Reactivity of Cyclothiaphosphazenes towards Alkyl-lithium Reagents

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Reactions of $(NPCl_2)_n(NSOPh)_{3-n}$ (n = 1 or 2) with 1 and 2 equivalents of LiMe or LiBu^t and an excess of 2-propanol in tetrahydrofuran lead to complex reaction mixtures, containing the hydridoisopropoxycyclothiaphosphazenes $NPH(OPr^i)(NPCl_2)_n(NSOPh)_{2-n}$ (n = 0 or 1) and several alkyl-substituted ring systems (based on ^{31}P and ^1H n.m.r. spectrometry). The structural characterization of the reaction products is described together with the appropriate reaction pathways, based on an initial metal–halogen exchange process. Reactions of the cyclothiaphosphazenes with alkyl-lithium reagents show a tendency to afford lower yields of cyclic derivatives than those previously reported for $(NPCl_2)_3$. This different behaviour is ascribed to competition between the metal–halogen exchange process and nucleophilic substitution, which is supposed to induce ring cleavage.

Several papers concerning the reactivity of hexachlorocyclotriphosphazene, $(NPCl_2)_3$ (**1**), towards Grignard and organolithium reagents have pointed to a metal–halogen exchange process as responsible for the formation of a large variety of organo-substituted cyclophosphazenes.[1–4] Recently, we have shown that reactions of compound (**1**) with LiR (R = Me or Bu^t) and 2-propanol lead to complex reaction mixtures, in which the presence of hydridocyclophosphazenes, *e.g.* $NPH(OPr^i)(NPCl_2)_2$, also points to a metal–halogen exchange process.[5,6]

In the scope of our investigations concerning the mixed N,P,S ring systems $NPCl_2(NSOX)_2$ and $(NPCl_2)_2NSOX$ (X = F, Cl, or Ph) we were interested in the reactivity of these cyclothiaphosphazenes towards alkyl-lithium reagents. In order to compare the results with those obtained with compound (**1**) it was necessary to restrict reactions, if any, to the PCl_2 centres. With respect to the compounds $NPCl_2(NSOX)_2$ and $(NPCl_2)_2NSOX$ (X = F, Cl, or Ph), nucleophilic substitution reactions take place at the PCl_2 centres as well as the SOX centres [*e.g.* phenylation of $(NPCl_2)_2NOSF$ (**2**) or aminolysis of $(NPCl_2)_2NSOCl$ (**3**)[7]], except for X = Ph. Hence, compounds $(NPCl_2)_n(NSOPh)_{3-n}$ (n = 1 or 2) were chosen as starting materials.

Results and Discussion

In order to obtain information about the reactivity of *trans*-$NPCl_2(NSOPh)_2$ (**4**), *cis*-$NPCl_2(NSOPh)_2$ (**5**), and $(NPCl_2)_2NSOPh$ (**6**) towards LiR (R = Me or Bu^t), thus allowing a comparison between the cyclothiaphosphazenes and the cyclophosphazene (**1**), all reactions were carried out according to the standard procedure as described for (**1**).[6] Crucial points in the procedure are (*i*) the use of tetrahydrofuran as a solvent, (*ii*) the reaction temperature, which must be kept below −60 °C, and (*iii*) the addition of an excess of 2-propanol at the same temperature (see Experimental section).

The composition of each reaction mixture was analysed by ^{31}P and ^1H n.m.r. spectrometry. The total yields (weight) and absolute yields (mol%) based on n.m.r. data, including those for reaction of (**1**) with LiR and 2-propanol,[6] are collected in Table 1.

(a) Reactions of Compounds (**4**)—(**6**) *with* LiMe, *in Molar Ratios* 1:1 *and* 1:2; *Subsequent Treatment with 2-Propanol.*— According to ^{31}P and ^1H n.m.r. spectrometry, reaction of compound (**4**) with LiMe, in molar ratio 1:1, and 2-propanol gave one cyclic compound in 50% yield. Comparison with n.m.r. data previously obtained from reactions of (**1**) with LiMe and 2-propanol[6] pointed to the presence of an hydridoisopropoxycyclothiaphosphazene, (1α,3β,5α)-$NPH(OPr^i)(NSOPh)_2$ (**7**) (Table 2). In the case of (**5**) also, one cyclic compound was obtained, *viz.* $NPH(OPr^i)(NSOPh)_2$ (**8**) (50%), which is one of the two possible isomers [see section (*d*)]. The residues (50%) consisted of a white sticky material, which was not analysed further. Both (**7**) and (**8**) (solids) could be purified by recrystallization and were completely characterized.

Reaction of compound (**6**) with LiMe, in molar ratio 1:1, and 2-propanol gave an oil (40%), which appeared to be a mixture of cyclic compounds containing the starting material (**6**) (10%) and two isomers (**a**) and (**b**) of $NPH(OPr^i)(NPCl_2)NSOPh$ (**9**) (30%), probably the *cis* and *trans* isomers in a ratio of 14:1 (based on ^{31}P and ^1H n.m.r. spectrometry, Table 2) [see also section (*d*)]. As observed for the reactions with compounds (**4**)

Table 1. Absolute yields (mol%) of reactions of $(NPCl_2)_3$ (**1**),[6] $(NPCl_2)_2NSOPh$ (**6**), *trans*-$NPCl_2(NSOPh)_2$ (**4**), and *cis*-$NPCl_2(NSOPh)_2$ (**5**) (500 mg) with LiR (R = Me or Bu^t) and 2-propanol.[a] Total yields (mg) in parentheses

