REACTION OF DIALKYLDITHIOTRIMETHYLSILYLPHOSPHITES WITH ACYL HALIDES

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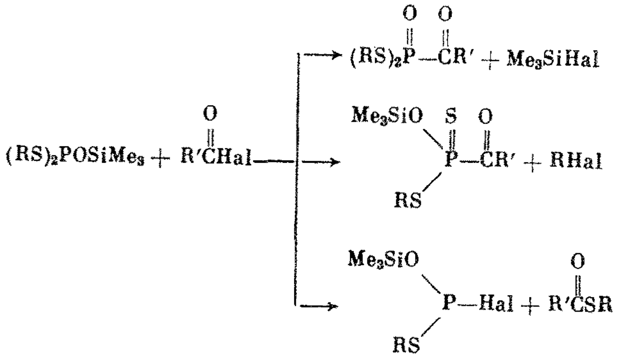
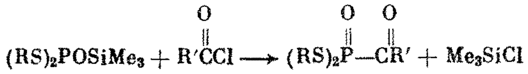
It has been established that S,S-dialkyltrimethylsilyldithiophosphites react with acyl halides in two directions, depending on the nature of the halogen in the acyl halide and on the reaction conditions, thus giving as the main reaction products either dialkyldithiohalophosphites or dialkyldithioacylphosphonates. The latter compounds react with acyl halides in accordance with a retro-Arbuzov reaction scheme, giving dialkyldithiohalophosphites.

Keywords: dialkyldithiotrimethylsilylphosphites, acyl halides, dialkyldithioacylphosphites, dialkyldithioacylphosphonates.

Reactions of siloxy derivatives of P(III) acids with acyl halides have been studied in considerable detail. In the case of mixed C, Si esters of phosphorous acid, these reactions proceed in accordance with the Arbuzov reaction scheme, depending on the nature of the halogen in the acyl halide, with participation of the alkoxyl or trimethylsiloxy group, forming acetylphosphonates [1]. The thio analogs of these compounds — dialkyldithiotrimethylsilylphosphites — have not been investigated with regard to their behavior in this reaction. By analogy with the alkoxysilylphosphites, we could expect in these reactions the formation of either dialkyldithioacylphosphonates or alkylthiotrimethylsiloxyacylphosphonates. However, in view of the ability of the akylthio group to be replaced under the influence of alkyl halides in thioesters of P(III) acids [2], we did not exclude the possibility of forming products in which the alkylthio group has been replaced by halogen, analogous to the replacement of the amido group in the case of amidosilylphosphites [3].



It was found that the interaction of the dialkyldithiotrimethylsilylphosphites **1** with acyl chlorides at −20°C proceeds in accordance with the Arbuzov reaction scheme with participation of the trimethylsiloxy group, forming the dithioacylphosphonates **2** [4]:



$$(RS)_2POSiMe_3 + R'\overset{O}{\overset{\|}{C}}Cl \longrightarrow (RS)_2\overset{O}{\overset{\|}{P}}-\overset{O}{\overset{\|}{C}}R' + Me_3SiCl$$

(**1**) (**2a, b**)

R=Et, R'=Ph (**2a**); R=*i*-Pr, R'=Me (**2b**).

The structure of the compounds obtained as products was established by means of physicochemical methods and elemental analysis.

In contrast, when the silylphosphites **1** react with acyl bromides under the same conditions, an unexpected reaction is realized, previously unknown in the chemistry of silylphosphites, namely the replacement of the trimethylsiloxy group by halogen.

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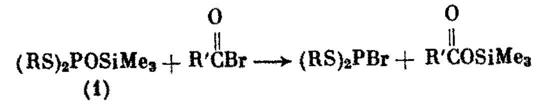
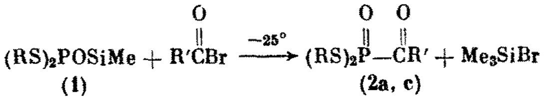


$$\underset{(1)}{(RS)_2POSiMe_3} + R'\overset{O}{\overset{\|}{C}}Br \longrightarrow (RS)_2PBr + R'\overset{O}{\overset{\|}{C}}OSiMe_3$$

R=Et, R'=Me, Ph.

The structure of the compounds that were obtained was established by means of physicochemical methods of investigation and by comparing the constants with literature data [2, 5]. In some cases, owing to the pronounced tendency of the dialkyldithiobromophosphite to disproportionate, it was characterized in the reaction mixture in the form of the crude product, with subsequent conversion to the trialkyltrithiophosphite through reaction with a mercaptan in the presence of triethylamine.

