REACTIONS OF MIXED O,S-ESTERS OF ACIDS OF TRIVALENT PHOSPHORUS WITH SUBSTITUTED 1-CHLOROACETYLENES

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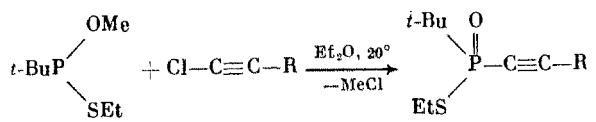
The reactions of mixed O,S-esters of tert*-butylthiophosphonous acid and dithiophosphorous acid with 1-chloro-2-organylacetylenes were studied. On the basis of them, a convenient method for the synthesis of thioesters of organylethynylthiophosphinic and dithiophosphonic acids, which are undescribed in the literature, was proposed. A difference was found in the chemical behavior of the methyl ester of S,S-diethyldithiophosphorous acid by comparison with the corresponding complete esters and thioesters of phosphorous acid in reactions with dichloroacetylene.*

Keywords: thioesters of P(III) acids, 1-chloroacetylenes, organylethynylthiophosphinates, organylethynyldithiophosphonates, Arbuzov reaction.

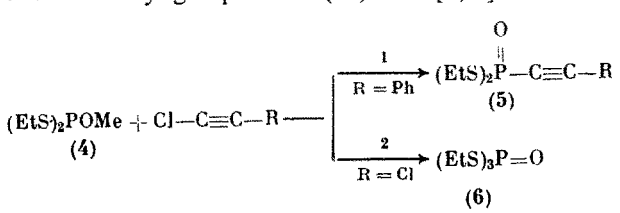
We previously showed that esters and ester-amides of thioacids of trivalent phosphorus react with substituted 1-chloroalkynes with the formation of unsaturated phosphorus–sulfur organic compounds for which the composition includes both acetylenic [1] and olefinic [2, 3] fragments. The mixed esters of thioacids of trivalent phosphorus were not studied for their reactions with 1-halogenoacetylenes. Meanwhile, the investigation of these reactions permits, on the one hand, a comparison of their chemical behavior with the behavior of complete esters of thioacids of P(III) in reactions with chloroacetylenes and, on the other hand, the finding of approaches to the synthesis of new unsaturated organophosphorus compounds.

It was established that the thiophosphonite (**1**) reacts with the 1-chloroalkynes (**2a-c**) according to the scheme of the Arbuzov reaction with the formation of the previously unknown thioesters of *tert*-butyl(organylethynyl)thiophosphinic acid (**3a-c**).



R=Ph (**2a**, **3a**); EtS (**2b**, **3b**); Cl (**2c**, **3c**)

In contrast, the interaction of the O-methyl ester of S,S-diethyldithiophosphorous acid (**4**) with 1-chloroacetylenes is accomplished by two routes — the scheme of the Arbuzov reaction when phenylchloroacetylene is utilized (route 1), and the scheme of the substitution reaction of the thioalkyl group at the P(III) atom [1, 4] when dichloroacetylene is applied (route 2).



The change in the course of the reaction is caused, in our opinion, by specific features of the electronic and steric structures of mono- and dihalogen-substituted acetylenes [5, 6] which exert a specified influence on the course of monotypic reactions in some cases [1, 3].

EXPERIMENTAL

The IR spectra of the compounds were recorded on the UR-20 and Specord 75 IR spectrometers in the range 400-3700 cm^{-1}. Samples of the compounds were investigated in the form of liquid films or suspensions in mineral oil between KBr tablets. The accuracy for the determination of the frequencies of the absorption bands was ± 2 cm^{-1}. The PMR spectra were obtained

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on the Varian T-60 spectrometer with the working frequency of 60 MHz. The 10-15% solutions of the compounds in inert solvents (CCl_4, C_6H_6) were utilized for the recording of the ^1H NMR spectra. Tetramethylsilane was utilized as the standard. The measurement of the chemical shifts of the ^{31}P nuclei was performed on the nonseries NMR-KGU-4 instrument with the working frequency of 10.2 MHz. The accuracy for the determination of the chemical shift was ±2 ppm. All reactions were performed in an atmosphere of dry argon.

S-Ethyl-*tert*-butyl(phenylethynyl)thiophosphinate (3a). To 6.5 g (0.04 mole) of the thiophosphonite **1** in 50 ml of ethyl ether were added, dropwise 5 g (0.04 mole) of phenylchloroacetylene **1a** so as to ensure that the temperature of the reaction mixture should not exceed 25-30°C. At the end of the addition the stirring was continued for an additional 1 h, after which the solvent was removed under reduced pressure, and the residue was fractionated. This led to the isolation of 6.4 g (77%) ofthe thiophosphinate **3a** having bp 154-157°C (0.01 mm Hg), n_D^{20} 1.5720, and δ_P 40 ppm. IR spectrum (ν, cm^{-1}): 490, 550 (P—S), 2180 (C≡C), and 1230 (P=O). PMR spectrum (CCl_4, δ, ppm; J, Hz): 1.5 t ($\underline{CH_3}CH_2S$, ^3J_H = 7, 3H), 1.33 d (Me_3C, $^3J_{HP}$ = 19, 9H), 3.03 d.q ($CH_3\underline{CH_2}S$, $^3J_{HH}$ = 7, $^3J_{HP}$ = 14, 2H), and 7.23-7.57 m (C_6H_5, 5H). Found, %: S 12.46, 12.37; P 11.26, 12.35. $C_{14}H_{19}OSP$. Calculated, %: S 12.03; P 11.65. *M* 266.

