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Derivatives of *cis*-$NPCL_2(NSOCl)_2$ and $(NPCl_2)_2NSOCl$. Part VIII*. Dimethylamino Derivatives of *cis*-$NPCl_2(NSOCl)_2$

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Cis-$NPCl_2(NSOCl)_2$ (I) reacts with dimethylamine in a molar ratio of 1:2 to give four isomeric mono-substituted compounds $N_3PS_2O_2Cl_3NMe_2$; the position of the substituent depends strongly on the solvent. The second reaction step leads to three isomeric bis(dimethylamino) derivatives. Furthermore, two trisubstituted and two tetrasubstituted derivatives are described. Structures are assigned on the basis of ^1H NMR spectra. A suggestion for the substitution mechanism of the first step is offered. The ^{31}P NMR spectra of the secondary-amino derivatives of the ring systems $(NPCl_2)_3$, $(NPCl_2)_2NSOCl$ and $NPCl_2(NSOCl)_2$, known up to now, are compared.

Introduction

In the past extensive studies have been made on the behaviour of dimethylamine towards $(NPCl_2)_3$ [1–4]. In the course of our investigations of the chemical properties of *cis*-$NPCl_2(NSOCl)_2$ (I) we performed a series of reactions of this ring compound with dimethylamine in order to elucidate the substitution pattern. Furthermore, we tried to clarify the structures of the derivatives on the basis of their ^1H NMR spectra, which have turned out to be very useful expedients for the identification of the dimethylamino derivatives of $(NPCl_2)_3$ [5–7].

Since the preparation of (I) [8, 9] a series of papers has appeared, which deal with its behaviour towards different reagents. It was observed that (I) could be converted into *cis*- and *trans*-$NPCl_2(NSOF)_2$ and *cis*- and *trans*-$NPCl_2(NSOPh)_2$ by reaction with SbF_3 or AgF_2 [10–12] and $C_6H_6/AlCl_3$ [13], respectively. Some attention has also been paid to the aminolysis of (I) and its derivatives mentioned above. Reaction of (I) with various amines in a molar ratio of 1:2 in diethyl ether leads to the formation of mono(amino) derivatives [10], in which the amino group is attached to the phosphorus atom. In acetonitrile, however, (I) reacts with piperidine (molar ratio 1:2) to form two isomeric mono(piperidino) derivatives [14], in which the amino group is attached to a sulphur atom. From an investigation of the reactivity of butylamines towards (I) [15] it was concluded that an increasing bulk of the amine leads to an increasing tendency to substitute a chlorine atom bonded to sulphur. *Cis*-$NPCl_2(NSOF)_2$ and *trans*-$NPCl_2(NSOPh)_2$ react with amines to form mono- and disubstituted derivatives, in which the F- and Ph-groups are not replaced [13, 14, 16].

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Experimental

All experiments were carried out under dry nitrogen. *Cis*-$NPCl_2(NSOCl)_2$ was prepared by the method of Clipsham and co-workers [9]. Dimethylamine (Fluka *purum*) was distilled via a KOH column into a calibrated glass tube, cooled at −10 °C, from which the desired amount of amine was drawn off. All solvents were purified and dried by conventional methods. Elemental analyses were carried out at the Microanalytical Department of this University under the supervision of Mr. A. F. Hamminga. Infrared spectra (4000–400 cm^{-1}) were recorded on a Hitachi EPI-G spectrophotometer, using KBr-optics. The spectra were calibrated by means of polystyrene film bands. Mass spectra were recorded on an AEI M.S. 9 mass spectrometer operating at 70 eV, using an accelerating voltage of 8 kV. The samples were introduced directly by a conventional inlet system at 100 °C (Mr. A. Kiewiet, Department of Organic Chemistry, this University). Melting points were determined on a Büchi melting point apparatus and are uncorrected.

Aminolysis

Procedure A.

A quantity of a mmol (a in the range 2–40) of ring compound was dissolved in $15a$ ml of solvent; the solution was cooled to −35 °C, and the amine was added in about 5 minutes under vigorous stirring. The

reaction mixture was allowed to warm up to room temperature and then stored overnight, all under continuous stirring. After evaporation of the solvent the residue was extracted twice with 10*a* ml of diethyl ether, leaving the insoluble dimethylamine hydrochloride (if diethyl ether was used as reaction medium, the salt was directly filtered off and washed with a second portion of ether). The ethereal filtrates were evaporated to dryness, the residue was characterized spectroscopically (^1H and ^{31}P NMR, IR), and recrystallized from a suitable solvent.