	$(NPCl_2)_3$ (**1**)		$(NPCl_2)_2$-NSOPh (**6**)		*trans*-$NPCl_2$-$(NSOPh)_2$ (**4**)		*cis*-$NPCl_2$-$(NSOPh)_2$ (**5**)
	1:1[b]	1:2	1:1	1:2	1:1	1:2	1:1
≡PCl_2	10		10				
≡$PH(OPr^i)$	60	50	30	20	50	10	50
≡PH(Me)	10	10					
$(\equiv PMe)_2$		15					
≡PMe_2		5				15	
	80	80	40	20	50	25	50
	(405)	(370)	(200)	(100)	(250)	(120)	(250)

	$(NPCl_2)_3$ (**1**)		$(NPCl_2)_2$-NSOPh (**6**)		*trans*-$NPCl_2$-$(NSOPh)_2$ (**4**)	
	1:1[c]	1:2	1:1	1:2	1:1	1:2
≡PCl_2	60	10	20			
≡$PH(OPr^i)$	20	50	30	20	30	
≡$PH(Bu^t)$	10	25	5	5	10	70
≡$PCl(Bu^t)$		5	5	5	40	10
	90	90	60	30	80	80
	(450)	(430)	(300)	(160)	(400)	(400)

[a] See Experimental section. [b] Molar ratio of ring: LiMe. [c] Molar ratio of ring: LiBu^t.

Table 2. ^{31}P and ^{1}H n.m.r. data[a] on compounds (**7**)—(**14**) and (**20**)

Compound[b]	δ(PR¹R²)	δ(PCl_2)	δ(H) Me	δ(H) CH	δ(H) PH	^{1}J(PH)	^{2}J(PP)	^{3}J(PH)	^{3}J(HH)
(**7**) (1α,3β,5α)-NPH(OPr^{i})(NSOPh)$_2$	−1.0		1.0/1.2[c]	4.3	6.8	732		11.7	5.8
(**8**) (1α,3α,5α)-NPH(OPr^{i})(NSOPh)$_2$	4.3		1.4	4.9	7.1	725		11.3	5.9
(**20**) (1α,3α,5β)-NPCl(OPr^{i})(NSOPh)$_2$	17.4		1.4	4.9				11.3	5.9
(**9a**) *cis*-NPH(OPr^{i})(NPCl$_2$)NSOPh	1.4	23.3	1.4	4.8	6.9	725	28.0	11.6	5.8
(**9b**) *trans*-NPH(OPr^{i})(NPCl$_2$)NSOPh	1.1	*d*	1.3	*d*	*d*	*d*	*d*	*d*	5.8
(**10**) *trans*-NPMe$_2$(NSOPh)$_2$	33.0		*d*						
(**11**) (1α,3β,5α)-NPCl(Bu^{t})(NSOPh)$_2$	51.5		1.2					22.6	
(**12**) (1α,3β,5α)-NPH(Bu^{t})(NSOPh)$_2$	26.7		1.0		6.6	533		19.7	
(**13**) NPH(Bu^{t})(NPCl$_2$)NSOPh	31.6	*d*	*d*		*d*	543	*e*	*d*	
(**14**) NPCl(Bu^{t})(NPCl$_2$)NSOPh	55.6	22.1	*d*				*e*	*d*	

[a] Chemical shifts (p.p.m.) positive to low field, coupling constants in Hz; solvent $CDCl_3$. [b] For the use of α and β descriptors, see B. de Ruiter and J. C. van de Grampel, *J. Chem. Soc., Dalton Trans.*, 1982, 1773. [c] Two ^{1}H n.m.r. signals were observed due to chirality of the ring system. [d] Hidden lines. [e] Unresolved lines.

and (**5**), the residue (60%) also consisted of polymer-like substances. The moisture sensitivity and instability of (**9a**) and (**9b**) prevented their separation by means of h.p.l.c.

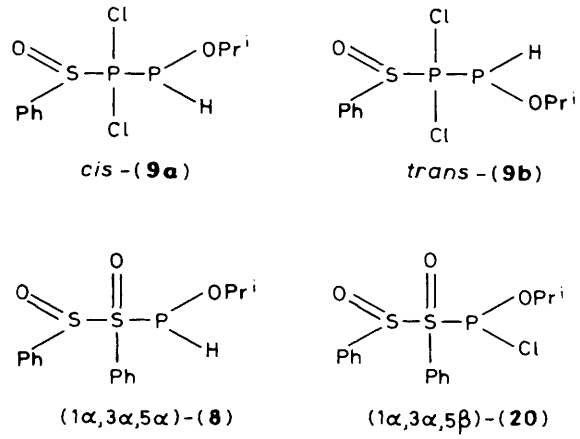
Decomposition predominated in reactions of compounds (**4**) and (**6**) with 2 equivalents of LiMe. Mixtures of cyclic compounds were obtained in only 20—25% yield (Table 1), mainly consisting of the hydridoisopropoxy derivatives (**7**) and (**9a**), (**9b**); in the case of (**4**), *trans*-NPMe$_2$(NSOPh)$_2$ (**10**) could be detected in the ^{31}P n.m.r. spectrum [Table 2, assignment by comparison with ^{31}P n.m.r. data for a pure sample obtained by reaction of (**4**) with MgMeCl[8]].

