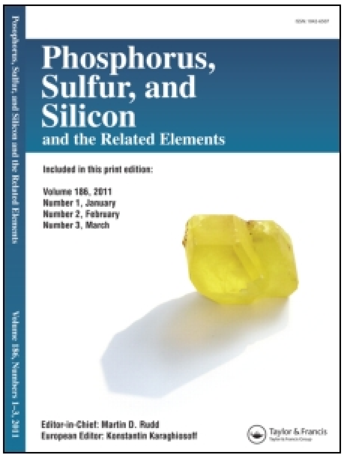

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THE REACTION OF PHOSPHORUS TRICHLORIDE WITH PROPANOLAMINE-1.3

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The reaction of PCl_3 with propanolamine-1.3 in the presence of NEt_3 was studied and found to form two heterocyclic compounds, the 2-chloro-3-dichlorophosphanyl-1.3.2-oxazaphosphorinane and the 2-aminopropoxy-1.3.2-oxazaphosphorinane, which could be isolated and characterized. By low-temperature NMR the formation of the 2-chloro-3-dichlorophosphanyl-1.3.2-oxazaphosphorinane was found to proceed via a diphosphanylated propanolamine-1.3.

Key words: Oxazaphosphorinanes; N-phosphanylphosphorinanes; 2-chloro-3-dichlorophosphanyl-1.3.2-oxazaphosphorinane; NMR data.

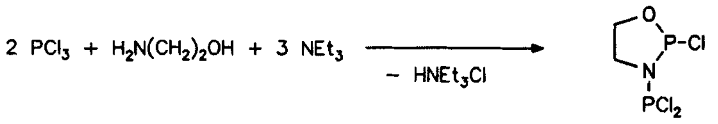
INTRODUCTION

In many cases the reactions of trivalent phosphorus compounds with primary amines don't give the expected monosubstituted phosphanes as final products of the reaction. Moreover these primary substitution products were observed to be formed as intermediates during the synthesis of a great variety of other linear and cyclic aminophosphanes.

It has been shown recently that the reaction behaviour in the system PCl_3/primary amine must be considered to be very complex,[1,2,3] which was especially pointed out by investigations concerning the reaction pathways in the system PCl_3/aniline.[4,5,6,7]

Also the synthesis of heterocyclic trivalent phosphorus compounds containing unsubstituted NH-functions in the ring often was found to be very difficult because secondary reactions based on the reactive centres in the molecule could not be prevented and therefore have to be considered, too.[8,9,10,11,12]

In this connection it was found by Pudovik and coworkers[13] that the reaction of PCl_3 with ethanolamine in the presence of NEt_3 as base doesn't lead to the expected compound, the 2-chloro-1.3.2-oxazaphospholane, but to its N-phosphanylated derivative **1**; Equation (1).

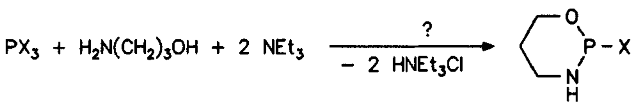


(1)

1

Investigations concerning the corresponding six-membered phosphorus heterocycles, the 1.3.2-oxazaphosphorinanes, have not been described in the literature yet.

Therefore the reactions of phosphorus(III)halides and phosphorus(III)amides with propanolamine-1.3 were thought to be a synthetic route for the halogen- and amino derivatives of the 1.3.2-oxazaphosphorinanes according to Equation (2).



(2)

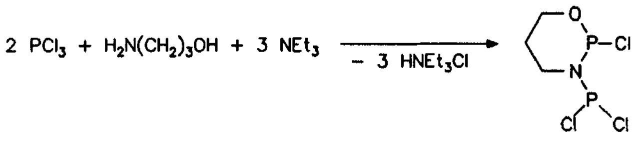
X = Cl, NR$_2$

2

RESULTS AND DISCUSSION

During the reaction of PCl_3 with propanolamine-1.3 at −20°C in diethyl ether, toluene or benzene a discolouring of the reaction mixture to light-green and the formation of a white solid can be observed immediately.