Procedure B

A solution of *a* mmol of ring compound in 10*a* ml of acetonitrile was added in about 15 minutes to a solution of the amine in 10*a* ml of acetonitrile, cooled at −35 °C, under vigorous stirring. The reaction mixture was treated as described under A. Procedure B was used only for reactions with an excess of amine.

Reaction of cis-$NPCl_2(NSOCl)_2$ *(I) with* $HNMe_2$ *in* Et_2O *(molar ratio 1:2)*

The crude reaction product contained two isomers, (II) and (III) (ratio 6:1), with formula $NPCl\text{-}NMe_2(NSOCl)_2$. Total yield of crystalline material after recrystallization from $Et_2O/n\text{-}C_5H_{12}$ (1:1) 26%. Only a small quantity of (II) could be isolated in a pure state; m.p. 66–67 °C.

Anal. $C_2H_6N_4PS_2O_2Cl_3$ (M.W. 319.56).

Calcd. C 7.52 H 1.89 N 17.53 S 20.07 Cl 33.28.

Found for (II): C 7.47, 7.29 H 1.89, 1.82 N 17.69, 17.71 S 20.43, 20.36 Cl 33.09, 33.25.

IR: 2935w 2013w 1991w 1890w 1472w 1450m 1319vs 1207m,br 1180s,br 1130s 1063s 1034s 1005s 855s 846s 751m 709vs 647vs 542m 530m 520s 502s 455m 427m.

Mass spectrum: m/e 318 $(M\ ^{35}Cl)^+$ 14%; m/e 283 $(M-{}^{35}Cl)^+$ 100%.

Reaction of cis-$NPCl_2(NSOCl)_2$ *(I) with* $HNMe_2$ *in MeCN (molar ratio 1:2)*

In this case the product contained two isomers, (IV) and (V) (ratio 2:1), with formula $NPCl_2NSO\text{-}ClNSONMe_2$. Total yield of crystalline material 51%. (IV) could be purified in reasonable yield (30%) by recrystallization from $Et_2O/n\text{-}C_5H_{12}$ (4:1); m.p. 104–105.5 °C (a small fraction of (IV), recrystallized from pure Et_2O gave m.p. 133–134 °C).

Anal. $C_2H_6N_4PS_2O_2Cl_3$ (M.W. 319.56).

Calcd. C 7.52 H 1.89 N 17.53 S 20.07 Cl 33.28.

Found for (IV): C 7.75, 7.76 H 1.96, 1.95 N 17.64, 17.64 S 20.40, 20.41 Cl 33.31, 33.03.

IR: 2935w 1975w 1880w 1460m 1315s 1298w 1260w 1174vs,br 1122vs 1040s 963s 851m 832s 759s 697s 648s 632w 607vs,br 543vs 527w 504w 453w 438w.

Mass spectrum: m/e 318 $(M\ ^{35}Cl)^+$ 20%; m/e 240 $(M-{}^{35}Cl-NC_2H_5)^+$ 51%; m/e 44 $(NC_2H_6)^+$ 100%.

Reaction of $NPCl_2NSOClNSONMe_2$ *(IV) with* $HNMe_2$ *in* Et_2O *(molar ratio 1:2)*

The crude product consisted mainly of two isomers, (VI) and (VII) (ratio 3:1), with formula $NPCl\text{-}NMe_2NSOClNSONMe_2$. Total yield of crystalline material 56%. (VI) could be purified by recrystallization from CCl_4 (yield 38%); m.p. 89–90 °C.

Anal. $C_4H_{12}N_5PS_2O_2Cl_2$ (M.W. 328.18).

Calcd. C 14.64 H 3.69 N 21.34 S 19.54 Cl 21.61.

Found for (VI): C 14.52, 14.63 H 3.71, 3.62 N 21.31, 21.36 S 19.68, 19.73 Cl 21.78, 21.77.

