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Letters to the Editor

Synthesis of polyfunctional methylphosphine oxides*

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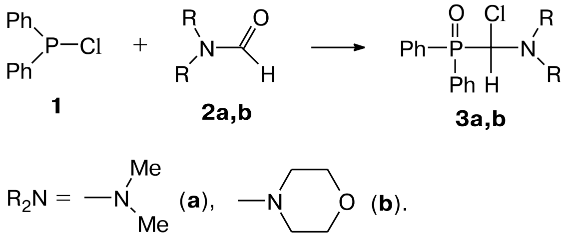
The synthesis and investigation of properties of polyheterofunctional methanes, including those containing phosphine and phosphine oxide moieties, are classical problems of organic chemistry. Previously, we have synthesized the first representatives of disubstituted methylphosphines, *viz.*, *N*,*N*-dialkyl(diphenylphosphinomethylene)iminium iodides $[Ph_2PC(H)=NR_2]^+I^-$, by the reaction of diphenylchlorophosphine (**1**) with *N*,*N*-dialkylformamides (**2**) in the presence of NaI and studied the structures of the reaction products.[1] Further studies of the reaction of Ph_2PCl with *N*,*N*-dialkylformamides showed that it can afford also other products.

In the present study, we performed a new reaction, which is of interest for the synthesis of functional phosphine oxides. Thus, the reaction of Ph_2PCl (**1**) with *N*,*N*-dialkylformamides (**2a,b**) in the presence of catalysts gives *N*,*N*-dialkylaminodiphenylphosphorylchloromethanes (**3a,b**) (Scheme 1). These compounds have been previously unknown, and only their phosphonate and amidophosphonate analogs were scarcely studied.[2—4]

Scheme 1



We used $PhP(O)Cl_2$ (**4**), $C_2O_2Cl_2$ (**5**), PCl_5 (**6**), $SOCl_2$ (**7**), and I_2 (**8**) as catalysts (5 mol.%). In the presence of these compounds, the iminium salts $[R_2N=C(H)X]^+X^-$ (**9**) known as Vilsmeier-Haack reagents are produced, in one way or another, in the reaction mixtures from *N*,*N*-dialkylformamides.[5,6] Phenylphosphonic dichloride $PhP(O)Cl_2$ (**4**) (as the phenyl-substituted analog of phosphorus oxychloride)** was proposed for the first time as a source of the Vilsmeier-Haack reagent. The iminium salt $[Me_2N=C(H)Cl]^+Cl^-$ (**9a**) can also be used as the reaction catalyst.

Apparently, the catalytic reaction has the following mechanism, as exemplified by $[Me_2N=C(H)Cl]^+Cl^-$ (**9a**) (Scheme 2). The reaction of Ph_2PCl (**1**) with $[Me_2N=C(H)Cl]^+Cl^-$ (**9a**) affords *N*,*N*-dimethylamino-

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* Dedicated to Academician A. I. Konovalov on his 75th birthday.

** Phosphorus oxychloride ($POCl_3$), which is generally used for this purpose, oxidizes Ph_2PCl (**1**) under the reaction conditions and is reduced to PCl_3.

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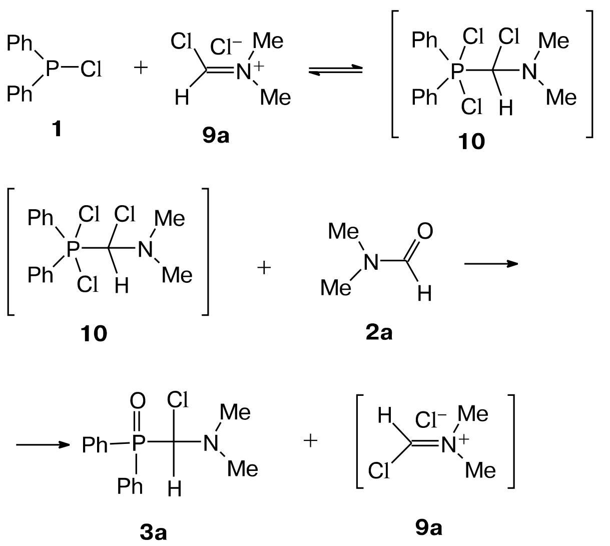
Scheme 2



(diphenyldichlorophosphorano)chloromethane (**10**). Then compound **10** reacts with DMF (**2a**) to form compound **3a** accompanied by regeneration of salt **9a**.