The ^{31}P-NMR spectrum of the reaction solution shows an AX-pattern at δ = 142 and δ = 160 (intensity 70%) with an unusually large coupling constant of 484 Hz, another signal with the chemical shift of 220 for PCl_3[14] (20% intensity) and some signals of lower intensity (4%) at $\delta = 49$, $\delta = 37$, $\delta = 3$ and $\delta = -10$. The main product of the reaction solution could be isolated as a colourless liquid; it was purified by repeated vacuum distillation. By means of several analytical methods (elemental analysis, mass spectrometry, ^{31}P-, ^{15}N-, ^{1}H- and ^{13}C-NMR spectroscopy) the product was proved to be the 2-chloro-3-dichlorophosphanyl-1.3.2-oxazaphosphorinane **3**; Equation 3).



(3)

3

For compound **3** the value of the two-bond phosphorus-phosphorus coupling of 484 Hz is very large. However, proof of a P—N—P-brigde with two nonequivalent phosphorus atoms could be obtained with a ^{15}N-NMR spectrum, wherein the P—N—P-brigde is characterized by two doublets with coupling constants of 76 Hz and 86 Hz. Similarly large $^{2}J_{PNP}$ coupling constants are reported in the literature for other N-brigded diphosphorus compounds of trivalent phosphorus, too.[15]

The ^{13}C-NMR spectrum of the considered compound **3** shows two singlets at δ = 26.5 ($CH_2\underline{C}H_2CH_2$), at δ = 39 ($\underline{C}H_2NP$) and a doublet at δ = 62.2 ($\underline{C}H_2OP$) with a $^{2}J_{PC}$ coupling constant of 5.2 Hz.

In the ^{1}H-NMR spectrum of **3** four multiplets at $\delta = 0.7$, $\delta = 1.5$, $\delta = 3.3$ and $\delta = 3.9$ with an intensity ratio of 1:1:3:1 were observed. In order to obtain an exact correlation between the ^{1}H-nuclei and the ^{13}C-nuclei a {^{13}C-^{1}H}-COSY experiment was carried out leading to the results represented in Table I.

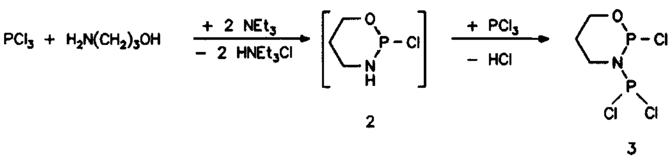
Whereas in the ^{1}H-NMR-spectrum a differentiation of the CH_2N-protons concerning their chemical shifts was found to be impossible, in the COSY-experiment a very small nonequivalence of both protons of the CH_2N-group could be established (see Table I).

TABLE I

Results of the {^{13}C-^{1}H}-COSY-experiment

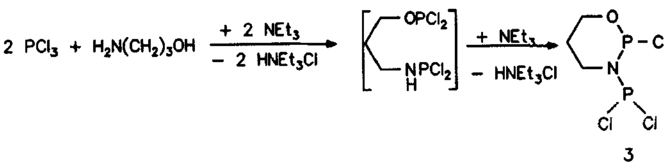
δ^{1}H [ppm]	δ^{13}C [ppm]	intensity	assignment
0.7	26.5	1 H	CH_2-$CH_A\underline{H}_B$-CH_2
1.5	26.5	1 H	CH_2-$CH_B\underline{H}_A$-CH_2
3.3	39.0	1 H	$C\underline{H}_AH_B$-N
3.4	39.0	1 H	$CH_A\underline{H}_B$-N
3.3	62.2	1 H	$CH_B\underline{H}_A$-O
3.9	62.2	1 H	$CH_A\underline{H}_B$-O

Relating to the way of formation of **3** two possibilities may be envisaged. On the one hand the intermediate formation of 2-chloro-1.3.2-oxazaphosphorinane **2** being unsubstituted on the ring nitrogen can be discussed. In the next step **2** is phosphanylated on the nitrogen of the ring by phosphorus trichloride forming **3**; Equation (4).



(4)

On the other hand a diphosphanylated propanolamine-1.3 could be formed as intermediate resulting in **3** by the elimination of hydrogen chloride and simultaneous cyclisation; Equation (5).



