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LETTERS
TO THE EDITOR

# Synthesis of Polyfunctional Methylphosphine Oxides

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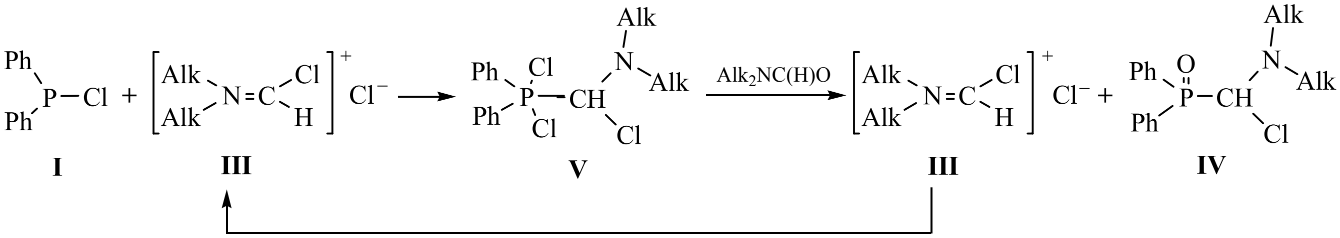
In previous communications [1–4] it was shown that the interaction of chlorodiphenylphosphine $Ph_2PCl$ (**I**) with an excess of a dialkylformamide $Alk_2NC(H)O$ (**II**) in the presence of catalytic amount (5–15 mol %) of a dialkylchloromethyleneiminium chloride $[Alk_2N{=}C(H)Cl]^+\ Cl^-$ (**III**) results in a high yield of the corresponding chloro(dialkylamino)(diphenylphosphoryl)methanes (**IV**). By an example of chloro(dialkylamino)(diphenylphosphoryl)methane (**IVa**) we have shown that the autocatalytic reaction of synthesis of compounds **IV** includes two stages (Scheme 1) [2]: the synthesis of (dichloro)(diphenyl)[chloro(dialkylamino)methyl]phosphoranes **V** in the reaction of **I** and **III**, and the synthesis of the final products **IV** in the reaction of halophosphorane **V** and amide **II** accompanied by the recover of compound **III**, which is involved in the next step of the interaction cycle.



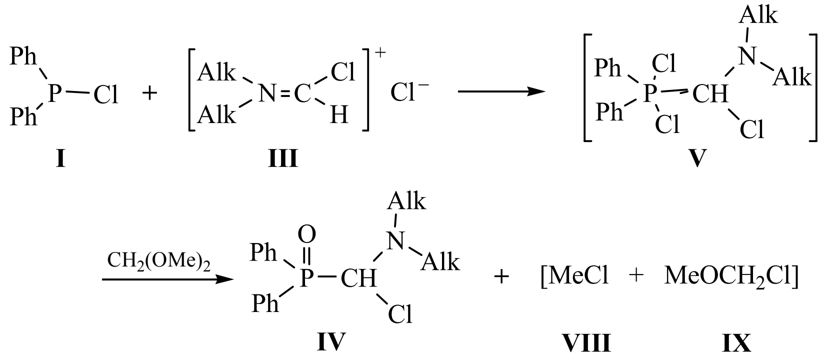
$Alk_2N$ denotes the residues of dimethylamine (**a**), diethylamine (**b**), *N*-pyrrolidine (**c**), *N*-piperidine (**d**), and *N*-morpholine (**e**).

It seems reasonable to check this scheme using a new synthetic method derived from this stepwise autocatalytic reaction scheme [4].

It follows from the scheme that compound **IV** can be synthesized without the excesses of **II**. To do this, one should add to the reaction medium a compound capable of replacing the chlorine atoms at the phosphorus atom of halophosphorane **V** by oxygen atom under mild conditions. Unfortunately, it was impossible to use water or alcohols for this purpose, since they led to a rupture of phosphorus–carbon bond in compound **IV** [5]. However, it was found empirically that, by analogy with $PCl_5$ [6, 7], for this purpose dimethoxymethane $(MeO)_2CH_2$ (**VI**) was suitable. It is known from the literature that at low temperatures **VI** does not react with **I** [8, 9] or **III** [10, 11]. Compounds **III** can be synthesized directly in the reaction medium by reaction of amides **II** with oxalyl chloride $(COCl)_2$ (**VII**) [12].

The new version of the synthesis of **IV** also consists of two stages: the synthesis of phosphorane **V** in the reaction of **I** with an equimolar amount of **III** and the synthesis of the final product **IV** in the reaction of **V** with **VI**. The expected reaction co-products are methyl chloride (**VIII**) and methoxy(chloro)methane (**IX**) [7].

Compounds **I** and **IIIa, IIIb, IIId** were introduced into the reaction in the presence of 4- to 6-fold excess of **VI** and a catalytic amount of dioxane [3] at 0°C. The reaction duration was 4–7 days. During this time, the $[Alk_2N{=}C(H)Cl]^+Cl^-$ (**III**) precipitate gradually



dissolved with simultaneous precipitation of **IV** (**a, b,** and **d**). The resulting compounds **IVa**, **IVb,** and **IVd** by melting points and $^1$H and $^{31}$P NMR spectra correspond to the products synthesized previously by the autocatalytic reaction [3]. The yields of products **IV** are in the range 46–72%. In the syntheses of chloro(dimethylamino)(diphenylphosphoryl)methane **IVa** and chloro(*N*-pyrrolidino)(diphenylphosphoryl)methane **IVc** a weak gas evolution was marked (presumably methyl chloride **VIII**).

