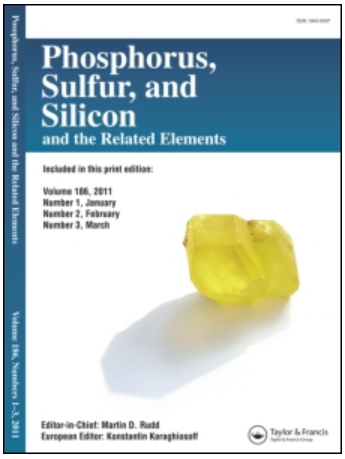

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ON DERIVATISATION REACTIONS OF 2-CHLORO-3-DICHLOROPHOSPHANYL-1.3.2- OXAZAPHOSPHORINANE

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ON DERIVATISATION REACTIONS OF 2-CHLORO-3-DICHLOROPHOSPHANYL-1.3.2-OXAZAPHOSPHORINANE

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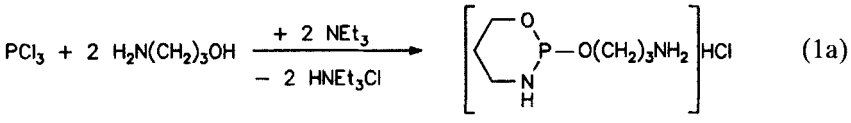
Derivatisation reactions of 2-chloro-3-dichlorophosphanyl-1.3.2-oxazaphosphorinane **1b** with protic nucleophiles like $HNEt_2$, C_2H_5OH, CH_3OH and the Franz-reagent $NEt_3 3HF$ forming the substituted N-phosphanylphosphorinanes **2–10** are described. Furthermore the temperature dependence of the $^2J_{PNP}$-coupling constant of 2-chloro-3-dichlorophosphanyl-1.3.2-oxazaphosphorinane **1b** and 2-diethylamino-3-bis(diethylamino)phosphanyl-1.3.2-oxazaphosphorinane **2** in a range from 203 K to 353 K was investigated.

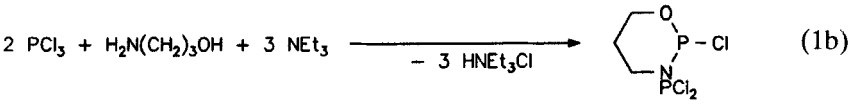
Key words: N-phosphanylphosphorinanes; 2-chloro-3-dichlorophosphanyl-1.3.2-oxazaphosphorinane; temperature dependence of $^2J_{PNP}$.

INTRODUCTION

The reaction of phosphorus trichloride with propanolamine-1.3 in the presence of NEt_3 was found to lead to the formation of two heterocyclic compounds, i.e. the hydrochloride of 2-aminopropoxy-1.3.2-oxazaphosphorinane **1a** and 2-chloro-3-dichlorophosphanyl-1.3.2-oxazaphosphorinane **1b**; Equation (1a) and (1b).[1]



(1a)



(1b)

For investigating the synthetic potential and the stability of the heterocyclic compound **1b** in replacement reactions as well as for obtaining statements concerning differences in the reactivity of the endocyclic and the exocyclic phosphorus atom, we carried out the reaction of **1b** with diethyl amine, methanol, ethanol and the Franz reagent $NEt_3 3HF$ as fluorinating agent.

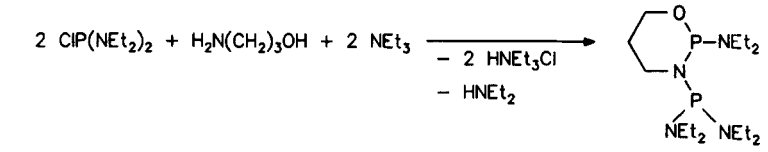
Considering the unusually large $^2J_{PNP}$ coupling constant ($^2J_{PNP}$ = 484 Hz) it was furthermore of special interest, how the value of the coupling constant is influenced by the partial or the complete replacement of chlorine by other substituents.

RESULTS AND DISCUSSION

The investigations concerning the reactions of **1b** with protic nucleophiles have shown, that a manifold derivatisation is possible according to Scheme 1.