(*b*) *Reactions of Compounds* (**4**) and (**6**) with LiBu^{t}, *in Molar Ratios* 1:1 *and* 1:2; *Subsequent Treatment with 2-Propanol.*—Reaction of compound (**4**) with LiBu^{t}, in molar ratio 1:1, and 2-propanol gave a mixture of cyclic compounds in 80% yield. This mixture was separated by means of h.p.l.c. giving (1α,3β,5α)-NPCl(Bu^{t})(NSOPh)$_2$ (**11**) (40%), (1α,3β,5α)-NPH(OPr^{i})(NSOPh)$_2$ (**7**) (30%), and (1α,3β,5α)-NPH(Bu^{t})(NSOPh)$_2$ (**12**) (10%), which were completely characterized (see also Tables 1 and 2). Using twice the amount of LiBu^{t} the reaction mixture (yield 80%) contained (**12**) (70%) and a small amount of (**11**) (10%).

Reaction of compound (**6**) with LiBu^{t}, in molar ratio 1:1, and 2-propanol gave a mixture of the starting material (**6**) (20%) and (**9a**), (**9b**) (30%, molar ratio 14:1). The ^{31}P n.m.r. spectra indicated that also small amounts of NPCl(Bu^{t})(NPCl$_2$)NSOPh (**14**) [assignment based on the δ(^{31}PClBu^{t}) values of NPCl(Bu^{t})(NPCl$_2$)$_2$[6] and (**11**)] and probably NPH(Bu^{t})(NPCl$_2$)NSOPh (**13**) [assignment based on ^{1}J(PH) = 543 Hz] were present. Using 2 equivalents of LiBu^{t} the yield of cyclic material decreased to 30% (Table 1).

(*c*) *Reactions of Compound* (**4**) with LiBu^{t}, *in Molar Ratio* 1:2; *Subsequent Treatment with Alkyl Iodides* RI (R = Me, Pr^{n}, *or* Pr^{i}), *Allyl Bromide, or Acetyl Chloride.*—Reaction mixtures of compound (**4**) and 2 equivalents of LiBu^{t} were also treated with RI (R = Me, Pr^{n}, or Pr^{i}), allyl bromide, or acetyl chloride instead of 2-propanol. All compounds NPRBu^{t}(NSOPh)$_2$ could be freed from (**11**) by means of h.p.l.c. and completely characterized. For ^{31}P n.m.r. data see the Experimental section. The compound (1α,3β,5α)-NP(COMe)Bu^{t}(NSOPh)$_2$ (**19**) appeared to be very moisture sensitive. Hydrolysis gave (**12**) and acetic acid (based on n.m.r.).

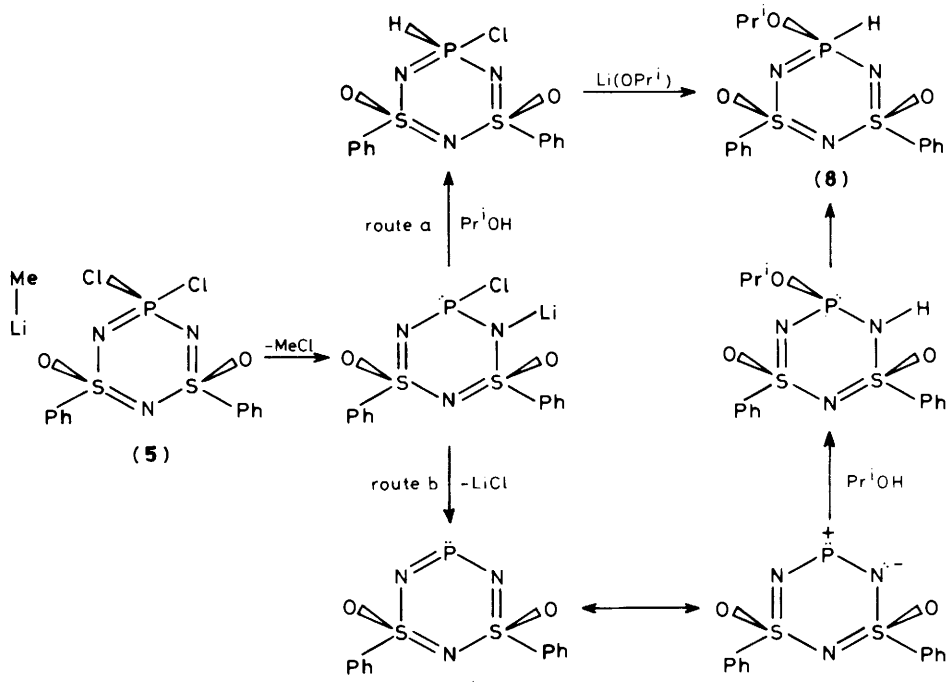
(*d*) *Reaction Routes and Mechanism.*—With respect to the amount of starting material left after reaction with 1 equivalent of LiMe (Table 1), it appears that compounds (**4**) and (**5**) are slightly more reactive than (**1**). The reactivity of (**6**) towards LiMe equals that of (**1**). However, the yields of the cyclic derivatives of (**4**) (50), (**5**) (50), and (**6**) (30) were considerably lower than for (**1**) (70%). Using 2 equivalents of LiMe the yields decreased even more drastically [compare (**4**) (25), (**6**) (20), and (**1**) (80%)].



