Heteroatom Chemistry
Volume 19, Number 2, 2008

Synthesis and Structure of Complexes of Phosphorus Pentachloride with 4-Dimethylaminopyridine and *n*-Methylimidazole

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Received 19 October 2006; revised 17 June 2007

ABSTRACT: *Complexes of phosphorus pentachloride with 4-dimethylaminopyridine and N-methylimidazole were synthesized. The molecular structure of the phosphorus pentachloride complex with N-methylimidazole was determined by single-crystal X-ray diffraction. In the cationic part of the complex, the phosphorus atom possesses four P—Cl bonds within the range 2.109–2.148 Å and two cis-P–N bonds (1.811 and 1.832 Å) with N-methylimidazole and exhibits slightly distorted octahedral coordination with angles at phosphorus atom in the range 87.57°–91.50°. The relative stability of the cis and trans conformations of the complex was studied by DFT calculations. The chemical properties and reactivity of the compounds obtained are determined; their utility as condensing agents in the synthesis of amides from acids and amines was shown.* © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:171–177, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20392

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INTRODUCTION

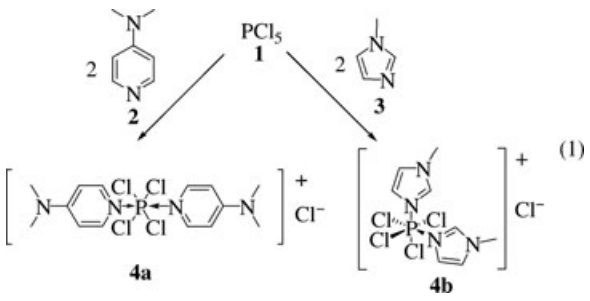
The ability of phosphorus halides to form complexes with amines was discovered a long-time ago. For the first time, the formation of complexes in the mixtures of triethylamine and phosphorus halides was postulated by W. R. Trost in 1954 [1]. Complexes of $PCl_3$and $PBr_3$with triethylamine [2–4], PCl_5 and PF_5 with pyridine [5–8], PCl_3, PBr_3, and PBr_5 with *N*,*N*-dimethylaminopyridine (DMAP) [9,10] were obtained later.

Interest in complexes of this type has originally arisen due to consideration of their possible role as transition state models for nucleophilic substitution reactions at phosphorus. Later, the catalytic properties of pyridine and other nitrogen-containing bases in phosphorylation reactions were discovered. The effect was explained by the formation of complexes as active electrophilic species [11–13].

However, all complexes obtained up to now were extremely easily hydrolyzable compounds. This created difficulties in their study and practical use. We have synthesized some new representatives of these complexes, which have unusual stability and chemical reactivity.

RESULTS AND DISCUSSION

Crystalline complexes **4a,b** of 1:2 composition, according to their elemental analysis, are formed by the interaction of PCl_5 **1** and DMAP **2** or *N*-methylimidazole **3** in chloroform.



In the NMR ^{31}P spectrum of complex **4a**, a signal of six-coordinated phosphorus at −195 ppm split into a quintet with a coupling constant $^3J_{PH} = 18$ Hz is observed. In the NMR ^1H spectrum, the corresponding splitting of the resonance of the α-protons of the pyridine ring is detected. This fact confirms the coordination of two molecules of the ligand with formation of a complex of six-coordinated phosphorus. The same situation is observed in the spectra of complex **4b**.

The molecular structure of compound **4b** was determined by single-crystal X-ray diffraction. The perspective view of molecule **4b** is given in Fig. 1. A fragment of molecular packing is presented in Fig. 2.

In the cationic part of the complex, the phosphorus atom possesses four P—Cl bonds within the range 2.109–2.148 Å and two *cis*-P—N bonds (1.811 and 1.832 Å) with *N*-methylimidazole and exhibits slightly distorted octahedral coordination with angles at phosphorus atom in the range 87.57°–91.50°.