In the reaction with diethyl amine in a molor ratio of 1:6 **1b** can be converted nearly quantitatively into the corresponding 2-diethylamino-3-bis(diethylamino)phosphanyl-1.3.2-oxazaphosphorinane **2**.

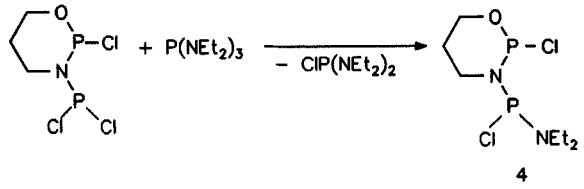
Furthermore the formation of **2** is also achieved by the reaction of $ClP(NEt_2)_2$ with propanolamine-1.3 in the presence of triethyl amine; Equation (2).



(2)

The preparation of the mono- and disubstituted cyclic compounds **3** and **4** according to Scheme 1 was found to be successful by the reaction of **1b** with diethyl amine in the presence of triethyl amine in the molar ratios 1:1:1 and 1:2:2, respectively.

The preparation of the monoamidated compound **4** can be realized by the reaction of **1b** with $P(NEt_2)_3$, too; Equation (3).



(3)

4

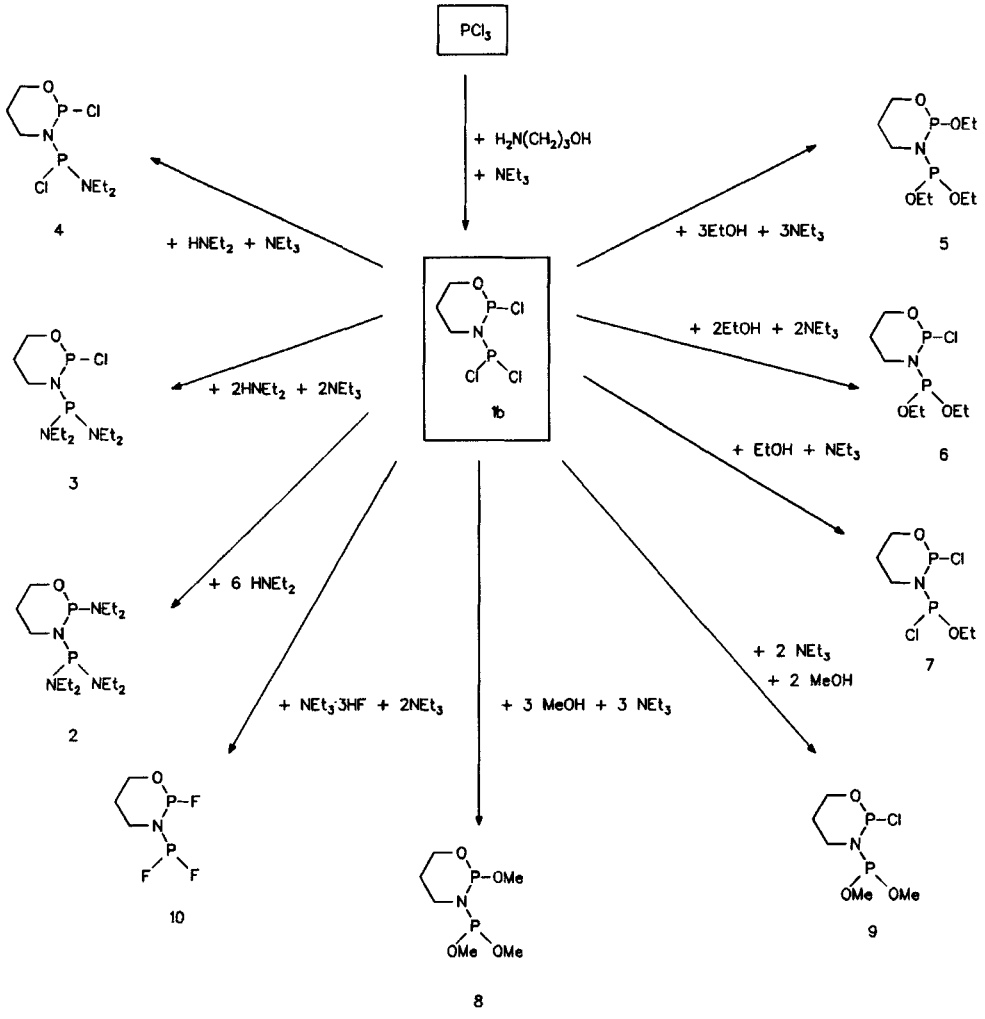
The assignment of the substituents to the exocyclic phosphorus atom for the compounds **3** and **4** represented in Table I results from a comparison of the ^{31}P-NMR chemical shifts of the cyclic chlorine compound **1b** with the corresponding values of the completely amidated compound **2**.