It could be assumed that the formation of the products through a reaction scheme of replacement of the siloxy group by halogen is accomplished directly by the interaction of the original reactants, possibly with the participation of acidic type catalysts [6, 7], or as the result of secondary conversions. With the aim of studying the scheme of formation of substitution products and trapping the intermediates, we investigated the interaction of these reactants at low temperatures. We found that the reaction proceeds at —25°C in accordance with a scheme analogous to that of the reaction with acyl chlorides, forming dialkyldithioacylphosphonates **2**, which can be recovered by rapid removal of residues of the original acyl bromide and the final trimethylbromosilane from the reaction sphere, under vacuum,

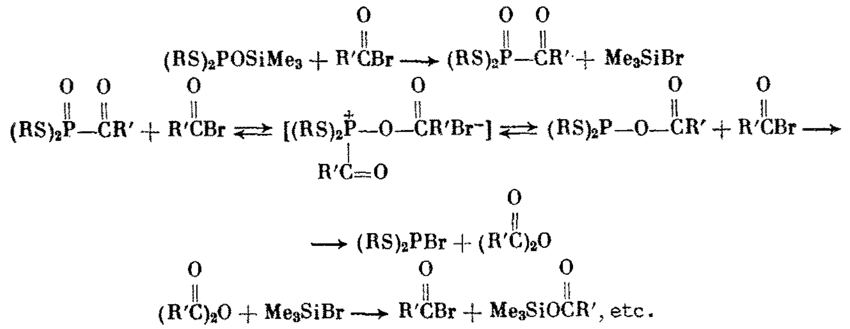


$$\underset{(1)}{(RS)_2POSiMe} + R'\overset{O}{\overset{\|}{C}}Br \xrightarrow{-25^\circ} \underset{(2a,\ c)}{(RS)_2\overset{O}{\overset{\|}{P}}-\overset{O}{\overset{\|}{C}}R'} + Me_3SiBr$$

R=Et, R'=Ph (**2a**); R=Et, R'=Me (**2c**).

When the reaction mixture temperature is brought up to approximately 20°C and held there for a short time, without removal of the low-boiling products, the acylphosphonates **2** are converted to dialkyldithiobromophosphites.

We believe on the basis of these results that the formation of bromophosphites in the reaction of the silylphosphites **1** with acyl bromides can be represented as a retro-Arbuzov interaction of the acylphosphonates **2** (formed in the first stage of the reaction) with the acyl halide, resulting in an acylotropic and possibly reversible phosphonate—phosphite rearrangement, with subsequent replacement of the acyloxy group by halogen. The latter reaction is described in [8]. The interaction of the bromosilane with the carboxylic acid anhydride leads to regeneration of the acyl bromide and the formation of a silyl ester of the carboxylic acid.



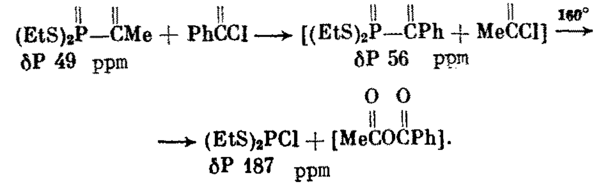
$$(RS)_2POSiMe_3 + R'\overset{O}{\overset{\|}{C}}Br \longrightarrow (RS)_2\overset{O}{\overset{\|}{P}}-\overset{O}{\overset{\|}{C}}R' + Me_3SiBr \quad (1)$$

$$(RS)_2\overset{O}{\overset{\|}{P}}-\overset{O}{\overset{\|}{C}}R' + R'\overset{O}{\overset{\|}{C}}Br \rightleftarrows [(RS)_2\underset{R'C=O}{\overset{+}{P}}-O-\overset{O}{\overset{\|}{C}}R'Br^-] \rightleftarrows (RS)_2P-O-\overset{O}{\overset{\|}{C}}R' + R'\overset{O}{\overset{\|}{C}}Br \longrightarrow$$

$$\longrightarrow (RS)_2PBr + (R'\overset{O}{\overset{\|}{C}})_2O \quad (2)$$

$$(R'\overset{O}{\overset{\|}{C}})_2O + Me_3SiBr \longrightarrow R'\overset{O}{\overset{\|}{C}}Br + Me_3SiO\overset{O}{\overset{\|}{C}}R', \text{ etc.} \quad (3)$$

