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SYNTHESIS AND REACTIONS OF S,S-DIALKYL TRIMETHYLSILYL DITHIOPHOSPHITES

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S,S-Dialkyl-O-trimethylsilyl dithiophosphites (III)-(VI) have been obtained by reacting dialkyl dithiochlorophosphites with bis(trimethylsilyl)acetamide. Compounds (III)-(VI) react with aldehydes in the presence of catalytic amounts of tertiary amines to give S,S-dialkyl-1-trimethylsilyloxyalkyldithiophosphonates (VII)-(IX) and (XII). Hydrolysis of (III) and (V) affords dialkyl dithiophosphites (XVI) and (XVII), which readily add to azomethines and chloral.

Silyloxy derivatives of P(III) thioacids with the SPOSi bond system have not been reported. The usual method of synthesis of silyl phosphites is by silylation of hydrophosphoryl compounds [1]. This method was, however, found to be inapplicable to the synthesis of silyl phosphites with alkylthio groups attached to phosphorus, since the requisite hydrophosphoryl compounds bearing alkylthio groups at phosphorus are extremely labile [2]. The best method was found to be by replacing the chlorine in P(III) acid chlorides by the trimethylsilyloxy group with bis(trimethylsilyl)acetamide [3]. We have found that the reaction of dialkyl dithiochlorophosphites with acetamide occurs in two steps. The first step occurs on mixing the reactants, under mild conditions, with the elimination of a molecule of trimethylchlorosilane, and phosphorylation of the ambident triad NCO system of the acetamide. This reaction could in theory give three isomers, namely the N-silylated-O-phosphoryl (a), the O-silylated-N-phosphoryl (b), or the N-silylated-N-phosphoryl compound (c) (see scheme at top of following page).

The ^{31}P NMR spectra of the reaction mixture at this stage showed clearly that compounds of two types were present, both containing three-coordinate phosphorus. When, for example, diisopropyl dithiochlorophosphite was used in this reaction, the spectrum showed two signals with δP 118 and 108 ppm in a ratio of 3:2. With diethyl dithiochlorophosphite, two products were formed with δP 128 and 117 ppm in a ratio of 4:1. Comparison of the chemical shifts of these signals with literature values [4] enables structure (a) to be excluded, since the S_2PO environment usually gives rise to a shift in the range 160-180 ppm. The IR spectra of the reaction mixtures show two bands at 1620 and 1660 cm^{-1}, clearly due to the C=N and C=O groups of isomers (b) and (c), respectively. This assignment is based on the fact that the carbonyl group absorbs at a longer wavelength than an azomethine group in approximately the same environment [5]. This assignment is supported by the absorptions of C=N and C=O groups

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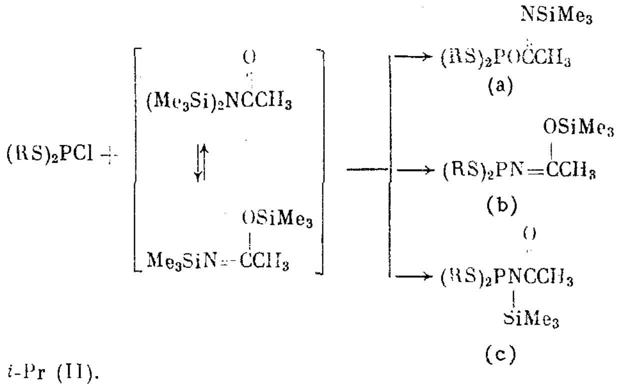
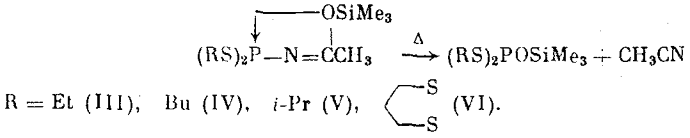


$$(RS)_2PCl + \left[(Me_3Si)_2NC(O)CH_3 \rightleftarrows Me_3SiN{=}C(OSiMe_3)CH_3 \right] \longrightarrow \begin{cases} (RS)_2POC(=NSiMe_3)CH_3 & (a) \\ (RS)_2PN{=}C(OSiMe_3)CH_3 & (b) \\ (RS)_2PN(SiMe_3)C(O)CH_3 & (c) \end{cases}$$

R = Et (I), *i*-Pr (II).