IR: 2940m 1460m 1309vs 1280s 1206vs 1179vs 1124vs 1060m 1047w 998s 956vs 861s 839s 763s 720vs 645w 621s 552vs 524s 507m 469m 424m.

Mass spectrum: m/e 327 $(M\ ^{35}Cl)^+$ 50%; m/e 249 $(M-{}^{35}Cl-NC_2H_5)^+$ 100%.

Recrystallization of the residue from $n\text{-}C_5H_{12}$ gave a small amount of pure (VII), m.p. 84–86 °C.

Anal. $C_4H_{12}N_5PS_2O_2Cl_2$ (M.W. 328.18).

Calcd. C 14.64 H 3.69 N 21.34 S 19.54 Cl 21.61.

Found for (VII): C 14.85, 14.96 H 3.67, 3.65 N 21.22, 21.21 S 20.05, 19.91 Cl 21.36, 21.35.

IR: 2935m 1460m 1320vs 1285vs 1209vs 1182vs 1130vs 1066m 1040m 1002s 954s 865s 841s 764s 722vs 698m 627/617vs 562w 534s 522vs 508s 472m 462w 422w.

Mass spectrum: m/e 327 $(M\ ^{35}Cl)^+$ 15%; m/e 249 $(M-{}^{35}Cl-NC_2H_5)^+$ 30%; m/e 44 $(NC_2H_6)^+$ 100%.

Reaction of $NPCl_2NSOClNSONMe_2$ *(1:1 mixture of (IV) and (V)) with* $HNMe_2$ *in* Et_2O *(molar ratio 1:2)*

Here, the crude product contained mainly three isomeric disubstituted derivatives $NPClNMe_2NSOCl\text{-}NSONMe_2$. In addition to (VI) and (VII), a third isomer (VIII) was also formed (ratio (VI):(VII):(VIII) = 2:1:3). (VIII) could however not be isolated in a pure state.

Reaction of $NPCl_2NSOClNSONMe_2$*(IV) with* $HNMe_2$*in MeCN (molar ratio 1:2)*

If the reaction of (IV) with $HNMe_2$ was carried out in acetonitrile, isomer (VIII) was also formed in addition to the main products (VI) and (VII) (ratio (VI):(VII):(VIII) = 7:5:1).

Reaction of cis-$NPCl_2(NSOCl)_2$ *(I) with* $HNMe_2$ *in* Et_2O *(molar ratio 1:4)*

In the crude reaction mixture the following derivatives were discernable: (II), (VI), (VII) and (VIII) in a ratio 2:1:3:3 (approximately).

TABLE I. ^1H and ^{31}P NMR Data.

Compound		^1H NMR Data[a]				^{31}P NMR Data[a]			Struct. Assignm.[b]
		δ(PNC*H*) ppm	$^3J_{PH}$ Hz	δ(SNC*H*) ppm	$^5J_{PH}$ Hz	δ(PCl_2) ppm	δ(PClAm) ppm	δ(PAm_2) ppm	
cis-$NPCl_2(NSOCl)_2$	I					27.6			
$NPClNMe_2(NSOCl)_2$	II	2.92	16.1				20.1		A or B
$NPClNMe_2(NSOCl)_2$	III	2.96	17.5				23.2		B or A
$NPCl_2NSOClNSONMe_2$	IV			2.89	1.0	28.8			E
$NPCl_2NSOClNSONMe_2$	V			2.99	1.0	28.4			D
$NPClNMe_2NSOClNSONMe_2$	VI	2.89	16.8	2.88	0.6		26.1		F
$NPClNMe_2NSOClNSONMe_2$	VII	2.85	16.7	2.84	0.6		25.3		G
$NPClNMe_2NSOClNSONMe_2$	VIII	2.86	16.1	2.96	0.5		24.1		H
$NPClNMe_2(NSONMe_2)_2$	IX	2.79	17.2	2.83	0.7		28.4		K
$NPClNMe_2(NSONMe_2)_2$	X	2.80	16.8	2.86	0.5		28.3		L
$NP(NMe_2)_2(NSONMe_2)_2$	XI	2.72	11.5	2.78	<0.5			19.5	P
		2.68	11.9						
$NP(NMe_2)_2(NSONMe_2)_2$	XII			2.83[c]	<0.5			19.3	N
		2.73[c]	11.5[c]						
$NPCl_2NSONMe_2NSOPh$	XIII			2.89	1.0	24.6			Q
$NPCl_2NSONMe_2NSOPh$	XIV			2.63	0.9	26.0			R

[a]δ-values defined as positive in low-field direction. [b]*Cf.* Figs. 1 and 2 and text. [c]Overlapping signals.