The possibility of such a course of the reaction is supported by a series of model conversions. We have found that the dialkyldithioacetylphosphonates **2** at ~20°C react with acyl bromides to form dialkyldithiobromophosphites in accordance with Eq. (2). Diethyldithioacetylphosphonate enters into an analogous reaction with benzoyl chloride, but under more severe conditions. It is interesting that in the early stages, a reaction previously unknown in the chemistry of acylphosphonates is observed — transacylation, with the formation of the corresponding benzoylphosphonate, identified by ^{31}P NMR:



$$\underset{\delta P\ 49\ \text{ppm}}{(EtS)_2\overset{O}{\overset{\|}{P}}-\overset{O}{\overset{\|}{C}}Me} + Ph\overset{O}{\overset{\|}{C}}Cl \longrightarrow [\underset{\delta P\ 56\ \text{ppm}}{(EtS)_2\overset{O}{\overset{\|}{P}}-\overset{O}{\overset{\|}{C}}Ph} + Me\overset{O}{\overset{\|}{C}}Cl] \xrightarrow{160^\circ}$$

$$\longrightarrow \underset{\delta P\ 187\ \text{ppm}}{(EtS)_2PCl} + [Me\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}Ph].$$

TABLE 1. Changes in ^{31}P NMR Spectrum in Reaction of Diethyldithiotrimethylsilylphosphite with Acetyl Bromide as the Temperature is Raised

T, °C	Intensity, %		
	$(\mathrm{EtS})_2\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{P}}}-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{CH_3}$ δp −49 ppm	$(\mathrm{EtS})_2\mathrm{PBr}$ 196 ppm	$(\mathrm{EtS})_2\mathrm{PO}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{CH_3}$ 174 ppm
−30	100.00	–	–
−5	70.64	11.37	17.99
0	70.07	15.91	14.02
30	4.26	95.74	

TABLE 2. Changes in ^{31}P NMR Spectrum in Reaction of Diethyldithioacetylphosphite with Benzoyl Bromide as the Temperature is Raised

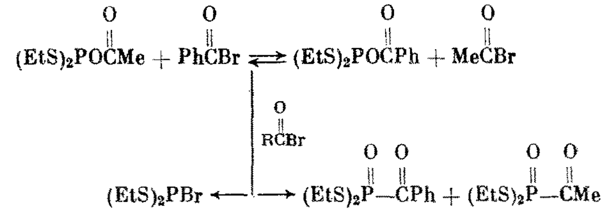
T, °C	Intensity, %				
	$(\mathrm{EtS})_2\mathrm{PO}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{Me}$ δP 174 ppm	$(\mathrm{EtS})_2\mathrm{PO}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{Ph}$ 177 ppm	$(\mathrm{EtS})_2\mathrm{PBr}$ 196 ppm	$(\mathrm{EtS})_2\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{P}}}-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{Me}$ 49 ppm	$(\mathrm{EtS})_2\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{P}}}-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{Ph}$ 56 ppm
−20	100.00	–	–	–	–
5	94.50	2.00	3.50	–	–
15	86.65	9.76	3.59	–	–
25	41.31	32.01	17.10	5.29	4.29

We have used ^{31}P NMR to study the interaction of diethyldithiotrimethylsilylphosphite with acetyl bromide in the temperature interval from −30 to +30°C. The reactants were mixed at −30°C, whereupon we observed that the signal from the original silylphosphite disappeared and a signal of the acetylphosphonate appeared, with δP 49 ppm. When the temperature was raised to −10°C, signals appeared with δP 196 and 174 ppm, assigned to the dialkyldithiobromophosphite and dialkyldithioacetylphosphite, respectively. Their ratio changed as the temperature was raised; at +30°C, essentially all that remained in the spectrum was a single signal with δP 196 ppm, assigned to the final dialkyldithiobromophosphite (Table 1).

Quite probably, the reaction of transacylation of acylphosphonates that we have discovered is also related to a reversible retro-Arbuzov conversion of the phosphonate to a phosphite, with the participation of the two different acyl halides. In this connection, an important factor is the possibility of rearrangement of the dithioacylphosphites to the corresponding acylphosphonates under the influence of the acyl halides, a rearrangement that had not been observed previously for this type of compound [8].

We have also used ^{31}P NMR in studying the interaction of diethyldithioacetylphosphite with benzoyl bromide in the temperature interval from −20 to +25°C. The reactants were mixed at −20°C, after which the spectrum was recorded as the temperature was raised. At +5°C, a signal appeared with δP 177 ppm, apparently pertaining to the product of transacylation of the acetylphosphite, i.e., the benzoylphosphite, with the intensity of this signal increasing rapidly as the temperature was raised. At the same time, a signal of the diethyldithiobromophosphite was observed, with δP 196 ppm. At a higher temperature (+25°C), signals of the acetyl- and benzoylphosphonates appeared in the spectrum, with δP 49 and 56 ppm, respectively (Table 2). The assignment of the signals in the spectra was based on a comparison of the chemical shifts given by the reaction mixture to those given by model compounds.