The 2-chloro-3-dichlorophosphanyl-1.3.2-oxazaphosphorinane **1b** was found to show two doublets at δ = 142 and δ = 160 in the ^{31}P-NMR spectrum. It is known from the literature,[2] that $NPCl_2$-groups are characterized by a chemical shift of about 160, so that the exocyclic dichlorophosphanyl group should be represented by the doublet at δ = 160.

For the completely amidated compound **2** two doublets at δ = 111.3 and at δ = 127.6 were observed in the ^{31}P-NMR spectrum. The signal at δ = 111.3 should be assigned to the exocyclic phosphanyl group, because δ-values in a range from 110 to 122 are typical for $P(NR_2)_3$-compounds.[2]

In the ^{31}P-NMR spectrum of the disubstituted compound **3** one of the two doublets is observed at δ = 111, too, which indicates, that a double substitution takes place on the exocyclic phosphorus atom.

Simultaneously it is also shown by the NMR-data, that the replacement, resulting in a change of the electronic conditions on the exocyclic phosphorus, likewise leads to a change of the chemical shift of the endocyclic phosphorus nucleus. This result is especially pointed out by the monoamidated compound **4**. By comparing the



SCHEME 1 Derivatisation reactions of 2-chloro-3-dichlorophosphanyl-1.3.2-oxazaphosphorinane **1b**.

$^2J_{PNP}$-coupling constants represented in Table I, it is generally noticed, that the $^2J_{PNP}$-values of the cyclic amino derivatives **2**, **3** and **4** are essentially smaller in comparison with the $^2J_{PNP}$-coupling constant of the 2-chloro-3-dichlorophosphanyl-1.3.2-oxazaphosphorinane **1b**. Hence the question arises, whether this result is only based on the change of the electronic conditions on the phosphorus nuclei or on the fact that in the case of the cyclic amino derivatives other conformers than in the case of **1b** are formed preferentially.

In this connection investigations concerning the temperature dependence of the $^2J_{PNP}$-coupling constants of 2-chloro-3-dichlorophosphanyl-1.3.2-oxazaphosphorinane **1b** and 2-diethylamino-3-bis(diethylamino)phosphanyl-1.3.2-oxazaphosphorinane **2** were carried out. As expected they led to different results according to Table II.

TABLE I

^{31}P-NMR data of the cyclic amino derivatives of **1b**

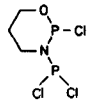
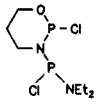
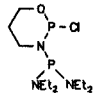
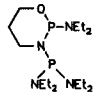
compound	δ^{31}P in ppm	$^2J_{PNP}$ in Hz
 **1b**	endo 142 (D) exo 160 (D)	484
 **4**	exo 134 (D) endo 149 (D)	270
 **3**	exo 111.8 (D) endo 158.6 (D)	159
 **2**	exo 111.3 (D) endo 127.6 (D)	239

TABLE II

Temperature dependence of the $^2J_{PNP}$ coupling constants of **1b** and **2**

temperature in Kelvin	$^2J_{PNP}$ [Hz] of **1b**	$^2J_{PNP}$ [Hz] of **2**
203	484	335
213	484	335
283	486	256
293	484	239
323	478	-
353	472	197

Concerning the $^2J_{PNP}$-coupling constant of **1b** nearly a temperature invariance was found, whereas for the completely amidated compound **2** in a range between 80°C and −70°C an increase of the coupling constant was observed with decreasing temperature. This result points out, that the $^2J_{PNP}$ values, measured for compound **2**, have to be considered to be only mean values representing a certain composition of the existing conformational equilibrium.

