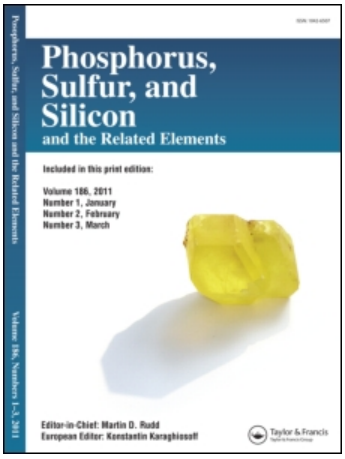

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PREPARATION AND SPECTROSCOPIC STUDIES OF SOME ESTERS OF N, N-DIBENZYL-, N-METHYL, N-BENZYL-, AND N, N-DIMETHYL-AMIDOPHOSPHORYLHALIDIC ACID ESTERS. THE EFFECT OF HALIDS AND AMINE DERIVATIVES ON THE P-N AND P=O BONDS

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PREPARATION AND SPECTROSCOPIC STUDIES OF SOME ESTERS OF N, N-DIBENZYL-, N-METHYL, N-BENZYL-, AND N, N-DIMETHYL-AMIDOPHOSPHORYLHALIDIC ACID ESTERS. THE EFFECT OF HALIDS AND AMINE DERIVATIVES ON THE P-N AND P=O BONDS

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The preparation of the compounds: $(C_6H_5CH_2)_2NP(O)Cl_2$, $(CH_3)(C_6H_5CH_2)NP(O)Cl_2$, $(C_6H_5CH_2)_2NP(O)(Cl)OC_6H_4CH_3$, $(CH_3)(C_6H_5CH_2)NP(O)(Cl)OC_6H_4CH_3$, $(C_6H_5CH_2)_2NP(O)(F)OC_6H_4CH_3$, $(CH_3)(C_6H_5CH_2)NP(O)(F)OC_6H_4CH_3$ and $(CH_3)_2NP(O)(F)OC_6H_4NO_2$ is described and they are characterized by ^{1}H-, ^{13}C-, ^{31}P-, ^{19}F-NMR and IR-spectroscopy. Acccording to their spectroscopic data the properties of the P-N and P=O bonds are strongly dependent on the substituents. Long-range couplings ($^7J_{PH}$) of some compounds have been measured. The ^{1}H-NMR spectra of the molecules were measured at different temperatures in order to study the rotation of P-N bond.

Keywords: Phosphoramidohalidic acid; NMR; IR spectra

INTRODUCTION

Many derivatives of phosphorylchloride have been known in the literature. Some of these derivatives act as pesticides and insecticides [1–10]. *Doak*

* Corresponding author.

and *Freed* have studied amides of arylphosphonic acid and observed antibacterial properties [11]. The preparation of series of alkyl-, arylphosphorylfluorides and thiolates from phosphorylhalides as starting material has been reported by *Olah* and *Oswald* [12]. *Perregaard* and co-workers described the synthesis of esters of N, N-dimethylphosphoramidic acid and N, N-dimethylamidophosphorylchloride from hexamethyl phosphoric acid triamids [13]. The influence of the substituents on the P=O stretching vibration in phosphorylchloride derivatives has been studied by some other authors [14]. *Robinson* and *Lavery* suggested that substitution of the chlorine in N-methyl- und N,N-dimethyl amidophosphoryl halides by fluorine lead to partial P-F multiple bonding and decrease of the $^3J_{PH}$ coupling constant and decrease of the proton chemical shift [15]. Long-range J_{PH} spin-spin coupling (more than over three bonds) have also been observed [16]. In continuation of our recent work on the preparation of $(CH_3)_2NP(O)(X)OC_6H_4CH_3$ (X = Cl, F) [17], we wish to report the synthesis and characterization of the previously unknown compounds $(C_6H_5CH_2)_2NP(O)Cl_2$ (II), $(CH_3)(C_6H_5CH_2)NP(O)Cl_2$ (III), $(C_6H_5CH_2)_2NP(O)(Cl)OC_6H_4CH_3$ (IV), $(CH_3)(C_6H_5CH_2)NP(O)(Cl)OC_6H_4CH_3$ (V), $(C_6H_5CH_2)_2NP(O)(F)OC_6H_4CH_3$ (VI), $(CH_3)(C_6H_5CH_2)NP(O)(F)OC_6H_4CH_3$ (VII), and $(CH_3)_2NP(O)(F)OC_6H_4NO_2$ (VIII). The compounds (VI) and (VII) were prepared by fluorination from the respective chlorine compounds (IV) and (V). Neat NaF, KF, and CsF as well as in presence of 18-crown-6 in various solvents were used for fluorination. The compounds (IV), (V), and $(CH_3)_2NP(O)(Cl)OC_6H_4CH_3$ show a long-range spin coupling ($^7J_{PH}$) which vaniches by substitution of chlorine by fluorine, in the compounds (II) – (VII) the P – N vibration is strongly dependent on the other substituents attached to the phosphorus and nitrogen atom. We measured the ^1H- NMR spectra of (IV), (V), and their fluorine derivatives at different temperatures in order to study the rotation along the P – N bond.

EXPERIMENTAL

Coution ! These types of compounds can be very toxic and should be handled with proper safety precautions and care.

