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REACTION OF DIPHENYLTHIOPHOSPHINOUS ESTERS

WITH DIPHENYLCHLOROPHOSPHINE

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It is known [1, 2] that the esters of P(III) acids react with halophosphines by the Arbuzov reaction to give compounds with a phosphorus—phosphorus bond. Aminophosphines are also capable of adding to chlorophosphines, but in this case the reaction stops at the step of forming quasiphosphonium compounds [3]. The reaction of the thioesters of P(III) acids with halophosphines has not been studied. Only the reactions of the trithioesters with PCl₃ are known, which lead to an exchange of the substituents [4].

We studied the reaction of the ethyl ester of diphenylthiophosphinous acid (I) with diphenylchlorophosphine (II). The derivatives of the same acid were chosen so as to not complicate the reaction due to the exchange processes of the thioalkyl group with the halide.

In contrast to the oxygen esters of P(III) acids, the reaction with thiophosphinite (I) proceeds under drastic conditions (250°C, neat) and leads to the formation of a mixture of tetraphenyldiphosphine (III) with $\delta^{31}P - 16$ ppm, ethyldiphenylphosphine sulfide (IV) with $\delta^{31}P + 45$ ppm, and diphenylchlorophosphine sulfide (V) with $\delta^{31}P + 79.5$ ppm [5]. It should be mentioned that (II) doesnot react completely. In addition, small amounts of S-ethyl di-

$$\begin{array}{ccc} & \mathbf{S} & \mathbf{S} \\ \mathbf{Ph_2PSEt} + \mathbf{Ph_2PCl} \longrightarrow \mathbf{Ph_2P-PPh_2} + \mathbf{Ph_2PEt} + \mathbf{Ph_2PCl} + \mathbf{EtCl} \\ (\mathbf{I}) & (\mathbf{II}) & (\mathbf{III}) & (\mathbf{IV}) & (\mathbf{V}) \end{array}$$

phenyldithiophosphinate were detected by the ³¹P NMR and TLC methods.

In contrast to this, the phenyl ester of diphenylthiophosphinous acid (VI) does not react with (II) even at 350°. Only the isomerization of (VI) to triphenylphosphine sulfide (VII) is observed under these conditions. The presence of (II) in the reaction mixture apparently has no effect on the isomerization process, since the heating of thiophoshinite (VI) to 350° in the absence of diphenylchlorophosphine also leads to the isomerization product.

 $\begin{array}{ccc} \mathrm{Ph_2PSPh} & \xrightarrow{350^{\circ}} & \mathrm{Ph_3PS} \\ \mathrm{(VI)} & \mathrm{(VII)} \\ & & & \\ \mathrm{EXPERIMENTAL} \end{array}$

The ³¹P NMR spectra were recorded on a nonserial KGU-4 NMR instrument at an operating frequency of 10.2 MHz. The external standard was 85% H₃PO₄. The PMR spectra were taken on a Varian T-60 spectrometer at an operating frequency of 60 MHz relative to TMS.

Reaction of Ethyl Diphenylthiophosphinite (I) with Diphenylchlorophosphine (II). A mixture of 7.5 g of (I) and 7.0 g of (II) was heated at 250° for 0.5 h, cooled, and 5 ml of benzene was added. On standing at 20° a product deposited from the mixture, which was recrystallized from ether to give 3.5 g (31%) of (III) withmp 121° (cf. [6]). PMR spectrum (CC1₄): δ 7.23-8.33 ppm. (C₆H₅); the mixed melting point was 120°. Fractional distillation of the

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 951-952, April, 1982. Original article submitted July 31, 1981. residue gave 2.9 g (43%) of (II) with bp 120-122° (0.7 mm), nD^{20} 1.6360, $\delta^{31}P + 82$ ppm (cf. [7]), and a fraction with bp 160-170° (0.7 mm), which crystallized on standing. Recrystallization from ether gave 1.6 g (21%) of (IV) with mp 65° (cf. [8]). PMR spectrum (CC1₄, δ , ppm): 1.13 (CH₃), $^{3}J_{\text{HH}} = 7.5$, $^{3}J_{\text{PH}} = 20$ Hz: 2.36 (CH₂), $^{2}J_{\text{PH}} = 12$ Hz; 7.2-8.0 (C₆H₅). Without isolation, (V) was identified via the ^{31}P NMR spectral data [5].

Reaction of Phenyl Diphenylthiophosphinite (VI). A mixture of 7.3 g of (VI) and 5.5 g of (II) was heated for 1 h at 350°. On cooling the reaction mixture crystallized. Treatment with ether and subsequent recrystallization from benzene gave 5.2 g of (VII) with mp 161°, $\delta^{31}P + 42.5$ ppm (cf. [9], $\delta^{31}P + 42.5$ ppm [5]). After removal of the solvent from the filtrate the fractional distillation of the residue gave 5.1 g (93%) of (II).

Thermal Isomerization of (VI). Here 0.2 g of (VI) was heated at 350° for 1 h, cooled, and recrystallized from benzene to give 0.14 g (70%) of (VII) with mp 161°.

CONCLUSIONS

The reaction of ethyl diphenylthiophosphinite with Ph₂PCl leads to the formation of tetraphenyldiphosphine, ethyldiphenylphosphine sulfide, and diphenylchlorophosphine sulfide. Phenyl diphenylthiophosphinite under drastic conditions undergoes isomerization to triphenyl-phosphine sulfide.

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