I) and six molar equivalents of dimethylamine is a result which bears a resemblance to the analogous reactions with $N_3P_3Cl_6$, in which no pentadimethylamino-derivative $N_3P_3Cl(NMe_2)_5$, has yet been detected from a reaction with 10 molar equivalents of dimethylamine. It is possible that the absence of the latter derivative is related to the ease with which the sixth chlorine atom may heterolyse.[3] However, the n.m.r. results of compound (V) described below indicate that, at least in chlorobenzene, the rate of chloride ion exchange is slow on the n.m.r. time scale, even at temperatures up to 150°.

Selected ^1H and ^{31}P n.m.r. data (Table 1) provided good evidence for the structures of the derivatives (I) to (VI), especially in the appearance of the *N*-methyl signal which was a 1 : 2 : 1 triplet due to coupling with equivalent phosphorus atoms in the symmetrical derivatives (I), (III), and (VI), and a four-line signal in (II), (IV), and (V). The coupling constant, $J_{P\text{-}N\text{-}C\text{-}H}$, for a given phosphorus atom in the $P\cdot N(Me)\cdot P$ grouping decreased on the introduction of dimethylamino-groups at that phosphorus atom as expected,[13] but increased on the introduction of dimethylamino-groups at the second phosphorus atom. A noteworthy feature of the dimethylamino-proton signals in the symmetrical derivatives (III) and (VI) was the appearance of a broad ' hump ' between the components of the spin-coupled doublet. This is the result of the fact that the compounds (III) and (VI) provide examples of second-order spin systems, $AA'X_6X_6'$ and $AA'X_{12}X_{12}'$, respectively[14] (neglecting the bridging *N*-methyl protons). The NMe_2-proton signals from the trisdimethylamino-derivative were unusual in that three doublets, of equal intensity were apparent. It seems unlikely that this is the result of hindered rotation about any of the bonds, or of slow inversion (on the n.m.r. time scale) at any of the nitrogen atoms, since the appearance of the spectrum only changed slightly as the temperature was raised to 150° in chlorobenzene solution. This behaviour is closely related to that in systems where, for example, methylene protons are rendered nonequivalent as a result of their proximity to an asymmetric centre.[15] Presumably, the dimethylamino-groups in the $P(:O)(NMe_2)_2$ grouping are nonequivalent due to their proximity to the $P(:O)ClNMe_2$ group. This conclusion is supported by the fact that the ^1H spectrum of the analogous *P*-phenyl compound, $(Me_2N)PhP(:O)\cdot NMe\cdot P(:O)(NMe_2)_2$, also shows three dimethylamino-proton signals whose separation varies only slightly with temperature. An interesting consequence of these observations in the case of compound (V) is that chloride ion exchange must be slow on the n.m.r. time scale under the conditions employed. This is because chloride ion exchange might be associated with fast inversion of configuration at phosphorus, or with the formation of a $(Me_2N)_2P(:O)\cdot NMe\cdot \overset{+}{P}(:O)\cdot NMe_2$ ion. Both of these possibilities would effectively introduce a plane of symmetry at the phosphorus atom undergoing exchange and rule out magnetic nonequivalence at the $(Me_2N)_2PO$-group.

TABLE 1

^1H and ^{31}P N.m.r. data *

Compound	NMe Signals		^{31}P shift (p.p.m.)
	τ	$^3J_{P\text{-}N\text{-}C\text{-}H}$ (Hz.)	
$Cl(Me_2N)P(:O)\cdot NHMe$	7·33	14·7	−28·2
$(Me_2N)_2P(:O)\cdot NHMe$	7·45	10·8	−22·9
$Cl(Me_2N)P(:O)\cdot NMe\cdot SiMe_3$	7·60	16·3	−29·4
$[Cl_2P(:O)]_2NMe$ (I) †	6·64	13·8	−10·3
$Cl_2P(:O)\cdot NMe\cdot P(:O)ClNMe_2$ (II)	6·76	15·7, 11·1	−12·3, −15·2
$Cl(Me_2N)P(:O)\cdot NMe\cdot P(:O)ClNMe_2$ (III) (m.p. 65—66°)	6·89 ‡	11·9	−19·2
$Cl(Me_2N)P(:O)\cdot NMe\cdot P(:O)ClNMe_2$ (III) (b.p. 116—118°/0·6 mm.)	6·89 ‡	11·2	−19·2
$Cl_2P(:O)\cdot NMe\cdot P(:O)(NMe_2)_2$ (IV)	6·89	16·8, 8·2	−13·0, −17·0
$Cl(Me_2N)P(:O)\cdot NMe\cdot P(:O)(NMe_2)_2$ (V)	7·00	12·5, 8·5	−19·1, −24·1
$[(Me_2N)_2P(:O)]_2NMe$ (VI)	7·18	9·2	−20·3
$Me_2N\cdot PhP(:O)\cdot NMe\cdot P(:O)(NMe_2)_2$		13·1, 9·0 §	