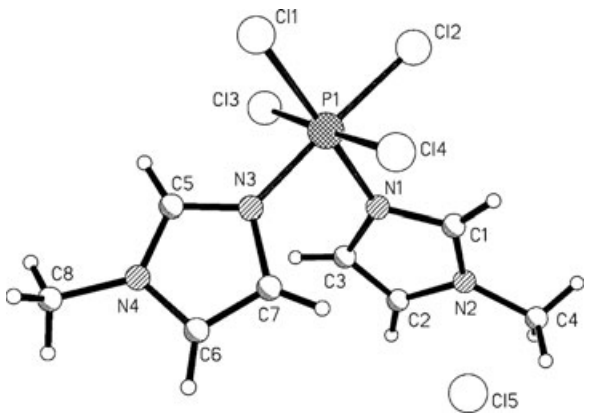


FIGURE 1 A perspective view of molecule **4b**.

Two *N*-methylimidazole ligands N1N2C1–C4 and N3N4C5–C8 are planar (mean deviation of atoms from least-squares planes of heterocycles do not exceed 0.014 and 0.007 Å, respectively), and the dihedral angle between planes is 59.6°.

A series of short CH···Cl contacts of the hydrogen atoms of *N*-methylimidazole with the chloride anion within the range of 2.65–2.85 Å have been found in crystals. Six of seven H···Cl contacts have "chelate"-like nature that may stabilize strongly the crystal topology of the cis-isomer. This supposition was studied by DFT calculations of conformations **A** (cis) and **B** (trans). Calculated conformations of **4b** with the $[Cl]^-$ anion are given in Fig. 3.

DFT calculations of the systems under study were carried out using the B3LYP and B3PW91 schemes incorporated in the Gaussian 98W program suite [14]. A standard basis set 6-31+G (2d,2p) was used throughout.

Values of the total energy of the conformers and ions are listed in Table 1. Calculations of **4b** without the $[Cl]^-$ anion show that conformation **B** is more stable by 6.45 kcal/mol at the B3LYP and by the 6.40 kcal/mol at the B3PW91 level. At the same time, calculations of **4b** with the $[Cl]^-$ anion demonstrate specific interactions between the anion and the hydrogen of the heterocyclic moieties making conformation **A** more stable by 15.80 kcal/mol at the B3LYP and by 15.90 kcal/mol at the B3PW91 level of the theory.

The calculation of the $[Cl]^-$ shows specific interactions between the hydrogen atom at the C_2 atom of the imidazole ring and the anion. The C—H bond lengths are listed in Table 2. The B3PW91 method shows greater changes in C—H bond lengths.

The distance between Cl–H(C_5) is 2.216 Å (B3LYP) and 2.176 Å (B3PW91) in conformation **A**. The distance between Cl–H(C_5) is 2.096 Å (B3LYP) and 2.037 Å (B3PW91) in conformation **B**. These changes in C—H bond length and such small distance between hydrogen atom and $[Cl]^-$ anion demonstrate the effect of H-bond formation.

Interactions between the $[Cl]^-$ anion and the cation lead to redistribution of electron density in **4b**. Electron density distribution was analyzed at the natural bond orbital framework [15] using the NBO 3.1 program [16]. The values of "natural charges" on atoms (further charges) in the species under discussion are presented in Table 3. The interaction of the cationic fragment with the $[Cl]^-$ anion decreases the moiety charge by 0.132 *e* (B3LYP) and 0.146 *e* (B3PW91) in conformation **A** and by 0.173 *e* (B3LYP) and 0.159 *e* (B3PW91) in conformation **B**.