^1H-, ^{13}C – NMR spectra were recorded on a JEOL- JUM- EX 90A FT-NMR and BRUKER 500 FT – NMR spectromerters and ^{19}F-, ^{31}P- NMR spectra on a Bruker AC- 80 FT- NMR spectrometer. ^1H, ^{13}C, ^{19}F or ^{31}P

chemical shifts are determined relative to TMS, $CFCl_3$ or 85% H_3PO_4 as external standard respectively. Infrared spectra were recorded on a Shimadzu Model IR- 60 spectrometer. Elemental analysis was performed using a Heraeus CHN-O-RAPID elemental analyser.

Materials

Chemicals were used without further purification and were obtained from the following companies. Fluka: (Tetrahydrofuran 99%, acetonitrile 99%, p-cresol sodiumfluoride 99%, potasiumfluoride 99%, cesiumfluoride 99%); Aldrich: (pentane 99%, phosphorylchloride 99.999, dibenzylamine 97%, methylbenzylamine 97%, pyridine 99%, triethylamine 99%, 18-crown-6 ether 99%); Merck: (benzene 99%. dried with sodium in tetrahydrofurane). N, N-dimethylamidophosphorylchloride was prepared by the literature method [20].

4-methylphenyl phosphorylchloride was prepared according to the reported method [18].

Syntheses

N, N-dibenzylamidophosphoryldichloride ($(C_6H_5CH_2)_2NP(O)Cl_2$, (II)

A mixture of 9.2 g (60 mmol) phosphorylchloride, 5.1 g (50 mmol) triethylamine and 9.7 g (50 mmol) dibenzylamine was stirred for 1/2h. After filteration of triethylaminehydrochloride and removal of the excess of phosphorylchloride in vacuo, colourless crystals were obtained (yield 85%). Anal. Calc. for $C_{14}H_{14}Cl_2NOP$: C,53.50; H,4.46;N,4.46;Found: C,54.12; H,4.42;N,4.50

Infrared spectrum:(KBr, cm^{-1}): 3090(m), 2945(m), 1500(m), 1491(m), 1237(s), 1095(s), 917(s), 543(s).

NMR- spectrum: ^{1}H-NMR($CDCl_3$); $\delta = 4.3$(d., $^3J_{P\text{-}H} = 14.5$ Hz), 7.4(mult). ^{13}C- NMR($CDCl_3$); $\delta = 48.9$(d., $^2J_{PC} = 4.55$ Hz), 134.4(d., $^3J_{PC} = 4.5$Hz), 128.8(s), 128.6(s), 128.2(s).

N-methyl, N-benzylamidophosphoryldichloride ($(CH_3)(C_6H_5CH_2)NP(O)Cl_2$, (III)

A mixture of 7.7 g (50 mmol) phosphorylchloride, 5.1 g (50 mmol) triethylamine and 6.1 g (50 mmol) N-methyl, N-benzylamine were placed in

a 500 ml round bottom flask and were stirred for 1/2h. After filtration of triethylamine hydrochloride and removal of the excess of phosphorylchloride by distillation in vacuo, colourless crystals of (III) were obtained (yield 85%). Anal. Calc. for $C_8H_{10}Cl_2NOP$: C,40.34; H,4.20; N,5.88;Found:C,40.10; H,4.35; N,5.92: Infrared spectrum; (KBr, cm^{-1}): 3005(m), 2915(m), 1549(m), 1491(m), 1268(s), 1127(m), 917(s), 599(s).

NMR-spectrum:^{1}H-NMR($CDCl_3$): $\delta = 2.7$(d., $^3J_{PH} = 15.8$ Hz), 4.4(d., $^3J_{PH} = 12.1$ Hz), 7.2(mult.). ^{13}C-NMR($CDCl_3$): $\delta = 33.5$(d., $^2J_{PC} = 4.6$ Hz), 53.2(d., $^2J_{PC} = 3.7$ Hz), 128.3, 128.8, 135.1(d., $^3J_{PC} = 6.4$ Hz).

N, N-dibenzylphosphoramidochloridic acid 4-methylphenyl ester $(C_6H_5CH_2)_2NP(O)(Cl)OC_6H_4CH_3$. (IV)

Two different procedures were used for the synthesis of compound (IV).

Procedure A:

13 g (100 mmol) of the sodium salt of p-cresol was added in small portions to a stirred solution of 50.2 g (160 mmol) N,N-dibenzyl amidophosphoryldichloride (II) in 20 ml benzen. After 1/2h the mixture was filtered and the solvent was distilled off in vacuo. The resulting product showed an oily consistence and was purified by column-chromatography (silica gel, solvent: ether/acetic acid ethyl ester 1:2)

Procedure B:

A mixture of 36 g (160 mmol) p-cresol phosphoryldichloride [18] in 20 ml benzene, 31.5 g (160 mmol) N, N-dibenzylamine and 16.2 g (160 mmol) triethylamine was stirred for 1/2h. After filtration and removal of the solvent by distillation in vacuo the compound (IV) was obtained. Anal. Calc. for $C_{21}H_{21}ClNO_2P$: C, 64.50; H, 5.45; N, 3.63; Found: C, 65.30; H, 5.35; N, 3.70.

Infrared-spectrum (KBr, cm^{-1}): 3020(m), 2980(m), 1590(m), 1498(s), 1268(ms), 1194(s), 1067(ms), 939(s), 819(ms), 532(ms).