* Obtained from $CDCl_3$ solutions (^1H) and CH_2Cl_2 solutions (^{31}P). † Data from ref. 1. ‡ Separated by 0·6 Hz. at 100 MHz. § In C_6H_5Cl solution. Three NMe_2 doublets (all $J_{P\text{-}N\text{-}C\text{-}H}$ 9·3 Hz.) whose separation changed by < 1 Hz. over the temperature range 30—140°.

Because of the poor resolution inherent in running ^{31}P n.m.r. spectra on samples contained in stationary tubes, and the broadening due to coupling with the *N*-methyl protons, *P*–N–*P* coupling was not clearly detected and generally assumed to be less than *ca.* 20 Hz. The presence of diastereoisomers was not detected in the ^{31}P spectrum of compound (III) and the shift between these may be assumed to be < 1 p.p.m. However, larger shifts *ca.* 3 p.p.m. are generally apparent[9,16] in the ^{31}P spectra of diastereomeric compounds based on the P^{III}–N–P^{III} unit.

The i.r. spectra of a series of compounds containing the P–N–P skeleton showed a strong band near 900 cm^{-1} which has been assigned[1,17,18] to the P–N–P asymmetric

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[13] R. Keat, *J. Chem. Soc. (A)*, 1970, 1795.

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

[15] M. van Gorkom and G. E. Hall, *Quart. Rev.*, 1968, **22**, 14.

[16] L. Maier, *J. Inorg. Nuclear Chem.*, 1962, **24**, 275.

[17] D. E. C. Corbridge, *Topics in Phosphorus Chem.*, 1970, **6**, 235.

[18] J. F. Nixon, *J. Chem. Soc. (A)*, 1968, 2689.

stretching mode. This band moved[1,18] to lower wavenumbers on passing from phosphorus(V) to phosphorus(III) compounds and by a reduction in the electronegativities of the substituents at phosphorus(V), changes which are probably related to a reduction in the strength of the bridging P–N bonds. Replacement of a chlorine atom by a dimethylamino-group may be expected to produce the same effect and Table 2 shows that this is broadly true. This trend may be compared with a reduction in ν(P=O), as expected,[17] and an increase in ν(C–N),[17] except in the case of the geminal compound (IV).

TABLE 2

Selected i.r. data *

Compound	ν(P=O) cm⁻¹	ν(C–N) cm⁻¹	$\nu_{as.}$ (P–N–P) cm⁻¹
$[Cl_2P(:O)]_2NMe$ †	1310, 1290	1040	912
$Cl_2P(:O)NMe\cdot P(:O)ClNMe_2$ ‡	1294, 1253	1055	901
$Cl(Me_2N)P(:O)\cdot NMe\cdot P(:O)ClNMe_2$ ‡ (± *meso*)	1250	1060	890
$Cl_2P(:O)\cdot NMe\cdot P(:O)(NMe_2)_2$ †	1310, 1200?	1060	918
$Cl(Me_2N)P(:O)\cdot NMe\cdot P(:O)(NMe_2)_2$ ‡	1250 (v. broad)	1063	888
$[(Me_2N)_2PO]_2NMe$ †	1236	1063	887

* See refs. 1, 17, 18 for related assignments. † Run as Nujol mulls. ‡ Run as liquid films.