With the aim of a further derivatisation of 2-chloro-3-dichlorophosphanyl-1.3.2-oxazaphosphorinane **1b** investigations concerning the alcoholysis of this compound with ethanol and methanol were carried out.

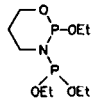
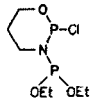
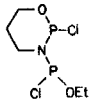
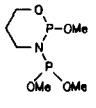
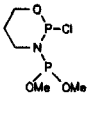
During these reactions it was of a great importance to scavenge the formed hydrogen chloride immediately and completely in order to prevent not only a P-N cleavage of the ring, but also to avoid secondary reactions of the formed alkoxyphosphanylphosphorinanes with hydrogen chloride in analogy to Michaelis-Arbuzov-reactions. In this way the cyclic di- and trialkoxy derivatives **5**, **6**, **8** and **9** were prepared in good yields at −20°C in toluene solution.

The monoethoxy derivative **7** is formed, however, in small yields only, and in the reaction of **1b** with methanol and triethyl amine in a molar ratio of 1:1:1 a mixture of products was obtained, which could not be identified.

Because of the ^{31}P-NMR chemical shift of 146 for $P(OEt)_2NEt_2$[2] the signal at δ = 139.2 for the cyclic triethoxyphosphane **5** (see Table III) should be assigned to the exocyclic phosphanyl group. A comparable signal is observed in the ^{31}P-NMR spectra of the compounds **6**, **8** and **9** (in Table III marked by underlining) and

TABLE III

^{31}P-NMR data of the cyclic alkoxy derivatives of **1b**

compound	δ^{31}P in ppm	$^2J_{PNP}$ in Hz
 **5**	129.6 (D) 139.2 (D)	325
 **6**	137.0 (D) 153.0 (D)	318
 **7**	125.0 (D) 161.9 (D)	435
 **8**	131.0 (D) 141.2 (D)	327
 **9**	139.0 (D) 154.1 (D)	321

therefore these compounds also possess the dialkoxylated exocyclic phosphanyl group.

Considering the structure of the completely alkoxylated compounds **5** and **8** two different O_2PN-groups containing an endocyclic and an exocyclic phosphorus atom can be recognized. The shift difference in the ^{31}P-NMR spectrum amounts to 10 ppm for the compounds **5** and **8**, which should correspond approximately to the difference of the chemical shifts between the oxazaphosphorinanes and the analogeous acyclic compounds. This result is in accordance with the observation of Jones and Katritzky,[3] reporting a high field shift of 6 to 11 for the phosphorus(III)derivatives of the dioxaphosphorinanes in comparison with the analogous acyclic compounds.

Furthermore we carried out investigations concerning the fluorination of **1b** with the Franz reagent $NEt_3 3HF$[4] in the presence of an excess of triethyl amine. The complete fluorination of **1b** proceeds at $-20°C$ in acetonitrile forming nearly quantitatively the 2-fluoro-3-difluorophosphanyl-1.3.2-oxazaphosphorinane **10** (see Scheme 1).

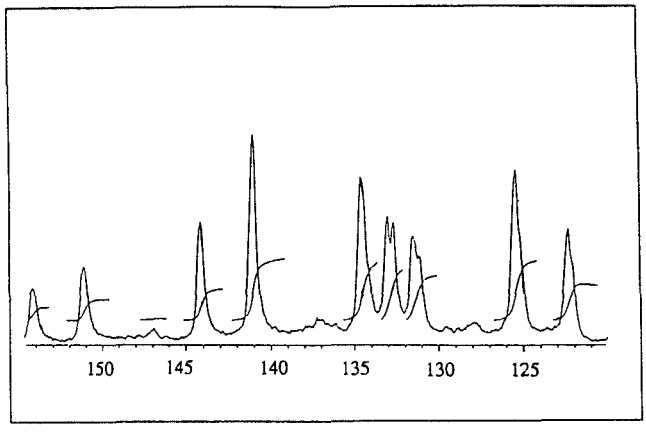


FIGURE 1a ^{31}P-NMR-spectrum of **10**.

