

## Dimethylaminolysis of Dichlorophosphinothioyl Compounds

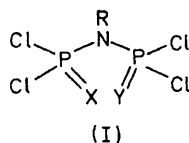
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The reactions of  $[\text{Cl}_2(\text{S})\text{P}]_2\text{NR}$  (I; R = Me or Ph) with dimethylamine have been investigated. When R = Me, mono-, non-geminal bis-, and tetrakis-dimethylamino-derivatives have been isolated, and the new ring compound

(II),  $\text{Me}_2\text{N}(\text{S})\text{P}(\text{NMe}_2)\text{P}(\text{S})\text{NMe}_2\text{S}$ , obtained by reaction with 6 mol dimethylamine heated under reflux in chloroform solution. The analogous *N*-ethyl ring compound has been obtained from (I; R = Et). Attempts to synthesise the geminal bis(dimethylamino) derivatives,  $\text{Cl}_2(\text{S})\text{P}(\text{NR})\text{P}(\text{S})(\text{NMe}_2)_2$ , have been unsuccessful, although the reaction of  $\text{Cl}_2(\text{S})\text{P}(\text{NHPH})$  with dimethylamine gives  $(\text{Me}_2\text{N})_2(\text{S})\text{P}(\text{NPh})\text{P}(\text{S})(\text{NMe}_2)(\text{NHPH})$ . Aminolysis of  $\text{Cl}_2(\text{O})\text{P}(\text{NMe})\text{P}(\text{S})\text{Cl}_2$  by dimethylamine, (dimethylamino)trimethylsilane, and (diethylamino)trimethylsilane initially occurs at the phosphinothioyl centre in non-donor solvents, but in diethyl ether solution dimethylaminolysis preferentially occurs at the phosphinoyl centre. Similar results have been obtained for  $\text{Cl}_2(\text{O})\text{P}(\text{NPh})\text{P}(\text{S})\text{Cl}_2$ .

By contrast, dimethylaminolysis of the cyclodiphosphazane  $\text{Cl}(\text{O})\text{P}(\text{NMe})\text{P}(\text{S})\text{Cl}(\text{NBU})$  occurs exclusively at the phosphonoyl centre in donor and non-donor solvents. Non-geminal bis- and tetrakis-dimethylamino-derivatives of  $\text{Cl}_2(\text{O})\text{P}(\text{NMe})\text{P}(\text{S})\text{Cl}_2$  have also been isolated.

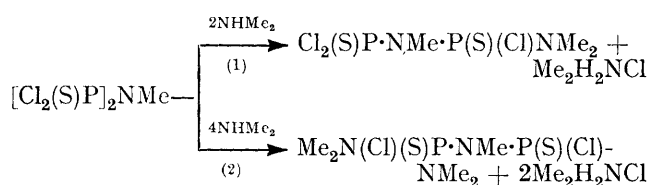
DIMETHYLAMINOLYSIS of halogenated compounds containing the P-N-P grouping has been studied<sup>1,2</sup> in some detail during recent years. It is established that the course of replacement of chlorine atoms in (I; X = Y = O) bears certain similarities to that which occurs<sup>3</sup> with



hexachlorocyclo(triphosphazene),  $\text{N}_3\text{P}_3\text{Cl}_6$ , perhaps the most important of which is a non-geminal chlorine-atom replacement scheme. Substrates of type (I) may also be expected to provide useful comparisons of the relative reactivity of phosphinoyl and phosphinothioyl groups to nucleophilic species, and with this in mind we undertook a study of dimethylaminolysis of (I; X = O or S, Y = S).

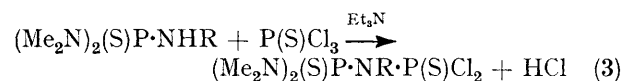
### RESULTS AND DISCUSSION

Bis(dichlorophosphinothioyl)methylamine, (I; X = Y = S, R = Me)<sup>4</sup> underwent ready reactions with dimethylamine in diethyl ether solution to give good yields of mono- and bis-dimethylamino-derivatives [equations (1) and (2)]. Although  $\text{Cl}_2(\text{S})\text{P}(\text{NPh})\text{P}(\text{S})(\text{Cl})\text{NMe}_2$  was

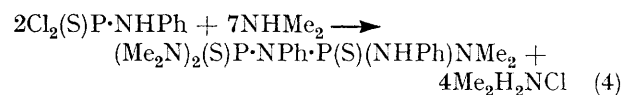


was obtained from (I; X = Y = S, R = Ph) in the

same way, it was necessary to heat under reflux in chloroform to effect formation of the bis(dimethylamino) derivative,  $\text{Me}_2\text{N}(\text{Cl})(\text{S})\text{P}(\text{NPh})\text{P}(\text{S})(\text{Cl})\text{NMe}_2$ . The formation of non-geminal bis(dimethylamino) derivatives as a mixture of diastereoisomers was readily confirmed by the appearance of two 1 : 2 : 1 triplets in the  $^1\text{H}$  n.m.r. spectrum of the *N*-methyl compound and two singlets in  $^1\text{H}$ -decoupled  $^{31}\text{P}$  n.m.r. spectra of the *N*-methyl and -phenyl compounds. The presence of diastereoisomers was also indicated by analytical-scale t.l.c., although *meso*- and *DL*-forms were not distinguished. It was hoped to synthesise the isomeric geminal bis(dimethylamino) derivatives by the route (3), but when R = Me an



adduct of triethylamine and thiophosphoryl chloride was obtained, and when R = Ph the synthesis of  $(\text{Me}_2\text{N})_2(\text{S})\text{PNHPh}$  proved impractical because of reaction (4).