Reaction of cis-$NPCl_2(NSOCl)_2$ *(I) with* $HNMe_2$ *in MeCn (molar ratio 1:13.6) by procedure A*

The crude reaction product consisted of two isomers (XI) and (XII) with formula $NP(NMe_2)_2(NSONMe_2)_2$ (ratio 3:1). All efforts to separate the components from the oily mixture failed and no satisfactory element analyses could be obtained. However, the identity of the products could be established unequivocally by spectroscopic measurements (^1H and ^{31}P NMR and mass spectra).

Mass spectrum: m/e 345 $(M)^+$ 21%; m/e 258 $(M-N_2C_4H_{11})^+$ 36%; m/e 44 $(NC_2H_6)^+$ 100%.

Reaction of cis-$NPCl_2(NSOCl)_2$ *(I) with* $HNMe_2$ *in MeCN (molar ratio 1:13.6) by procedure B*

Again, the two isomers (XI) and (XII) were formed, but their ratio (10:1) differed considerably from that formed by procedure A.

Reaction of $NPCl_2NSOClNSONMe_2$ *(IV) with* $HNMe_2$ *in MeCN (molar ratio 1:4.5)*

The crude product contained mainly four different compounds. In addition to the tetrasubstituted derivatives (XI) and (XII) two new compounds were present, which turned out to be trisubstituted derivatives (IX) and (X) with formula $NPClNMe_2(NSONMe_2)_2$. Recrystallization from Et_2O afforded a first fraction of crystalline material, which after repeated crystallization yielded 15% of pure (IX), m.p. 128–129 °C.

Anal. $C_6H_{18}N_6PS_2O_2Cl$ (M.W. 336.80).

Calcd. C 21.40 H 5.39 N 24.95 S 19.04 Cl 10.53.

Found for (IX): C 21.40, 21.57 H 5.36, 5.42 N 24.87, 24.99 S 18.94, 18.84 Cl 10.62, 10.59.

IR: 3025w 2930m 1460s 1264vs 1238m 1168vs 1140vs 1061w 1031m 992s 955m 931s 860s 845s 796s 713s 690s 607vs 529m 513vs 450w 430w 415w.

Mass spectrum: m/e 336 $(M\ ^{35}Cl)^+$ 2%; m/e 249 $(M-N_2C_4H_{11})^+$ 62%; m/e 44 $(NC_2H_6)^+$ 100%.

A second crystalline fraction from Et_2O consisted of (X), but this compound could not be purified to a constant melting point.

Anal. $C_6H_{18}N_6PS_2O_2Cl$ (M.W. 336.80).

Calcd. C 21.40 H 5.39 N 24.95 S 19.04 Cl 10.53

Found for (X): C 21.32, 21.34 H 5.54, 5.45 N 24.92, 24.68 S 19.23, 19.23 Cl 10.50, 10.60

IR: 2975w 2920m 2845w 2815w 1268s 1242sh 1191sh 1170s 1145vs 1055m 1010m 997w 951s 860w 850s 793m 721s 698s 595m 544m 525m 508m 470m 446w 432w.

Mass spectrum: m/e 336 $(M\ ^{35}Cl)^+$ 1%; m/e 249 $(M-N_2C_4H_{11})^+$ 44%; m/e 44 $(NC_2H_6)^+$ 100%.

Friedel–Crafts Reaction of $NPCl_2NSOClNSONMe_2$ *(IV)*

1.00 g (3.13 mmol) of (IV) and 0.84 g (6.26 mmol) of anhydrous $AlCl_3$ were boiled under reflux in 20 ml of benzene during 48 hours. The resulting brown solution was hydrolyzed with a hydrochloric acid/ice mixture and the layers were separated. After

washing of the benzene layer with water and drying over $CaCl_2$ the organic phase was evaporated to dryness. A spectroscopic study of the resulting crude product showed the presence of two isomeric forms (XIII) and (XIV) of $NPCl_2NSOPhNSONMe_2$ (ratio 6:1). (XIII) could be isolated in 10% yield after repeated recrystallization from n-C_5H_{12}; m.p. 45–46.5 °C.