in the structural isomers formed on O,N-acylotropic rearrangement in amide–imide systems [6]. In some instances, it is possible by careful distillation in a high vacuum to isolate the isomers with the lower chemical shift values for the phosphorus atom in a pure state. The IR spectra of these compounds show absorption at 1620 cm^{-1} only. Examination of these findings shows that the isomers with the higher shift values have structure (c), and those with the lower values, structure (b). The fact that only isomer (b) is isolable by distillation shows that in all likelihood the isomers (c) and (b) are interconvertible, and that isomer (b) is the more thermodynamically stable. A similar result indicating the interconversion of the isomers has been obtained on prolonged storage (three months) or heating to 100°C of a mixture of isomers (b) and (c). When this is done, the signal with the high shift in the ^{31}P NMR spectrum disappears, and the intensity of the low shift value is increased. The high thermodynamic stability of (b) is probably due to the high silicophilicity of oxygen and to steric requirements, in accordance with which the presence of two bulky substituents, trimethylsilyl and dithiophosphite, at the amide nitrogen is hindered.

In the second stage of the reaction, occurring at high temperatures, the intermediates (b) and (c) decompose with the elimination of a molecule of acetonitrile to give S,S'-dialkyl O-trimethylsilyl dithiophosphites, probably as a result of intramolecular nucleophilic attack of the trimethylsilyloxy group on phosphorus in isomer (b).



$$(RS)_2P{-}N{=}C(OSiMe_3)CH_3 \xrightarrow{\Delta} (RS)_2POSiMe_3 + CH_3CN$$

R = Et (III), Bu (IV), *i*-Pr (V), (VI).

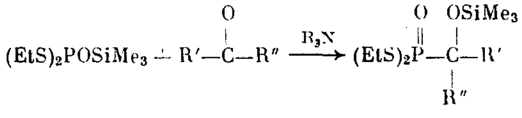
The structures of the products were confirmed by physicochemical methods and elemental analysis. The chemical shifts for the phosphorus nucleus in the acyclic dithiosilylphosphites (III)-(V) lie in the range 160-170 ppm. The PMR spectrum of the diethyl trimethylsilyl phosphite (III) consists of a singlet with δ 0.32 ppm for the trimethylsilyloxy group protons, a triplet with δ 1.32 ppm and a doublet of quartets with δ 2.77 ppm for the ethylthio group protons ($^3J_{HH}$ = 7.5, $^3J_{HP}$ = 9 Hz). The IR spectra of these compounds show absorption at 855 and 1255 cm^{-1} (CH_3Si), 958 cm^{-1} (POSi), 650 cm^{-1} (CS), and 580-480 cm^{-1} (PS).

In this reaction, the phosphorus atom functions as an electrophile, as is shown in [3], in which the effects of substituents at phosphorus on the ease of decomposition of compounds of type (b) was examined. Comparison of the present findings with those reported in [3] shows that the alkylthio group at phosphorus occupies a position intermediate between alkyl and alkoxy groups in order of increasing tendency to decompose (R < RS < RO). This indicates that the alkylthio group does not have a very high electron-acceptor influence on the phosphorus atom in this intramolecular nucleophilic replacement.

The reactions of silyloxy derivatives of P(III) acids with carbonyl compounds have received the greatest attention. Usually, 1-silyloxyphosphonic acid derivatives are obtained [7]. Aldehydes are the more reactive than ketones in such reactions, occurring at temperatures below 0°C [8].

It has been found that in contrast to sulfur-free silyl phosphites, which react with aldehydes under mild conditions, dialkyl dithiotrimethylsilylphosphites are inert towards deactivated and unreactive carbonyl compounds such as benzaldehyde, acetaldehyde, and o-nitrobenzaldehyde. No reaction occurs with these reactants at ~20°C, and only partial reaction at 100°C.

We have, however, found that the addition of catalytic amounts of tertiary amines to the reaction mixture results in a spontaneous reaction at ~20°C. In some instances, the reaction is exothermic. The silyl phosphite adds to the carbonyl group to give 1-trimethylsilyloxyalkyldithiophosphonates (VII)-(IX).



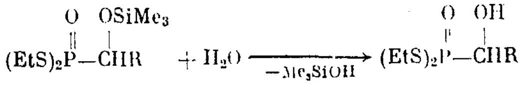
$$(EtS)_2POSiMe_3 + R'-\overset{\overset{O}{|}}{C}-R'' \xrightarrow{R_3N} (EtS)_2\overset{\overset{O}{\|}}{P}-\underset{\underset{R''}{|}}{\overset{\overset{OSiMe_3}{|}}{C}}-R'$$

(VII)—(IX)

$R' = H$, $R'' = CH_3$ (VII), Ph (VIII), $C_6H_4NO_2$-*o* (IX).