The ^{31}P NMR spectra of compounds **3a,b** have two signals at δ 25.9 (80%) and 21.1 (20%) for **3a** and at δ 34.9 (11%) and 25.9 (89%) for **3b**. Conceivably, both compounds exist as equilibrium mixtures of two conformers.[7] As exemplified by compound **3a**, this is confirmed by the fact that the ^{31}P NMR spectra recorded in DMF have only one signal at δ 26.1, which evidently corresponds to the more stable conformation in this solvent. Analogously, the ratio of the signals at δ 26.5 and 20.6 corresponding to the conformers in CH_2Cl_2 is 1 : 1.

The structure of compound **3a** was established by X-ray diffraction (at 100 K, space group $P2_1/c$, $Z = 4$, $a = 16.217(12)$ Å, $b = 8.136(6)$ Å, $c = 11.127(8)$ Å, $\beta = 99.701(14)°$, $V = 1447.1(18)$ Å^3, $R_1 = 0.0813$) and is presented in Fig. 1. It should be noted that the C(1)—Cl(1) bond in molecule **3a** is abnormally long (1.899(5) Å), which is apparently attributed to the anomeric interaction between the lone pair (Lp) of the nitrogen atom and the antibonding orbital of the C—Cl bond. The stereoelectronic interaction is additionally confirmed by the antiperiplanar orientation of Lp of the N(1) atom with respect to the C—Cl bond (the Lp—N(1)—C(1)—Cl(1) pseudotorsion angle is 173°) and a substantial shortening of the N(1)—C(1) bond to 1.384(7) Å.

The ^{1}H and ^{31}P NMR spectra were recorded on a Bruker Avance 400 spectrometer operating at 400.13 and 161.98 MHz, respectively. The ^{31}P and ^{1}H NMR spectra of the individual compounds were measured in $CDCl_3$. The ^{31}P NMR spectra of compound **1a** were recorded also in DMF and CH_2Cl_2 with the use of 85% H_3PO_4 as the external standard. *N*-Formylmorpholine was prepared according to a procedure described earlier.[8] Toluene, CH_2Cl_2, and DMF were twice distilled over CaH_2; $CDCl_3$ was distilled over P_2O_5. Diphenylchlorophosphine (Aldrich), $C_2O_2Cl_2$, PhP(O)Cl_2, PCl_5, $SOCl_2$, and I_2 (Acros Organics) were used as received. The X-ray diffraction study of compound **3a** was carried out on a Smart APEX II CCD diffractometer (MoKα radiation, graphite monochromator, ω-scanning technique). All calculations were performed with the use of the SHELXTL PLUS program package.

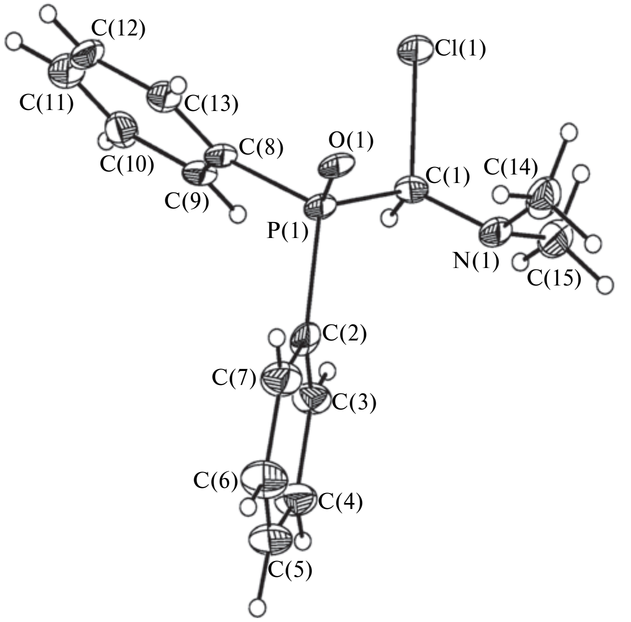


Fig. 1. Structure of (diphenylphosphoryl)-*N*,*N*-dimethylaminochloromethane (**3a**).