The formation of the hydridoisopropoxy derivatives (**7**), (**8**), and (**9a**), (**9b**) points to the same reaction mechanism, *i.e.* a metal–halogen exchange process as described for the reactions of (**1**) with LiMe.[5,6]

Compounds (**9a**) and (**9b**) (molar ratio 14:1, according to ^{31}P and ^{1}H n.m.r. spectrometry) probably represent the *trans* and *cis* isomers of NPH(OPr^{i})(NPCl$_2$)NSOPh. In the ^{1}H n.m.r. spectrum (Table 2), the resonances (doublet) of the Me moieties of the isopropoxy group of the most abundant isomer (**9a**) {δ[^{1}H(Me)] = 1.4 p.p.m.} are found at lower field compared with (**9b**) {δ[^{1}H(Me)] = 1.3 p.p.m.}. It has been argued before that a phenyl group exerts a shielding effect towards another substituent in *cis* position.[9,10] Therefore we presume that (**9a**) has the structure in which the oxygen and isopropoxy groups are in *cis* position and consequently (**9b**) possesses the *trans* structure.

In the reaction of *cis*-NPCl$_2$(NSOPh)$_2$ (**5**) with LiMe, in molar ratio 1:1, and 2-propanol only one isomer is formed. According to the arguments (shielding) mentioned above, we presume that this compound (**8**) has the (1α,3α,5α) structure. The δ[^{1}H(Me)] value of (**8**) (1.4 p.p.m.) equals that of (**9a**) and is found at lower field compared with (**7**) (1.1 p.p.m.). In order to confirm this assignment we carried out a reaction of (**5**) with sodium isopropoxide, in molar ratio 1:1. From our experience



Scheme 1.

in the field of nucleophilic substitution reactions of cyclothiaphosphazenes,[7] the (1α,3α,5β) structure can be assigned to the predominant product $NPCl(OPr^i)(NSOPh)_2$ (**20**). As the δ[^{1}H(Me)] value of compound (**20**) (1.4 p.p.m.) approaches that of (**8**) {Δδ[^{1}H(Me)] is 0.02 p.p.m.} and keeping in mind that Δδ[^{1}H(Me)] for $NPCl(OPr^i)(NPCl_2)_2$ and $NPH(OPr^i)(NPCl_2)_2$ is 0.03 p.p.m. we conclude that (**8**) has indeed the (1α,3α,5α) structure.

As stated before reactions of compounds (**4**) and (**6**) with 2 equivalents of LiMe were accompanied by extensive decomposition of the starting materials; only small amounts (20—25%) of mainly hydridoisopropoxy derivatives could be obtained. This is in sharp contrast with the reaction of (**1**) with LiMe, in molar ratio 1:2, and 2-propanol, where a considerable amount of cyclic derivatives was detected.

Considering these results two questions arise: (*i*) why do (**5**) and (**6**) give one or predominantly one isomer of the possible two in reactions with LiMe and 2-propanol, assuming a metal–halogen exchange process; and (*ii*) why do (**4**)—(**6**) give lower yields of cyclic derivatives than does the cyclophosphazene (**1**), particularly when 2 equivalents of LiMe are used?

In the case of a metal–halogen exchange process the incoming LiMe is supposed to attack a ring nitrogen and a chlorine atom simultaneously as has been described for reactions of compound (**1**) with [{CuI(PBu^n_3)}$_4$]–MgRCl[1] (Scheme 1). The oxygen atoms of the SOPh moieties of (**5**) are less bulky than the phenyl groups. Hence, it can be expected that the exchange process involves the chlorine atom at the oxygen side of the ring system, leading to $NLiPCl(NSOPh)_2$ as depicted in Scheme 1.

For the second step, ultimately leading to the hydridoisopropoxy derivative, two possibilities were proposed in a previous paper,[6] *viz.* (*a*) protonation or (*b*) elimination of lithium chloride. We presume that during the protonation of the lithiated complex to $NPH(Cl)(NSOPh)_2$ the configuration is retained. From a stereochemical point of view [compare the molecular structure of *cis*-$NPCl_2(NSOPh)_2$[11]], the incoming nucleophile lithium isopropoxide will attack at the oxygen side of the ring system giving (1α,3α,5α)-$NPH(OPr^i)(NSOPh)_2$ (**8**).

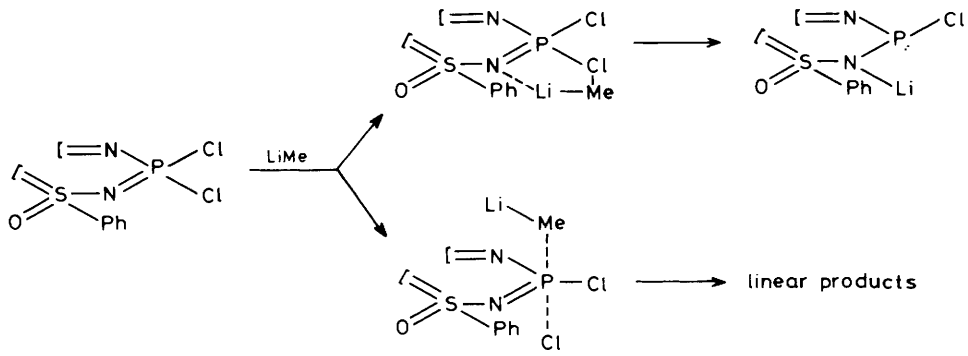
As depicted in Scheme 1, elimination of lithium chloride should lead to the intermediate $NP(NSOPh)_2$. During the rearrangement of the addition complex $NP(NSOPh)_2$·$HOPr^i$ again steric factors may force the alkoxy group into a *cis* position with respect to the oxygen atoms.

The same reasoning can be followed for compound (**6**). However, the preference for a *cis* configuration is less pronounced, as only one SOPh moiety is present, thus leading to the formation of two isomers of $NPH(OPr^i)(NPCl_2)NSOPh$.