The structures of the products were established by ^{31}P, ^1H, and IR spectroscopy. The chemical shifts of the phosphorus in these compounds lay in the region 64-70 ppm. The PMR spectrum of the phosphonate (VIII) showed a singlet for the protons of the trimethylsilyl group with δ 0.42 ppm. The methyl protons of the ethylthio group were present as two triplets as a result of anisochronicity due to the presence of an asymmetric carbon atom with δ 1.35 and 1.62 ppm, $^3J_{HH} = 7.5$ Hz. The methylene protons occurred as a multiplet at 2.50-3.40 ppm, and the methine protons as a doublet with δ 5.36 ppm, $^2J_{HP} = 5.0$ Hz. A multiplet for the phenyl protons was seen at δ 7.37-7.84 ppm. The IR spectrum of this compound showed absorption at 1599, 1493 cm^{-1} (arom. C=C), 1255 cm^{-1} ($SiMe_3$), 1209 cm^{-1} (P=O), 650 cm^{-1} (CS), 557 and 528 cm^{-1} (PS).

These compounds were hydrolytically unstable, undergoing hydrolysis in air at the O—Si bond to give the 1-hydroxyalkyldithiophosphonic acids (X) and (XI).

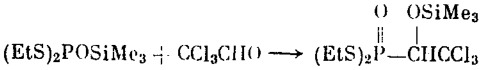


$$(EtS)_2\overset{\overset{O}{\|}}{P}-\overset{\overset{OSiMe_3}{|}}{C}HR + H_2O \xrightarrow[-Me_3SiOH]{} (EtS)_2\overset{\overset{O}{\|}}{P}-\overset{\overset{OH}{|}}{C}HR$$

$R = C_6H_4NO_2$-*o* (X); CCl_3 (XI).

The structures of the hydrolysis products were confirmed by physicochemical methods, and by comparison of their constants with the literature values [2].

In contrast to the reactions with carbonyl compounds of low electrophilicity, that of diethyl dithiotrimethylsilylphosphite with chloral was exothermic even at 20°C, giving the addition product S,S'-diethyl 1-trimethylsilyloxy-2,2,2-trichloroethyldithiophosphonate (XII).



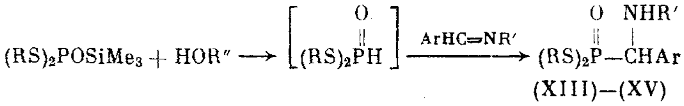
$$(EtS)_2POSiMe_3 + CCl_3CHO \longrightarrow (EtS)_2\overset{\overset{O}{\|}}{P}-\overset{\overset{OSiMe_3}{|}}{C}HCCl_3$$

(XII)

The formation of 1-silyloxyalkyl compounds in the reaction of silylphosphites with carbonyl compounds with nucleophilic catalysis is the first instance of catalytic reactions of this type.

It is noteworthy that increasing the basicity of the amine enhances its catalytic activity. The catalytic activity decreases in the sequence triethylamine > diethylaniline > pyridine, resulting in a decrease in completeness of reaction, as shown by ^{31}P NMR spectroscopy of the reaction mixtures.

Unlike the reactions with carbonyl compounds, the dithiosilylphosphites failed to react with azomethines, either on heating, or in the presence of a catalyst. Addition occurred only in the presence of proton donors (water or alcohol), to give high yields of products with the 1-aminobenzyldithiophosphonate structure (XIII)-(XV) which did not contain silicon. The reaction apparently occurs via an intermediate dialkyldithiophosphorous acid formed by reaction of the silylphosphites with the proton donor, followed by addition of this to the azomethine:



$$(RS)_2POSiMe_3 + HOR'' \longrightarrow \left[(RS)_2\overset{O}{\overset{\|}{P}}H\right] \xrightarrow{ArHC{=}NR'} (RS)_2\overset{O}{\overset{\|}{P}}-\overset{NHR'}{\overset{|}{C}}HAr$$

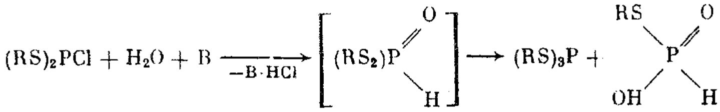
(XIII)—(XV)

R″ = H, Alk; R = Et, R′ = Ar = Ph (XIII); R = Et, R′ = *o*-ClC$_6$H$_4$, Ar = *o*-NO$_2$C$_6$H$_4$ (XIV); R = *i*-Pr, R′ = Ar = Ph (XV).