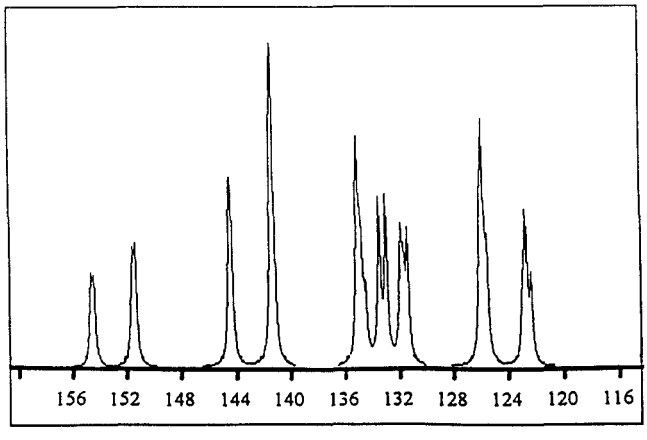


FIGURE 1b Simulation of the ^{31}P-NMR-spectrum of **10**.

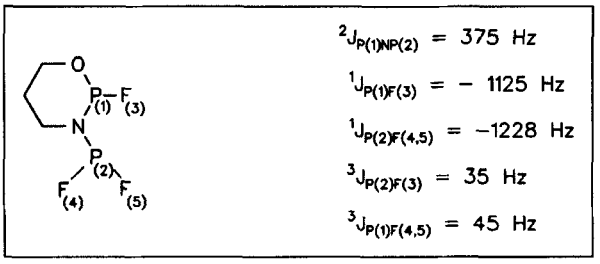


FIGURE 2 PP- and PF-coupling constants of **10**.

In the ^{31}P-NMR-spectrum **10** is characterized by a spectrum of higher order of the type A_2XBY (see Figure 1a).

The Y-part of the spectrum consists of a further splitted doublet at δ = 129 for the endocyclic phosphorus atom P_1 and the X-part consists of a further splitted triplet at δ = 142 for the exocyclic phosphorus atom P_2.

The values for the chemical shifts of the phosphorus nuclei and the coupling constants $^2J_{P(1)NP(2)}$, $^1J_{P(1)F(3)}$, $^1J_{P(2)F(4,5)}$, $^3J_{P(1)F(4,5)}$, $^3J_{P(2)F(3)}$ were determined by a simulation of the spectrum (see Figure 1b and 2).

In the ^{19}F-NMR-spectrum of **10** two doublets further splitted in multiplets at δ = −71.2 for the two fluorine atoms on the exocyclic phosphorus atom P_2 and at δ = −76.3 for the fluorine atom on the endocyclic phosphorus atom P_1 in the expected intensity ratio of 2:1 were observed.

The investigations concerning the preparation of the mono- and difluorinated compound resulted in a great variety of products, which could not be separated and identified.

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 and ^{19}F: 282 MHz). The resonance frequencies are given in δ (ppm) and referenced to 85% H_3PO_4 (^{31}P), to tetramethyl silane (^{1}H, ^{13}C) and to fluortrichlormethane (^{19}F).

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

The preparation of the 2-chloro-3-dichlorophosphanyl-1.3.2-oxazaphosphorinane **1b** was carried out by the published procedure.[1]

1. Preparation of 2 from $ClP(NEt_2)_2$ and propanolamine-1.3. A mixture of 0.21 mol (16.1 g) of propanolamine-1.3, 0.43 mol (43.3 g) of NEt_3 and 100 ml of benzene is added dropwise to a solution of 0.43 mol (90 g) of $ClP(NEt_2)_2$ in 800 ml of benzene at 30°C under vigorous stirring. During the reaction a warming up to 40°C is observed. After 2 h additional stirring the mixture is filtered and the separated solid is washed 3 times with 50 ml of benzene. The solvent of the combined filtrates is removed in the vacuum (40 Torr). The residue is distilled 2 times in a vacuum of 0.05 Torr, whereby the compound is obtained as a viscous, dark-yellow oil (yield: 39% = 30 g).