Anal. $C_8H_{11}N_4PS_2O_2Cl_2$ (M.W. 361.20).

Calcd. C 26.60 H 3.07 N 15.51 S 17.75 Cl 19.63.

Found for (XIII): C 26.45, 26.51 H 3.02, 3.00 N 15.61, 15.39 S 17.85, 17.87 Cl 19.48, 19.48.

IR: 2000w 1905w 1475w 1455m 1445m 1276vs, br 1179sh 1155vs,br 1066w 997m 941s 833s 751s 710s 686s 643s 589s 550s 525s 468w.

Mass spectrum: m/e 360 $(M\ ^{35}Cl)^+$ 21%; m/e 225 $(M-C_8H_{11}N_2)^+$ 69%; m/e 44 $(NC_2H_6)^+$ 100%.

NMR Spectra

Both the purified compounds and the crude reaction products were subjected to ^1H and ^{31}P NMR measurements. The ratio of formation of the isomers, as given in the experimental part, were calculated from the ^1H NMR spectra of the crude reaction products.

^1H NMR spectra were recorded at 35 °C on a Varian A-60 spectrometer, using TMS as internal reference; ^{31}P NMR spectra were recorded by Mr. R. H. Fokkens (University of Amsterdam) at 37 °C on a Varian XL-100 FT spectrometer, operating at 40.5 MHz, using 85% H_3PO_4 as external standard. In all cases $CDCl_3$ was used as solvent. The NMR data are summarized in Table I.

Discussion

^1H NMR Spectra

The proton resonance spectra of the dimethylamino derivatives of *cis*-$NPCl_2(NSOCl)_2$ are relatively easy to be interpreted. Since only one phosphorus atom is present in the ring system, no complicating long-range coupling effects occur as in the derivatives of the cyclophosphazenes [17]. Sulphur-bonded groups can be readily distinguished from phosphorus-bonded ones from their very small values of J_{PH} (^{31}P-decoupling experiments with compounds (IV) and (V) confirmed that the splitting of the signals is caused by a five-bond P–H coupling). As for the dimethylamino derivatives of $(NPCl_2)_3$ the mean position of the signals shifts upfield with increasing degree of aminolysis. The magnitude of $^3J_{PH}$ is dependent on the degree of aminolysis of the phosphorus atom: The $^3J_{PH}$ values for $\equiv PClNMe_2$ groups all lie above 16 Hz, those for $\equiv P(NMe_2)_2$ groups below 12 Hz. The $^5J_{PH}$ values tend to decrease with increasing degree of aminolysis (Table I).

Structures

The investigations of the NMR spectra of the dimethylamino phosphazenes by Shaw and coworkers [5] have shown that NMe_2 groups are shielded to some extent by other NMe_2 groups. This shielding effect depends markedly on the relative position of the groups; if a group is situated *trans* to a second one the effect does not exceed the value of 0.02 ppm, a *cis*-situated group exercises a shielding effect of about 0.05 ppm and a geminally situated one an effect of about 0.10 ppm. In the following these observations will be applied to elucidate the structures of the dimethylamino derivatives of *cis*-$NPCl_2(NSOCl)_2$, since no other possibilities are present for the moment.