The structures of the products were proved by physicochemical methods and elemental analysis. The PMR spectrum of (XIV) showed a triplet for the methyl protons with δ 1.20 ppm, $^3J_{HH}$ = 7.5 Hz, a multiplet for the methylene protons with δ 2.27-3.00 ppm, and a doublet for the methine proton with δ 4.87 ppm, $^2J_{HP}$ = 16 Hz. The phenyl protons were seen as a multiplet at 6.40-7.63 ppm, and the NH proton occurred as a broadened singlet at 5.40 ppm. The IR spectrum of this product showed absorption at 3315 (NH), 1190 (P=O), 575 (CS), 540 and 525 cm^{-1} (PS).

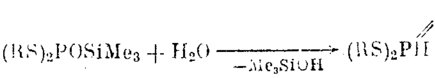
In order to establish this reaction mechanism, it was necessary to examine the behavior of dithiosilylphosphites towards proton donors.

It is known that the hydrolysis [9, 10], alcoholysis [11], and in some cases aminolysis [12] of silylphosphites occurs readily to give the corresponding hydrophosphoryl compounds. By analogy, it would be expected that dialkyldithiophosphorous acids would be formed in the reaction of dialkyl dithiotrimethylsilyl phosphites with protonic nucleophiles. No dialkyl dithiophosphites have hitherto been obtained in a stable state. Attempts have been made [13, 14] to obtain such compounds by hydrolyzing the appropriate P(III) thioacid chlorides in the presence of a base. It was not, however, possible to isolate and characterize these compounds in consequence of the formation of disproportionation products.



It was found that reaction of dialkyl dithiotrimethylsilylphosphites with diethylamine and aniline failed to occur even under severe conditions, in contrast to the reaction with diamidosilylphosphites. With proton donors containing an OH group such as water or aliphatic alcohols, however, the reaction took place vigorously at ~20°C.

Hydrolysis of the silylphosphites (III) and (V) proceeded cleanly to give the dialkyldithiophosphorous acids (XVI) and (XVII), which are quite stable under normal conditions, thus enabling their physicochemical properties and reactivity to be examined.



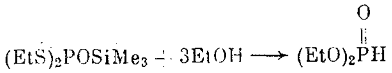
$$(RS)_2POSiMe_3 + H_2O \xrightarrow[-Me_3SiOH]{} (RS)_2\overset{O}{\overset{/\!/}{P}}H$$

R = Et (XVI); *i*-Pr (XVII).

The chemical shifts of the phosphorus atom were 28 ppm for the diethyldithiophosphite (XVI) (J_{HP} = 632 Hz), and 27 ppm for diisopropyl dithiophosphite (XVII) (J_{HP} = 632 Hz). The IR spectra of these compounds showed weak absorption at 2380 cm^{-1} attributed to P—H vibrations. The Raman spectrum of (XVI) in a sealed capillary showed strong absorption at 2380 cm^{-1} for PH, and three bands at 495, 520, and 555 cm^{-1} (P—S—C).

The dialkyldithiophosphorous acids were quite stable, remaining unchanged on storage for periods of from 2-3 h to 2-3 days. On attempted distillation, they decomposed with the formation of a complex mixture of phosphorus-containing products which could not be separated.

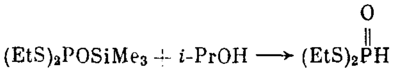
It was assumed that the formation of dithiophosphorous acids by reaction of dithiosilylphosphites with alcohols would proceed more smoothly. It was, however, found that the reaction of diethyl dithiotrimethylsilylphosphite with ethanol proceeded further than the reaction with water, giving diethylphosphorous acid irrespective of the proportions of the reactants.



$$(EtS)_2POSiMe_3 + 3EtOH \longrightarrow (EtO)_2\overset{O}{\overset{\|}{P}}H$$

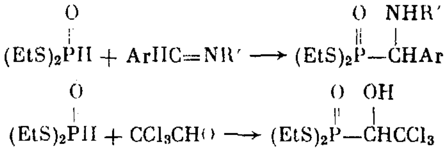
When the proportion of reactants in this reaction was 1:1, two-thirds of the silylphosphite remained unreacted, one third being converted into diethyl phosphite.