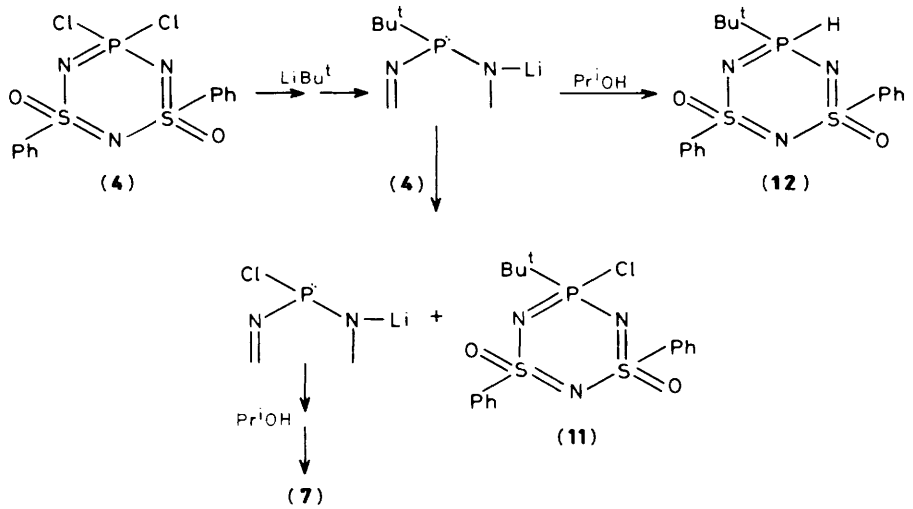
The relatively low stability of the cyclothiaphosphazenes in reactions with LiMe still remains a point of discussion. From our experimental data it can be assumed that the intermediates $NLiPCl(NPCl_2)_n(NSOPh)_{2-n}$ [or $NP(NPCl_2)_n(NSOPh)_{2-n}$] ($n$ = 0 or 1) are stable when kept at −60 °C. This should be particularly true for $NLiPCl(NSOPh)_2$ [or $NP(NSOPh)_2$] where no reactive PCl_2 moieties, responsible for intra- or intermolecular decomposition reactions, are present. Hence, another mechanism induces ring-opening reactions.

Apart from the sideways interaction between LiMe and the ring system, another mode of action can be visualized, *viz.* perpendicular to the ring plane, which is characteristic of nucleophilic substitution[12] (Scheme 2). The small size of the oxygen atom(s) in comparison with chlorine makes the cyclothiaphosphazenes more sensitive to such an attack than (**1**). Although no convincing evidence is available, pseudo-rotation in the five-co-ordinated phosphorus intermediate, as proposed by Westheimer[13] for the hydrolysis of phosphate esters, may be responsible for ring opening, and subsequent polymerization reactions.

Compounds (**1**), (**6**), and (**4**) show an increasing reactivity towards $LiBu^t$ on going from (**1**) to (**4**). Again it can be argued that the presence of SOPh moieties, exerting less steric hindrance than PCl_2 groups, facilitates the interaction between the organometallic reagent and the ring system. With respect to a nucleophilic substitution (perpendicular attack), it is well known that this mode of reaction will be sterically hindered by the presence of a bulky Bu^t group. In other words, reactions with $LiBu^t$ can be expected to proceed with minor decom-



Scheme 2.



Scheme 3.

position, which is true for the ring systems (**1**) and (**4**) (Scheme 3), when compared with the analogous reactions with LiMe.

Surprisingly, reactions of compound (**6**) with LiBu^t, in molar ratio 1:1 or 1:2, and 2-propanol gave substantial amounts of polymeric material, besides low yields of cyclic derivatives. We assume that in this case the configuration of NLiPBu^t(NPCl$_2$)-NSOPh allows a nucleophilic attack at the remaining PCl_2 centre as only very small amounts of NPH(Bu^t)(NPCl$_2$)NSOPh (**13**) could be detected. The large PCl_2 groups in the lithio derivative of (**1**) prevent such an attack; NLiPBu^t(NSOPh)$_2$ is stable due to the absence of an additional reactive centre.

Considering the reaction of compound (**4**) with LiBu^t (1:1) in more detail, one observes, besides the presence of (1α,3β,5α)-NPH(OPr^i)(NSOPh)$_2$ (**7**), the formation of a monosubstituted derivative (1α,3β,5α)-NPCl(Bu^t)(NSOPh)$_2$ (**11**) in a relatively high yield (40%). As nucleophilic substitution by LiBu^t is excluded, (**11**) must be formed by a metal–halogen exchange process between NLiPBu^t(NSOPh)$_2$ and the starting material (**4**) (Scheme 3). Therefore NLiPBu^t(NSOPh)$_2$ was generated from compound (**12**) and LiBu^n, treated with (**4**) and finally with 2-propanol. According to ^{31}P and ^1H n.m.r. spectrometry the crude reaction mixture again contained (**11**) in about 40% yield. Reaction of (**4**) with LiBu^t, in molar ratio 1:2, and 2-propanol predominantly gave (**12**) (Scheme 3).

