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LETTERS TO THE EDITOR

Reactions of Chlorophosphonium Compounds with Sodium *N,N*-Diethylamidodithiocarbamate

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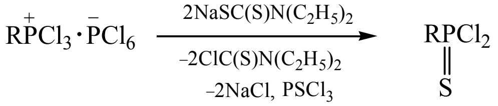
The reactions of phosphorus pentachloride with various C-, N-, O-, and S-nucleophiles are widely used for the synthesis of compounds containing one or more phosphorus-carbon bonds [1]. A feature of this method is its proceeding in two stages: the first is the formation of organyltrichlorophosphonium hexachlorophosphates **Ia**–**Ie**, and the second is the formation of the stable phosphorus chlorides **III** and **IV** at the treatment of the hexachlorophosphates with appropriate reagents [2]. However, the universal transformers that meet the modern production requirements were not developed so far despite a wide range of those proposed. Analysis of published data showed that the stage of hexachlorophosphates **Ia**–**Ie** transformation into organyldichlorothiophosphonates is the least known. The known reagents (phosphorus pentasulfide, hydrogen sulfide, ethylene sulfide, alkanethiols, and sodium alkylxanthogenates) are of limited use due to the different reasons: low accessibility, high toxicity, flammability, multistage process, a large number of unutilizable waste, the process duration, and in some cases because of low yields. Therefore, in order to find new, more efficient and technologically advanced transformers, we studied the reaction of hexachlorophosphates **Ia**–**Ie** with sodium *N,N*-diethylamidodithiocarbamate.

The interaction of organyltrichlorophosphonium compounds **Ia**–**Ie** with sodium *N,N*- diethylamidodithiocarbamate was performed at a molar ratio of reagents 1:2. The reaction proceeds rapidly at 20–25°C for 0.1–0.2 h after the reagents mixing. The yellow-orange solutions and sodium chloride precipitate are formed, which is confirmed by a qualitative detection of sodium and chloride ions, as well as by the quantitative determination of chlorine. After the precipitate separation, the filtrate was distilled to isolate the organylphosphonic acids dichlorides **IIa–IIe**.



$$R\overset{+}{P}Cl_3\cdot\overset{-}{P}Cl_6 \xrightarrow[\substack{-2ClC(S)N(C_2H_5)_2\\ -2NaCl,\ PSCl_3}]{2NaSC(S)N(C_2H_5)_2} \underset{\substack{\|\\ S}}{RPCl_2}$$

Ia–Ie **IIa–IIe**

R = $C_6H_5CH{=}CH$ (**a**), $C_6H_5C(CH_3){=}CH$ (**b**), $C_2H_5OCH{=}CH$ (**c**), $C_4H_9CHClCH_2$ (**d**), $C_5H_{11}CHClCH_2$ (**e**).

The structure of the synthesized compounds was confirmed by the IR and NMR spectroscopy, and the composition, by the elemental analysis. The IR spectra of dichlorides **IIa–IIe** contain the characteristic absorption bands originating from the stretching vibrations of P=S (680–685 cm^{-1}) and P–Cl bonds (475–525 cm^{-1}) together with the absorption bands of the hydrocarbon substituent (R). In the ^{31}P NMR spectra the phosphorus atom is characterized by the chemical shift of 66–82 ppm, which is consistent with the published data [3].

The IR spectra were recorded on an infrared Fourier spectrometer FSM (KBr prisms, thin film). The ^1H NMR spectra were registered on a Bruker WM-250 (250 MHz) instrument with internal reference dimethyl sulfoxide, the solvent $(CD_3)_2SO$, the ^{31}P NMR spectra, on a Bruker WP-80 (32.44 MHz) instrument with external reference 85% phosphoric acid.

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