With 2-propanol, however, the reaction stopped at the stage of formation of diethyl dithiophosphite, as shown by the ^{31}P NMR spectrum, apparently as a result of the steric hindrance of the isopropyl group of the alcohol.



$$(EtS)_2POSiMe_3 + i\text{-}PrOH \longrightarrow (EtS)_2\overset{O}{\overset{\|}{P}}H$$

These dialkyl dithiophosphites were highly reactive compounds which added readily to azomethines and chloral. It is likely that these reactions are models for the reaction of silylphosphites with azomethines in the presence of water or alcohol.



$$(EtS)_2\overset{O}{\overset{\|}{P}}H + ArHC{=}NR' \longrightarrow (EtS)_2\overset{O}{\overset{\|}{P}}-\overset{NHR'}{\overset{|}{C}}HAr$$

$$(EtS)_2\overset{O}{\overset{\|}{P}}H + CCl_3CHO \longrightarrow (EtS)_2\overset{O}{\overset{\|}{P}}-\overset{OH}{\overset{|}{C}}HCCl_3$$

The structures of these products were confirmed by comparing their physicochemical characteristics with samples of compounds obtained in preceding experiments.

These studies have thus led to the synthesis of new representatives of thio-derivatives of trivalent phosphorus, namely the dialkyl dithiotrimethylsilyl phosphites. The potential value of these compounds for the synthesis of organothiophosphorus compounds by addition to electrophiles has been shown.

EXPERIMENTAL

^{31}P NMR spectra were obtained on a KGU-4 NMR spectrometer (USSR) at a frequency of 10.2 MHz, standard 85% H_3PO_4. IR spectra were recorded on a UR-20, and PMR spectra on a Varian T-60 (solvent CCl_4) relative to TMS as external standard.

S,S'-Diethyl O-Trimethylsilylacetimidoyldithiophosphite (Ib). To 8.3 g (0.04 mole) of bis(trimethylsilyl)acetamide was added dropwise with stirring 7.5 g (0.04 mole) of S,S-diethyl dithiochlorophosphite at 45°C. The mixture was held under vacuum (0.02 mm) at 45°C, and the liquid which condensed in a trap cooled in liquid nitrogen was redistilled to give 3.0 g (70%) of trimethylchlorosilane, bp 58°C, n_D^{20} 1.3875. The residue contained two isomers (Ib and Ic), δ 128 and 117 ppm, in a ratio of 4:1. Fractionation of this residue gave 4.1 g (35.3%) of S,S'-diethyl O-trimethylsilylacetimidoyldithiophosphite (Ib), bp 108°C (0.02 mm), n_D^{20} 1.5274. PMR spectrum (δ, ppm, J, Hz): 0.23 s (CH_3Si), 1.26 t (CH_3C, $^3J_{HH}$ = 7.2), 2.10 d ($CH_3C{=}N$, $^4J_{HP}$ = 3.5), 2.30-3.00 m (CH_2S), δP 128 ppm. Found, %: C 38.65; H 7.33; N 5.21; P 11.42; S 23.28; Si 10.05. $C_9H_{22}NOPS_2Si$. Calculated, %: C 38.13; H 7.33; N 4.95; P 10.93; S 22.63; Si 9.91.

S,S'-Diisopropyl O-Trimethylsilylacetimidoyldithiophosphite (IIb). To 10.6 g (0.05 mole) of bis(trimethylsilyl)acetamide was added with stirring 13.2 g (0.05 mole) of S,S'-diisopropyl dithiochlorophosphite. The reaction mixture was evacuated at 10 mm. The residue contained two isomers (IIb and IIc), δP 118 and 108 ppm in a ratio of 3:2. Fractionation of the residue gave 8.6 g (53%) of S,S'-diisopropyl O-trimethylsilylacetimidoyldithiophosphite (IIb), bp 95°C (0.002 mm), n_D^{20} 1.5163, d_4^{20} 1.0054. PMR spectrum (δ, ppm, J, Hz): 0.20 s (CH_3Si), 1.10 d (CH_3C, $^3J_{HH}$ = 7.0), 2.07 d ($CH_3C{=}N$, $^4J_{HP}$ = 3.5); 3.11 d. sept. (CH, $^3J_{HP}$ = 7.0), δP 118 ppm. Found, %: C 42.21; H 8.54; N 4.40; P 9.84. $C_{11}H_{26}NOPS_2Si$. Calculated, %: C 42.44; H 8.36; N 4.50; P 9.97.