It has been described previously[6] that treatment of the intermediate NLiPCl(NPCl$_2$)$_2$ [or NP(NPCl$_2$)$_2$] with alkyl iodides or allyl bromide instead of 2-propanol induces ring cleavage. The reaction of compound (**4**) with 2 equivalents of LiBu^t offers an excellent opportunity to investigate the reactivity of NLiP-Bu^t(NSOPh)$_2$. Treatment with alkyl iodides RI (R = Me, Pr^n, or Pr^i), allyl bromide, or acetyl chloride gave a series of compounds (1α,3β,5α)-NPR(Bu^t)(NSOPh)$_2$ (**14**)—(**18**) in about 60% yield [overall yield 70%: 60% of (1α,3β,5α)-NPR(Bu^t)-(NSOPh)$_2$ plus 10% of (**11**)], except for (**18**) (yield 26%). These results confirm the conclusion that a large difference in reactivity exists between a =P(:)Cl [or ≡P(:)] and a =P(:)R (R = alkyl) moiety.

Experimental

All experiments were carried out in an atmosphere of dry, oxygen-free nitrogen applying gas-vacuum techniques in combination with Schlenk-type glassware. Liquids were transferred with syringes.

Solvents (tetrahydrofuran, diethyl ether, and pentane) were distilled prior to use under nitrogen from sodium potassium benzophenone. 2-Propanol (Merck) was dried on molecular sieves. A solution of LiMe in diethyl ether (1.6 mol dm^{-3}) was prepared from lithium and methyl chloride according to standard procedures.[14] Solutions of LiBu^t in pentane (1.6 mol dm^{-3}) or LiBu^n in hexane (1.6 mol dm^{-3}) were obtained commercially from Janssen. The concentrations of the LiR solutions were checked regularly by titration. The compounds *trans*- and

cis-$NPCl_2(NSOPh)_2$ (**4**) and (**5**) and $(NPCl_2)_2NSOPh$ (**6**) were prepared according to published methods.[11,15]

Purification by h.p.l.c. was carried out using a Waters system consisting of two 6000 A pumps, combined with a R401 RI detector. Separations were performed on LiChrosorb Si 60/10 columns (internal diameter 22 mm, length 30 cm).

Proton n.m.r. (60 MHz) spectra were recorded on a Perkin-Elmer R-24B instrument using $SiMe_4$ as internal reference; ^{31}P n.m.r. spectra were recorded on a Nicolet NT 200 spectrometer, operating at 81 MHz [$(NPCl_2)_3$ (**1**) was used as external reference (19.9 p.p.m. with respect to 85% H_3PO_4 solution in $CDCl_3$)]. In all cases the ^2H resonance line of the solvent was used for field–frequency lock. Chemical shifts are positive to low field. Mass spectra were obtained with an AEI Ms9 mass spectrometer (Mr. A. Kiewiet, Department of Organic Chemistry, this University). I.r. spectra were recorded with a Pye-Unicam SP3-300 spectrophotometer, using KBr discs, and calibrated by means of polystyrene film bands. These spectra were utilized for fingerprint purposes only (characteristic bands: 1 280—1 200, SO; 1 200—1 100 cm^{-1}, PNS ring).

Elemental analyses were carried out at the Microanalytical Department of this University under supervision of Mr. A. F. Hamminga.

(*a*) *Analysis of the Crude Reaction Mixtures by N.M.R. Methods.*—Reactions of compounds (**4**)—(**6**) (0.5 g) in tetrahydrofuran (20 cm^3) with LiR, in molar ratio 1:1 or 1:2 (R = Me or Bu^t), in diethyl ether or pentane (5 cm^3) and 2-propanol (0.49 cm^3, 6.5 mmol) were carried out under standard conditions. After the reaction the solvent was removed *in vacuo*. In the case of (**6**) the remainder was extracted with pentane. The reaction products from (**4**) and (**5**) appeared to be poorly soluble in pentane. Hence, the residues were dissolved in dichloromethane and filtered through neutral alumina to remove salts and polymeric substances (for a typical reaction procedure see below). The reaction mixtures, thus obtained, could be dissolved completely in $CDCl_3$ (2.5 cm^3). The composition of each reaction mixture was analysed by ^{31}P and ^1H n.m.r. spectrometry. In order to overcome differences in relaxation time and to obtain a reasonable intensity–concentration correlation from the ^{31}P n.m.r. spectra it was necessary to compare the ^{31}P and ^1H n.m.r. spectra of a well defined mixture of compounds (**11**), (**7**), and (**12**). Absolute yields (mol%) as well as total yields of cyclic material are collected in Table 1.

(*b*) *Reactions of* trans *and* cis-$NPCl_2(NSOPh)_2$ (**4**) *and* (**5**) *with* LiMe, *in Molar Ratio* 1:1, *and* 2-*Propanol.*—Methyllithium (1.3 mmol) in diethyl ether (5 cm^3) was added dropwise to a stirred solution of compound (**4**) or (**5**) (0.5 g, 1.3 mmol) in tetrahydrofuran (20 cm^3) at −78 °C. After stirring for 2 h at −60 °C, 2-propanol (0.5 cm^3) was added dropwise. The reaction mixture was allowed to warm to room temperature within 1.5 h, after which the solvent was removed by evaporation. Filtration of a solution of the remainder in dichloromethane through neutral alumina and subsequent evaporation gave a white solid (0.25 g). Recrystallization from diethyl ether afforded pure compound (**7**) or (**8**).

