Derivatives of $NPCl_2(NSOCl)_2$ and $(NPCl_2)_2NSOCl$. Part 19.[1] Reactions of $(NPCl_2)_2NSOCl$† with Secondary Amines

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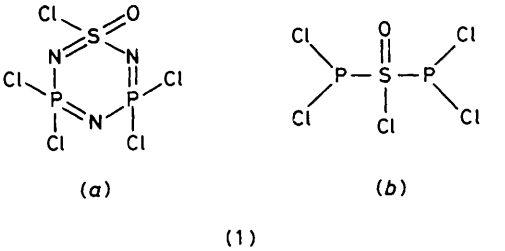
Substitution reactions of $(NPCl_2)_2NSOCl$ with pyrrolidine (Hpyr) or dimethylamine proceed according to a non-geminal pathway; the order of reactivity is PCl_2 > SOCl > PClR (R = pyr or NMe_2). The nucleophilic attack at the phosphorus centres preferably takes place from the oxygen side of the ring plane, resulting in a preponderance of the mono- and di-substituted derivatives which have their amino-group(s) *cis* with respect to the oxygen ligand. The substitution of the sulphur-bonded chlorine atom occurs with inversion of configuration and is probably attended by an important change in the geometry of the sulphur centre. The reactivity of the tri- and tetra-substituted compounds is dependent on the mutual position of the amino-substituents; if three amino-groups are placed at the same side of the ring plane, the compound is less reactive towards further substitution than its isomer(s), in which such an arrangement of substituents is not present. The ^1H n.m.r. spectra of the dimethylamino derivatives show the same additivity of mutual shielding of the amino-groups as previously observed for derivatives of $(NPCl_2)_3$ and *cis*-$NPCl_2(NSOCl)_2$. This can be considered as a strong support for the correctness of the structure assignments based on chemical considerations.

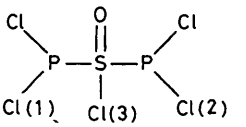
Reactions of the inorganic ring systems $(NPCl_2)_2NSOX$ (X = F or Ph) with simple secondary amines such as pyrrolidine [2] and dimethylamine [3] have shown that the pattern of chlorine substitution is essentially non-geminal; X is not replaced. It has also been noticed that in the ring system $NPCl_2(NSOCl)_2$ the sulphur-bonded chlorine ligands are readily replaceable by secondary amines; [4–6] therefore, it is to be expected that in $(NPCl_2)_2NSOX$ (X = Cl) the substitution pattern will be more complicated compared with $(NPCl_2)_2NSOX$ (X = F or Ph) by the intervenient substitution of the sulphur-bonded chlorine atom.

In order to clarify its behaviour in substitution reactions with secondary amines we have investigated the reactivity of $(NPCl_2)_2NSOCl$ (1) (Figure 1) towards dimethylamine and pyrrolidine. Structural assignments have been made on the grounds of ^1H and ^{31}P n.m.r. parameters. The results of the consecutive substitution steps were compared with those observed for $NPCl_2(NSOCl)_2$, whereas some aspects have been connected with the behaviour of the closely related and more familiar ring system $(NPCl_2)_3$.[7]



(1)

Figure 1. Representations of $(NPCl_2)_2NSOCl$ (1) (1,3,3,5,5-pentachloro-1λ^6,2,4,6,3λ^5,5λ^5-thiatriazadiphosphorine 1-oxide). In (*b*) the nitrogen atoms are omitted for clarity



Cl(1)···Cl(2) = 4·916 Å
Cl(1)···Cl(3) = 4·015 Å
Cl(2)···Cl(3) = 4·058 Å

van der Waals radius of Cl = 1·80 Å

Figure 2. Non-bonded Cl–Cl distances in $(NPCl_2)_2NSOCl$ (1) in the solid state (data from ref. 9)