B.p. = 102°C (0.05 Torr = 6.6 Pa)

Anal. Calcd. for $C_{15}H_{36}N_4P_2O$ (350): C, 51.43, H, 10.28, N, 16.00, P, 17.71

Found: C, 51.38, H, 10.34, N, 15.97, P, 17.50

^{31}P-NMR data (benzene): δ: 111.3 (D); 127.6 (D); $^2J_{PNP}$ = 239 Hz (293 K)

^{1}H-NMR data (C_6D_6): δ: 1.05 (M) 6 × $C\underline{H}_3$ + $CH_2C\underline{H}_2CH_2$; 3.04 (M) 6 × NCH_{2exo} + NCH_{2endo}; 3.62 (M) $CH_B\underline{H}_AO$; 4.09 (M) $C\underline{H}_BH_AO$

^{13}C-NMR data (C_6D_6): δ: 14.9 (S) $\underline{C}H_3$; 27.5 (S) $\underline{C}H_2$; 40.0 (D) (J = 21 Hz $N\underline{C}H_2$); 60.0 (S) $O\underline{C}H_2$

2. Preparation of **2** *from the reaction of* **1b** *with* $HNEt_2$. A solution of 0.01 mol (0.73 g) of $HNEt_2$ in 3 ml of benzene is dropwise added to a solution of 1.7 mmol (0.4 g) of **1b** in 4 ml of benzene at 0°C. After 2 h stirring the reaction mixture is filtered and the resulting solution is concentrated in the vacuum. **^{31}P-NMR-data:** 2 doublets at δ = 111.3 and δ = 127.6 for the diphosphorus compound **2** (90% of total amount of phosphorus); $^2J_{PNP}$ = 239 Hz; by-products (10%) represented by singlets between δ = 5 and 20.

3. Preparation of **3** *by the reaction of* **1b** *with* $HNEt_2$. A solution of 3.3 mmol (0.24 g) of $HNEt_2$ and 3.3 mmol (0.34 g) of NEt_3 in 3 ml of toluene is added dropwise to a solution of 1.7 mmol (0.4 g) of **1b** in 4 ml of toluene at −20°C.

After 2 h stirring the reaction mixture is filtered and the filtrate is concentrated in the vacuum. **^{31}P-NMR data:** 2 doublets at δ = 111.8 and 158.6 for the diphosphorus compound **3** (70% of total amount of phosphorus); $^2J_{PNP}$ = 159 Hz; by-products represented by singlets between δ = 125 and 155.

TABLE IV

Reactions of **1b** with ethanol and methanol in the presence of NEt_3

kind and amount of the alcohol	amount of compound **1b**	amount of NEt_3	^{31}P-NMR data of the reaction solutions
0.09 g (2.1 mmol) ethanol in 3 ml toluene	0.5 g (2.1 mmol) in 5 ml toluene	0.21 g (2.1 mmol)	2 doubl. 125.0; 161.9 ppm (J_{PNP}=435 Hz); intensity:70% side prod.: signals from 0 to 10 ppm
0.19 g (4.2 mmol) ethanol in 3 ml toluene	0.5 g (2.1 mmol) in 5 ml toluene	0.42 g (4.2 mmol)	2 doubl. 137.0; 153.0 ppm J_{PNP}=318 Hz; intensity:75% side prod.: signals from 0 to 10 ppm
0.29 g (6.25 mmol) ethanol in 3 ml toluene	0.5 g (2.1 mmol) in 5 ml toluene	0.63 g (6.25 mmol)	2 doubl. 129.6; 139.2 ppm J_{PNP}=325 Hz; intensity: 80% side prod.: signals from -5 to +15 ppm
0.13 g (4.2 mmol) methanol in 3 ml toluene	0.5 g (2.1 mmol) in 5 ml toluene	0.42 g (4.2 mmol)	2 doubl. 139.0; 154.1 ppm J_{PNP}=321 Hz; intensity: 75% side prod.: signals from -10 to +10 ppm
0.2 g (6.25 mmol) methanol in 3 ml toluene	0.5 g (2.1 mmol) in 5 ml toluene	0.63 g (6.25 mmol)	2 doubl. 131.0; 141.2 ppm J_{PNP}=327 Hz intensity: 80% side prod.: signals at 125, 128 ppm and from 0 to 10 ppm

4. Preparation of **4** *by the reaction of* **1b** *with* $HNEt_2$. A solution of 1.6 mmol (0.12 g) of $HNEt_2$ and 1.6 mmol (0.17 g) of NEt_3 in 3 ml of toluene is dropwise added to a solution of 1.7 mmol (0.4 g) of **1b** in 4 ml of toluene at −20°C under vigorous stirring. After 2 h stirring the reaction mixture is filtered and the filtrate is concentrated in the vacuum.
^{31}P-NMR data: 2 doublets at δ = 134.0 and 149.0 for the diphosphorus compound **4** (80% of total amount of phosphorus); $^2J_{PNP}$ = 270 Hz; by-products represented by singlets between δ = 0 and 20.