Different directions of electron density redistribution with changing conformation from **A** to **B**

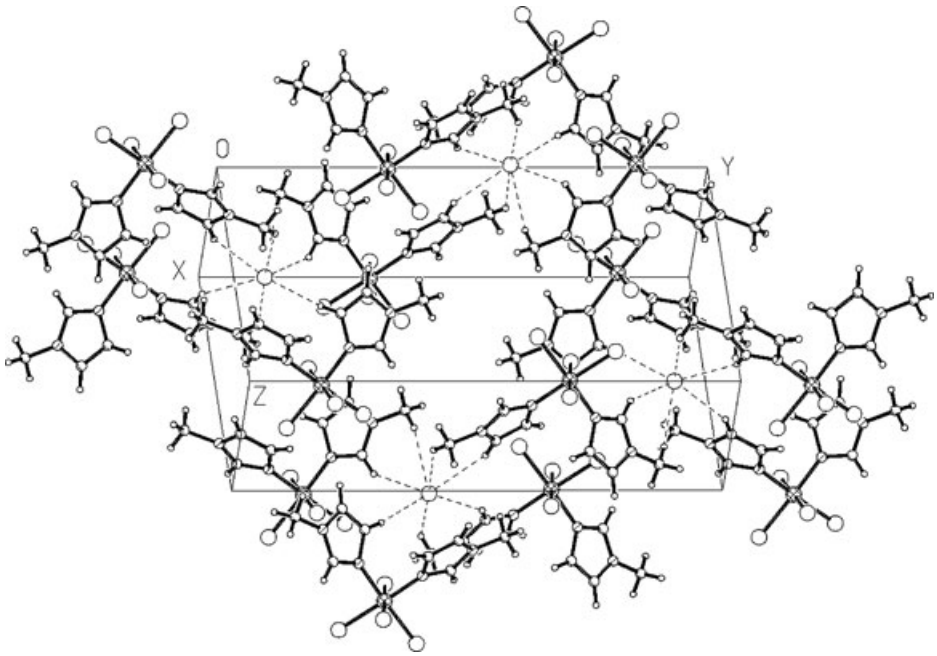


FIGURE 2 Molecular packing of **4b**.

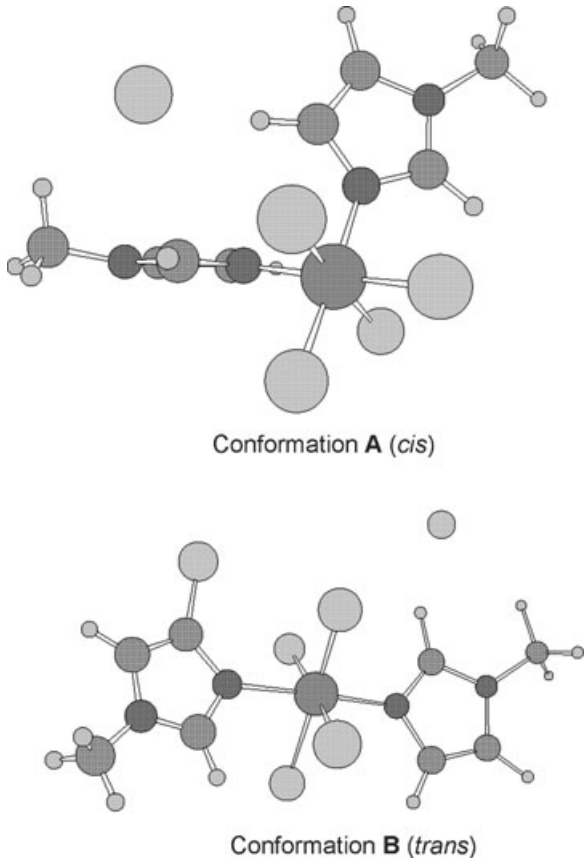


FIGURE 3 Calculated conformations of **4b** with the Cl^- anion.

were found for cation and neutral molecule. The charge on the phosphorus atom increases when the conformation changes from **A** to **B** in the cation opposite to the neutral molecule. Although charges on N_{pyr} decrease when the conformation of the cation changes from **A** to **B**, the changes are opposite in the neutral molecule.

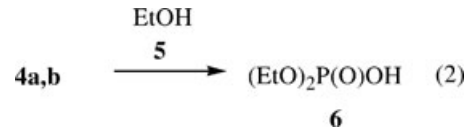
The energy of the donor–acceptor interaction between a p-type orbital of a lone pair of $[Cl]^-$ anion and the antibonding orbital of the $H{-}C_5$ bond is 17.74 kcal/mol (B3LYP) and 20.07 kcal/mol (B3PW91) in conformation **A** and 24.87 kcal/mol (B3LYP) and 33.14 kcal/mol (B3PW91) in conformation **B**. These values correlate with changes in distance between $[Cl]^-$ anion and H atom.