The condensation product formed was identified by elemental analysis, and  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r. spectroscopy. A feature of the  $^1\text{H}$  n.m.r. spectrum was the presence of three dimethylamino-proton doublets, two of which were assignable to a  $(\text{Me}_2\text{N})_2(\text{S})\text{P}$  group adjacent to an asymmetric  $(\text{Me}_2\text{N})(\text{PhNH})(\text{S})\text{P}$  centre. The spectrum was only slightly temperature and solvent dependent, inconsistent with hindered rotation about the P-N bonds.

<sup>3</sup> R. Keat and R. A. Shaw in 'Organic Phosphorus Compounds,' eds. G. M. Kosolapoff and L. Maier, Wiley, New York, 1973, vol. 6, p. 833.

<sup>4</sup> R. Keat, *J.C.S. Dalton*, 1972, 2189.

<sup>1</sup> I. Irvine and R. Keat, *J.C.S. Dalton*, 1972, 17.

<sup>2</sup> R. Keat, *J.C.S. Dalton*, 1974, 876.

Other minor products were also obtained but not identified.

Attempts to synthesise tris(dimethylamino) derivatives of (I;  $X = Y = S$ ) were also unsuccessful, although when  $R = Me$  the major products from the reaction with 6 mol dimethylamine heated under reflux in chloroform solution were the cyclic compound (II;  $R = Me$ ),

expected for diastereotopic  $-CH_2-$  protons. Both cyclic compounds showed a complex set of dimethylamino-proton signals which formed the X part of an  $(AX_6)_2$  spin system.<sup>5</sup>

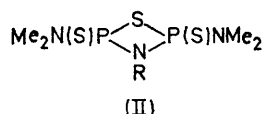
The tetrakis(dimethylamino) derivative,  $(Me_2N)(S)P \cdot NMe \cdot P(S)(NMe_2)_2$ , was readily obtained by reaction with excess of dimethylamine heated under reflux in chloro-

TABLE I  
N.m.r. data <sup>a</sup>

| Compound  | <sup>1</sup> H                            |  |   |  | <sup>31</sup> P                                     |                      |
|---|---|--|---|--|---|----------------------|
|   | $\delta(NMe)$ <sup>b</sup> /<br>p.p.m.    | $^3J(P-N-C-H)$ /<br>Hz                   | $\delta(NMe_2)$ /<br>p.p.m.                     | $^3J(P-N-C-H)$ /<br>Hz   | $\delta(^{31}P)$ <sup>c</sup> /<br>p.p.m.           | $^2J(P-N-P)$ /<br>Hz |
| $Cl_2(O)P \cdot NMe \cdot P(S)Cl_2$             | 3.46                                      | 13.7 (PO),<br>16.2                       |   |  | 10 (PO),<br>49                                      | 3                    |
| $Cl_2(O)P \cdot NMe \cdot P(S)(Cl)NMe_2$        | 3.21                                      | 15.9 (PO),<br>13.2                       | 2.95  | 14.1   | 10 (PO),<br>69                                      | 15.7                 |
| $Me_2N(Cl)(O)P \cdot NMe \cdot P(S)Cl_2$        | 3.32                                      | 11.3 (PO),<br>15.9                       | 2.81  | 12.9,<br>0.5 <sup>d</sup>  | 16.5 (PO),<br>51                                    | 14.5                 |
| $Me_2N(Cl)(O)P \cdot NMe \cdot P(S)(Cl)NMe_2$   | 3.10 (2)                                  | 12.1 (PO),<br>13.0                       | 2.79 (PO),<br>2.92                              | 13.3 (PO),<br>14.6,<br>0.3 <sup>d</sup>                            | 19 (PO),<br>74                                      | 13.9                 |
| $(Me_2N)_2(O)P \cdot NMe \cdot P(S)(NMe_2)_2$   | 3.11 (1)                                  | 12.2 (PO),<br>13.2                       | 2.80 (PO),<br>2.94                              | 13.3,<br>14.2  | 20 (PO),<br>77                                      | 9.7                  |
| $Cl_2(O)P \cdot NMe \cdot P(S)(Cl)NEt_2$        | 3.20                                      | 16.0 (PO),<br>13.4                       | 3.43 (CH <sub>2</sub> )                         | 16.4   | 9 (PO),<br>67                                       | 13.3                 |
| $Cl_2(O)P \cdot NPh \cdot P(S)Cl_2$             |   |  |   |  | 8 (PO),<br>45                                       | 30                   |
| $Cl_2(O)P \cdot NPh \cdot P(S)(Cl)NMe_2$        |   |  |   |  | 8 (PO),<br>67                                       | 35                   |
| $Cl(O)P \cdot NMe \cdot P(S)Cl \cdot NBu^t$     | 2.90 (2)<br>2.92 (1)                      | 16.1 (PO),<br>16.9<br>16.8 (PO),<br>17.2 | 1.65<br>[ $\delta(Bu^t)$ ]<br>(both<br>isomers) | 0.7<br>[ $\{^4J-$<br>(O)P-N-C-C-H]<br>$ca. ^4J-$<br>(S)P-N-C-C-H}] | -1.5 (PO),<br>40<br>-2 (PO),<br>43                  | 31.5<br>43.0         |
| $Me_2N(O)P \cdot NMe \cdot P(S)Cl \cdot NBu^t$  | 2.8                                       | <i>e</i>                                 | 2.82  | 11.2   | 6.5 (PO),<br>46.5<br>79.5                           | 32.8                 |
| $(Me_2N)_2(S)P \cdot NHMe$                      | 2.63                                      | 11.9                                     | 2.63  | 11.9   |   |                      |
| $Me_2N(S)P \cdot NMe \cdot P(S)NMe_2 \cdot S$   | 2.58                                      | 15.3                                     | 2.97  | 15.2 <sup>f</sup>  | 59  | 9.8                  |
| $Me_2N(S)P \cdot NEt \cdot P(S)NMe_2 \cdot S$   | <i>ca.</i> 3.15 (CH <sub>2</sub> )        | <i>e</i>                                 | 2.99  | 15.2 <sup>g</sup>  | 58  | 9.0                  |
| $(Me_2N)_2(S)P \cdot NPh \cdot P(S)(NMe_2)NHPH$ | 2.81 [P(S)-<br>(NMe <sub>2</sub> )(NHPH)] | 12.0                                     | 2.53<br>2.42                                    | 14.0,<br>1.0 <sup>d</sup><br>14.2,<br>0.8 <sup>d</sup>             | 75 [P(S)-<br>(NMe <sub>2</sub> ) <sub>2</sub> ], 60 | 6.0                  |