S-Ethyl-*tert*-butyl(ethylthioethynyl)thiophosphinate (3b). The reaction was performed by analogy with the reaction described above. The thiophosphonite **1** (5.6 g, 0.03 mole) and 3.8 g (0.03 mole) of ethylthiochloroacetylene **2b** afforded 5.5 g (72%) of the product **3c** with bp 120-124°C (0.01 mm Hg), n_D^{20} 1.5512, δP 40 ppm. IR spectrum (ν, cm^{-1}): 515 (P—S), 2110 (C≡C), 1220 (P=O). PMR spectrum (C_6H_6, δ, ppm; J, Hz): 1.17 t ($\underline{CH_3}CH_2SC{\equiv}C$, $^3J_{HH}$ = 7), 2.93 d.q ($CH_3\underline{CH_2}SP$, $^3J_{HH}$ = 7, $^3J_{HP}$ = 14, 2H), 1.3 t ($\underline{CH_3}CH_2SP$, $^3J_{HH}$ = 7), and 1.23 d (Me_3C, $^3J_{HP}$ = 19, 9H). Found, %: S 25.83, 25.71; P 12.00, 12.25. $C_{10}H_{19}OS_2P$. Calculated, %: S 25.60; P 12.40. M 250.

S-Ethyl-*tert*-butyl(chloroethynyl)thiophosphinate (3c). The reaction was performed by analogy with the reaction described above. The thiophosphonite **1** (9.8 g, 0.05 mole) and 5.2 g (0.05 mole) of dichloroacetylene **2c** afforded 8.3 g (68%) of the product **3b** with bp 83-85°C (0.01 mm Hg), n_D^{20} 1.5355, δP 40 ppm. IR spectrum (ν, cm^{-1}): 490, 550 (P—S), 2180 (C≡C), 1230 (P=O). PMR spectrum (δ, ppm; J, Hz): 1.5 t ($\underline{CH_3}CH_2S$, $^3J_{HH}$ = 7, 3H), 3.03 d.q ($CH_3\underline{CH_2}S$, $^3J_{HH}$ = 7, $^3J_{HP}$ = 14, 2H), and 1.33 d (Me_3C, $^3J_{HP}$ = 19, 9H). Found, %: P 14.05, 14.11; Cl 15.79, 15.92. $C_8H_{14}ClOSP$. Calculated, %: P 13.81; Cl 15.81%. M 224.5.

S,S-Diethyl(phenylethynyl)dithiophosphonate (5). The mixture consisting of 12.8 g (0.07 mole) of the dithiophosphite **4** and 9.5 g (0.07 mole) of phenylchloroacetylene **2a** was maintained for 3 h at 60°C. At the end of the process, fractionation led to the isolation of 10.8 g (81%) of the product **5c** with bp 170-171°C (0.05 mm Hg) and δ_P 22 ppm. IR spectrum (ν, cm^{-1}): 490, 515 (P—S), 2180 (C≡C), 1210 (P=O). PMR spectrum (δ, ppm; J, Hz): 1.7 t (CH_3, $^3J_{HH}$ = 7, 3H), 3.2 d.q (CH_2S, $^3J_{HH}$ = 7, $^3J_{HP}$ = 16, 2H), and 7.37-7.8 m (C_6H_5, 5H). Found, %: C 53.11, 53.28; S 23.52, 23.76; P 11.18, 11.35. $C_{12}H_{15}OS_2P$. Calculated, %: C 53.33; S 23.70; P 11.48. M 270.

S,S,S-Triethyltrithiophosphate (6). To 10 g (0.05 mole) of the dithiophosphite **4** in 50 ml of ethyl ether were added, dropwise, 4.8 g (0.05 mole) of dichloroacetylene etherate. At the end of the addition, the reaction mixture was stirred for an additional 2 h. The solvent was then removed under reduced pressure, and the residue was fractionated. This led to the isolation of 4.1 g (32.8%) of the phosphate **6** with bp 90-92°C (0.05 mm Hg), n_D^{20} 1.5459, and δP 62 ppm. IR spectrum (ν, cm^{-1}): 490, 515 (P—S), 1270 (P=O). PMR spectrum (δ, ppm; J, Hz): 1.67 t (CH_3, $^3J_{HH}$ = 7, 3H) and 3.21 d.q (CH_2S, $^3J_{HH}$ = 7, $^3J_{HP}$ = 14, 2H). Found, %: S 41.76, 41.82; P 13.41, 13.46. $C_6H_{15}OS_3P$. Calculated, %: S 41.56; P 13.42. M 231.

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