NMR-spectrum: ^{1}H NMR(CDCl3): $\delta = 2.2$(d., $^7J_{PH} = 1.5$ Hz), 4.3(mult.), 6.8(mult.), 7.2(mult.). ^{13}C-NMR($CDCl_3$): $\delta = 19.9$(s), 48.1(d., $^2J_{PNC} = 4.42$ Hz), 119.3(d., $^3J_{POC} = 5.47$ Hz), 127.3(s), 127.6(s), 128.0(s), 129.7(s), 134.8(s), 147.3(d., $^2J_{POC} = 8.2$ Hz). ^{31}P – NMR ($CDCl_3$): $\delta = 11.6$(quint).

N-methyl, N-benzylphosphoramidochloridic acid 4-methylphenyl ester $(CH_3)(C_6H_5CH_2)NP(O)(Cl)OC_6H_4CH_3$, (V)

The compound (V) was prepared in the same way as (IV) by using either N-methyl, N-benzylphosphoramidodichloride with sodiumsalt of p-cresol (procedur A) or 4-methyl phenyl phosphoryldichloride and N-methyl, N-benzylamine (procedure B). Anal. Calc. for $C_{15}H_{17}ClNO_2P$: C, 58.15; H, 5.49; N, 4.53; Found : C, 57.76; H, 5.55; N, 4.60.

Infrared-spectrum (KBr,cm^1): 3010(m), 2800(m), 1509(m), 1499(vs), 1268(s), 1193(s), 1089(s), 943(s), 818(s), 539(m).

NMR-spectrum: ^{1}H-NMR($CDCl_3$): $\delta = 2.2$(d., $^7J_{PH} = 1.2$ Hz), 2.7(d., $^3J_{PH} = 3.4$ Hz), 4.4(d., $^3J_{PH} = 11.6$ Hz), 7.2(s), 7.4(s). ^{13}C-NMR($CDCl_3$): $\delta = 20.6$(s), 33.5(d., $^2J_{PNC} = 3.65$ Hz), 52.9(d., $^2J_{PNC} = 4.6$ Hz), 120.2(d., $^3J_{POC} = 4.6$ Hz), 127.6(s), 128.6(s), 128.6(s), 130.4(s), 135.5(s), 136.0(d., $^5J_{POC} = 6.4$ Hz), 147.8(d., $^2J_{POC} = 8.2$ Hz). ^{31}P-NMR ($CDCl_3$): $\delta = 12.5$(sext.).

N, N-dibenzyl phosphoramidofluoridic acid 4-methyl phenyl ester $(C_6H_5CH_2)_2NP(O)(F)OC_6H_4CH_3$, (VI)

39.9 g (100 mmol) N, N-dibenzyl phosphoramidochloridic acid 4-methyl phenyl ester and 17.4 g (300 mmol) KF in the presence of 18-crown-6 ether were refluxed in 100 ml benzene for 1/2h. After removing the solvent by distillation in vacuo the residue was purified by running through a silica gel column eluated with $CHCl_3$.

Infrared spectrum (KBr, cm^{-1}): 3010(s), 2950(s), 1600(m), 1501(s), 1324(s) 1197(vs), 1017(s), 867(s), 817(ms).

NMR-spectrum: ^{1}H-NMR($CDCl_3$): $\delta = 2.4$(s), 4.2(mult.), 7.2, 7.4. ^{13}C-NMR($CDCl_3$): $\delta = 20.2$(s), 48.0(d., $^2J_{PNC} = 4.6$ Hz), 119.4(d., $^3J_{POC} = 4.5$ Hz), 127.2(s), 128.0(s), 129.9(s), 134.9(s), 147.5(d., $^2J_{POC} = 7.3$ Hz). ^{31}P-NMR($CDCl_3$): $\delta = -0.9$(d., $J_{PF} = 970.4$ Hz, obtained from ^{19}F spectrum)

N-methyl, N-benzylphosphoramidofluoridic acid 4-methyl phenyl ester $(CH_3)(C_6H_5CH_2)NP(O)(F)OC_6H_4CH_3$, (VII)

A mixture of 30.9 g (100 mmol) N-methyl, N-benzyl phosphoramidochloridic acid 4-methyl phenyl ester and 17.4 g (300 mmol) KF in 100 ml benzene was refluxed in the presence of 18-crown-6 ether for 5 h. The

reaction mixture was treated as described previously for the preparation of compound (VI).

Infrared-spectrum, (KBr, cm^{-1}): 3020(m), 2950(m), 1610(m), 1502(s), 1304(s), 1198(s), 1017(s), 930(s), 888(s), 820(m).

NMR-Spectrum: ^{1}H-NMR($CDCl_3$): δ = 2.3(s), 2.7(d.of 1:1d., $^{3}J_{PH}$ = 10.7, $^{4}J_{FH}$ = 1.3 Hz), 4.3(d. of 1:1 d., $^{3}J_{PH}$ = 10.7, $^{4}J_{FH}$ = 1.3 Hz), 7.2(s), 7.3(s).

^{13}C-NMR($CDCl_3$): δ = 19.8(s), 32.1(d., $^{2}J_{PNC}$ = 4.6 Hz), 52.2(d, $^{2}J_{PNC}$ = 5.5 HZ), 119.0(d., $^{3}J_{POC}$ = 4.6 Hz), 127.2(s), 127.5(s), 128.0(s), 129.8(s), 134.6(s), 135.7(s), 147.2(d., $^{2}J_{POC}$ = 6.4 Hz). ^{31}P-NMR($CDCl_3$): δ = –0.5 (d., J_{PF} = 965.4 obtained from ^{19}F-spectrum).

