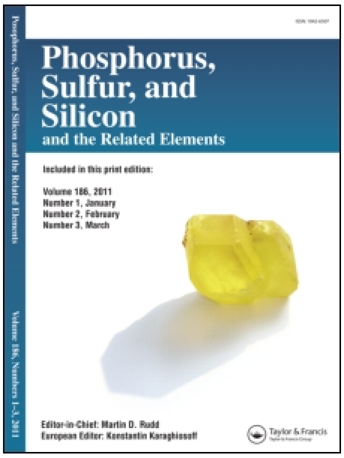

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N-PHOSPHANYLATED 1.3.2-OXAZA- AND 1.3.2-DIAZAPHOSPHOLANES AND -PHOSPHORINANES

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N-PHOSPHANYLATED 1.3.2-OXAZA- AND 1.3.2-DIAZAPHOSPHOLANES AND -PHOSPHORINANES

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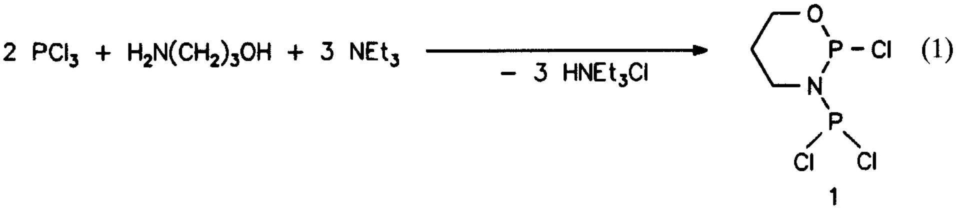
The formation of the *N*-phosphanyl derivatives of the oxaza- and diazaphosphorinanes and -phospholanes **2–10** by the reaction of PX_3 (X = Cl, Br) with alcoholamines and diamines is described. The unusually large $^2J_{PNP}$ coupling constants of the products are discussed.

Key words: *N*-phosphanyloxazaphosphorinanes; *N*-phosphanyldiazaphosphorinanes; $^2J_{PNP}$ coupling constants.

INTRODUCTION

Recently we have found that the reaction of phosphorus trichloride with propanolamine-1.3 in the presence of NEt_3 leads apart from 2-aminopropoxy-1.3.2-oxazaphosphorinane-hydrochloride to 2-chloro-3-dichlorophosphanyl-1.3.2-oxazaphosphorinane **1**; Equation (1).[1]



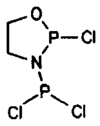
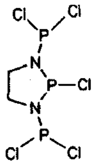
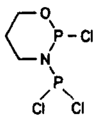
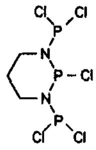
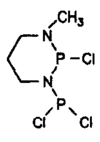
In further investigations we studied the reactions of PCl_3 and PBr_3 with other bifunctional primary amines aiming to obtain the corresponding *N*-phosphanylated cyclic derivatives.

RESULTS AND DISCUSSION

The reaction of PCl_3 with bifunctional protic nucleophiles like ethanolamine, ethylenediamine, propanediamine-1.3 and *N*-methyl-propanediamine-1.3 in the presence of NEt_3 was found to form the corresponding heterocyclic dichlorophosphanyl compounds **2–5** (see Table I).

TABLE I

^{31}P-NMR data of the dichlorophosphanyl compounds **1–5**

compound	$\delta^{31}P$ in ppm	$^2J_{PNP}$ in Hz
 **2**	155.0 (D) 158.7 (D)	254
 **3**	134 (T) 158.4 (D)	312
 **1**	142.6 (D) 160.4 (D)	484
 **4**	113.4 (T) 162.2 (D)	527
 **5**	128.9 (D) 162.2 (D)	517

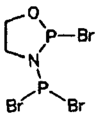
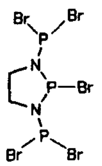
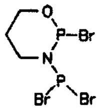
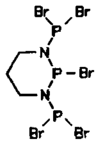
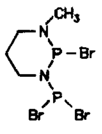
(D = doublet; T = triplet)

As reported in Table I the products of the reactions of PCl_3 with alcoholamines are represented by typical AX-pattern in their ^{31}P-NMR spectra, whereas the resulting products of the reactions with diamines are found to be characterized by typical AX_2-pattern.