<sup>a</sup> All data obtained from  $CH_2Cl_2$  solutions. <sup>b</sup> Figures in parentheses indicate isomer ratios. <sup>c</sup> Relative to 85%  $H_3PO_4$ . <sup>d</sup>  $^5J[(S)P-N-P-N-C-H]$ . <sup>e</sup> Not measured. <sup>f</sup>  $^3J(P-N-C-H) + ^5J(P-N-P-N-C-H)$ .

$Me_2N(Cl)(S)P \cdot NMe \cdot P(S)(Cl)NMe_2$ , and  $(Me_2N)_2(S)P \cdot NMe \cdot P(S)(NMe_2)_2$ . The reaction was repeatable when



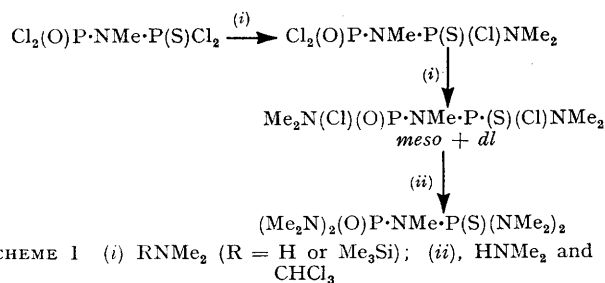
$R = Et$ , but not when  $R = Ph$ , which gave mainly  $Me_2N(Cl)(S)P \cdot NPh \cdot P(S)(Cl)NMe_2$ . Only one of the two possible geometrical isomers of (II) was apparently formed in each case. Evidence for formation of the centrosymmetric *trans*-isomer (or less likely the *cis*-isomer without a plane of symmetry) of (II;  $R = Et$ ) was obtained from the  $^{31}P$ -decoupled  $^1H$  n.m.r. spectrum. This showed two quartets in a 1 : 1 ratio, assignable to inner quarters of the AB part of an  $ABX_3$  spin system

form solution. This derivative was used in an attempt to prepare the tris(dimethylamino) derivative by heating together bis- and tetrakis-dimethylamino-derivatives, a method which proved successful in the preparation of  $Cl(Me_2N)(O)P \cdot NMe \cdot P(O)(NMe_2)_2$ ,<sup>1</sup> but here the starting materials were recovered unchanged.

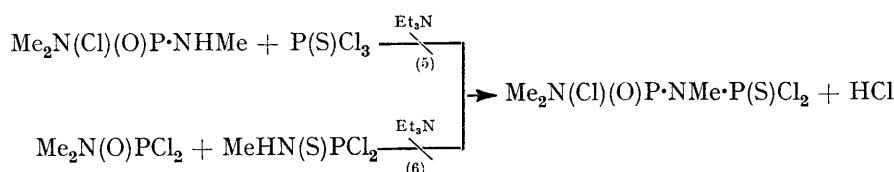
(Dichlorophosphinothioyl)(dichlorophosphinoyl)-methylamine, (I;  $X = O$ ,  $Y = S$ ,  $R = Me$ ), reacted with dimethylamine or (dimethylamino)trimethylsilane in chloroform, methylene chloride, or carbon tetrachloride solution to give good yields of mono-, bis-, and tetrakis-dimethylamino-derivatives [Scheme 1]. The fact that aminolysis occurs initially at the phosphinothioyl centre was unambiguously established from the multiplicity of lines associated with the low-field (phos-

<sup>5</sup> R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

phinothiyl) signal in the  $^{31}\text{P}$  n.m.r. spectrum, and by  $^1\text{H}\{^{31}\text{P}\}$  double resonance which clearly established that



the dimethylamino-proton doublet collapsed on irradiation at the higher  $^{31}\text{P}$ -decoupling frequency (lower field). Attempts to prepare the isomeric monodimethylamino-derivative by the reactions (5) and (6) were unsuccessful.