N, N-dimethylphosphoramidofluoridic acid 4-nitro phenyl ester $(CH_3)_2NP(O)(F)OC_6H_4NO_2$, (VIII)

A mixture of 9.9 g (27 mmol) N, N-dimetyl phosphoramidic acid bis (4-nitro phenyl) ester [19] and 3.1 g (54 mmol) KF was refluxed in 50 ml benzene in the presence of 18-crown-6 ether for 5 days. After filtration of potasium salts and evaporation of the solvent the product (VIII) was obtained. TLC-chromatography was used for purification (solvent: ether/ petrolether 1:2), (yield, 36%). Anal. Calc. for $C_{14}H_{14}NO_7P$: C,45.78; H,3.82; N,11.44; Found: C,45.69; H,3.89; N,11.42.

Infrared-spectrum, (KBr,cm^{-1}): 1582(s), 1514(s), 1277(s), 931(s), 860(s), 766(m).

NMR-spectrum: ^{1}H-NMR($CDCl_3$): δ = 2.8(d.of 1:1 d., $^{3}J_{PH}$ = 10.7, $^{4}J_{FH}$ = 1.9 Hz), 7.4, 8.2. ^{13}C-NMR($CDCl_3$): δ = 36.4(d., $^{2}J_{PNC}$ = 4.5 Hz), 120.4(d., $^{3}J_{POC}$ = 5.4 Hz), 125.9(s), 144.5(s), 154.7(d., $^{2}J_{POC}$ = 6.4 Hz).

RESULTS AND DISCUSSION

Phosphoryltrichloride is used as starting material for the preparation of various esters of phosphoramidohalidic acids. The reaction of phosphoryl-trichloride with hydrochloridsalt of dimethylamine, N, N-dibenzylamine and N-methyl, N-benzylamine yielded N, N-dimethyl-, N, N-dibenzyl-, N-methyl-, N-benzyl amidophosphoryldichloride with the following formula : $(CH_3)_2NP(O)Cl_2$ (I), $(C_6H_5CH_2)_2NP(O)Cl_2$(II), $(CH_3)(C_6H_5CH_2)NP(O)Cl_2$(III).

Two methods are successfully used to synthesize N, N-dibenzyl phosphoramidochloridic acid 4-methyl phenyl ester (IV) and N-methyl, N-benzyl phosphoramidochloridic acid 4-methyl phenyl ester(V).

A: Reaction between sodium salt of p-cresol and amidophosphoryldichloride

$$R_1R_2NP(O)Cl_2 + NaOC_6H_4CH_3 \rightarrow R_1R_2NP(O)(Cl)OC_6H_4CH_3 + NaCl$$

$R_1 = R_2 = C_6H_5CH_2$ (IV); $R_1 = CH_3$, $R_2 = C_6H_5CH_2$ (V)

B: Reaction between 4-methyl phenylphosphoryldichloride and corresponding amine in the presence of triethylamine

$$CH_3C_6H_4OP(O)Cl_2 + R_1R_2NH + Et_3N \rightarrow Et_3NH^+ Cl^- + R_1R_2NP(O)(Cl)OC_6H_4CH_3.$$

The compounds (VI), (VII) and $(CH_3)_2NP(O)(F)OC_6H_4NO_2$ (VIII) were synthesized by fluorination of (IV), (V), and $(CH_3)_2NP(O)(OC_6H_4NO_2)_2$(IX).

The alkalimetalfluorides (NaF, KF, CsF) in the presence or absence of 18-crown-6 ether were used as fluorinating agents. The results are summarized in Table I.

TABLE I Results of the fluorination of (IV) and (V) with different fluorinating agents and solvents

Fluorination agent	*Solvent*	*Reflux time (h)*	*yield(%)*
NaF	Benzene	5	46
NaF, 18-crown-6	Benzene	5	55
KF	Benzene	5	65
KF, 18-crown-6	Benzene	5	90
CsF	Benzene	5	70
CsF, 18-crown-6	Benzene	5	88
KF, 18-crown-6	Acetonitrile	5	90
CsF, 18-crown-6	Acetonitrile	5	90

Many articles have described the substitution effect on the P=O vibrational wavenumber in phosphorylchloride derivatives. *Wagner* calculated

the strengths of a series of symmetrically substituted phosphoryl moleculs $Y_3P(O)$. He found, that the P=O bond characters are directly related to the electronegativities of substituent [3]. This phenomenon is experimentally reported for organic derivates of phosphoric acid by *Leonard* [5]. As is illustrated in table II an increase in the P=O vibrational wavenumber can be observed by substitution of chlorine with fluorine in amidophosphoryl-halides (Table II).