TABLE 3

Summary of aminolysis reactions

Substrate (moles)	Amine (moles)	Solvent (ml.)	Conditions	Products %	M.p./b.p.° (mm. Hg)
(I) (0·038)	Me_3SiNMe_2 (0·038)	Et_2O (50)	0°, stirred 20° (1 hr.)	(I) (~30), (II) (~40), (III) (~30) [a]	90—96 (0·6)
(I) (0·024)	$NHMe_2$ (0·096)	Et_2O (50)	0°, reflux (1 hr.)	(III) (63) [b]	95—100 (0·01)
(I) (0·011)	$NHMe_2$ (0·044)	Toluene (60)	reflux [d]	(III)	
(I) (0·012)	$NHMe_2$ (0·072)	Et_2O (40)	0°, stirred 20° (1 hr.)	(III) (~45), (V) (<10), (VI) (~45) [a,c]	
(I) (0·019)	$Me_3Si\cdot NMe_2$ (0·057)	Et_2O (50)	0°, reflux (6 hr.)	Unidentifiable	
(I) (0·012)	$NHMe_2$ (excess)	Et_2O (100)	0°, reflux (1 hr.)	(IV) (79)	54—56/120 (0·1) [e,h]
$Cl_2P(O)\cdot NHMe$ (0·136)	$NHMe_2$ (0·279)	Et_2O (250)	0°, stirred 20° (1 hr.)	$Cl_2(Me_2N)P(\cdot O)\cdot NHMe$ (76)	75—80 (0·1)
$Cl_2P(:O)\cdot NHMe$ (0·10)	$NHMe_2$ (excess)	Et_2O (200)	0°, reflux (1 hr.)	$(Me_2N)_2P(:O)\cdot NHMe$ (72)	110 (0·1)
$Cl_2P(:O)\cdot NMe_2$ (0·0080)	$Cl_2P(\cdot O)\cdot NHMe$ (0·0080) [f]	Et_2O (50)	0°, reflux (½ hr.)	$Cl_2P(:O)\cdot NMe_2$	
$ClP(:O)(NMe_2)_2$ (0·018)	$Cl_2P(:O)\cdot NHMe$ (0·018) [f]	Et_2O (60)	0°, stirred 20° (1 hr.)	$ClP(:O)(NMe_2)_2$	
$Cl_2P(:O)\cdot NMe_2$ (0·020)	$(Me_3Si)_2NMe$ (0·020)		20°, stirred (24 hr.)	$Cl(Me_2N)P(:O)\cdot NMe\cdot SiMe_3$ (74)	68—72 (0·1)
$P(:O)Cl_3$ (excess)	$Cl(Me_2N)P(:O)\cdot NMe\cdot SiMe_3$ (0·0022)		20°, stirred (½ hr.)	(II) (84)	85 (0·1)
$P(:O)Cl_3$ (0·019)	$(Me_2N)_2P(:O)\cdot NHMe$ (0·019) [f]	C_6H_6 (15)	0°, stirred 50° (6 hr.)	(IV) (20)	52—55/130 (0·05) [g]
$Cl_2P(:O)\cdot NMe_2$ (0·042)	$(Me_2N)_2P(:O)\cdot NHMe$ (0·042) [f]	n-Hexane (100)	20°, reflux (1 hr.)	$Cl(Me_2N)P(:O)\cdot NMe\cdot P(:O)(NMe_2)_2$ (54)	130 (0·05)
$ClPhP(\cdot O)\cdot NMeP(O)Cl_2$ (0·010)	$NHMe_2$ (excess)	Et_2O (20)	20°, reflux (1 hr.)	$(Me_2N)PhP(:O)\cdot NMe\cdot P(:O)(NMe_2)_2$ (43)	150—160 (0·1)

[a] Ratios established from ^1H and ^{31}P n.m.r. spectra. [b] Gave diastereoisomer m.p. 65—66°. [c] After distillation ratio was (III) (~33), (V) (~33), (VI) (~33). [d] Dimethylamine distilled into refluxing toluene solution. [e] Very hygroscopic. [f] Condensation accomplished by addition of one molar equivalent of triethylamine. [g] Unaffected on heating 120°/12 hr. (^1H n.m.r.). [h] Lit.,[8] b.p. 145—149° (1·0 mm.Hg).

TABLE 4

Analytical data

	Found					Calculated				
Compound	C	H	Cl	N	m/e †	C	H	Cl	N	m/e †
$Cl_2P(:O)\cdot NMe\cdot P(:O)ClNMe_2$ (II)	12·7	3·4	38·7		272	13·2	3·3	38·9		272
$Cl(Me_2N)P(:O)\cdot NMe\cdot P(:O)ClNMe_2$ (III) (liquid + solid)	21·6	5·65	25·1	21·4 *	281 ‡	21·3	5·3	25·2	22·0 *	281
$Cl_2P(:O)\cdot NMe\cdot P(:O)(NMe_2)_2$ (IV)	21·9	5·4	25·0		281 §	21·3	5·3	25·2	22·0 *	281
$Cl(Me_2N)P(:O)\cdot NMe\cdot P(:O)(NMe_2)_2$ (V)	28·4	6·7	12·25		290	28·9	7·2	12·2		290
$[(Me_2N)_2PO]NMe$ (VI)	35·8	9·0		20·4 *	299	36·1	9·0		20·7 *	299
$Me_2NPhP(:O)\cdot NMeP(:O)(NMe_2)_2$	46·6	8·0		16·1		47·0	7·9		16·9	
$Cl(Me_2N)P(:O)\cdot NHMe$	22·6	6·2			156	23·0	6·4			156
$(Me_2N)_2P(:O)\cdot NHMe$	36·0	9·8		25·6	165	36·4	9·7		25·4	165
$Cl(Me_2N)P(:O)\cdot NMe\cdot SiMe_3$	31·0	7·8	15·8		228	31·5	7·8	15·5		228