These data are in support of a strong stabilization of the cis-isomer crystal topology by interactions between the $[Cl]^-$ anion and H-atoms of the cationic part.

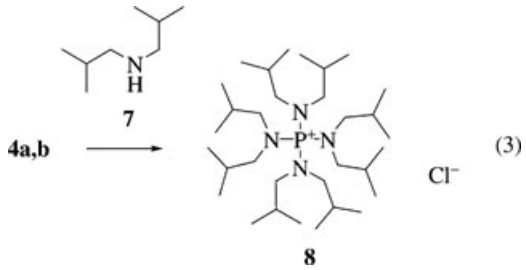
The complexes **4a,b** are incomparably more stable to hydrolysis than the starting phosphorus pentachloride and all known complexes of phosphorus halides. In DMSO solution with 3% of water by volume, the hydrolysis of compound **4a** proceeds to an extent of 75% during 12 h, and for compound **4b** to an extent of 50% during 10 days. The suspension of complexes **4a,b** in ethanol **5** is stable at ambient temperature. The alcoholysis with formation of diethylphosphate **6** starts only when heated to boiling point.

TABLE 1 Total Energies (in hartree) of **4b**

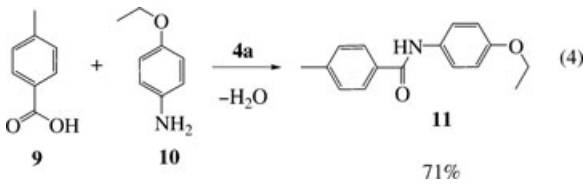
	Conformation **A**		*Conformation* **B**	
Method	*Cation*	*Neutral*	*Cation*	*Neutral*
B3LYP	−2713.1022662	−3173.5160436	−2712.6538131	−3173.0106928
B3PW91	−2713.1125376	−3173.4908691	−2712.6640084	−3172.9853555

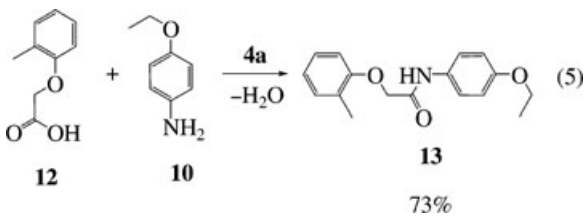


In chloroform solution at ambient temperature, complexes **4a,b** do not react with diisobutylamine **7**. The reaction proceeds only after boiling the reaction mixture for 1 h. Tetrakis(diisobutylamino)phosphonium chloride **8** is the product of the reaction.



The unusual stability of the complexes **4a,b** allows to use them as new condensation reagents in organic synthesis, for example, in obtaining amides from carboxylic acids and amines. Test reactions of derivatives of benzoic **9** and phenoxyacetic **12** acids with *p*-phenetidin **10** in the presence of complex **4a** give the corresponding amides **11,13** in good yields.





The method is more useful for preparative use than condensation with standard reagents such as carbodiimides or carbonyldiimidazole, where the reaction must be conducted in two steps: at the first stage, an activated derivative of the acid is produced, at the second stage the amine is added and the acylation is carried out. The condensation with the help of complex **4a** allows us to avoid the intermediate stage and to carry out the synthesis simply by heating all three components together.

The optimal conditions of the reaction, and area of its application are under study.