The significantly reduced endocyclic OPN-bond angle of 93° to 103°[2] is considered to be an essential feature of the structure of the oxazaphospholanes compared to the phosphorinanes as well as the acyclic analogous compounds. Consequently the electron density on the endocyclic phosphorus atom is decreased, which is indicated by a low-field shift in the ^{31}P-NMR spectrum. Accordingly the endocyclic phosphorus atom of compound **2** shows with δ = 155 the highest value for the ^{31}P-NMR chemical shift in comparison with the other compounds represented in Table I. The ^{31}P-NMR chemical shift for the exocyclic phosphorus atoms was found to be nearly constant (δ = 158 to 162). As expected it is independent of the kind of the ring and of the ring size. In comparison with the reactivity of the alcoholamines with PCl_3 the reactivity of the diamines was observed to be essentially higher, apparently due to the additional free aminofunction. Therefore during the reactions of the diamines polymeric products are also formed in all these cases, whereby the yield of the heterocyclic compound is simultaneously decreased.

TABLE II

^{31}P-NMR data of the dibromophosphanyl compounds **6–10**

compound	δ^{31}P [ppm]	$^2J_{PNP}$ [Hz]
 **6**	153.6 (D) 172.2 (D)	238
 **7**	140.4 (T) 157.2 (D)	298
 **8**	149.5 (D) 160.4 (D)	483
 **9**	110.8 (T) 162.5 (D)	538
 **10**	136.7 (D) 164.2 (D)	521

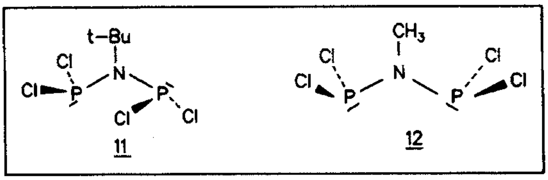


FIGURE 1 *Trans*- and *cis*-orientation of the phosphorus lone-pairs in bis(phosphino)amines.

Furthermore the reactivity of the ethane derivatives with PCl_3 was observed to be comparatively higher than the reactivity of the propane derivatives.

The substitution of PCl_3 by PBr_3 leads to the corresponding bromine compounds **6–10**, which are characterized by similar ^{31}P-NMR spectra (see Table II).

Not only the ^{31}P-NMR chemical shifts but also the $^2J_{PNP}$ coupling constants of the formed heterocyclic compounds containing bromine differ only weakly from their analogous chlorine compounds. Considering the bromine compounds it is also noticed, that the 6-membered heterocyclic compounds formed by the reaction with propane derivatives are characterized by larger ^{31}P-NMR coupling constants than the corresponding 5-membered heterocyclic products.

As before the products formed in the reactions with the diamines are characterized by higher coupling constants relative to the compounds obtained with the alcoholamines.

However, generally the $^2J_{PNP}$ coupling constants are particularly large for the 6-membered chlorine and bromine derivatives.

It is known from the literature, that the amount of the two-bond phosphorus-phosphorus coupling constant is considerably influenced by the orientation of the lone-pairs on the phosphorus nuclei.[3–5]

Very large two-bond phosphorus-phosphorus coupling constants are always measured in the case, where the preferential conformation of the compound is connected with a *cis*-orientation of the lone-pairs on the phosphorus nuclei.

In their studies concerning the NMR data of bisphosphinoamines it was successfully demonstrated by Keat and coworkers,[6] that the preferential conformation of compound **11** in solution containing a *trans*-orientation of the lone-pairs leads to a two-bond phosphorus-phosphorus coupling with a very small value of -20 Hz. In contrast to that the analogous *N*-methyl derivative exists in the conformation **12**, for which a very large $^2J_{PNP}$ coupling constant with a positive value of more than 400 Hz could be measured (see Figure 1).

Consequently the formed *N*-phosphanyl derivatives of the oxaza- and diazaphosphorinanes are assumed to prefer a conformation containing a *cis*-orientation of the lone-pairs at the phosphorus atoms.

EXPERIMENTAL

All experiments were carried out under an atmosphere of nitrogen with dry solvents and starting materials. 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; ^{1}H: 300 MHz; ^{13}C: 75 MHz).