The tetrasubstituted derivatives are the only compounds in the series, the structures of which can be clarified unambiguously by means of the ^1H NMR measurements; compound (XII) contains two chemically different phosphorus-bonded substituents (Table I) and will therefore possess structure N (Fig. 1). The group at the oxygen side of the ring plane undoubtedly will be the less shielded one and the low-field NMR signal (2.73 ppm, Table I) can be assigned to this group. Structure P can then be assigned to compound (XI). In Figure 1 the calculated chemical shifts for the tri-, di-, and monosubstituted derivatives are given, using the "shielding values" as obtained from the derivatives of $(NPCl_2)_3$, and starting from the δ-values of the fully aminolysed derivatives. From the observed equivalence of the protons of the sulphur-bonded dimethylamino groups in the two trisubstituted derivatives isolated, (IX) and (X), it can be derived that these compounds have the sulphur-bonded groups in *cis*-positions (structures K and L). It is easily derived that in structure K ("all-*cis*") the dimethylamino protons will be somewhat more shielded than in structure L (Fig. 1) and hence we assign structure K to compound (IX) and structure L to compound (X) (compare Table I). The disubstituted derivatives (VI) and (VII) are formed in ether from one monosubstituted derivative (IV). As it does not seem very likely that an inversion of a sulphur centre occurs during substitution at the phosphorus atom (during the reaction of (I) with $HNMe_2$ in Et_2O again only two derivatives are formed, it can be assumed that the configurations around the sulphur centres of compounds (VI), (VII) and (IV) are the same. Comparison of the observed shifts of (VI) and (VII) with the shifts calculated for the structures F, G, H, and J (Fig. 1) leads to the conclusion that (VI) has structure F and (VII) structure G (substituents *cis*: more shielded); consequently (IV) will have structure E and, therefore, its isomer (V) structure D. The third disubstituted derivative (VIII) (formed from (V) in the reaction of a 1:1 mixture of (IV) and (V) with $NHMe_2$) probably has structure H, the calculated δ-values of which agree better with

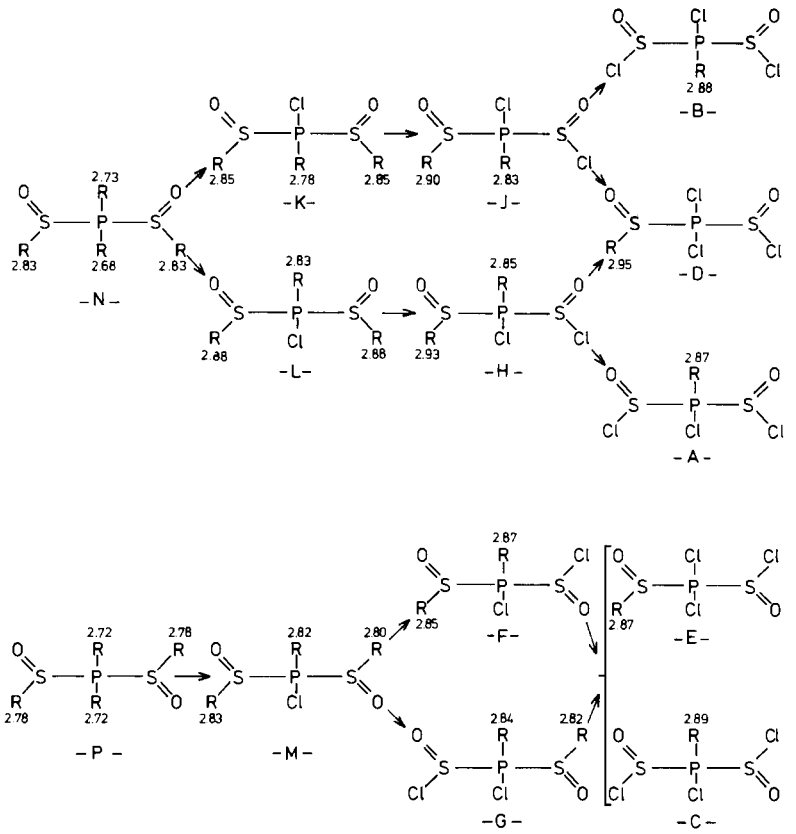

Figure 1. Calculated δ-values for all possible structures, using shielding values of 0.05, 0.02 and 0.10 ppm for *cis*-, *trans*-, and geminally-situated groups (R = NMe_2), respectively, starting from the observed values for the tetrasubstituted isomers (XI) (=P) and (XII) (=N).