Synthesis of *N*,*N*-dimethylamino(diphenylphosphoryl)chloromethane (3a). Method *A*. Phenylphosphonic dichloride PhP(O)Cl_2 (**4**) (0.03 g, 0.15 mmol) was added with stirring to a solution of DMF (**2a**) (0.53 mL, 0.5 g, 7 mmol) in toluene (3 mL) at room temperature in an inert atmosphere. After 20 min, diphenylchlorophosphine (**1**) (0.4 mL, 0.5 g, 2.3 mmol) was added. After 3 h, the reaction mixture turned red-brown and the precipitation of analytically pure compound **3a** started. The precipitation ceased within 18 h. The precipitate was filtered off, washed with toluene (3S5 mL), and dried *in vacuo*. Compound **3a** was obtained in a yield of 0.61 g (91%) as colorless needle-like crystals, m.p. 92—94 °C (with decomp.). Compound **3a** is hygroscopic. Found (%): C, 61.44; H, 5.79; N, 4.68; P, 10.40. $C_{15}H_{17}ClNOP$. Calculated (%): C, 61.34; H, 5.83; N, 4.77; P, 10.55. ^{31}P NMR, δ: 25.9 (20%), 21.1 (80%). ^{1}H NMR, δ: 8.2 (m, 0.2 H, P—C(H)); 7.96 (m, 4 H, *o*-H_{arom}); 7.89 (m, 0.8 H, P—C(H)); 7.51 (m, 6 H, *m*-H_{arom}, *p*-H_{arom}); 3.06 (d, 6 H, N—CH_3). M 293.74.

Method *B*. Oxalyl chloride $C_2O_2Cl_2$ (**5**) (0.012 mL, 0.015 g, 0.15 mmol) was added with stirring to DMF (**2a**) (3 mL) in an inert atmosphere. After the gas evolution ceased, diphenylchlorophosphine (**1**) (0.4 mL, 0.5 g, 2.3 mmol) was added. After 30 min, the reaction mixture turned red-brown and the precipitation of compound **3a** started. The precipitation ceased within 8 h. The precipitate was filtered off, washed with toluene (3×5 mL), and dried *in vacuo*. Compound **3a** was obtained in a yield of 0.63 g (94%).

Compound **3a** was synthesized also according to the method ***B*** with the use of PCl_5 (**6**), $SOCl_2$ (**7**), I_2 (**8**), or $[Me_2N=C(H)Cl]^+Cl^-$ (**9a**) as the catalyst. The yields were 68%, 80%, 54%, and 75%, respectively.

N*-Morpholino(diphenylphosphoryl)chloromethane (3b)**. Compound **9b** was synthesized according to the method ***A. The reaction time was 3 days. The yield was 86%, colorless needle-like crystals, m.p. 70—71 °C (with decomp.). Compound **9b** is hygroscopic. Found (%): C, 60.32; H, 5.90; N, 4.10; P, 9.11. $C_{17}H_{19}ClNPO_2$. Calculated (%): C, 60.71; H, 5.70; N, 4.17; P, 9.22. ^{31}P NMR, δ: 34.9 (11%), 25.9 (89%). ^1H NMR, δ: 8.15 (s, 0.3 H, P—C(H)); 7.95 (m, 0.7 H, P—C(H)); 7.82 (m, 4 H, *o*-H_{arom}); 7.52 (m, 2 H, *m*-H_{arom}); 7.44 (m, 4 H, *p*-H_{arom}); 3.59 and 3.08 (both m, 4 H each, CH_2). M 319.75.

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