Results and Discussion

First Substitution Step.—Reactions of (1) with HR [R = pyrrolidin-1-yl (pyr) or NMe_2] in a 1 : 2 molar ratio in acetonitrile afford a mixture of two isomers of $(NPCl_2)(NPClR)NSOCl$ [(2) and (3)]; the ratio of isomers for the pyr derivatives (series a), as estimated from the ^{31}P n.m.r. spectrum of the crude reaction product, is (2a) : (3a) = 2 : 1; for the dimethylamino-derivatives (series b) the ratio was determined from the ^1H n.m.r. spectrum [(2b) : (3b) = 3 : 1]. On the analogy of the assignments to the derivatives of *cis*-$NPCl_2(NSOCl)_2$ we assume that the predominant isomers, (2a) and (2b), have their amino-substituent *cis* with respect to the oxygen ligand (*cis* structure ‡ in the Scheme); consequently (3a) and (3b) are the *trans* isomers. The steric effect of the oxygen ligand is, as expected, less directive than in *cis*-$NPCl_2(NSOCl)_2$ (ratio of isomers 6 : 1),[4] where two such ligands are present.

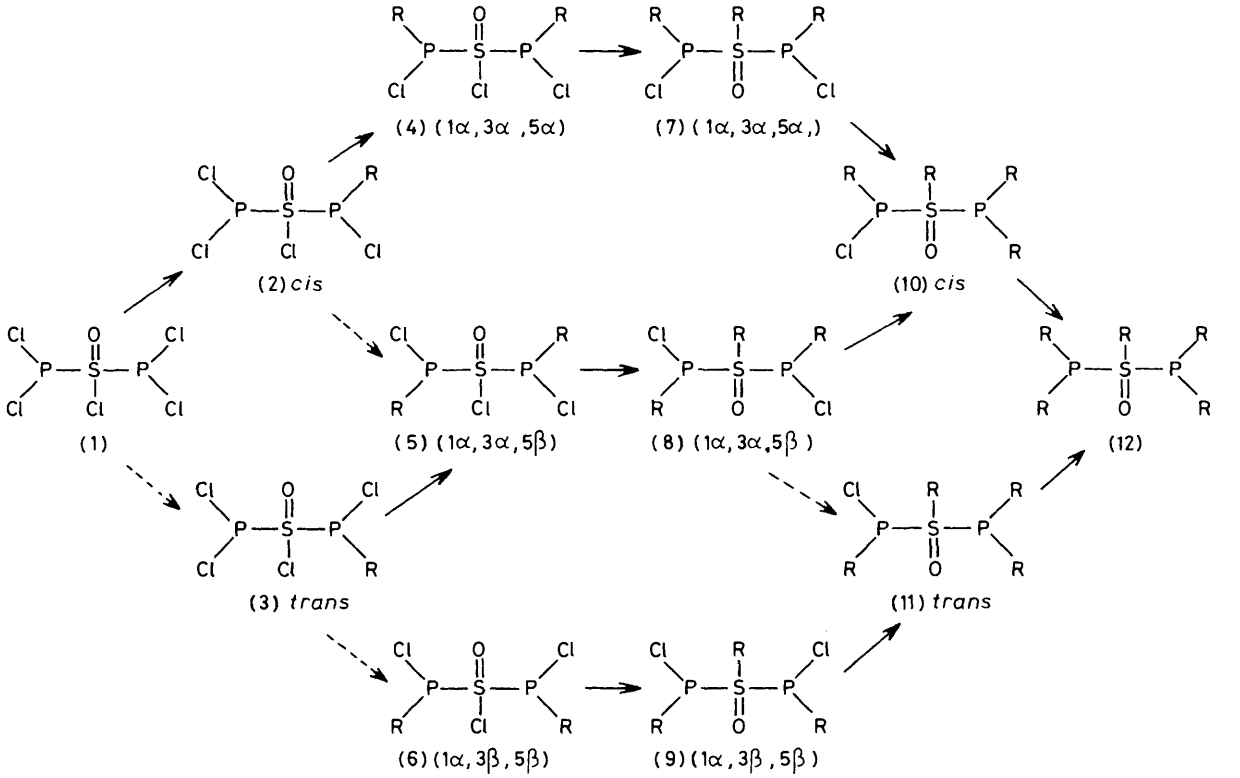
Whereas in *cis*-$NPCl_2(NSOCl)_2$ the first chlorine atom to be substituted by secondary amines is a sulphur-bonded one (acetonitrile as solvent), in $(NPCl_2)_2NSOCl$ the first substitution step takes place at a phosphorus centre. The unexpected behaviour of *cis*-$NPCl_2(NSOCl)_2$ has been suggested to be due to a combination of labile S–Cl bonds and short non-bonded Cl–Cl distances.[4,6,8] In (1) the Cl–Cl distances are substantially larger [9] (Figure 2), no longer hampering the formation of S_N2-type transition states with five-co-ordinated phosphorus.