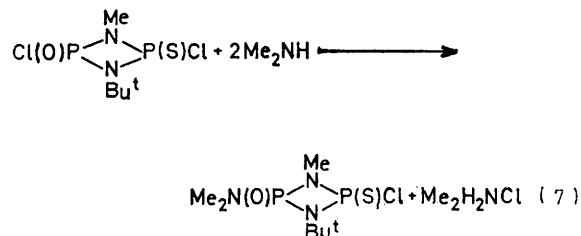
The starting dimethylamino-derivatives were recovered unchanged and unidentified adducts or condensation products were precipitated.

The presence of a mixture of diastereoisomers showed again that the dimethylamino-groups were non-geminal in the bis(dimethylamino) derivative. No tris(dimethylamino) derivative was identified. Preferential reactions at the phosphinothiyl centre appear to be a general feature of this class of compound because  $\text{Cl}_2(\text{O})\text{P}\cdot\text{NMe}\cdot\text{P}(\text{S})(\text{Cl})\text{NEt}_2$  and  $\text{Cl}_2(\text{O})\text{P}\cdot\text{NPh}\cdot\text{P}(\text{S})(\text{Cl})\text{NMe}_2$  were obtained in a similar way using non-donor solvents. The use of diethyl ether, however, had a very marked effect on the course of the reaction of (I;  $\text{X} = \text{O}$ ,  $\text{Y} = \text{S}$ ,  $\text{R} = \text{Me}$ ) with  $\text{Me}_2\text{NH}$ . The relative molar proportions (3 : 2 : 1 : 3) of the products  $\text{Cl}_2(\text{O})\text{P}\cdot\text{NMe}\cdot\text{P}(\text{S})\text{Cl}_2$ ,  $\text{Me}_2\text{N}(\text{Cl})(\text{O})\text{P}\cdot\text{NMe}\cdot\text{P}(\text{S})\text{Cl}_2$ ,  $\text{Cl}_2(\text{O})\text{P}\cdot\text{NMe}\cdot\text{P}(\text{S})(\text{Cl})\text{NMe}_2$ , and  $\text{Me}_2\text{N}(\text{Cl})(\text{O})\text{P}\cdot\text{NMe}\cdot\text{P}(\text{S})(\text{Cl})\text{NMe}_2$ , estimated by  $^1\text{H}$  n.m.r. spectroscopy, suggest that preferential reaction with dimethylamine now occurs at the phosphinothiyl centre. There seems little doubt that the small proportion of  $\text{Cl}_2(\text{O})\text{P}\cdot\text{NMe}\cdot\text{P}(\text{S})(\text{Cl})\text{NMe}_2$  is not due to facile conversion to the bis(dimethylamino) derivative, because reaction of  $\text{Cl}_2(\text{O})\text{P}\cdot\text{NMe}\cdot\text{P}(\text{S})\text{Cl}_2$  with 3.6 mol dimethylamine in diethyl ether gave only this mono(dimethylamino) derivative and the bis(dimethylamino) derivative in a 1 : 5 molar ratio. It was not possible to separate the components of the mixture to obtain a pure sample of  $\text{Me}_2\text{N}(\text{Cl})(\text{O})\text{P}\cdot\text{NMe}\cdot\text{P}(\text{S})\text{Cl}_2$ , but comparisons of the results of  $^1\text{H}$ ,  $^{31}\text{P}$ , and  $^1\text{H}\{^{31}\text{P}\}$  n.m.r. experiments left little doubt as to its identity. The same mixture of bis(dimethylamino) derivative diastereoisomers was obtained with excess of dimethylamine in diethyl ether, but, as with (I;  $\text{X} = \text{Y} = \text{S}$ ,  $\text{R} = \text{Me}$ ), complete replacement of all the chlorine atoms was only achieved on heating under reflux in chloroform solution.

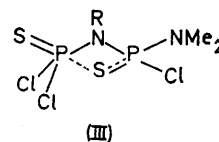
Finally, a comparison was made of the results of dimethylaminolysis of (I;  $\text{X} = \text{O}$ ,  $\text{Y} = \text{S}$ ) with that of the cyclodiphosphazane  $\text{Cl}(\text{O})\text{P}\cdot\text{NMe}\cdot\text{P}(\text{S})\text{Cl}\cdot\text{NBu}^t$ .<sup>6</sup> In this case n.m.r. experiments showed that dimethylaminolysis occurred exclusively at the phosphonoyl centre, irrespective of whether the experiment was carried out in methylene chloride or diethyl ether solution [equation (7)].

The ease with which the mono(dimethylamino) derivatives,  $\text{Cl}_2(\text{S})\text{P}\cdot\text{NR}\cdot\text{P}(\text{S})(\text{Cl})\text{NMe}_2$ , were isolated contrasts with the difficulties experienced<sup>1</sup> in obtaining pure samples of  $\text{Cl}_2(\text{O})\text{P}\cdot\text{NMe}\cdot\text{P}(\text{O})(\text{Cl})\text{NMe}_2$  which was always accompanied by substantial proportions of starting material and the bis(dimethylamino) derivative. It is difficult to understand why steric effects should make such a difference and we are tempted to conclude that

electron density is transmitted more effectively from one phosphorus atom to the next in the  $\text{>P}(\text{S})\cdot\text{NR}\cdot\text{P}(\text{S})\text{<}$  system than in  $\text{>P}(\text{O})\cdot\text{NR}\cdot\text{P}(\text{O})\text{<}$ . An alternative explanation for this behaviour, that deactivation of the second



phosphorus atom to nucleophilic attack by an intramolecular interaction, (III), is discounted on the basis of the 'hard-soft' nature of the phosphorus and sulphur atoms (see also below).