(5)

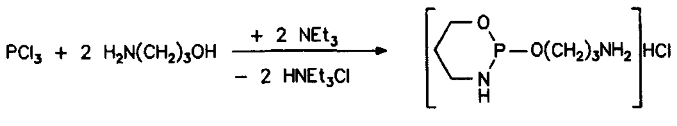
During a low-temperature-^{31}P-NMR investigation of the reaction solution of the system PCl_3/propanolamine-1.3/NEt_3 at −20°C in toluene two singlets of the same intensity at $\delta = 163$ and $\delta = 176$ were observed apart from the typical signal for PCl_3 at $\delta = 220$[14] (intensity 61%) and the two doublets for the disphosphorus compound **3** with about 12% intensity.

It is known from the literature[14] that $NPCl_2$-groups are characterized by signals at about $\delta = 163$, while a $OPCl_2$-group is represented by a signal at $\delta = 176$.

Accordingly the considered reaction is assumed to proceed after the second pathway, in the course of which the propanolamine-1.3, phosphanylated on nitrogen and on oxygen, acts as intermediate during the formation of **3**.

The white solid precipitating during the reaction of phosphorus trichloride with propanolamine-1.3 was found to be a mixture of two components, which could be separated based on their different density in methylenechloride.

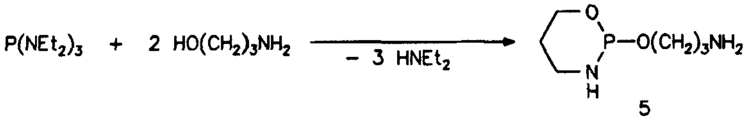
As expected one of the solids could be identified as $HNEt_3Cl$. By elemental analysis the second solid was found to be the hydrochloride of 2-aminopropoxy-1.3.2-oxazaphosphorinane **4** formed according to Equation (6).


4 (6)

Because of the extremely poor solubility of **4** in common organic solvents it was impossible to carry out NMR-spectroscopic investigations. Consequently the hydrochloride **4** was transformed into the corresponding cyclic nitrogen base by treatment with a strong base (DBN) in acetonitrile.

The ^{31}P-NMR spectrum of this reaction shows one singlet at $\delta = 140$ with an intensity of 90%. The corresponding compound which was isolated by distillation and characterized by means of elemental analysis and NMR-spectroscopy could be shown to be the 2-aminopropoxy-1.3.2-oxazaphosphorinane **5**.

In a direct way the preparation of **5** is also possible by the reaction of $P(NEt_2)_3$ with propanolamine-1.3; Equation (7).


5 (7)

EXPERIMENTAL

All experiments were carried out under an atmosphere of nitrogen. The solvents were dried by standard methods. Standard Schlenk procedures were used for all syntheses. The NMR-spectra were recorded on a Bruker AM 300 spectrometer (operating frequencies ^{31}P: 121.5 MHz; ^1H: 300 MHz; ^{13}C: 75 MHz).

The resonance frequencies are given in δ (ppm) and referenced to 85% H_3PO_4 (^{31}P) and tetramethyl silane (^1H, ^{13}C), respectively.

A positive value of δ corresponds to a shift to lower field.

1a. Preparation of 2-chloro-3-dichlorophosphanyl-1.3.2-oxazaphosphorinane **3**. A mixture of 0.44 mol (32.8 g) of propanolamine-1.3 and 0.88 mol (88.5 g) of triethyl amine in 100 ml of toluene is added dropwise at −20°C to a solution of 0.44 mol (60 g) of phosphorus trichloride in 500 ml of toluene under vigorous stirring. After 2h additional stirring the white precipitate is filtered and washed 3 times with 50 ml of toluene and dried *in vacuo*. The resulting yellow-green filtrate is concentrated by removing the solvent under vacuum (10 Torr). The residue is repeatedly distilled under vacuum (1 Torr) yielding the product as a colourless liquid (yield: 12% (6.2 g)).