† 1,3,3,5,5-Pentachloro-1λ^6,2,4,6,3λ^5,5λ^5-thiatriazaphosphorine 1-oxide.
‡ For a definition of the stereochemical nomenclature, see ref. 5.

Table 1. Phosphorus-31 n.m.r. data of mono- and di-substituted derivatives of $(NPCl_2)_2NSOCl$

Compound	δ(PCl_2)/p.p.m.	δ(PClR)[a]/ p.p.m.	^2J(PP)/Hz
(1) $(NPCl_2)_2NSOCl$	26.3		
(2a) *cis*-$(NPCl_2)$[NPCl(pyr)]NSOCl	27.0	18.2	70.8
(2b) *cis*-$(NPCl_2)(NPClNMe_2)$NSOCl	27.1	23.4	72.0
(3a) *trans*-$(NPCl_2)$[NPCl(pyr)]NSOCl	27.1	19.6	66.4
(3b) *trans*-$(NPCl_2)(NPClNMe_2)$NSOCl	27.0	24.7	70.2
(4a) (1α,3α,5α)-$[NPCl(pyr)]_2$NSOCl		21.1	
(4b) (1α,3α,5α)-$(NPClNMe_2)_2$NSOCl		26.1	
(5a) (1α,3α,5β)-$[NPCl(pyr)]_2$NSOCl		21.5—22.4	*b*
(5b) (1α,3α,5β)-$(NPClNMe_2)_2$NSOCl		25.9—27.6	60.8
(6a) (1α,3β,5β)-$[NPCl(pyr)]_2$NSOCl		22.5	
(6b) (1α,3β,5β)-$(NPClNMe_2)_2$NSOCl		27.4	

[a] R = pyr or NMe_2. [b] Outer lines not observed.



Scheme. Aminolysis pattern of $(NPCl_2)_2NSOCl$ (1). The dotted lines represent the less probable of two substitution possibilities (R = pyr or NMe_2); the nitrogen atoms are omitted for clarity

Therefore, a ' normal ' reaction pattern is possible, according to a reactivity order PCl_2 > SOCl > PClR.

Second Substitution Step.—Three isomers of $(NPClR)_2$-NSOCl, (4), (5), and (6), are formed during reactions of (1) with pyrrolidine or dimethylamine in a 1 : 4 molar ratio, again carried out in acetonitrile. The three dimethylamino-derivatives could be separated by means of h.p.l.c. The most abundant isomers, (4a), (4b), show a singlet in their ^{31}P n.m.r. spectrum (Table 1), while the ^1H n.m.r. spectrum of the dimethylamino-derivative (4b) indicates a chemical equivalence of the two amino-groups. As the most abundant mono-substituted isomer (2) will undoubtedly be the precursor of the most abundant disubstituted one, (4) will have both amino substituents *cis* with respect to the oxygen ligand [(1α,3α,5α) structure, see Scheme]. Isomer (5), second in order of abundance, has, according to its n.m.r. spectra, chemically inequivalent phosphorus nuclei as well as inequivalent amino groups. Therefore, it will have the (1α,3α,5β) structure with the amino-groups in mutual *trans* position; consequently, the least abundant isomer (6) will have the (1α,3β,5β) structure.

Obviously, the preferential formation of the (1α,3α,5α) isomer is again caused by the steric directive effect of the oxygen ligand.