TABLE 2 The Bond Lengths (in angstroms) in the Cation of **4b** and in the Neutral Molecule Obtained at B3LYP and B3PW91 Levels

	Conformation **A**		*Conformation* **B**	
Method	*Cation*	*Neutral*	*Cation*	*Neutral*
B3LYP	1.074	1.097, 1.073	1.074	1.111, 1.074
B3PW91	1.075	1.103, 1.073	1.075	1.123, 1.075

EXPERIMENTAL

General Remarks

All reactions were performed under an inert atmosphere of Ar in predried glassware. The solvents were dried by distillation over the following drying agents and were transferred under Ar: chloroform (P_4O_{10}), acetonitrile (P_4O_{10}), ethanol (Na). Residual of water in 4-dimethylaminopyridine and *N*-methylimidazole was removed by azeotropic distillation with CCl_4. ^1H and ^{31}P NMR spectra were recorded on $CDCl_3$ and DMSO-d_6 solutions on a Varian VXR-300 spectrometer operating at 299.95 and 121.42 MHz, respectively. Chemical shifts (δ) are given in ppm relative to TMS and 85% H_3PO_4. Melting points were determined in closed tubes and were uncorrected. Elementary analyses were performed at the Micronalysis Services of the Institute of Organic Chemistry of National Academy of Sciences of Ukraine.

*Tetrachlorobis(4-dimethylaminopyridine)phosphorus(V) Chloride (**4a**).* A solution of 4-dimethylaminopyridine **2** (5 g, 40.9 mmol) in

TABLE 3 The Values of the Natural Charges (*q*, *e*) on the Atoms for the **4b** Species

	Cationic Fragment				*Cationic Fragment with Cl⁻*			
	B3LYP		*B3PW91*		*B3LYP*		*B3PW91*	
Atom	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
q(P)	1.207	1.240	1.213	1.234	1.254	1.234	1.248	1.239
Cl	−0.256	−0.249	−0.255	−0.246	−0.229	−0.224	−0.228	−0.216
	−0.256	−0.249	−0.255	−0.246	−0.298	−0.225	−0.293	−0.296
Cl′	−0.210	−0.249	−0.211	−0.246	−0.242	−0.303	−0.238	−0.216
	−0.210	−0.249	−0.211	−0.246	−0.268	−0.303	−0.263	−0.296
$q(N_{pyr})$	−0.614	−0.612	−0.615	−0.615	−0.622	−0.630	−0.624	−0.637
	−0.614	−0.612	−0.615	−0.615	−0.647	−0.585	−0.650	−0.592
$q(N_{py})$	−0.358	−0.358	−0.354	−0.354	−0.368	−0.367	−0.365	−0.363
	−0.358	−0.358	−0.354	−0.354	−0.354	−0.371	−0.352	−0.367
C_5	−0.048	−0.033	−0.056	−0.040	−0.032	−0.021	−0.040	−0.030
	−0.048	−0.033	−0.056	−0.040	−0.060	−0.032	−0.068	−0.039
Cl					−0.868	−0.827	−0.854	−0.841

chloroform (10 mL) was added to a suspension of PCl_5**1** (1.7 g, 8.19 mmol) in chloroform (20 mL) with intensive stirring. The solid phase was dissolved quickly, then the product was precipitated. After 2 h, the precipitate was filtered and washed with chloroform. Complex **4a** was obtained as white crystals (4.7 g, 99%) (solvate with one molecule of chloroform); mp = 155°C–160°C. Elemental analysis Calcd for $C_{15}H_{21}Cl_8N_4P$ (571.955): C 31.50, H 3.70, Cl 49.59, N 9.80, P 5.42; Found C 31.24, H 3.74, Cl 49.45, N 9.81, P 4.19. NMR (DMSO-d_6): ^{1}H, δ (ppm) = 3.27s (12H, N-CH_3), 6.96d (4H, CH (β-aromatic) (J_{HH} = 7 Hz)), 8.28s (1H, $CHCl_3$), 9.30dd (4H, CH (α-romatic), (J_{PH} = 17 Hz), (J_{HH} = 7 Hz)). ^{31}P, δ (ppm) = −196 quintet, $^3J_{PH}$ = 17 Hz.