(1α,3β,5α)-$NPH(OPr^i)(NSOPh)_2$ (**7**) (0.2 g, 41%), colourless crystals, m.p. 77.5—79.5 °C [Found: C, 46.95; H, 4.75; N, 11.05; S, 16.70. $C_{15}H_{18}N_3O_3PS_2$ (*M* = 383.43) requires C, 47.00; H, 4.75; N, 10.95; S, 16.70%]. Mass spectrum: *m/e* 383 (M^+, 35) and 342 ($M - C_3H_5$, 100%). (1α,3α,5α)-$NPH(OPr^i)(NSOPh)_2$ (**8**) (0.2 g, 41%), white crystals, m.p. 130.5—132.5 °C [Found: C, 46.65; H, 4.75; N, 11.10; S, 16.80. $C_{15}H_{18}N_3O_3PS_2$ (*M* = 383.43) requires C, 47.00; H, 4.75; N, 10.95; S, 16.70%].

(*c*) *Reactions of* trans-$NPCl_2(NSOPh)_2$ (**4**) *with* LiBu^t *in Molar Ratio* 1:1 *or* 1:2, *and* 2-*Propanol.*—For procedure see above. Reaction of compound (**4**) (2.0 g, 5.1 mmol) in tetrahydrofuran (80 cm^3) with LiBu^t (5.1 mmol, 10.2 mmol) in pentane (20 cm^3) gave the crude products (1.6, 1.7 g). Both mixtures were subjected to h.p.l.c. using a hexane–tetrahydrofuran (8:2) eluant.

In case of the 1:1 reaction three fractions were isolated. Fraction 1: 0.85 g, (40%). Recrystallization from diethyl ether afforded colourless crystals of (1α,3β,5α)-$NPCl(Bu^t)(NSOPh)_2$ (**11**) (0.8 g, 38%), m.p. 166—168 °C [Found: C, 46.20; H, 4.60; Cl, 8.65; N, 10.15; S, 15.35. $C_{16}H_{19}ClN_3O_2PS_2$ (*M* = 415.90) requires C, 46.20; H, 4.60; Cl, 8.50; N, 10.10; S, 15.40%]. Mass spectrum: *m/e* 415 (M^+, 38), 359 ($M - C_4H_8$, 68), 324 [$M-(^{35}Cl + C_4H_8)$, 61], 77 (Ph, 64), and 57 (Bu^t, 100%). Fraction 2: 0.55 g (30%). Recrystallization from diethyl ether afforded colourless crystals of (1α,3β,5α)-$NPH(OPr^i)(NSOPh)_2$ (**7**) (0.5 g, 27%). Fraction 3: 0.2 g (10%). Recrystallization from diethyl ether afforded white crystals of (1α,3β,5α)-$NPH(Bu^t)(NSOPh)_2$ (**12**) (0.16 g, 8%), m.p. 125—127 °C [Found: C, 50.60; H, 5.15; N, 10.75; S, 16.80. $C_{16}H_{20}N_3O_2PS_2$ (*M* = 381.46) requires C, 50.40; H, 5.30; N, 11.00; S, 16.80%]. Mass spectrum: *m/e* 381 (M^+, 60), 325 ($M - C_4H_8$, 100), 248 [$M-(Ph + C_4H_8)$, 48], 77 (Ph, 97), and 57 (Bu^t, 98%).

In case of the 1:2 reaction two fractions were isolated. Fraction 1: (1α,3β,5α)-$NPCl(Bu^t)(NSOPh)_2$ (**11**) (0.2 g, 10%). Fraction 2: 1.35 g (70%). Recrystallization from diethyl ether afforded white crystals of (1α,3β,5α)-$NPH(Bu^t)(NSOPh)_2$ (**12**) (1.2 g, 62%).

(*d*) *Reactions of* trans-$NPCl_2(NSOPh)_2$ (**4**) *with* LiBu^t, *in Molar Ratio* 1:2, *and* RX.—Reaction mixtures obtained from compound (**4**) (1.0 g, 2.5 mmol) and LiBu^t (5.0 mmol) [see procedure (*b*)] were treated at −60 °C with a five-fold excess of RI (R = Me, Pr^n, or Pr^i), allyl bromide, or acetyl chloride. Stirring was continued for 17 h at room temperature. Crude products were separated from the reaction mixtures by means of h.p.l.c. using hexane–tetrahydrofuran (8:2) as eluant and recrystallized from diethyl ether.

(1α,3β,5α)-$NPMe(Bu^t)(NSOPh)_2$ (**15**) (0.6 g, 60%), white crystals, m.p. 155.5—157 °C [Found: C, 52.00; H, 5.60; N, 10.60; S, 16.25. $C_{17}H_{22}N_3O_2PS_2$ (*M* = 395.48) requires C, 51.65; H, 5.60; N, 10.60; S, 16.20%]. Mass spectrum: *m/e* 395 (M^+, 31), 339 ($M - C_4H_8$, 100), 324 [$M-(C_4H_8 + Me)$, 69], and 262 [$M-(C_4H_8 + Ph)$, 64%]. N.m.r. ($CDCl_3$): ^1H, δ 1.0 [9 H, d, ^3J(PH) 17.3, Bu^t], 1.4 [3 H, d, ^2J(PH) 15.4 Hz, Me], and 7.7 (10 H, m, Ph); ^{31}P, 44.3.

(1α,3β,5α)-$NPPr^n(Bu^t)(NSOPh)_2$ (**16**) (0.65 g, 60%), white crystals, m.p. 143—144.5 °C [Found: C,53.90; H, 6.20; N, 9.80; S, 15.10. $C_{19}H_{26}N_3O_2PS_2$ (*M* = 423.54) requires C, 53.90; H, 6.20; N, 9.90; S, 15.15%]. Mass spectrum: *m/z* 423 (M^+, 8), 381 ($M - C_3H_6$, 34), and 324 [$M-(C_6H_3 + C_4H_9)$, 100%]. N.m.r. ($CDCl_3$): ^1H, δ *ca.* 0.9 (3 H, Me), 1.0 [9 H, d, ^3J(PH) 15.8 Hz, Bu^t], 1.7 (4 H, m, CH_2), and 7.7 (10 H, m, Ph); ^{31}P, 46.9.