Third Substitution Step.—From the reaction of (1) with pyrrolidine in a 1 : 6.5 molar ratio in acetonitrile a yield of 45% of one pure isomer of $[NPCl(pyr)]_2NSO(pyr)$ (7a) is obtained. According to its ^{31}P n.m.r. spectrum (Table 2) this compound possesses chemically equivalent phosphorus nuclei. In addition to (7a) a yellowish oil can be obtained in *ca.* 35% yield, mainly consisting of two other trisubstituted com-

Table 2. Phosphorus-31 n.m.r. data of $N_3P_2SOR_nCl_{5-n}$ (n = 3, 4, or 5, R = NMe_2 or pyr)

Compound	δ(PClR)/p.p.m.	δ(PR_2)/p.p.m.	^2J(PP)/Hz
(7a) (1α,3α,5α)-[NPCl(pyr)]$_2$NSO(pyr)	23.7		
(7b) (1α,3α,5α)-(NPClNMe$_2$)$_2$NSONMe$_2$	28.6		
(8a) (1α,3α,5β)-[NPCl(pyr)]$_2$NSO(pyr)	23.3—23.4		*a*
(8b) (1α,3α,5β)-(NPClNMe$_2$)$_2$NSONMe$_2$	27.9		*b*
(9a) (1α,3β,5β)-[NPCl(pyr)]$_2$NSO(pyr)	22.9		
(10a) *cis*-[NPCl(pyr)][NP(pyr)$_2$]NSO(pyr)	27.7	13.4	47.8
(10b) *cis*-(NPClNMe$_2$)[NP(NMe$_2$)$_2$]NSONMe$_2$	31.7	21.8	51.6
(11a) *trans*-[NPCl(pyr)][NP(pyr)$_2$]NSO(pyr)	27.1	13.8	47.8
(11b) *trans*-(NPClNMe$_2$)[NP(NMe$_2$)$_2$]NSONMe$_2$	31.3	21.7	48.8
(12a) [NP(pyr)$_2$]$_2$NSO(pyr)		14.2	
(12b) [NP(NMe$_2$)$_2$]$_2$NSONMe$_2$		22.9	

[a] Outer lines not observed. [b] Singlet observed.

pounds (ratio *ca.* 2 : 1), while two tetrasubstituted derivatives are also present, in much lower concentration however (^{31}P n.m.r. and mass spectrum). The predominant trisubstituted component of this oily fraction, (8a), exhibits an AB pattern in its ^{31}P n.m.r. spectrum. In this compound the phosphorus bonded amino-groups will therefore be in mutual *trans* position (*cf.* disubstituted derivatives) which means that it has the (1α,3α,5β) structure (see Scheme). The spectra of (7a) and (9a) show identical patterns (singlets), which apply to both the (1α,3α,5α)- and the (1α,3β,5β)-structure. In order to gain more information concerning the structures of (7a) and (9a) some further reactions were carried out: (*a*) purified (7a) appears to be relatively unreactive towards further aminolysis. It reacts only partly with an excess of pyrrolidine (acetonitrile, 20 h, 20 °C) to give one isomer of [NPCl(pyr)][NP(pyr)$_2$]NSO(pyr) (10a); the greater part of (7a) remains unchanged; (*b*) on the contrary, the oily mixture containing (8a) and (9a) affords, under the conditions of (*a*), a roughly equimolar mixture of (10a) and the pentasubstituted derivative [NP(pyr)$_2$]$_2$NSO-(pyr) (12a), while no trisubstituted starting materials can be discerned in the mixture. Isomer (7a) apparently is less sensitive to further substitution than (9a) [and (8a)].

How can the above difference in substitution rate be rationalized? In the (1α,3α,5α) structure the three dimethylamino-ligands are placed at the same side of the ring plane; in a second-order reaction with inversion of configuration around phosphorus (which is the only mode of aminolysis reaction with secondary amines hitherto known in phosphazene chemistry) the nucleophilic attack has to occur at this ' amino-side '; this is unfavourable as compared with the situation in the (1α,3β,5β) isomer, where this attack can only occur at the ' oxygen side ' (see Scheme).

It should be emphasized that such a retardation of the substitution process has also been noticed for *cis* tri- and *cis* tetra-substituted amino-derivatives of $(NPCl_2)_3$ (relative to their *trans* isomers);[10,11] this has been ascribed to a steric screening of the molecule by the three amino-substituents in mutual *cis* position,[11] although the theories of the ' *cis* effect '[12] or ' substituent solvating effect '[13] can also be used in order to explain this phenomenon. In view of the results of reactions (*a*) and (*b*), it seems obvious to ascribe the (1α,3α,5α) structure to isomer (7a), and the (1α,3β,5β) structure to (9a); moreover, it will be shown afterwards that these assignments are in harmony with the observed shielding effects in the ^{1}H n.m.r. spectra of the analogous dimethylamino-derivatives.