These results indicate that in the first stage of this reaction a reversible transacylation of the acetylphosphite takes place under the influence of the benzoyl bromide, with the formation of the benzoylphosphite, which then apparently interacts with both acyl halides in accordance with the Arbuzov reaction scheme:



$$(EtS)_2P\overset{O}{\overset{\|}{O}}\overset{O}{\overset{\|}{C}}Me + Ph\overset{O}{\overset{\|}{C}}Br \rightleftarrows (EtS)_2P\overset{O}{\overset{\|}{O}}\overset{O}{\overset{\|}{C}}Ph + Me\overset{O}{\overset{\|}{C}}Br$$

$$\xrightarrow{R\overset{O}{\overset{\|}{C}}Br} (EtS)_2PBr + (EtS)_2\overset{O}{\overset{\|}{P}}-\overset{O}{\overset{\|}{C}}Ph + (EtS)_2\overset{O}{\overset{\|}{P}}-\overset{O}{\overset{\|}{C}}Me$$

It is highly probable that reactions in which the coordination of the phosphorus atom is preserved are catalyzed by acids, in particular HBr [2, 8].

EXPERIMENTAL

^{31}P NMR spectra were registered in a KGU-4 NMR spectrometer at a frequency of 10.2 MHz and in a Bruker CXP-100 spectrometer at a frequency of 36.5 MHz, relative to an 85% solution of H_3PO_4. PMR spectra were recorded in a Varian T-60 spectrometer with a working frequency of 60 MHz, with TMS as an internal standard. IR spectra were recorded in a UR-20 spectrometer.

Reaction of S,S-Diethyltrimethylsilyldithiophosphite with Acetyl Bromide. a. To 10.0 g (0.04 mole) of S,S-diethyltrimethylsilyldithiophosphite, 5.1 g (0.04 mole) of acetyl bromide was added rapidly (but dropwise). The reaction mixture was heated to 34°C. The light fractions were removed under vacuum (0.02 mm Hg) and condensed in a liquid nitrogen trap. By distillation of the contents of the trap, 2.5 g (46%) of trimethylsilyl acetate was recovered, with bp 95°C (160 mm) and n_D^{20} 1.3940 [5]. By fractionation of the residue, obtained 5.5 g (57%) of S,S-diethyldithiobromophosphite with bp 64°C (0.03 mm), n_D^{20} 1.6155, δP 196 ppm [2]. For proof of the structure, 4.0 g (0.017 mole) of the bromophosphite was converted to triethyltrithiophosphite by reaction with 1.1 g (0.017 mole) of ethyl mercaptan in the presence of 1.75 g (0.017 mole) of triethylamine. Recovered 1.5 g (52%) of triethylamine hydrobromide with mp 240°C [9] and 3.2 g (87%) of triethyltrithiophosphite with bp 85°C (0.04 mm), n_D^{20} 1.5691, δP 116 ppm [10].

b. To 10.0 g (0.04 mole) of S,S-diethyltrimethylsilyldithiophosphite, 5.1 g (0.04 mole) of acetyl bromide was added dropwise, with cooling of the reaction mixture to —25°C, after which the temperature was increased smoothly to approximately +20°C. The light fractions were removed under vacuum (0.02 mm) and condensed in a liquid nitrogen trap. By distillation of the contents of the trap, obtained 5.1 g (80.7%) of trimethylbromosilane with bp 77°C, n_D^{20} 1.4195 [11]. In the residue was undistilled S,S-diethylacetyldithiophosphonate **2c**, n_D^{20} 1.5165. PMR spectrum (CCl_4, δ, ppm, J, Hz): 1.33 t (CH_3C), $^3J_{HH}$ = 7.5; 2.51 d ($CH_3C{=}O$), $^3J_{HP}$ = 5.0; 2.87 d.q (CH_2S), $^3J_{HP}$ = 12.0. IR spectrum (ν, cm^{-1}): 1710 (C=O); 1210 (P=O); 580, 490 (PSC). δP 49 ppm. In an attempt at fractionation, the substance decomposed.