*cis-Tetrachlorobis(1-methylimidazole)phosphorus(V) Chloride (***4b***).* Compound **4b** was prepared as described for **4a.** Complex **4b** was obtained as white crystals, yield 97.8%; mp = 131.5°C–137°C (dec.). Elemental analysis Calcd for $C_8H_{12}Cl_5N_4P$ (372.448): C 25.80, H 3.25, Cl 47.59, N 15.04, P 8.32; Found C 25.51, H 3.21, Cl 50.91, N 12.97, P 7.29. NMR (DMSO-d_6): ^{1}H, δ (ppm) = 3.86s (3H, N—CH_3), 7.56m (2H, CH (4-aromatic),J_{PH} = 5 Hz), 7.78m (2H, CH (5-aromatic),J_{PH} = 6 Hz), 9.80d (2H, CH (2-aromatic), J_{PH} = 4 Hz). ^{31}P, δ (ppm) = −231 pseudo-heptet, $^3J_{PH}$ = 5.8 Hz. Yellowish crystals suitable for X-ray analysis were obtained by growing in methylene chloride/chloroform (1:1).

X-ray Structure Determination of **4b**. *Crystal Data:* $C_{8.50}H_{13}Cl_6N_4P$ (**4b**·$\frac{1}{2}CH_2Cl_2$), M 414.90, monoclinic, space group $P2_1/c$ (N 14), a = 7.056(2), b = 19.139(3), c = 13.186(3) Å, β = 104.24(2)°, V = 1726.0 (7) Å^3, Z = 4, d_c = 1.597 g cm^{-3}, μ = 9.915 mm^{-1}, $F(000)$ = 836. To avoid the decomposition of the yellowish crystal of compound **4b** with size ca. 0.40 × 0.45 × 0.45 mm, it was placed in a glass capillary. All crystallographic measurements were performed at room temperature on a CAD4 Enraf–Nonius diffractometer operating in the ω – 2θ scan mode (the scanning ratio was $\omega/2\theta$ = 1.2). Intensity data were collected within range 4.6 ≤ θ ≤ 64.9° using Cu K_α radiation (λ = 1.54178 Å). Intensities of 3182 reflections (2931 unique reflections, R_{int} = 0.058) were measured. Data were corrected for Lorenz and polarization effects. The azimuthal absorption correction by PSI-scan (T_{min} 0.0156, T_{max} 0.0704) was applied. The structure was solved by direct methods and refined by full-matrix least-squares technique in the anisotropic approximation for non-hydrogen atoms using SHELXS97 and SHELXL97 programs. In the refinement, 2931 reflections (1973 reflections with $I \geq 2\sigma(I)$) were used. All hydrogen atoms were placed at calculated position as "riding" model with $U_{iso} = 1.2U_{iso}$ of supporting carbon atoms. During the structure refinement, the atoms of the methylene chloride solvent molecule were observed close to inversion center, but could not be modeled satisfactorily. The SQUEEZE routine in PLATON was used to modify the HKL file and the solvent equated to a half molecule of methylene chloride per molecule of complex. Convergence was obtained at R = 0.0567 and $R_w(F^2)$ = 0.1429, GOF = 0.984 (166 parameters; observed/variable ratio 11.9; the largest and minimal peaks in the final difference map 0.55 and −0.51 eÅ^3, weighting scheme $\omega = 1/[\sigma^2(F_o^2) + (0.0943)P^2]$, where $C = (F_o^2 + 2F_c^2)/3$). Full crystallographic

parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for these materials should quote the full literature citation and reference number CCDC 624161. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

General Procedure for Reaction of Complexes **4a,b** *with Ethanol*

Compound **4a** (or **4b**) (1.59 mmol) was added to dry ethanol **5** (108.5 mmol). The reaction mixture was stirred at ambient temperature for 1 h, compound **4a (**or **4b)** was not dissolved. According to the ^{31}P NMR spectrum, there was no phosphorus compound in the reaction mixture at this point. The mixture was stirred at 60°C for 4.5 h until **4a (**or **4b)** was completely dissolved. The yield of diethylphosphate **6** was more than 95% according to the ^{31}P NMR spectrum. The identity of the product was established by spectral comparison to diethylphosphate, which was obtained by the hydrolysis of diethylchlorophosphate. NMR ($CDCl_3$): ^{1}H, δ (ppm) = 4.12 quintet (4H, OCH_2, ($J_{HH} = J_{HP} = 7$ Hz)), 1.35t (6H, CH_3), ($J_{HH} = 7$ Hz)). ^{31}P, δ (ppm) = −1m, $^2J_{PH} = 12$ Hz.