The most abundant trisubstituted derivative (7a) (1α,3α,5α) logically is formed *via* the most abundant disubstituted one (4a) (1α,3α,5α); this is confirmed by the result of a reaction of purified (4a) with pyrrolidine in a 1 : 2 molar ratio, which affords (7a) as the only trisubstituted product. The substitution of the sulphur-bonded chlorine atom is, therefore, attended with inversion of the configuration around sulphur. This means that substitution of a chlorine ligand of a SOCl unit apparently proceeds *via* a mechanism comparable with that of the substitution at the isoelectronic PCl_2 unit.

The results of reactions with dimethylamine show great similarities with those with pyrrolidine. The main product (over 50% purified yield) of a reaction of (1) with dimethylamine (molar ratio 1 : 7) is a trisubstituted compound, to which we tentatively ascribe the (1α,3α,5α) structure (7b). Besides the singlet due to (7b) a second, low-intensity, singlet is observed in the ^{31}P n.m.r. spectrum of the crude reaction product, in view of the results of the reactions with pyrrolidine, probably belonging to the (1α,3α,5β) isomer (8b) (with a casual magnetic equivalence of the chemically inequivalent phosphorus nuclei). The signal of the third trisubstituted isomer (1α,3β,5β) is not observed; either it is hidden by another peak, or its absence is caused by a relatively high reactivity for this isomer. Indeed, signals due to tetra- and penta-substituted derivatives are also present. No attempts were made to substantiate the structure assignments to the dimethylamino derivatives any further.

Fourth and Fifth Substitution Steps.—In the preceding section it was shown that (1α,3α,5α)-[NPCl(pyr)]$_2$NSO(pyr) (7a) can be converted into a single tetrasubstituted isomer (10a) [reaction (*a*)]. The only tetrasubstituted compound which can result from a further substitution reaction of (7a) is the *cis* isomer (see Scheme); therefore, a *cis* structure can be attributed to (10a). This compound is also the main component (*ca.* 60%) of the crude product of a 1 : 17 molar ratio reaction (acetonitrile, room temperature); in addition, considerable quantities of (7a), and the pentasubstituted (12a), are present (^{31}P n.m.r.). A low-intensity AB system is tentatively ascribed to the *trans*-isomer of [NPCl(pyr)][NP(pyr)$_2$]-NSO(pyr) (11a). The (near) absence of the trisubstituted isomers (8a) and (9a), and of the tetrasubstituted (11a) is undoubtedly the consequence of their relatively high reactivity; they can be considered to be the precursors of (12a) in this reaction.

The reaction with dimethylamine shows a quite similar result, although in this case the *cis* tetrasubstituted isomer (10b) could not be obtained in a pure state.

The pentasubstituted derivatives (12a) and (12b) can be prepared selectively in reactions of (1) with the desired amine in a 1 : 17 molar ratio in boiling acetonitrile.

^{1}H *N.M.R. Spectra of Dimethylamino-derivatives.*—Table 3 summarizes the ^{1}H n.m.r. data of the dimethylamino-derivatives, excluding those of the trisubstituted compounds (8b)

Table 3. Proton n.m.r. data of dimethylamino-derivatives of (1) (in $CDCl_3$)

Compound	δ(PNC*H*) [a]/ p.p.m.	^3J(PH) + ^5J(PH) [b]/ Hz	δ(SNC*H*)/ p.p.m.	^5J(PH)/ Hz
(2b)	2.82	16.7		
(3b)	2.86	17.0		
(4b)	2.79	16.9		
(5b)	2.85 (1)	17.0		
	2.82 (1)	16.4		
(6b)	2.83	16.9		
(7b)	2.74	17.2	2.70	0.6
(10b)	2.73 (1)	16.4 + 0.4 [c]		
	2.69 (1)	11.5 + 0.5 [c]	2.70	0.5
	2.68 (1)	10.9 + 0.4 [c]		
(12b)	2.69 (1)	11.7	2.70	<0.4
	2.65 (1)	11.9		

[a] Relative intensity in parentheses. [b] Apparent coupling constant J(PH)* given, except for (10b) (first-order spectrum). [c] ^5J(PH) determined in C_6H_6 solution (in $CDCl_3$, coincidence of peaks).