It is not surprising to find that dimethylaminolysis of the bis(dichlorophosphinothiyl)amines (I;  $\text{X} = \text{Y} = \text{S}$ ) proceeds by a non-geminal reaction scheme. This suggests that, as in the case of the phosphinothiyl analogues (I;  $\text{X} = \text{Y} = \text{O}$ ), the rate of replacement of the first chlorine atom at each phosphorus is determined by an associative process, as is common to most nucleophilic displacements at phosphorus(v).<sup>7</sup> A further similarity to the phosphinothiyl analogues is apparent in the absence of a tris(dimethylamino) derivative.

<sup>6</sup> G. Bulloch and R. Keat, unpublished work.

<sup>7</sup> R. F. Hudson, 'Structure and Mechanism in Organophosphorus Chemistry,' Academic, London, 1965.

The isolation of the ring compound (II) during attempts to synthesise the tris(dimethylamino) derivative is somewhat surprising since P-S bond formation and cleavage evidently occurs. Although we have no evidence relating to the mechanism of cyclisation, it is interesting to note that formation of this ring system seems particularly

The observation that the compounds (I; X = O, Y = S, R = Me or Ph) undergo preferential reactions at the phosphinothioyl centre in non-donor solvents is totally unexpected since phosphoryl halides are generally more readily aminolysed than thiophosphoryl halides.<sup>9</sup> These findings, and the pronounced solvent dependence