TABLE II P=O stretching wavenumber of N, N-dimethylamino -compounds

compounds	$\nu_{P=O}/cm^{-1}$	ν_{P-N}/cm^{-1}	*ref.*
$(CH_3)_2NP(O)Cl_2$	1275	722	[22,25]
$(CH_3)_2NP(O)F_2$	1340	842	[21]
$[(CH_3)_2]_2NP(O)Cl$	1241	758	[22,25]
$[(CH_3)_2N]_2P(O)F$	1315	760	[21]

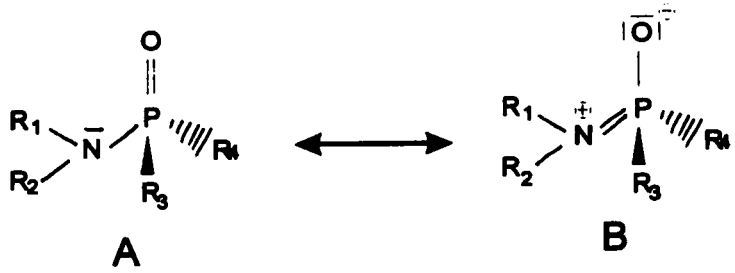
Moreover, in addition to this increase a similar situation is valid for the P-N vibrations. Therefor we can use the wavenumber of the P-N bond for characterization of the P-N bond in the amidophosphoryl compounds. It is widely believed that due to its isolated mode P=O vibration is more characteristic than P-N. Hence it is neccessary to use the P-N vibrational wavenumber with care. The molecule $(CH_3)_2NP(O)Cl_2$ (I) is considered, as reference molecule. Bonding changes in the P-N bond and also in the P=O bond are evaluated by substitution of methyl groups in the amine ligand and chlorine atoms connected to phosphorus. The molecule (III) is obtained by substitution of one methyl- by benzyl group in the reference molecule. In this case, the vibrational wavenumber of ν(P-N) shifts by about 200 cm^{-1} in comparison with our reference molecule (I). By substitution of two methyl- by two benzyl groups in the reference molecule, molecule (II) is formed. The IR-spectra of molecule (II) shows an increase of ν(P-N) by about 200 cm^{-1} and also a decrease of ν(P=O) by about 30 cm^{-1} in comparison with the reference molecule. In table III the ν(P=O), and ν(P-N) stretching wavenumbers of compounds (I) – (IX) are listed.

The vibrational wavenumbers are compared to previously reported data [7, 10, 11, 21–26]. The increase of ν(P-N) and decrease of ν(P=O) are probably related to the donor character of the benzyl group in the molecules (II) and (III), which favours resonance structure B.

TABLE III P=O and P-N stretching wavenumbers of compounds (I)--(IX)

Compounds	$\nu_{P=O}/cm^{-1}$	ν_{P-N}/cm^{-1}	*ref.*
$(CH_3)_2NP(O)Cl_2$(I)	1268	722	22,25
$(C_6H_5CH_2)_2NP(O)Cl_2$(II)	1237	917	a
$(CH_3)(C_6H_5CH_2)NP(O)Cl_2$(III)	1268	917	a
$(C_6H_5CH_2)_2NP(O)(Cl)OC_6H_4CH_3$(IV)	1268	819	a
$(CH_3)(C_6H_5CH_2)NP(O)(Cl)OC_6H_4CH_3$(V)	1268	818	a
$(C_6H_5CH_2)_2NP(O)(F)OC_6H_4CH_3$(VI)	1324	817	a
$(CH_3)(C_6H_5CH_2)NP(O)(F)OC_6H_4CH_3$(VII)	1304	850	a
$(CH_3)_2NP(O)(F)OC_6H_4NO_2$(VIII)	1277	766	a
$(CH_3)_2NP(O)(OC_6H_4NO_2)_2$(IX)	1267	776	19

a. this work.



With increase of electron donor ability of R_1 and R_2 the double bond character of the P-N bond increases While the double bond character of P=O bond decreases. If one of the chlorine atoms in compound (II), and (III) is substituted by a π-donor group (p-cresol) the molecules (IV) and (V) are obtained. The IR-spectra of the compounds (IV) and (V) shows a significant reduction in the vibration wavenumber of P-N (about 100 cm^{-1}) in comparison to (II) and (III). Although p-cresol is a π-donor ligand, still ν(P=O) increases compared to (II), while the change between (III) and (V) is small. Despite p-cresol being more electropositive than chlorine, the P=O stretch shifts to higher wavenumber. The compound (VI) and (VII) are obtained by substitution of chlorine in compound (IV)

and (V) by fluorine. In these cases there is no change in ν(P-N) but we witness an increase in the P=O wavenumber by fluorination. If one para nitrophenol in the molecule $(CH_3)_2NP(O)(OC_6H_4NO_2)_2$ (IX) [19] is replaced by fluorine we are dealing with compound (VIII).