Table 4. Shielding effects (in p.p.m.) in dimethylamino-derivatives of (1)

Observed group	Shielding group: *trans* *S*-bonded	*cis* *S*-bonded	*trans* *P*-bonded	*cis* *P*-bonded	*gem* *P*-bonded
P-bonded	0.09	0.09	0.00	0.03	0.05
S-bonded	—	—	0.00	no data	—

and (9b), and the tetrasubstituted (11b), the sets of peaks of which could not be identified in the obtained mixtures. Apart from (10b) all compounds show second-order effects, closely resembling those observed for the derivatives of $(NPCl_2)_2$NSOPh.[3]

Structures have been successfully assigned to dimethylamino derivatives of $NPCl_2(NSOCl)_2$ on the grounds of the additivity of mutual shielding of the amino-substituents in their ^{1}H n.m.r. spectra.[4] From the data in Table 3 it appears that a similar additivity is present in the derivatives of $(NPCl_2)_2$NSOCl. If the structure assignments of the preceding paragraphs are used, it is possible to derive a set of 'best values' for the different types of shielding, exercised by dimethylamino-groups on one another (Table 4). Comparison of the calculated chemical shifts (using the shielding values of Table 4) with the experimental ones (Table 3) shows a very close conformity for all compounds, the values never differing by more than 0.02 p.p.m. This observation, combined with the impossibility to arrive at a reasonable set of best values, if an alternative set of structural proposals is applied, can be considered as a strong support for the correctness of the assignments, given in the preceding paragraphs.

From the values in Table 4 it is obvious that sulphur-bonded groups exercise a markedly larger shielding effect than phosphorus-bonded ones. This phenomenon, which has also been observed for the derivatives of *cis*-$NPCl_2(NSOCl)_2$,[4] is very probably connected with an important alteration of the geometry around the sulphur centre during substitution of a chlorine ligand by an organic group. Crystal structure determinations of compounds containing a ring system with one or more NSOX units have demonstrated that the oxygen ligand of this NSOX unit takes an equatorial position if X = Cl [9,14-18] or X = F,[19,20] while the configuration around sulphur is almost tetrahedral (in one example [20] the oxygen is even axial) if X = NMe_2 [16] or X = Ph.[20,21] The n.m.r. data for derivatives of $(NPCl_2)_2NSOCl$ and *cis*-$NPCl_2(NSOCl)_2$ suggest that similar geometry alterations take place during the substitutions of the sulphur-bonded chlorine ligands in these compounds by dimethylamino-groups.

Experimental

General.—All experiments were carried out under dry nitrogen. Pyrrolidine was purified by distillation over KOH pellets. About 1 mol dm^{-3} solutions of dimethylamine in acetonitrile were prepared by distillation of the amine through a KOH column into a vessel containing the solvent. The concentration was determined by way of titration prior to use. Solvents were purified and dried by conventional methods. The compound $(NPCl_2)_2NSOCl$ was prepared as described elsewhere.[22]

Proton n.m.r. spectra were recorded with a Varian A-60 instrument, using $SiMe_4$ as internal reference; ^{31}P n.m.r. spectra (proton-noise decoupled) were taken with a Varian XL-100 FT spectrometer, operating at 40.5 MHz; 85% H_3PO_4 was used as external reference. In all cases spectra were taken of solutions in $CDCl_3$; the ^{2}H resonance line of the solvent was used for field frequency lock (^{31}P). Chemical shifts are positive in the low-field direction.

Preparation of Pyrrolidin-1-yl Derivatives.—(*i*) $(NPCl_2)$-[NPCl(pyr)]NSOCl [*mixture of* (2a) *and* (3a)]. A solution of pyrrolidine (4.8 mmol) in acetonitrile (40 cm^3) was added dropwise, over a period of *ca.* 30 min, to a stirred solution of (1) (2.43 mmol) in acetonitrile (30 cm^3), cooled at −15 °C. The mixture was allowed to warm slowly to room temperature and was stirred for *ca.* 17 h at this temperature. After evaporation of the solvent under reduced pressure the residue was extracted twice with diethyl ether. The combined extracts were evaporated to dryness; the crude reaction product thus obtained consisted mainly (*ca.* 85%) of (2a) and (3a) (ratio *ca.* 2 : 1; ^{31}P n.m.r.). The isomers could not be separated.