TABLE III

Results of the reactions of PX_3 with bifunctional amines

Amount of PX_3	Kind and amount of amine	Amount of NEt_3	^{31}P-NMR data of the reaction solutions
PCl_3 1 g (7.3 mmol)	$H_2N(CH_2)_2OH$ 0.44 g (7.3 mmol)	1.5 g (0.015 mol)	**2**: 155.0 (*D*); 158.7 (*D*) $^2J_{PNP}$ = 254 Hz Intensity: 90% By-products: at $\delta = -40$, 0 and $\delta = 220$ (PCl_3)
PCl_3 2 g (14.6 mmol)	$H_2N(CH_2)_2NH_2$ 0.9 g (15 mmol)	2.9 g (0.03 mol)	**3**: 134.0 (*T*); 158.4 (*D*) $^2J_{PNP}$ = 312, intensity: 75%; Amount PCl_3 < 5% By-products: singlets at $\delta = -10$; 3; 38; 50; 170; 175
PCl_3 2 g (14.6 mmol)	$H_2N(CH_2)_3NH_2$ 1.1 g (15 mmol)	2.9 g (0.03 mol)	**4**: 113.4 (*T*); 162.2 (*D*) $^2J_{PNP}$ = 527 Hz, intensity: 70%; $\delta = 220$ PCl_3 5% By-products: signals between $\delta = -10$ and 100
PBr_3 1 g (3.7 mmol)	$H_2N(CH_2)_2OH$ 0.22 g (3.7 mmol)	0.74 g (7.4 mmol)	**6**: 153.6 (*D*); 172.2 (*D*) $^2J_{PNP}$ = 238 Hz, intensity: 80%; $\delta = 230$ PBr_3 10% By-products: signals between $\delta = 0$ and 20
PBr_3 2 g (7.4 mmol)	$H_2N(CH_2)_2NH_2$ 0.44 g (7.4 mmol)	1.49 g (0.015 mol)	**7**: 140.4 (*T*); 157.2 (*D*) $^2J_{PNP}$ = 298 Hz, intensity: 65%; $\delta = 230$ PBr_3 20% By-products: signals between $\delta = 160$ and 200
PBr_3 1 g (3.7 mmol) in 8 ml benzene at 0°C	$H_2N(CH_2)_3NH_2$ 0.27 g (3.7 mmol) in 2 ml benzene at 0°C	0.74 g (7.4 mmol)	**9**: 110.8 (*T*); 162.5 (*D*) $^2J_{PNP}$ = 538 Hz, intensity: 70%; $\delta = 230$ PBr_3 15% By-products: signals between $\delta = 70$ and 130

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.

Compound **1** was prepared by the published procedure.[1]

Reactions of PX_3 (X = Cl, Br) with ethanolamine, ethylenediamine and propanediamine-1.3. A solution of the bifunctional amine and triethylamine is added dropwise to a solution of the phosphorus(III)halide in toluene at −20°C. The formed $HNEt_3Cl$ is filtered. The reaction solution was investigated by ^{31}P-NMR-spectroscopy (Table III).

The reactions were carried out in diethyl ether at −20°C, too, whereby comparable results were obtained.

Preparation of 2-chloro-3-dichlorophosphanyl-1-methyl-1.3.2-diazaphosphorinane **5**. A solution of 0.36 mol (32 g) of *N*-methyl-propanediamine-1.3 and 0.73 mol (73.8 g) of NEt_3 in 100 ml of benzene is added dropwise to a solution of 0.36 mol (50 g) of PCl_3 in 400 ml of benzene at 0°C under vigorous stirring.

After 2 h of additional stirring the reaction mixture, consisting of a light yellow-green liquid, $HNEt_3Cl$ and brown, insoluble polymeric product, is filtered and the solid is washed 3 times with 50 ml of benzene. The combined filtrates are evaporated under vacuum. The residue is repeatedly distilled (0.05 Torr) yielding the product as a colourless liquid (yield: 35% (16.3 g).

B.p. (0.05 Torr = 6.6 Pa): 68–70°C

Anal. Calcd. for $C_4H_9N_2P_2Cl_3$ (253.35):
C, 18.95; H, 3.55; N, 11.05; P, 24.47; Cl, 41.97
Found: C, 18.87; H, 3.66; N, 11.21; P, 24.10; Cl, 42.01
^{31}P-NMR data (C_6D_6): $\delta^{31}P_{endo}$: 128.9 (D); $\delta^{31}P_{exo}$: 162.2 (D); $^2J_{PNP}$ = 517 Hz
^1H-NMR data (C_6D_6): δ: 1.0 (M) (1 H) $CH_2C(H_A\underline{H}_B)CH_2$; 1.41 (M) (1 H) $CH_2{-}C(H_B\underline{H}_A)CH_2$; 2.0 (M) (4 H) $NC\underline{H}_3$; $N(CH_3){-}C(H_B\underline{H}_A)CH_2$; 2.55 (M) (1 H) $N(CH_3)C(H_A\underline{H}_B)CH_2$; 3.2 (M) (1 H) $CH_2{-}N(CH_B\underline{H}_A){-}PCl_2$; 3.55 (M) (1 H) $CH_2{-}N(CH_A\underline{H}_B){-}PCl_2$
^{13}C-NMR data (C_6D_6): δ: 25.7 (S) $CH_2{-}\underline{C}\underline{H}_2{-}CH_2$; 38.9 (S) $\underline{C}H_2{-}N{-}PCl_2$; 39.7 (D, $^2J_{PC}$ = 30.9 Hz) $N{-}\underline{C}H_3$; 46.2 (S) $\underline{C}H_2{-}N(CH_3){-}P$