TABLE 2  
Preparative details

| Substrate<br>(amount/mmol)   | Reactants<br>(amount/mmol)  | Solvent<br>V/cm <sup>3</sup>                                     | $\theta_c/^\circ\text{C}$ | Subsequent<br>treatment<br>(t/h) | Products (%) <sup>a</sup>  | M.p.,<br>$\theta_c/^\circ\text{C}$<br>or b.p.,<br>$\theta_c/^\circ\text{C}$<br>(p/mmHg) |
|--|---|--|---------------------------|----------------------------------|--|---|
| Cl <sub>2</sub> (S)P·NMe·P(S)Cl <sub>2</sub> (30)<br>(120)                               | NHMe <sub>2</sub> (60)<br>(480)                                     | Et <sub>2</sub> O (250)<br>(500)                                 | -78                       | Stirred (½)<br>Stirred (½)       | Cl <sub>2</sub> (S)P·NMe·P(S)(Cl)NMe <sub>2</sub> (35)<br>Me <sub>2</sub> N(Cl)(S)P·NMe·P(S)(Cl)NMe <sub>2</sub> (46)<br>(both diastereoisomers) <sup>b</sup>  | 72—73<br>49—50  |
| (25)   | (excess)  | CHCl <sub>3</sub> (150)  | -78                       | Refluxed<br>(24)                 | (Me <sub>2</sub> N) <sub>2</sub> (S)P·NMe·P(S)(NMe <sub>2</sub> ) <sub>2</sub> (40)  | 85—86   |
| Cl <sub>2</sub> (S)P·NPh·P(S)Cl <sub>2</sub> (13)<br>(20)                                | (30)<br>(80)  | Et <sub>2</sub> O (200)<br>CHCl <sub>3</sub> (200)               | -78                       | Stirred (2)<br>Refluxed (3)      | Cl <sub>2</sub> (S)P·NPh·P(S)(Cl)NMe <sub>2</sub> (71)<br>Me <sub>2</sub> N(Cl)(S)P·NPh·P(S)(Cl)NMe <sub>2</sub><br>(64)<br>(both diastereoisomers) <sup>b</sup>   | 84—85<br>119—120  |
| Cl <sub>2</sub> (S)P·NMe·P(S)Cl <sub>2</sub> (24)  | (146)   | (150)  | -78                       | Refluxed<br>(12)                 | Me <sub>2</sub> N(S)P·NMe·P(S)NMe <sub>2</sub> ·S (3)  | 130—150   |
| Cl <sub>2</sub> (S)P·NEt·P(S)Cl <sub>2</sub> (365)                                       | (220)   | (150)  | -78                       | Refluxed<br>(12)                 | Me <sub>2</sub> N(S)P·NEt·P(S)NMe <sub>2</sub> ·S (2.5)  | 93—97   |
| Cl <sub>2</sub> P(S)·NPh·P(S)Cl <sub>2</sub> (18)  | (111)   | (100)  | -78                       | Refluxed<br>(15)                 | Me <sub>2</sub> N(Cl)(S)P·NPh·P(S)(Cl)NMe <sub>2</sub><br>(major product)  |   |
| (Me <sub>2</sub> N) <sub>2</sub> (S)P·NMe·P(S)-<br>(NMe <sub>2</sub> ) <sub>2</sub> (15) | Me <sub>2</sub> N(Cl)(S)P·NMe·<br>P(S)(Cl)NMe <sub>2</sub> (15)     | (100)  | 25                        | Refluxed<br>(24)                 | No reaction  |   |
| Cl <sub>2</sub> (S)P·NHPh (43)   | NHMe <sub>2</sub> (excess)  | (200)  | -78                       | Refluxed (1)                     | (Me <sub>2</sub> N)(S)P·NPh·P(S)(NMe <sub>2</sub> )NHPh<br>(50)  | 142—143   |
| Cl <sub>2</sub> (S)P·NHMe (92)   | (400)   | (200)  | -78                       | Refluxed (4)                     | (Me <sub>2</sub> N) <sub>2</sub> (S)P·NHMe (74)  | 79—80   |
| (Me <sub>2</sub> N) <sub>2</sub> (S)P·NHMe (14)  | PSCl <sub>3</sub> (14),<br>Et <sub>3</sub> N (15)                   | (100)  | 25                        | Refluxed (3)                     | (Me <sub>2</sub> N) <sub>2</sub> (S)P·NHMe,<br>Et <sub>3</sub> N·P(S)Cl <sub>2</sub> ?   |   |
| Cl <sub>2</sub> (O)P·NMe·P(S)Cl <sub>2</sub> (10)<br>(11)                                | NHMe <sub>2</sub> (21)<br>Me <sub>3</sub> SiNEt <sub>2</sub> (11)   | CH <sub>2</sub> Cl <sub>2</sub> (250)<br>(100)                   | -78                       | Stirred (1)<br>Refluxed (1)      | Cl <sub>2</sub> (O)P·NMe·P(S)(Cl)NMe <sub>2</sub> (68)<br>Cl <sub>2</sub> (O)P·NMe·P(S)(Cl)NEt <sub>2</sub> (72)   | 68 (0.05)<br>107 (0.05)   |
| Cl <sub>2</sub> (O)P·NPh·P(S)Cl <sub>2</sub> (14)  | NHMe <sub>2</sub> (28)  | (100)  | -78                       | Stirred (1)                      | Cl <sub>2</sub> (O)P·NPh·P(S)(Cl)NMe <sub>2</sub><br>(not purified)  |   |
| Cl <sub>2</sub> (O)P·NMe·P(S)Cl <sub>2</sub> (11)  | (22)  | Et <sub>2</sub> O (300)  | -78                       | Stirred (1)                      | Cl <sub>2</sub> (O)P·NMe·P(S)Cl <sub>2</sub> [3],<br>Me <sub>2</sub> N(Cl)(O)P·NMe·P(S)Cl <sub>2</sub> [2],<br>Cl <sub>2</sub> (O)P·NMe·P(S)(Cl)NMe <sub>2</sub> [1],<br>Me <sub>2</sub> N(Cl)(O)P·NMe·P(S)(Cl)-<br>NMe <sub>2</sub> [3] |   |
| (15)   | (18)  | (250)  | -78                       | Stirred (1)                      | Cl <sub>2</sub> (O)P·NMe·P(S)(Cl)NMe <sub>2</sub> [1],<br>Me <sub>2</sub> N(Cl)(O)P·NMe·P(S)(Cl)-<br>NMe <sub>2</sub> [5]  |   |
| (15)   | (61)  | (250)  | -78                       | Stirred (2)                      | Me <sub>2</sub> N(Cl)(O)P·NMe·P(S)(Cl)NMe <sub>2</sub><br>(67) (both diastereoisomers)   | 54—55.5°  |
| (22)   | (132)   | CHCl <sub>3</sub> (200)  | -78                       | Refluxed<br>(15)                 | Me <sub>2</sub> N(Cl)(O)P·NMe·P(S)(Cl)NMe <sub>2</sub><br>[1], (Me <sub>2</sub> N) <sub>2</sub> (O)P·NMe·<br>P(S)(NMe <sub>2</sub> ) <sub>2</sub> [1]  |   |
| (20)   | (Excess)  | (200)  | -78                       | Refluxed<br>(10)                 | (Me <sub>2</sub> N) <sub>2</sub> (O)P·NMe·P(S)(NMe <sub>2</sub> ) <sub>2</sub> (56)  | 115 (0.1)   |
| Me <sub>2</sub> N(Cl)(O)P·NHMe (35)  | PSCl <sub>3</sub> (35),<br>Et <sub>3</sub> N (35)                   | Et <sub>2</sub> O (150)  | 0                         | Refluxed<br>(0.5)                | Me <sub>2</sub> N(Cl)(O)P·NHMe,<br>Et <sub>3</sub> N·P(S)Cl <sub>2</sub> ?   |   |
| Cl <sub>2</sub> (S)P·NHMe (18)   | Me <sub>2</sub> NP(O)Cl <sub>2</sub> (18)<br>Et <sub>3</sub> N (18) | C <sub>6</sub> H <sub>6</sub> (75)                               | 20                        | Refluxed (3)                     | Me <sub>2</sub> N·P(O)Cl <sub>2</sub> , [Cl(S)P·NMe] <sub>n</sub> ?  |   |
| Cl(O)P·NMe·P(S)Cl·NBut <sup>t</sup><br>(10)  | NHMe <sub>2</sub> (21)  | Et <sub>2</sub> O or<br>CH <sub>2</sub> Cl <sub>2</sub><br>(100) | -78                       | Stirred (1)                      | Me <sub>2</sub> N(O)P·NMe·P(S)Cl·NBut <sup>t</sup><br>(not purified)   |   |

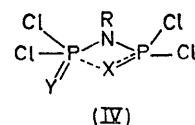
<sup>a</sup> Relative proportions are indicated in square brackets. <sup>b</sup> Separated by t.l.c. [alumina plates, eluted with light petroleum (b.p. 60—80 °C)]. <sup>c</sup> Major diastereoisomer; separated by fractional crystallisation from light petroleum.

favoured because the closely related heterocycle Me(S)P·NSiMe<sub>3</sub>·P(S)Me·S was recently obtained<sup>8</sup> from the reaction of trimethylsilyl azide with Me(S)-P·S·P(S)Me·S.