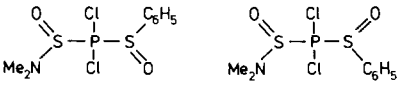

Figure 2. Possible structures of $NPCl_2NSOPhNSONMe_2$.

the observed ones than those of structure J. Moreover, the formation of an isomer with *trans*-situated substituents from (V) is in agreement with the results of reaction of (IV) with $HNMe_2$, in which again the formation of a *trans*-isomer is preferred to the formation of a *cis*-isomer (see the structural assignments above). The structures of the isomers of $NPClNMe_2(NSOCl)_2$, (II) and (III), cannot be resolved properly in this way. Since inversion of a sulphur centre during substitution at the phosphorus atom seems very unlikely, the two isomers formed from *cis*-$NPCl_2(NSOCl)_2$ in reaction of (I) with $HNMe_2$ will have structures A and B, but not structure C.

The structural assignments of the phenylated derivatives (XIII) and (XIV) present no difficulties. A study of the mixed dimethylaminophenyl derivatives

TABLE II. Best Shielding Values (in ppm) for the Phosphorus- and Sulphur-bonded Dimethylamino Groups.

Observed Group	Shielding Group				
	trans S-bd.	*cis* S-bd.	*trans* P-bd.	*cis* P-bd.	*gem.*
P-bonded	0.05	0.08			0.09
S-bonded	0.05	0.10	0.01	0.05	

of $(NPCl_2)_3$ has shown [18] that phenyl groups exercise a considerable shielding effect on *cis*-situated dimethylamino groups, and therefore structure Q can safely be ascribed to (XIII) and R to (XIV) (Figure 2).

As mentioned above we used in our structural assignments shielding constants as observed for the derivatives of $(NPCl_2)_3$. It is now possible to evaluate the "best shielding values" of the differently situated dimethylamino groups for the derivatives of (I). From these values (Table II) it is apparent that the sulphur-bonded groups exercise a larger shielding effect than the phosphorus-bonded ones. This phenomenon may be caused by a difference in con-

TABLE III. Observed and Calculated Proton δ-Values (in ppm) of the NMe_2 Derivatives of $NPCl_2(NSOCl)_2$.

Compound	Nr. of NMe_2 gr.	Assigned Structure	Observed		Calculated	
			P-bonded	S-bonded	P-bonded	S-bonded
XII	4	N	2.68; 2.73	2.83	2.68; 2.73	2.83
XI	4	P	2.72	2.78	2.72	2.78
X	3	L	2.80	2.86	2.82	2.88
IX	3	K	2.79	2.83	2.77	2.84
	3	M			2.81	2.79; 2.83
VIII	2	H	2.86	2.96	2.87	2.98
VII	2	G	2.85	2.84	2.86	2.84
VI	2	F	2.89	2.88	2.89	2.88
	2	J			2.85	2.94
V	1	D		2.99		2.99
IV	1	E		2.89		2.89
III[a]	1	B	2.96		2.93	
II[a]	1	A	2.92		2.92	
	1	C			2.94	

[a]Assignments doubtful, see text.

figuration around the sulphur atoms and the phosphorus atom, as is found in (I) [20]. In Table III the δ-values, calculated with the aid of the values of Table II (and again starting from the observed values for the tetrasubstituted derivatives), are compared with the experimental ones. As may be seen the calculated values agree in a satisfactory way with the experimental ones for all assigned structures. However, definite structure determinations of the derivatives can only be achieved by means of an X-ray structure determination (*e.g.* of the key compound (IV)).

Substitution Pattern

The most striking result of this investigation is the completely different behaviour of (I) towards dimethylamine in the solvents diethyl ether and acetonitrile, particularly in the first substitution step. In diethyl ether the first substitution takes place at the phosphorus atom, while in acetonitrile substitution occurs at a sulphur centre. This difference in behaviour strongly suggests that two different reaction mechanisms operate. Only a few kinetic data have been published concerning substitution reactions with $(NPCl_2)_3$. It was observed that the first steps of substitution with dimethylamine proceed via a second-order reaction rate law, if carried out in tetrahydrofuran [19]. We assume that the first substitution of (I) in ether also will proceed via an S_N2 type mechanism, while an S_N1 type reaction mechanism is proposed for the first substitution step in the more polar solvent acetonitrile.