(*ii*) (1α,3α,5α)-$[NPCl(pyr)]_2NSOCl$ (4a). Reaction conditions as under (*i*): pyrrolidine (49.6 mmol) in acetonitrile (60 cm^3) and (1) (12.1 mmol) in acetonitrile (240 cm^3). The crude reaction product was recrystallized twice from diethyl ether and afforded (4a) in 34% yield. Evaporation of the mother-liquors afforded a yellow oil, consisting of (4a), (5a), and (6a) (^{31}P n.m.r.).

(*iii*) (1α,3α,5α)-$[NPCl(pyr)]_2NSO(pyr)$ (7a). Reaction conditions as under (*i*): pyrrolidine (79.0 mmol) in acetonitrile (60 cm^3) and (1) (12.1 mmol) in acetonitrile (240 cm^3). Recrystallization of the crude product from diethyl ether afforded 45% of pure (7a). Evaporation of the remaining diethyl ether solution gave a yellow oil, consisting of a mixture of (8a) and (9a), contaminated with (10a) and (11a) (^{31}P n.m.r.); this oil was used as the starting material in reaction (*vi*).

(*iv*) (1α,3β,5β)-$[NPCl(pyr)]_2NSO(pyr)$ (9a). The yellow oil described under (*iii*) gave a 7% yield of pure (9a) after several recrystallizations from a diethyl ether–n-pentane mixture (1 : 1).

(*v*) *Reaction* (a) (*see text*). To a stirred solution of pyrrolidine (12.7 mmol) in acetonitrile (30 cm^3), cooled at −15 °C, a solution of (7a) (1.15 mmol) in acetonitrile (30 cm^3) was added dropwise, over a period of *ca.* 30 min. The mixture was allowed to warm slowly to room temperature and was stirred for *ca.* 17 h at this temperature. After evaporation of the solvent under reduced pressure the residue was extracted twice with diethyl ether. The combined extracts were evaporated to dryness. The crude product consisted of (7a) (55%) and (10a) (45%).

Table 5. Analytical data of purified compounds

Compound	M.p.[b]/°C	Analysis (%) [a] C	H	N	S	Cl
(2b),(3b)	oil	7.40 (7.10)	1.90 (1.80)	16.40 (16.60)	9.30 (9.50)	41.90 (41.95)
(4a)	117.0—118.0	24.20 (24.10)	4.00 (4.05)	17.65 (17.55)	8.20 (8.05)	26.75 (26.70)
(4b)	113.5—115.0	14.20 (13.85)	3.55 (3.50)	20.20 (20.20)	9.40 (9.25)	31.00 (30.70)
(5b)	67.0—68.5	14.45 (13.85)	3.60 (3.50)	20.20 (20.20)	9.35 (9.25)	30.70 (30.70)
(6b)	130.0—133.0	13.60 (13.85)	3.60 (3.50)	*c*	*c*	30.55 (30.70)
(7a)	140.0—141.5	33.40 (33.25)	5.55 (5.60)	19.15 (19.40)	7.30 (7.40)	16.50 (16.35)
(7b)	115.0—116.5	20.20 (20.30)	5.10 (5.10)	23.65 (23.65)	9.00 (9.05)	19.80 (19.95)
(9a)	128.0—130.0	33.25 (33.25)	5.55 (5.60)	19.20 (19.40)	7.50 (7.40)	16.35 (16.35)
(10a) [d]	79.0—80.0 or 98.0—100.0	41.10 (41.05)	6.90 (6.90)	20.85 (20.95)	6.70 (6.85)	7.65 (7.60)
(12a)	106.5—107.5	47.75 (47.80)	8.00 (8.00)	22.35 (22.40)	6.30 (6.40)	
(12b)	58.5—60.0	32.20 (32.25)	7.95 (8.10)	30.05 (30.10)	8.85 (8.60)	

[a] Calculated values in parentheses. [b] Uncorrected. [c] Not carried out. [d] Two crystal modifications.