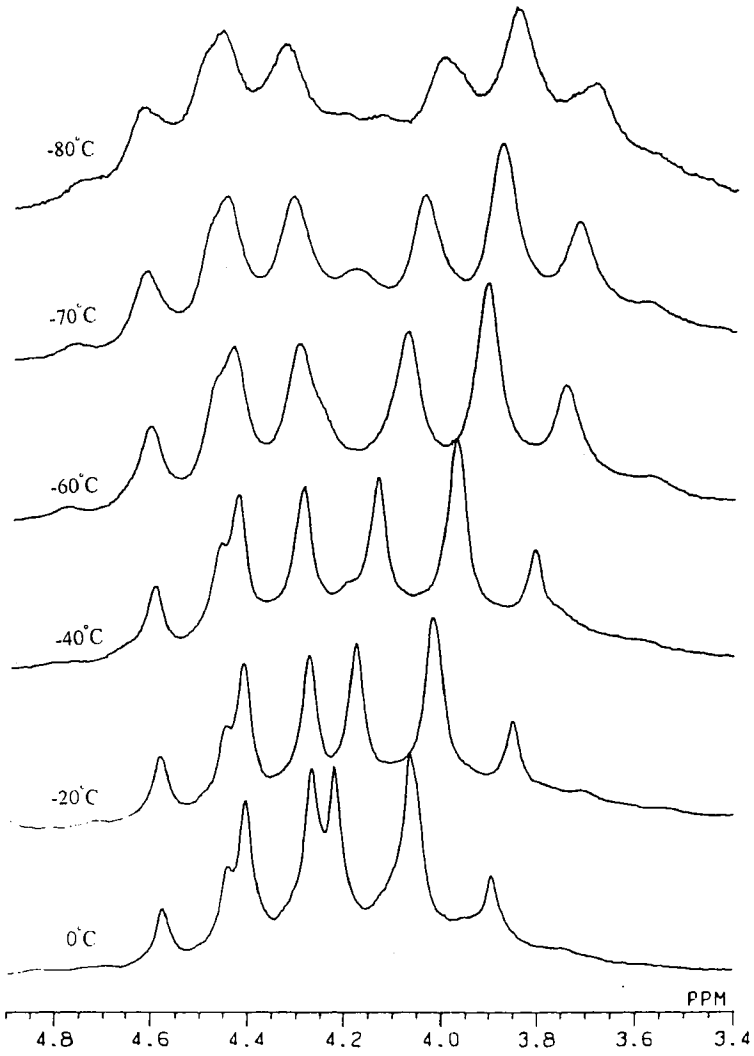


FIGURE 1 ^{1}H-NMR spectra of CH_2-proto in $(C_6H_5CH_2)_2NP(O)(Cl)OC_6H_4CH_3$(IV) at low temperatures

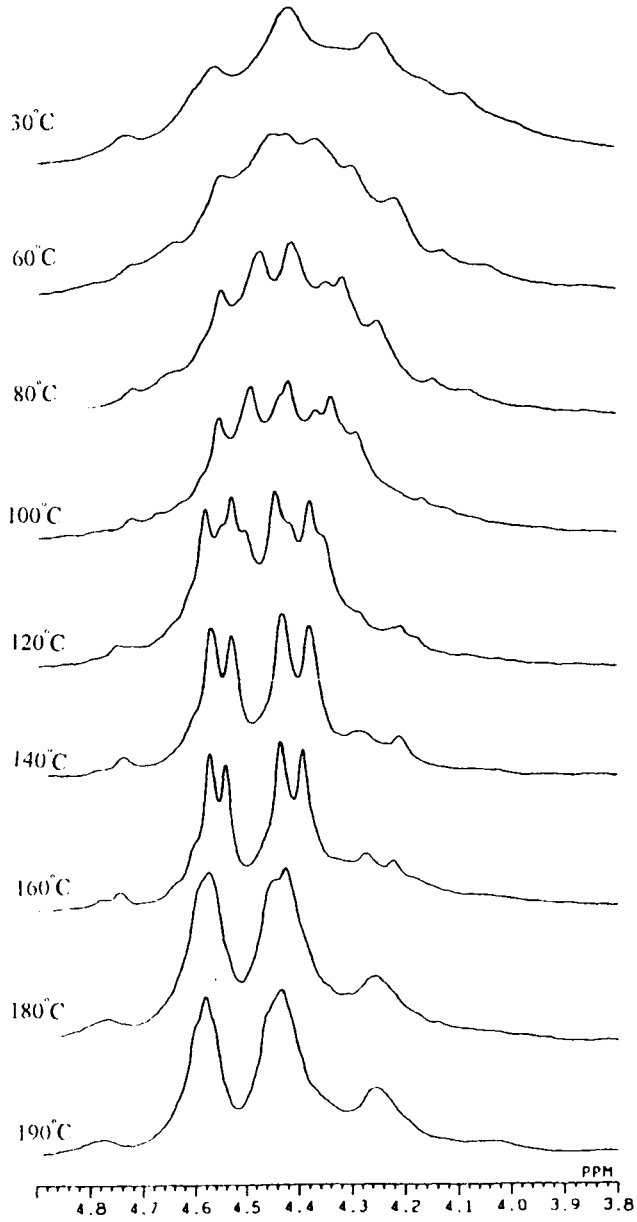


FIGURE 2 ^{1}H-NMR spectra of CH_2-proton in $(C_6H_5CH_2)_2NP(O)(Cl)OC_6H_4CH_3$ (IV) at high temperatures

The IR spectra of (VIII) and (IX) show that ν(P=O) increases and ν(P-N) decreases by fluorination. By substitution of nitrophenol by fluorine in molecule (IX) ν(P=O) increases based on *Wagner* calculation [3] and ν(P-N) decreases according to *Robinson*'s suggestions [5]. Increase of P=O frequency in molecule (IX) is about 50 cm^{-1} in comparison to molecule (I). According to single-crystal X-ray data of the molecule (IX) the P-N bond length is 1.62 Å [19]. This bond length is located between P-N single bond (1.77 Å in $NaHPO_3NH_2$) and P=N double bond (1.57 Å, in Ph_3P=N-) [26]. Therefore, the partial multiple (P-N) bond in (IX) is more than (I).