<sup>8</sup> H. W. Roesky and M. Dietl, *Angew. Chem. Internat. Edn.*, 1973, **12**, 425.

<sup>9</sup> E. Fluck, *Topics Phosphorus Chem.*, 1967, **4**, 332.

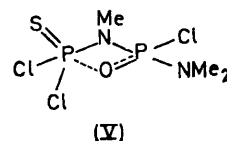
of the reaction, lead us to believe that an intramolecular associative effect is responsible for the enhanced reactivity of the phosphinothioyl centre as shown in (IV) with





X = O, Y = S, or X = S, Y = O. The former interaction is favoured since  $(\text{Me}_2\text{N})_3\text{PO}$  is known<sup>10</sup> to form an adduct with thiophosphoryl chloride,  $[(\text{Me}_2\text{N})_3\text{P}\cdot\text{O}\cdot\text{P}(\text{S})\text{Cl}_2]\text{Cl}^-$ , but there is no evidence (n.m.r.) for any reaction between  $(\text{Me}_2\text{N})_3\text{PS}$  and phosphoryl chloride at ambient temperatures. An interaction (IV; X = O, Y = S) would be favoured over an intermolecular interaction on entropy grounds, and would increase the importance of heterolysis of the (S)P-Cl bond in the rate-determining step of the reaction. We further suggest that in diethyl ether, a donor solvent, the importance of intramolecular effects are diminished and more 'normal' orders of reactivity are observed. Intramolecular effects of this type will not be possible in the cyclodiphosphazane  $\text{Cl}(\text{O})\text{P}\cdot\text{NMe}\cdot\text{P}(\text{S})\text{Cl}\cdot\text{NBu}^t$ , which is consistent with the fact that it undergoes reactions with dimethylamine at the phosphonoyl-centre in both

structure of the tris(dimethylamino) derivative, but no evidence for its presence in reaction mixtures was obtained.



N.m.r. data for the (phosphinothioyl)(phosphinoyl)-amines are given in Table 1 and analogous data for the bis(phosphinothioyl)amines will be published elsewhere.<sup>12</sup>

#### EXPERIMENTAL

Solvents were dried by conventional means. Ethanol was removed from chloroform by contact with basic alumina. Phosphoryl chloride and thiophosphoryl chloride were purified by distillation. Triethylamine was dried by distillation from sodium. Dimethylamine and  $\text{Et}_2\text{N}\cdot\text{SiMe}_3$  were

TABLE 3  
Analytical data<sup>a</sup>  
Found

| Compound  | C     | H    | N     | Cl                | m/e | Calc. | C     | H    | N    | Cl                | m/e <sup>b</sup> |
|---|-------|------|-------|-------------------|-----|-------|-------|------|------|-------------------|------------------|
| $\text{Cl}_2(\text{S})\text{P}\cdot\text{NMe}\cdot\text{P}(\text{S})(\text{Cl})\text{NMe}_2$                    | 11.7  | 3.2  |       | 33.5              | 304 |       | 12.0  | 3.0  |      | 33.8              | 304              |
| $[\text{Me}_2\text{N}(\text{Cl})(\text{S})\text{P}]_2\text{NMe}$  | 18.8  | 4.8  |       |                   | 313 |       | 19.1  | 4.8  |      |                   | 313              |
| $[(\text{Me}_2\text{N})_2(\text{S})\text{P}]_2\text{NMe}$   | 32.7  | 8.25 | 21.4  |                   | 331 |       | 32.6  | 8.2  | 21.1 |                   | 331              |
| $\text{Me}_2\text{N}(\text{S})\text{P}\cdot\text{NMe}\cdot\text{P}(\text{S})\text{NMe}_2\cdot\text{S}$          | 22.1  | 5.5  | 15.5  | 35.1 <sup>c</sup> | 275 |       | 21.8  | 5.5  | 15.3 | 34.9 <sup>c</sup> | 275              |
| $\text{Me}_2\text{N}(\text{S})\text{P}\cdot\text{NPh}\cdot\text{P}(\text{S})\text{NMe}_2\cdot\text{S}$          | 25.2  | 5.8  | 14.95 |                   | 289 |       | 24.9  | 5.9  | 14.5 |                   | 289              |
| $\text{Cl}_2(\text{S})\text{P}\cdot\text{NPh}\cdot\text{P}(\text{S})(\text{Cl})\text{NMe}_2$                    | 26.35 | 3.15 | 7.8   | 29.05             | 366 |       | 26.15 | 3.0  | 7.6  | 28.9              | 366              |
| $[\text{Me}_2\text{N}(\text{Cl})(\text{S})\text{P}]_2\text{NPh}$  | 32.0  | 4.55 |       | 18.7              | 393 |       | 31.9  | 4.55 |      | 18.85             | 393              |
| $(\text{Me}_2\text{N})(\text{S})\text{P}\cdot\text{NPh}\cdot\text{P}(\text{S})(\text{NMe}_2)\text{NHPh}$        | 49.0  | 6.5  | 16.1  | 13.9 <sup>d</sup> | 441 |       | 48.95 | 6.6  | 15.9 | 14.0 <sup>d</sup> | 441              |
| $\text{Cl}_2(\text{O})\cdot\text{P}\cdot\text{NMe}\cdot\text{P}(\text{S})(\text{Cl})\text{NMe}_2$               | 12.5  | 3.2  | 9.5   |                   |     |       | 12.4  | 3.1  | 9.7  |                   |                  |
| $\text{Me}_2\text{N}(\text{Cl})(\text{O})\text{P}\cdot\text{NMe}\cdot\text{P}(\text{S})(\text{Cl})\text{NMe}_2$ | 20.0  | 5.1  | 14.2  |                   | 297 |       | 20.15 | 5.1  | 14.1 |                   | 297              |
| $(\text{Me}_2\text{N})_2(\text{O})\text{P}\cdot\text{NMe}\cdot\text{P}(\text{S})(\text{NMe}_2)_2$               | 32.9  | 8.5  | 20.5  |                   | 315 |       | 34.3  | 8.6  | 22.2 |                   | 315              |
| $\text{Cl}_2(\text{O})\text{P}\cdot\text{NMe}\cdot\text{P}(\text{S})(\text{Cl})\text{NMe}_2$                    | 20.0  | 4.1  | 8.5   | 32.3              | 316 |       | 18.9  | 4.1  | 8.8  | 33.5              | 316              |
| $\text{Cl}(\text{O})\text{P}\cdot\text{NMe}\cdot\text{P}(\text{S})\text{Cl}\cdot\text{NBu}^t$                   | 20.8  | 4.7  | 8.7   |                   | 280 |       | 21.4  | 4.3  | 10.0 |                   | 280              |
| $\text{Me}_2\text{N}(\text{O})\text{P}\cdot\text{NMe}\cdot\text{P}(\text{S})\text{Cl}\cdot\text{NBu}^t$         |       |      |       |                   | 289 |       |       |      |      |                   | 289              |
| $(\text{Me}_2\text{N})_2(\text{S})\text{P}\cdot\text{NMe}$  | 33.3  | 8.95 | 23.05 |                   | 181 |       | 33.15 | 8.9  | 23.2 |                   | 181              |