Reaction of S,S-Diethyltrimethylsilyldithiophosphite with Benzoyl Bromide. a. To 5.0 g (0.02 mole) of S,S-diethyltrimethylsilyldithiophosphite, with stirring and cooling to 0°, 3.8 g (0.02 mole) of benzoyl bromide was added. The reaction temperature was brought up to ~20°C, and the volatile products were removed under vacuum at 0.02 mm Hg and condensed in a liquid nitrogen trap. The residue contained unpurified S,S-diethylbenzoyldithiophosphonate **2a** with δP 56 ppm. By distillation of the contents of the trap, recovered 2.6 g (85.0%) of trimethylbromosilane with bp 77°C, n_D^{20} 1.4255 [11]. From the residue, by means of a molecular distillation apparatus, recovered 4.2 g (74.2%) of the phosphonate **2a** with a coil temperature of 107°C (0.03 mm), n_D^{20} 1.5885 [4].

b. To the unpurified phosphonate **2a** that was obtained by the method described above, 3.8 g (0.02 mole) of benzoyl bromide was added at ~20°C. In the ^{31}P NMR spectrum of the crude reaction mixture, the only signal was that of diethyldithiobromophosphite with δP 196 ppm. By fractionation, recovered 3.5 g (72.7%) of diethyldithiobromophosphite with bp 60°C (0.02 mm) [2]. The diethyldithiobromophosphite product, through the action of 0.93 g of ethyl mercaptan and 1.52 g of triethylamine in 15 ml of hexane, was converted to triethyltrithiophosphite 2.5 g (78.0%) with bp 85°C (0.04 mm), n_D^{20} 1.5695, δP 116 ppm [10].

Reaction of S,S-Diethylacetyldithiophosphonate (2c) with Acetyl Bromide. To 8.0 g (0.033 mole) of S,S-diethyltrimethylsilyldithiophosphite, 2.6 g of acetyl chloride was added rapidly but dropwise. The trimethylchlorosilane was removed under vacuum (0.04 mm) and condensed in a liquid nitrogen trap. Recovered 3.1 g (86%) of trimethylchlorosilane with bp 58°, n_D^{20} 1.3892 [12]. The residue contained S,S-diethylacetyldithiophosphonate **2c**, n_D^{20} 1.5193. To the unpurified phosphonate **2c** obtained in this manner, 4.06 g (0.033 mole) of acetyl bromide was added dropwise with cooling to 0°C, after which the temperature was brought up slowly to ~20°C. The volatile components were removed under vacuum (0.02 mm) at 50°C and condensed in a liquid nitrogen trap. By distillation of the contents of the trap, recovered 2.1 g (62.3%) of acetic anhydride with bp 140°C, n_D^{20} 1.3975 [13]. The residue contained diethyldithiobromophosphite with δP 196 ppm. By fractionation of the residue, recovered 6.4 g of a fraction with bp 65-80°C (0.06 mm), which, as indicated by ^{31}P NMR spectra, consisted of triethyltrithiophosphite (δP 116 ppm) and diethyldithiobromophosphite (δP 196 ppm) in a 3:2 ratio. A 5.4-g quantity of this fraction (cooled and stirred) was treated with a mixture of 0.58 g of ethyl mercaptan and 0.95 g of triethylamine in 10 ml of hexane. The precipitate that was formed was filtered off. Recovered 1.6 g (93.0%) of triethylamine hydrobromide with mp 240°C [9]. The solvent was removed from the filtrate under vacuum. By fractionation of the residue, recovered 4.5 g (63.6%) of triethyltrithiophosphite with bp 84-85°C (0.04 mm), n_D^{20} 1.5695, δP 116 ppm [10].

Reaction of S,S-Diethylacetyldithophosphonate (2c) with Benzoyl Chloride. A 4.4-g quantity (0.02 mole) of the phosphonate **2c**, obtained in the same manner as described for the previous experiment, was mixed with 2.9 g (0.02 mole) of benzoyl chloride. The reaction mixture was heated for 10 min at 150°C. The ^{31}P NMR spectrum of the reaction mixture contained mainly a signal with δP 187 ppm, pertaining to diethyldithiochlorophosphite. By subsequent fractionation, recovered a fraction with bp 45-50°C (0.03 mm), which, according to ^{31}P NMR data, consisted of diethyldithiochlorophosphite (δP 187 ppm) and triethyltrithiophosphite (δP 116 ppm) in a 2:1 ratio. A 2.5-g quantity of this fraction was treated with a mixture of 0.6 g of ethyl mercaptan and 1.0 g of triethylamine in 10 ml of hexane. The precipitate was filtered off, and the solvent was removed under vacuum. By fractionation of the residue, recovered 2.2 g (49.8%)of triethyltrithiophosphite with bp 86°C (0.04 mm), n_D^{20} 1.5698, δP 116 ppm [10].

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