The synthesis of compounds **IV** along the proposed scheme confirms the presence in the reaction medium of **V**, being the adduct of **I** and **III**. Further **V**, as expected, reacts with **VI** to give the final reaction product **IV**. This in turn confirms the previously proposed [1, 2] and later experimentally confirmed [4] scheme of autocatalytic synthesis of chloro(dialkylamino)(diphenylphosphoryl) methanes **IV**.

The $^1$H and $^{31}$P NMR spectra (δ, ppm) were registered on a Bruker Avance 300 spectrometer, operating frequency 300.11 and 121.50 MHz, respectively, solvent $CDCl_3$. The registration of $^1$H and $^{31}$P NMR spectra of **IV** was performed immediately after their dissolution in $CDCl_3$ [3]. Dialkylformamides used in the study were twice distilled over $CaH_2$; dimethoxymethane, $CDCl_3$, $CH_2Cl_2$, benzene, and hexane were distilled over $P_2O_5$.

**Synthesis of chloro(dialkylamino)(diphenylphosphoryl)methane (IVa).** To a solution of 0.33 g (0.35 ml, 0.0045 mol) of DMF (**IIa**) in 5 ml of $CH_2Cl_2$ at 0°C, was slowly added dropwise at vigorous stirring 0.7 g (0.48 ml, 0.0055 mol) of oxalyl chloride $(COCl)_2$ (**VII**) in 5 ml of $CH_2Cl_2$. After the end of gas evolution, $CH_2Cl_2$ was distilled off in a vacuum of 50 mm Hg (strong foaming) at 25°C. To the solid residue of dialkylchloromethyleneiminium **IIIa** cooled to 0°C was successively added 1.2 g (0.96 ml, 0.0054 mol) of chlorodiphenylphosphine $Ph_2PCl$ **I**, 1,5 g (1.74 ml, 0.0202 mol) of dimethoxymethane and 5 drops of dioxane. The reaction mixture was left at 0°C while intermittently stirring. After 8 h a weak gas evolution began, which ended after four days. The mixture left standing for 1 day more at 0°C, then it was diluted with 5 ml of benzene–hexane mixture, 5:1, cooled to 0°C, stirred for 1 min, and the liquid layer was decanted. The operation was repeated four times. The solid residue was dried in a vacuum of 12 mm Hg for 1 h, than 2 days at 1 mm Hg over $P_2O_5$ and NaOH. We obtained 1.91 g (72%) of compound **IVa**. Colorless needles, mp 90–94°C with decomposition [2–5]. The compound is hygroscopic. $^{31}$P NMR spectrum, δ, ppm: 22.0 d ($^2J_{PH}$ = 11.0 Hz). $^1$H NMR spectrum, δ, ppm: 8.00–7.93 m (4H, *o*-H, Ph), 7.89 d (1H, CH, $^2J_{PH}$ = 11.0 Hz), 7.56–7.49 m (6H, *m,p*-H, Ph), 3.08 s [6H, N $(CH_3)_2$].

By similar procedure also compounds **IVc** and **IVd** were synthesized.

**(Diphenylphosphoryl)(*N*-pyrrolidino)chloromethane (IVc)**. The reaction duration 4 days. Yield 53%. A pale yellow hygroscopic substance, mp 79–82°C with decomposition [3]. $^{31}$P–{$^1$H} NMR spectrum, δ, ppm: 19.3 s. $^1$H NMR spectrum, δ, ppm: 10.31 d (1H, CH, $^2J_{PH}$ = 23.0 Hz), 8.20–8.13 m (4H, *o*-H,Ph), 7.61–7.49 m (6H, *m,p*-H, Ph), 4.22 s (4H, $2NCH_2$), 1.35 d (4H, $2CH_2$).

**(Diphenylphosphoryl)(*N*-piperidino)chloromethane (IVd)**. The reaction time 7 days. Yield 46%. A light yellow hygroscopic substance, mp 85–88°C with decomposition [3]. $^{31}$P–{$^1$H} NMR spectrum, δ, ppm: 20.2 s. $^1$H NMR spectrum, δ, ppm: 9.78 d (1H, CH, $^2J_{PH}$ = 21.0); 8.17–8.09 m ( 4H, *o*-H, Ph), 7.62–7.51 m (6H, *m,p*-H, Ph), 4.12 t (4H, $2NCH_2$, $^3J_{HH}$ = 6.0 Hz), 1.82 br.s ($\Delta\nu_{1/2}$ = 11 Hz, 4H,$C\underline{H_2}CH_2C\underline{H_2}$), 1.64 quintet (2H,$CH_2C\underline{H_2}CH_2$, $^3J_{HH}$ = 6.0 Hz).

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