<sup>a</sup> Elemental analyses figures are given in %. <sup>b</sup> For ions containing <sup>35</sup>Cl. <sup>c</sup> S analysis. <sup>d</sup> P analysis.

methylene chloride and diethyl ether solutions. Nucleophilic displacements at phosphorus(v) in four-membered rings generally take place with retention of configuration.<sup>11</sup> This may be the case here, but we have no reason to believe that formation of the expected trigonal-bipyramidal intermediate and any subsequent pseudo-rotation step will invalidate the conclusion that, in general, the phosphonoyl centre is more reactive than the phosphinothioyl centre to dimethylamine.

The formation of a bis(dimethylamino) derivative,  $\text{Me}_2\text{N}(\text{Cl})(\text{O})\text{P}\cdot\text{NMe}\cdot\text{P}(\text{S})(\text{Cl})\text{NMe}_2$ , is anticipated in terms of the reduced electrophilic nature of the phosphinothioyl centre in non-donor solvents. An interaction of the type (V) might be possible even in diethyl ether solution, and may, in part, be responsible for the relative ease with which the bis(dimethylamino) derivative is formed in this solvent. It would also be instructive to know the

obtained commercially and used without further purification. The compounds  $\text{Me}_2\text{N}\cdot\text{SiMe}_3$ ,<sup>13</sup>  $\text{Cl}_2(\text{O})\text{P}\cdot\text{NMe}_2$ ,<sup>14</sup>  $\text{Cl}_2(\text{S})\text{P}\cdot\text{NHMe}$ ,<sup>4</sup>  $\text{Cl}_2(\text{S})\text{P}\cdot\text{NHPh}$ ,<sup>4</sup>  $[\text{Cl}_2(\text{S})\text{P}]_2\text{NMe}$ ,<sup>4</sup>  $[\text{Cl}_2(\text{S})\text{P}]_2\text{NEt}$ ,<sup>4</sup>  $\text{Cl}_2(\text{O})\text{P}\cdot\text{NMe}\cdot\text{P}(\text{S})\text{Cl}_2$ ,<sup>4</sup>  $\text{Cl}_2(\text{O})\text{P}\cdot\text{NPh}\cdot\text{P}(\text{S})\text{Cl}_2$ ,<sup>4</sup> and  $\text{Cl}(\text{O})\text{P}\cdot\text{NMe}\cdot\text{P}(\text{S})\text{Cl}\cdot\text{NBu}^t$ <sup>6</sup> were prepared by literature methods.

<sup>1</sup>H and <sup>31</sup>P N.m.r. spectra were recorded on a Jeol C60HL spectrometer and selective-noise <sup>31</sup>P and <sup>1</sup>H decoupling carried out with a Schomandl ND100M frequency synthesiser and a Jeol SDHC unit. Aminolysis reactions were carried out as previously described<sup>1,2</sup> and details are given in Table 2. Analytical data are given in Table 3 and n.m.r. data in Table 1.

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<sup>14</sup> E. Fluck and W. Haubold in 'Organic Phosphorus Compounds,' eds. G. M. Kosolapoff and L. Maier, Wiley, New York, 1973, vol. 6, p. 579.