General Procedure for Reaction of Complexes **4a,b** *with Diisobutylamine*

Compound **4a** (or**4b**) (0.965 g, 1.69 mmol) was added to a solution of diisobutylamine **7** (1.635 g, 12.7 mmol) in chloroform (5 mL). The reaction mixture was stirred at ambient temperature for 0.5 h, compound **4a** (or **4b**) was not dissolved. According to the ^{31}P NMR spectrum, there was no phosphorus compound in the reaction mixture at this point. Then the mixture was heated to the boiling point, but no signal of phosphorus was detected after 1 h of boiling the reaction mixture. Compound **4a** (or **4b**) was dissolved completely only after 6 h of boiling the reaction mixture. The yield of tetrakis(diisobutylamino)phosphonium chloride **8** was more than 95% according to the ^{31}P NMR spectrum. The identity of the product was established by spectral comparison to tetrakis(diisobutylamino)phosphonium chloride, which was obtained by the reaction of PCl_5 with diisobutylamine. ^{31}P NMR ($CHCl_3$), δ (ppm) = 58.5 m, $^3J_{PH} = 12$ Hz.

(4′-Ethoxy)-4-methylbenzanilide **11**. A mixture of 4-methylbenzoic **9** acid (0.384 g, 2.82 mmol), *p*-phenetidin **10** (0.322 g, 2.35 mmol), **4a** (1.344 g, 2.35 mmol), and diisopropylethylamine (1.52 g, 11.75 mmol) in acetonitrile (2 mL) was heated in a boiling water bath for 1 h. A solution of 1 g K_2CO_3 in water (20 mL) was added to the reaction mixture. The mixture was stirred for 0.5 h. The precipitate was filtered off and was washed with a mixture of water and acetonitrile (1:1) (0.43 g, 71%). NMR ($CDCl_3$): ^{1}H, δ (ppm) = 1.41t (3H, O—CH_2—C$\underline{H}_3$, ($J_{HH} = 7$ Hz)), 2.42s (3H, Ar—C$\underline{H}_3$), 4.03 q (2H, O—C$\underline{H}_2$—CH_3, ($J_{HH} = 7$ Hz)), 6.88d (2H, CH (3′-aromatic), ($J_{HH} = 8.5$ Hz)), 7.27d (2H, CH (2′-aromatic), ($J_{HH} = 8.5$ Hz)), 7.52d (2H, CH(3-aromatic), ($J_{HH} = 8.5$ Hz)), 7.76d (2H, CH(2-aromatic), ($J_{HH} = 8.5$ Hz)), 7.71s (1H, NH).

(4′-Ethoxy)-2-methylphenoxyacetanilide **13**. Compound **13** was prepared as described for **11**. 0.54 g, 73%. NMR ($CDCl_3$): ^{1}H, δ (ppm) = 1.41t (3H, O—CH_2—C$\underline{H}_3$, ($J_{HH} = 6.85$ Hz)), 2.36s (3H, Ar—C$\underline{H}_3$), 4.02q (2H, O—C$\underline{H}_2$—CH_3, ($J_{HH} = 6.85$ Hz)), 4.61s (2H, —CH_2—CO—), 6.85d (1H, CH(6-aromatic), ($J_{HH} = 8.1$ Hz)), 6.88d (2H, CH(3′-aromatic), ($J_{HH} = 8.72$ Hz)), 6.97m (1H, CH(3-aromatic), ($J_{HH} = 7.3$ Hz)), 7.2m (2H, CH(4,5-aromatic), ($J_{HH} = 7.3$ Hz)), 7.48d (2H, CH(2′-aromatic), ($J_{HH} = 8.72$ Hz)), 8.23s (1H, NH).

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