The ^{1}H-NMR spectra of compounds (IV), (V), (VI), and (VII) were measured at different temperatures in order to get more information about the P-N bond. The ^{1}H-NMR spectra of the above mentioned compounds with methylene proton signals at 4–4.5 ppm were considered (Fig. 4). In the 1H – NMR spectra of the fiourine compounds (VI) and (VII) were no change up to –80 °C. As shown in the ^{1}H-NMR of (IV), the rotation along the P-N bond, even at 0 °C is quite slow (Fig. 1). As the temperature increases the spectra becomes simpler, which can be interpreted by faster rotation. At 190 °C free rotation accurs on the NMR time scale and the spectra becomes simple and almost show a doublet (Fig. 2). In compound (V) the rotation along P – N axis starts to slow down at – 30 °C and the rotation becomes very slow at –80 °C (Fig. 3). The slow rotation along the P-N bond in chlorine molecules (IV), and (V) is probably a result of partial multiple-bond between phosphorus and nitrogen. It can be found, that a suitable π-donation ligand connected to nitrogen in phosphoramide molecules produced the resonance structure B. Since there are two π-donating groups (benzyl groups) in compound (IV) and only one in compound (V) the resonance structure B is more prefered by (IV) than by (V). Probably the steric hindrance plays an additional role. On the other hand the fluorinated compounds (VI) and (VII) do not show any changes in the ^{1}H-NMR spectra at low temperatures. If the slow down of the P-N rotation is due to space restrictions in compound (IV) and (V), the same restrictions should exist in compound (VI) and (VII). The comparison of phosphor-proton couplings constant $^3J_{PH}$ of molecules (III), (V), and (VII) shows that $^3J_{PH}$ (III) > $^3J_{PH}$ (V) > $^3J_{PH}$(VII). The coupling constant reduction in (V) in comparison to (III) is due to replacement of chlorine by the M-electron donation group p-cresol. It means, that the partial multiple-bond between phosphorus and nitrogen is reduced. This reduction of partial multi-

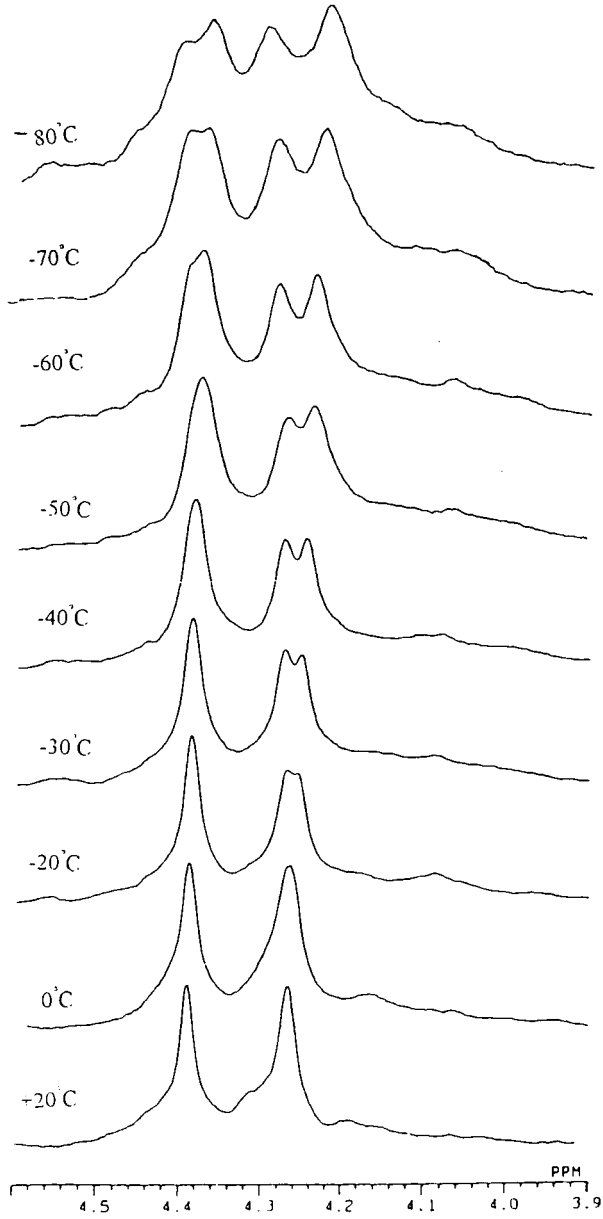


FIGURE 3 ^{1}H-NMR spectra of CH2-proto in $(CH_3)(C_6H_5CH_2)NP(O)(Cl)OC_6H_4CH_3$(V) at different temperatures

ple-bond is clearly shown by IR spectroscopy $\nu_{P\text{-}N}(III) = 917\ cm^{-1} > \nu_{P\text{-}N}(V) = 818\ cm^{-1}$.