5. Preparation of **4** *by the reaction of* **1b** *with* $P(NEt_2)_3$. A solution of 1.7 mmol (0.41 g) of $P(NEt_2)_3$ in 4 ml of benzene is dropwise added to a solution of 1.7 mmol (0.4 g) of **1b** in 4 ml of benzene at 0°C. After 2 h stirring the solvent is removed in the vacuum.
^{31}P-NMR data: 2 doublets at δ = 134.0 and 149.0 for the diphosphorus compound **4**; $^2J_{PNP}$ = 270 Hz; 1 singlet at δ = 154 for $ClP(NEt_2)_2$.[2]

6. Reactions of 2-chloro-3-dichlorophosphanyl-1.3.2-oxazaphosphorinane **1b** *with methanol and ethanol.* Under vigorous stirring a solution of the corresponding alcohol in toluene is dropwise added to a solution of **1b** and NEt_3 in toluene at −20°C. After 2 h additional stirring the formed $HNEt_3Cl$ is separated by filtration. The liquid residue was investigated by ^{31}P-NMR spectroscopy (see Table IV).
The content of the formed diphosphorus compound is indicated relative to the total amount of phosphorus in the solution.

7. Preparation of 2-fluoro-3-difluorophosphanyl-1.3.2-oxazaphosphorinane **10**. Under vigorous stirring a solution of 8.3 mmol (1 g) of $NEt_3$3HF and 0.025 mol (2.5 g) of NEt_3 in 5 ml of acetonitrile is added dropwise to a solution of 8.3 mmol (2 g) of **1b** in 20 ml of acetonitrile at −20°C. The formed $HNEt_3Cl$ is separated by filtration and the resulting solution is liberated from NEt_3 and acetonitrile in a weak vacuum (20 Torr), whereby the diphosphorus compound **10** is obtained as a red-brown oil (yield: 80%).
^{31}P-NMR data (CH_3CN): δ: 129 (D); 142 (T); $^2J_{PNP}$ = 375 Hz; $^1J_{P(1)F(3)}$ = −1125 Hz; $^1J_{P(2)F(4,5)}$ = −1228 Hz; $^3J_{P(2)F(3)}$ = 35 Hz; $^3J_{P(1)F(4,5)}$ = 45 Hz
^{19}F-NMR data (CH_3CN): δ: −71.2 (D); −76.3 (D)
Anal. Calcd. for $C_3H_6NOP_2F_3$ (191): C, 18.85, H, 3.14, N, 7.33
Found: C, 18.70, H, 3.28, N, 7.45
^{1}H-NMR data (CD_3CN): δ: 1.2 (M) $CH_2C\underline{H}_2\text{-}CH_2$; 2.0 (M) $C\underline{H}_AH_BN$; 3.0 (M) $CH_A\underline{H}_BN$; 3.5(M) $C\underline{H}_AH_BO$; 4.3 (M) $CH_A\underline{H}_BO$
^{13}C-NMR data (CD_3CN): δ: 27.5 (S) $CH_2\underline{C}H_2CH_2$; 46.5 (S) $\underline{C}H_2\text{-}N$; 63.5 (S) $\underline{C}H_2\text{-}O$

REFERENCES

1. C. Mundt and L. Riesel, Phosphorus, Sulfur and Silicon, in press.
2. M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark and J. R. van Wazer, Topics in Phosphorus Chemistry, Compilation of ^{31}P-NMR Data, (Interscience Publishers: a Division of Wiley and Sons, New York, London, Sidney, 1967), pp. 253–275.
3. R. A. Y. Jones and A. R. Katritzky, *J. Chem. Soc.*, 4376 (1960).
4. R. Franz, *J. Fluorine Chem.*, **15,** 423 (1980).