* P Analyses. † For ^{35}Cl and ^{28}Si containing ions where relevant. ‡ $P(:O)^{35}ClNMe_2$ ion (*m/e* 126) identified, but no related metastable. § $P(:O)(NMe_2)_2$ ion (*m/e* 135) identified, but no related metastable.

EXPERIMENTAL

Solvents were dried by conventional means. Phosphoryl chloride was purified by distillation. Dimethylamino-derivatives of phosphoryl chloride,[19] $Cl_2P(:O)\cdot NHMe$, $Cl(Ph)$-$P(:O)\cdot NMe\cdot P(:O)Cl_2$,[1] $Me_2N\cdot SiMe_3$,[20] and $(Me_3Si)_2NMe$[21] were prepared by literature methods. All experiments were carried out under a flush of dry nitrogen. ^1H and ^{31}P Spectra were measured on a Perkin-Elmer R10 spectrometer at 60 and 24·3 MHz, respectively. The ^{31}P spectra were obtained from samples contained in 8·5 mm o.d. non-spinning tubes and 85% H_3PO_4 was used as an external standard. I.r. spectra were recorded on Perkin-Elmer 225 or 457 spectrometers. Mass spectra were obtained from an A.E.I. MS12 spectrometer.

Reactions of Compound (I) *with Amines.*—Two examples of the procedures employed are given below and the details of the other reactions are summarised in Table 3. Analytical data are given in Table 4.

Reaction of Compound (I) *with Two Molar Equivalents of*

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Dimethylamine.—Bis(dichlorophosphinyl)methylamine (6·0 g., 0·023 mole) was dissolved in diethyl ether (100 ml.) and cooled (0°). Dimethylamine (2·0 g., 0·046 mole) was added slowly with stirring and the mixture was allowed to come to room temperature (*ca.* 1 hr.). The precipitate of dimethylamine hydrochloride was filtered off and washed with ether (50 ml.); the washings were combined with the filtrate. The ether was removed from the combined solutions leaving a colourless oil which was distilled *in vacuo* to give a mixture of bis(dichlorophosphinyl)methylamine, (I), *dichlorophosphinyl(chlorodimethylaminophosphinyl)methylamine*, (II), and *bis(chlorodimethylaminophosphinyl)methylamine* (III) in an approximate 1 : 2 : 1 molar ratio respectively (^{31}P n.m.r.), b.p. 86—96°/0·6 mmHg. The proportion of (II) was not significantly increased when the reaction was carried out at −78°. Repeated attempts at fractional distillation did give an analytically pure sample of (II), but see Table 3.

Reaction of Compound (I) *with Two Molar Equivalents of* NN-*Dimethyl(trimethylsilyl)amine.*— *NN*-Dimethyl(trimethylsilyl)amine (4·5 g., 0·038 mole) was added dropwise to a stirred solution of bis(dichlorophosphinyl)methylamine (5·0 g., 0·019 mole) in ether (40 ml.). The solution was boiled under reflux (1 hr.), and ether and trimethylsilyl chloride distilled off leaving an oily residue which was distilled *in vacuo* to give *bis(chlorodimethylaminophosphinyl)-methylamine*, b.p. 114—116°/0·6 mmHg (4·8 g., 90%). The distillate was found (^1H n.m.r.) to consist of a 1 : 1 mixture of two isomers and this mixture, on standing (48 hr., 0°), gave colourless crystals (1·6 g.). These were recrystallised from pentane to give a pure diastereoisomer of the above compound, m.p. 65—66°. The liquid isomer was not completely freed from the solid. The solid isomer (0·102 g.) was converted into a 1 : 1 mixture (^1H n.m.r.) of diastereoisomers when boiled under reflux (64 hr.) in acetonitrile (3 ml.) with tetraethylammonium chloride (0·015 g.). The same result was achieved when the solid isomer was heated (100°, 24 hr.).

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