Preparation of 2-bromo-3-dibromophosphanyl-1.3.2-oxazaphosphorinane **8**. A solution of 0.18 mol (13.8 g) of propanolamine-1.3 and 0.37 mol (37.2 g) of NEt_3 in 100 ml of benzene is dropwise added to a solution of 0.18 mol (50 g) of PBr_3 in 400 ml of benzene at 0°C under vigorous stirring. After 2 h of additional stirring the reaction mixture consisting of $HNEt_3Cl$ and a green-yellow liquid as well as a brown, insoluble polymeric product is filtered and the solid is washed 3 times with 50 ml of benzene. The combined yellow-green filtrates are concentrated by removing the solvent and PBr_3 under vacuum (1 Torr = 133.3 Pa) yielding the product as a dark-red, viscous oil (yield: 6.5 g (19%)).

By the elemental analysis the oily product was found to be relatively pure. During a further vacuum distillation decomposition took place at 0.05 Torr and 101°C.

Anal. Calcd. for $C_3H_6NOP_2Br_3$ (373.7):
C, 9.63; H, 1.60; N, 3.75; P, 16.59; Br, 64.14
Found: C, 9.75; H, 1.81; N, 3.60; P, 16.30; Br, 64.30
^{31}P-NMR data (benzene): δ: 149.5 (D); 160.4 (D); $^2J_{PNP}$ = 483 Hz
^1H-NMR data (C_6D_6): δ: 0.7 (M) (1 H) $CH_2C(\underline{H}_AH_B)CH_2$; 1.5 (M) (1 H) $CH_2C(H_A\underline{H}_B)CH_2$; 3.4 (M) (3 H) $C\underline{H}_2N$, $C(\underline{H}_AH_B)O$; 3.8 (M) (1 H) $C(H_A\underline{H}_B)O$
^{13}C-NMR data (C_6D_6): δ: 26.5 (S) ($CH_2\underline{C}H_2CH_2$); 39.1 (S) ($\underline{C}H_2{-}N{-}P$); 62.5 (D); J = 5.2 Hz ($\underline{C}H_2{-}O{-}P$)

Preparation of 2-bromo-3-dibromophosphanyl-1-methyl-1.3.2-diazaphosphorinane **10**. A solution of 0.18 mol (15.7 g) of *N*-methyl-propanediamine-1.3 and 0.37 mol (37.2 g) of NEt_3 in 100 ml of benzene is added dropwise to a solution of 0.18 mol (50 g) of PBr_3 in 400 ml of benzene at 0°C under vigorous stirring. After 2 h of additional stirring the reaction mixture is filtered and the solid phase is washed 3 times with 50 ml of benzene.

The solvent of the combined filtrates is removed in the vacuum. The orange residue is distilled yielding the product at 0.05 Torr and 116°C as a white solid (yield: 21% 7.4 g). B.p. (0.05 Torr = 6.6 Pa): 116°; M.p.: 162°C (decomposition).

Anal. Calcd. for $C_4H_9N_2P_2Br_3$ (386.7):
C, 12.41; H, 2.32; N, 7.24; P, 16.03; Br, 61.97
Found: C, 12.47; H, 2.43; N, 7.28; P, 16.10; Br, 62.20
^{31}P-NMR data: δ: 136.7 (D); 164.2 (D); $^2J_{PNP}$ = 521 Hz

^{1}H-NMR data: δ: 1.2 (M) $CH_2C(H_B\underline{H}_A)CH_2$; 1.45 (M) $CH_2C(\underline{H}_BH_A)CH_2$; 2.0 (M) $NC\underline{H}_3$ and $C(H_B\underline{H}_A)NCH_3$; 2.35 (M) $C(\underline{H}_BH_A)NCH_3$; 3.25 (M) $CH_2—C(H_B\underline{H}_A)NP$; 3.65 (M) $CH_2—C(H_A\underline{H}_B)NP$

^{13}C-NMR data: δ: 25.5 (S) $CH_2\underline{C}H_2CH_2$; 38.9 (S) $\underline{C}H_2N—PBr_2$; 39.5 (D) $^{2}J_{PC}$ = 30.2 Hz $\underline{C}H_3N—PBr$; 46.2 (S) $\underline{C}H_2—N(CH_3)—PBr$

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