(*vi*) *Reaction* (b) (*see text*). Reaction conditions as under (*v*): pyrrolidine (18.7 mmol) in acetonitrile (30 cm^3) and the yellow oil obtained in reaction (*iii*) (1.71 mmol) in acetonitrile (30 cm^3). The crude product consisted of (10a) (55%) and (12a) (45%), and traces of (11a).

(*vii*) *cis*-[NPCl(pyr)][NP(pyr)$_2$]NSO(pyr) (10a). Reaction conditions as under (*v*): pyrrolidine (41.3 mmol) in acetonitrile (30 cm^3) and (1) (2.43 mmol) in acetonitrile (30 cm^3). The crude product consists mainly (50%) of (10a), while (7a) and (12a) are present in *ca.* 25% each. Recrystallization from diethyl ether affords 33% of pure (10a).

(*viii*) [NP(pyr)$_2$]$_2$NSO(pyr) (12a). To a stirred solution of (1) (3.04 mmol) in acetonitrile (50 cm^3) pyrrolidine (51.0 mmol) was added at once. The mixture was boiled under reflux for 19 h, evaporated to dryness, and extracted with diethyl ether. The crude product was recrystallized from diethyl ether–n-pentane (1 : 1). Yield 70% of pure (12a).

Preparation of Dimethylamino-derivatives.—(*ix*) (NPCl$_2$)(NPClNMe$_2$)NSOCl [*mixture of* (2b) *and* (3b)]. A 1 N solution of dimethylamine (6.1 cm^3) in acetonitrile was mixed with the same solvent (20 cm^3) and added dropwise in 30 min to a stirred solution of (1) (3.04 mmol) in acetonitrile (30 cm^3), cooled at −35 °C. The mixture was allowed to warm slowly to room temperature and was stirred for *ca.* 17 h at this temperature. After evaporation of the solvent under reduced pressure the residue was extracted twice with diethyl ether. The combined extracts were evaporated to dryness. An analytically pure mixture of (2b) and (3b) (yield 40%, ratio *ca.* 3 : 1) remained.

(*x*) (NPClNMe$_2$)$_2$NSOCl (4b),(5b),(6b). Reaction conditions as under (*ix*): amine solution (12.2 cm^3) and (1) (3.04 mmol). The resulting mixture consisted mainly of (4b), (5b), and (6b). They were separated by means of h.p.l.c. using a Polygosil 60-D-10 CN 25-cm column (diameter 10 mm), and using a 9 : 1 mixture of n-hexane and diethyl ether as eluant. Flow-rate 4.0 cm^3 min^{-1}. The sequence of retention times is (5b) < (6b) < (4b). Recrystallization of (5b) from a 2 : 1 mixture of n-pentane and diethyl ether gave a yield of 14% of pure product; (6b) was purified by recrystallization from n-pentane (5% yield), and (4b) by recrystallization from a 1 : 1 mixture of n-pentane and diethyl ether (20% yield).

(*xi*) (1α,3α,5α)-(NPClNMe$_2$)$_2$NSONMe$_2$ (7b). Reaction conditions as under (*ix*): amine solution (21.0 cm^3) and (1) (3.04 mmol). Recrystallization of the crude reaction product, consisting of (7b) (75%), (10b) (20%), and traces of (8b), (11b), and (12b), from diethyl ether afforded 55% of pure (7b).

(*xii*) *cis*-(NPClNMe$_2$)[NP(NMe$_2$)$_2$]NSONMe$_2$ (10b). Reaction conditions as under (*ix*): amine solution (1 N, 51 cm^3) and (1) (3.04 mmol). The crude product consisted of (10b) (65%), (7b) (15%), and (12b) (20%). All attempts to purify (10b) by recrystallization failed.

(*xiii*) [NP(NMe$_2$)$_2$]$_2$NSONMe$_2$ (12b). Amine solution (1 N, 51 cm^3) was added at once to a stirred solution of (1) (3.04 mmol) in acetonitrile (30 cm^3) at room temperature. The mixture was then kept under reflux for 17 h. After evaporation of the solvent under reduced pressure the residue was extracted twice with diethyl ether. The combined extracts were evaporated to dryness; crystallization of the crude product in n-pentane afforded an oily precipitate, which solidified after several days at −20 °C. Yield 45% of pure (12b).

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