(1α,3β,5α)-$NPPr^i(Bu^t)(NSOPh)_2$ (**17**) (0.5 g, 47%), white crystals, m.p. 156.5—159 °C [Found: C, 53.75; H, 6.30; N, 9.90; S, 15.05. $C_{19}H_{26}N_3O_2PS_2$ (*M* = 423.54) requires C, 53.90; H, 6.20; N, 9.90; S, 15.15%]. Mass spectrum: *m/e* 423 (M^+, 8), 381 ($M - C_3H_6$, 48), 367 ($M - C_4H_8$, 57), and 324 [$M-(C_3H_6 + C_4H_9)$, 100%]. N.m.r. ($CDCl_3$): ^1H, δ 1.0 [3 H, m, ^3J(PH) 16.8, ^3J(HH) 6.2, Pr^i], 1.05 [9 H, d, ^3J(PH) 16.3, Bu^t], 1.1 [3 H, m, ^3J(PH) 16.8, ^3J(HH) 6.2 Hz, Pr^i], 2.1 (1 H, m, CH), and 7.7 (10 H, m, Ph); ^{31}P, 50.0.

(1α,3β,5α)-$NPC_3H_5(Bu^t)(NSOPh)_2$ (**18**) (0.64 g, 60%), white crystals, m.p. 132—134 °C [Found: C, 54.30; H, 5.60; N, 9.95; S, 15.25. $C_{19}H_{24}N_3O_2PS_2$ (*M* = 421.52) requires C, 54.15; H, 5.75; N, 9.95; S, 15.2%]. Mass spectrum: *m/e* 421 (M^+, 4), 365 ($M - C_4H_8$, 34), and 324 [$M-(C_4H_8 + C_3H_5)$, 100%]. N.m.r. ($CDCl_3$): ^1H, δ 1.0 [9 H, d, ^3J(PH) 17.7 Hz, Bu^t], 2.7 (2 H, m, CH_2), 5.1 (2 H, m, CH_2), 5.6 (1 H, m, CH), and 7.7 (10 H, m, Ph); ^{31}P, 44.0.

(1α,3β,5α)-NP(COMe)Bu^t(NSOPh)$_2$ (**19**) (0.28 g, 26%). The comparatively low yield is due to hydrolysis during the h.p.l.c. N.m.r. ($CDCl_3$): ^{1}H, δ 1.1 [9 H, d, ^3J(PH) 17.8, Bu^t] and 2.2 [3 H, d, ^3J(PH) 4.3 Hz, Me]; ^{31}P, 29.2.

(*e*) *Reaction of* (1α,3β,5α)-NPH(Bu^t)(NSOPh)$_2$ (**12**) *with* LiBu^n, trans-$NPCl_2$(NSOPh)$_2$ (**4**), *and* 2-*Propanol*.—n-Butyllithium (1.0 mmol) in pentane (5 cm^3) was added dropwise to a stirred solution of compound (**12**) (0.4 g, 1.0 mmol) in tetrahydrofuran (15 cm^3) at −78 °C. After stirring for 0.8 h at −60 °C, (**4**) (0.41 g, 1.0 mmol) in tetrahydrofuran (5 cm^3) was added dropwise. Stirring was continued for 2 h at −60 °C. After addition of 2-propanol (0.38 cm^3, 5 mmol) the reaction mixture was allowed to warm to room temperature within 1.5 h. The solvent was removed by evaporation. A solution of the remainder in dichloromethane was filtered through neutral alumina. Subsequent evaporation afforded a white solid (0.5 g). According to ^{31}P and ^{1}H n.m.r. spectrometry the mixture contained the (1α,3β,5α) isomers of NPCl(Bu^t)(NSOPh)$_2$ (**11**) (35%), NPH(OPr^i)(NSOPh)$_2$ (**7**) (22%), and NPH(Bu^t)-(NSOPh)$_2$ (**12**) (6%).

(*f*) *Preparation of* (1α,3α,5β)-NPCl(OPr^i)(NSOPh)$_2$ (**20**).—Sodium isopropoxide [prepared from sodium (0.03 g, 1.3 mmol) and 2-propanol (0.1 cm^3, 1.3 mmol) in tetrahydrofuran (8.5 cm^3)] was added dropwise to a stirred solution of compound (**5**) (0.5 g, 1.3 mmol) in tetrahydrofuran (20 cm^3). Stirring was continued for 17 h. The solvent was removed by evaporation. A solution of the remainder in dichloromethane gave after filtration through neutral alumina and subsequent evaporation the crude product. Recrystallization from diethyl ether afforded white crystals of (1α,3α,5β)-NPCl(OPr^i)(NSOPh)$_2$ (**20**) (0.3 g, 57%), m.p. 107—108 °C [Found: C, 43.05; H, 4.00; Cl, 8.85; N, 10.00. $C_{15}H_{17}ClN_3PO_3S_2$ (M = 417.89) requires C, 43.10; H, 4.10; Cl, 8.50; N, 10.05%].

Acknowledgements

This investigation was supported by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization of Advancement of Pure Research (Z.W.O.).

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Received 19*th August* 1985; *Paper* 5/1444