A second-order reaction at the phosphorus atom of (I) will not proceed very easily. From the structural data of (I) [20] it can be seen that the non-bonded Cl–Cl distances are short ((P)–Cl–(S)–Cl distances *trans* to oxygen 4.342 and 3.893 Å). The formation of an S_N2 type transition state with five-coordinated phosphorus will be unfavourable, but in ether no alternative reaction route seems to be present. Two isomers are formed and we tentatively ascribe structure A (Fig. 1) to compound (II) (the most abundant one), which is formed if the incoming group attacks the ring molecule from the oxygen side of the ring plane (the oxygen atoms are in "equatorial" positions [20]). Consequently structure B is assigned to compound (III), which is formed if the incoming group attacks from the unfavourable side of the ring. From the results of the reaction in which a molar ratio of 1:4 is used, starting from (I), it appears that in ether the second substitution step takes place at a sulphur atom ($NPClNMe_2(NSOCl)_2$ is converted into $NPClNMe_2NSOClNSONMe_2$); however, more experiments are needed to elucidate the mechanism of this step.

From the present experimental data it is evident that in acetonitrile the course of the reaction(s) is completely different from that in ether. Possibly, strong interaction of (I) with the polar solvent leads to the formation of an ion pair $NPCl_2NSOClNSO^+ Cl^-$, the cation of which reacts with the nucleophilic species available. The formation of two isomers of the monosubstituted derivative (in comparable quantities), substituted at a sulphur atom, supports this view. The second substitution step (both in acetonitrile and in ether), starting from $NPCl_2$-$NSOClNSONMe_2$ (IV), takes place at the phosphorus atom; the isomers observed in ether can again be accounted for by assuming an S_N2 type mechanism for this step.

More reactions (*e.g.* with $(NPCl_2)_2NSOCl$) and kinetic studies will be necessary to give a definite

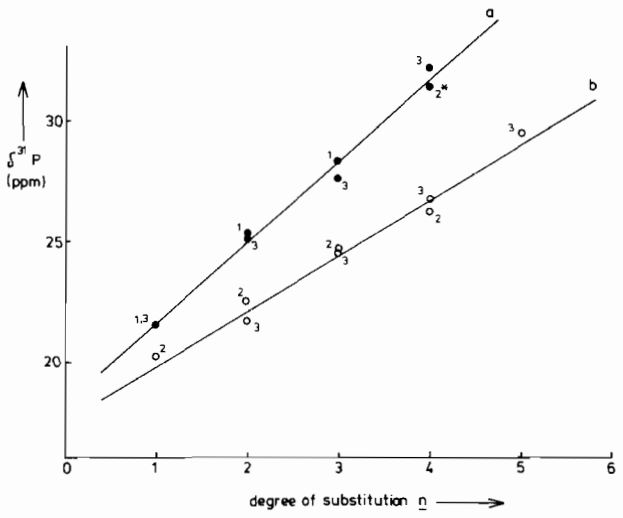

Figure 3. Graph of $\delta(PClNR_2)$ *versus* n for NR_2 equal to (a) NMe_2 and (b) morpholine. The numbers refer to derivatives of (1) $NPCl_2(NSOCl)_2$, (2) $(NPCl_2)_2NSOCl$, and (3) $(NPCl_2)_3$.

explanation for the solvent effect, particularly for the different substitution patterns in ether and acetonitrile.

^{31}P *NMR Spectra*

Recently, Keat *et al.* [21] showed the existence of a linear relationship between the ^{31}P chemical shift of the $\equiv PClNR_2$ signals and the degree of aminolysis n of secondary-amino derivatives of $(NPCl_2)_3$. This relationship is also a conspicuous feature of the dimethylamino derivatives of (I). It is remarkable that the graphs of ^{31}P chemical shift for the $\equiv PClNMe_2$ signals *versus* n for the two ring systems nearly coincide. This prompted us to check this relationship for other known secondary-amino derivatives of $(NPCl_2)_3$ [21, 22] $(NPCl_2)_2NSOCl$ [14], and $NPCl_2(NSOCl)_2$ [14]. It appeared that for each investigated amine (piperidine, morpholine, pyrrolidine) the plots of $\delta(PClAm)$ *versus* n for all three ring systems nearly coincide. In Figure 3 the plots of $\delta(PClAm)$ *versus* n are depicted for the amines dimethylamine and morpholine, the two amines of which the largest number of δ-values are known. The behaviour of the ^{31}P NMR shifts in derivatives of the three ring systems is subject to further investigation.

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