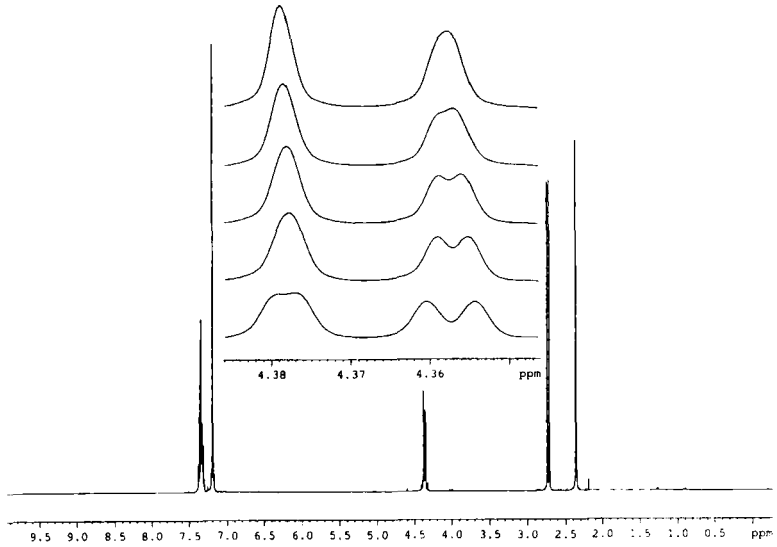


FIGURE 4 ^{1}H-NMR spectra of $(CH_3)(C_6H_5CH_2)NP(O)(Cl)OC_6H_4CH_3$

The further reduction of the $^3J_{PH}$ of (V) compared to (VII) can be rationalized by *Robinson*'s suggestion [15], since a partial multiple-bond between phosphorus and fluorine is formed, which can weaken the P-N bond. In addition, the behavior of halids in species (IV), (V), (VI), and (VII) is interesting in regard to long-rang NMR coupling of phosphorus-proton $^7J_{PH}$. The ^{1}H-NMR spectra of chloride compounds (IV), (V) and the reported compound $(CH_3)_2NP(O)(Cl)OC_6H_4CH_3$ [17] show that the proton signal of the methyl group of p-cresol is splitted by phosphorus into a doublet with a coupling constant of about $^7J_{PH} = 1.2 - 1.5$Hz. The ^{1}H-NMR of homologous fluoride compounds (VI), (VII) and the reported $(CH_3)_2NP(O)(F)OC_6H_4CH_3$ [17] show only a singulet and there is no sign of any split in the NMR peak. The chemical shift and coupling constant for methyl, and methylen groups of the compound (II)---(VII) are summarized in table (4).

TABLE IV Chemical shifts and coupling constants $^3J_{PH}$

Compound		*CH2R/ppm*	$^3J_{P\text{-}N\text{-}CH2R/Hz}$	$J_{F\text{-}H/Hz}$	*splitting*
(II)	(CH_2R)	4.28	14.5		doublet
(III)	(CH_3)	2.27	15.8		doublet
	(CH_2R)	4.4	12.07		doublet
(IV)	(CH_2R)	4.26	——		mult.
(V)	(CH_3)	2.69	13.41		doublet
	(CH_2R)	4.35	11.63		doublet
(VI)	(CH_2R)	4.18	——		mult.
(VII)	(CH3)	2.66	10.73	1.31	d. of d.
	(CH_2R)	4.29	10.73	1.31	d. of d.
1)	(CH_3)	2.81	13.7		d.
2)	(CH_3)	2.78	10.59	1.92	d. of d.

1) = $(CH_3)_2NP(O)(Cl)OC_6H_4CH_3$ [17]

2) = $(CH_3)_2NP(O)(F)OC_6H_4CH_3$ [17]

Finally it is concluded that:

1: Replacement of methyl group in $(CH_3)_2NP(O)Cl_2$ (I) by a benzyl group causes an increase in ν(P-N) and decrease in ν(P=O).

2: Replacement of chlorine in (II) by p-cresol results in strong reduction in ν(P-N) and an increase in ν(P=O).

3: Replacement of p-nitrophenol in (IX) by fluorine results in a reduction in ν(P-N) and an increase in ν(P=O).

Therefore, decrease or increase of the wavenumber of the (P-N) stretching mode is associated with increase and decrease of ν(P=O) and the wavenumber of both bonds are correlated with the replacement group in molecule(I). Since the vibrational wavenumber of species (IX) $\nu_{P\text{-}N} = 776\ cm^{-1}$ and the lenght of this bond is located between a single- and a double bond, it is possible that the P-N bond lengths of products (II) – (VII) are shorter than in compound (IX). At the end with different selection of R_1, R_2, R_3, and R_4 groups in the molecule $R_1R_2NP(O)R_3R_4$ one can design and synthesize molecules which have very weak P-N bonds (resonance structure A) or have partial multiple bond (resonance structure B).

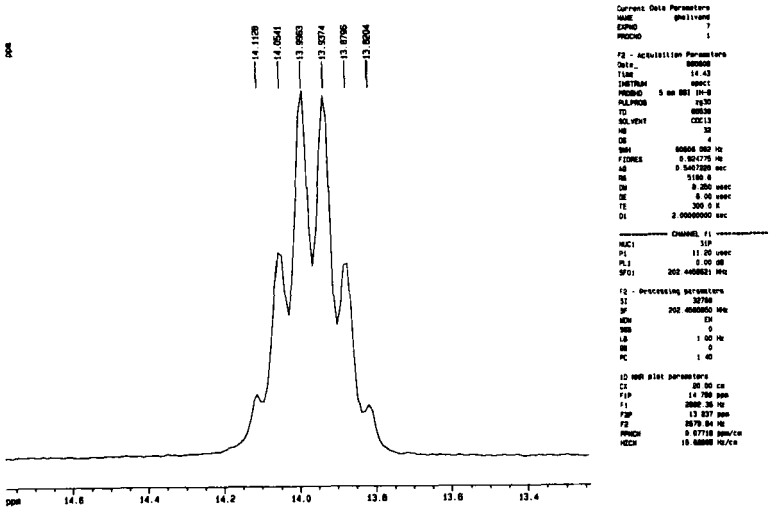


FIGURE 5 ^{31}P NMR spectra of $(CH_3)(C_6H_5CH_2)NP(O)(Cl)OC_6H_4CH_3$

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