B.p. (1 Torr; 133,3 Pa) = 75–76,5°C

^{31}P-NMR data (toluene): δ: 142.6 (D); 160.4 (D), $^2J_{PNP} = 484$ Hz

^1H-NMR data (C_6D_6): δ: 0.7 (M) (1 H); 1.5 (M) (1 H); 3.3 (M) (3 H); 3.9 (M) (1 H)

^{13}C-NMR data (C_6D_6): δ: 26.5 (S); 39.0 (S); 62.2 (D); $J = 5.2$ Hz

^{15}N-NMR data (30.4 MHz; C_6D_6): DD $J_1 = 76$ Hz; $J_2 = 86$ Hz (δ-values [ppm] have not been estimated)

Anal. Calcd. for $C_3H_6NOP_2Cl_3$ (240,35):

C, 14.97; H, 2.49; N, 5.82; P, 25.79; Cl, 44.30

Found: C, 14.93; H, 2.51; N, 5.81; P, 25.60; Cl, 44.30

Mass spectrum: m/z (%) = 240 (12, M^+), 104 (5, M^+-PCl_3), 72 (17, $[N(CH_2)_3O]^+$), 66 (51, $[PCl]^+$), 61 (12, $[OPN]^+$), 42 (28, $[(CH_2)_3]^+$), 35 (21, $[Cl]^+$), 31 (28, $[P]^+$)

1b. Preparation of 2-aminopropoxy-1.3.2-oxazaphosphorinane-hydrochloride **4**. 180 g of the white solid obtained under 1a are separated by suspending in 600 ml of CH_2Cl_2 into two solids due to their

different density. The supernatant $HNEt_3Cl$ (114 g = 95% relative to NEt_3) is separated. The second solid isolated is a light-brown powder (35 g) with a low solubility in common organic solvents.
M.p. = 253°C (decomposition)
Anal. Found: C, 36.2; H, 8.11; N, 14.02; P, 15.4; Cl, 17.5
Because of the C/H/N/P/Cl ratio of 6:16:2:1:1 the product is assumed to be the hydrochloride of the 2-aminopropoxy-1.3.2-oxazaphosphorinane [$C_6H_{16}N_2O_2PCl$; 214.45 g/mol].

1c. Preparation of 2-aminopropoxy-1.3.2-oxazaphosphorinane **5**. The light-brown product of 1b is suspended in acetonitrile and treated with an excess of DBN (1.5-diazabicyclo[4.3.0.]non-5-en) at room temperature. **5** is isolated and purified by vacuum distillation (yield: 28.8 g = 37% relative to PCl_3).
B.p. (1 Torr = 133,3 Pa) = 61–63°C
Anal. Calcd. for $C_6H_{15}N_2O_2P$ (178): C, 40.45; H, 8.43; N, 15.73; P, 17.41
Found: C, 40.53; H, 8.57; N, 15.67; P, 17.20
^{31}P-NMR data (benzene): δ = 140 (S)
^{1}H-NMR data (C_6D_6): δ: 1.45–1.6 (M) $CH_2C\underline{H}_2CH$ (4H); 2.45–2.85 (M) $NC\underline{H}_2$, $N\underline{H}_2$, $N\underline{H}$ (7H); 3.4–3.55 (M) $OC\underline{H}_2$ (4H)
^{13}C-NMR data (C_6D_6): δ: 26.5 (S) $(CH_2\underline{C}H_2CH_2)_{ring}$; 36.5 (S) $(CH_2\underline{C}H_2CH_2)_{exo}$; 41.5 (S) $\underline{C}H_2N$; 61 (S) $\underline{C}H_2O$

2. Preparation of 2-aminopropoxy-1.3.2-oxazaphosphorinane **5** *from $P(NEt_2)_3$ and propanolamine-1.3.* 0.14 mol (10.2 g) of propanolamine-1.3 are added dropwise to a solution of 0.068 mol (16.8 g) of $P(NEt_2)_3$ in 40 ml of benzene under vigorous stirring at 50°C. After 6h stirring at 50°C the reaction solution consists of two phases. The upper phase is clear and yellow and the other is oily and dark-red. The two phases are separated and individually distilled. The supernatant yellow phase contains mainly benzene with a little $P(NEt_2)_3$, while from the other dark-red phase **5** is obtained as a colourless, oily liquid (yield: 71% (8.6 g).

Analytical characterization under 1c.

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