S,S'-Diethyl Trimethylsilyl Dithiophosphite (III). To 17.4 g (0.09 mole) of S,S'-diethyl dithiochlorophosphite was added slowly with stirring and cooling in a water bath 18.7 g (0.09 mole) of bis(trimethylsilyl)acetamide. When the addition was complete, the mixture was held under vacuum at 10 mm. The liquid condensing in a trap cooled in liquid nitrogen was distilled to give 6.8 g (68.0% of trimethylchlorosilane, bp 58°C, n_D^{20} 1.3880. The residue was heated at 150-180°C until volatile products had been removed. Fractionation of these volatiles gave 2.0 g (52.6%) of acetonitrile, bp 82°C, n_D^{20} 1.3437. Redistillation of the residue gave 12.0 g (53.6%) of S,S'-diethyl trimethylsilyl dithiophosphite (III), bp

118-120°C (10 mm), n_D^{20} 1.4936, d_4^{20} 0.9891. Found, %: C 35.01; H 7.86; P 14.09; S 25.92; Si 12.80. $C_7H_{19}OPS_2Si$. Calculated, %: C 34.71; H 7.85; P 12.81; S 26.44; Si 11.57.

S,S'-Di(n-butyl) Trimethylsilyl Dithiophosphite (IV). Similarly, from 30.6 g (0.13 mole) of di-n-butyl dithiochlorophosphite and 25.4 g (0.13 mole) of bis(trimethylsilyl)-acetamide there was obtained 20.7 g (55.5%) of S,S'-di-n-butyl trimethylsilyl dithiophosphite (IV), bp 94°C (0.03 mm), n_D^{20} 1.4970, d_4^{20} 0.9794. PMR spectrum (δ, ppm, J, Hz): 0.25 t (CH_3Si), 0.74-1.10 m (CH_3C), 1.25-1.82 m (CCH_2), 2.73 d.t (CH_2S), $^3J_{HH}$ = 7.5, $^3J_{HP}$ = 9.0). IR spectrum (ν, cm^{-1}): 1255 (CH_3Si); 956 (POSi); 580-480 (PSC). δP 163 ppm. Found, %: C 44.59; H 9.10; P 10.71; Si 9.66. $C_{11}H_{27}OPS_2Si$. Calculated, %: C 44.30; H 9.06; P 10.40; Si 9.40.

S,S'-Diisopropyl Trimethylsilyl Dithiophosphite (V). Similarly, from 11.5 g (0.05 mole) of S,S-diisopropyl dithiochlorophosphite and 10.8 g (0.05 mole) of bis(trimethylsilyl)-acetamide there was obtained 9.1 g (63.4%) of S,S'-diisopropyl trimethylsilyl dithiophosphite (V), bp 81°C (0.06 mm), n_D^{20} 1.4970, d_4^{20} 0.9966. PMR spectrum (δ, ppm, J, Hz): 0.51 s (CH_3Si), 1.66 d (CH_3C, $^3J_{HH}$ = 7.5), 3.09-3.76 m (CHS). IR spectrum (ν, cm^{-1}): 1255 (CH_3Si); 960 (POSi); 580 (PSC). δP 158 ppm. Found, %: C 41.90; H 8.26; P 11.43; S 23.90, Si 10.30. $C_9H_{23}OPS_2Si$. Calculated, %: C 40.00; H 8.51; P 11.48; S 23.70; Si 10.37.

2-Trimethylsilyloxy-1,3,2-dithiaphosphorinane (VI). To 12.0 g (0.07 mole) of 2-chloro-1,3,2-dithiaphosphorinane was added dropwise with stirring 14.1 g (0.07 mole) of bis(trimethylsilyl)acetamide. The volatile components were removed under vacuum. The residue, containing a compound with δP 78 ppm, was fractionated to give 4.4 g (28.0%) of 2-trimethylsilyloxy-1,3,2-dithiaphosphorinane (VI), bp 116°C (0.03 mm), n_D^{20} 1.6683. PMR spectrum (δ, ppm, J, Hz): 0.12 s (CH_3Si); 2.93-3.59 m (CH_2S); 1.76-2.57 m (CH_2C). IR spectrum (ν, cm^{-1}): 1255 (CH_3Si); 943 (POSi); 446, 482 (PS). δP 139 ppm. Found, %: P 13.28; S 14.64. $C_6H_{15}OPS_2Si$. Calculated, %: P 13.72; S 14.16.

Reaction of S,S'-Diethyl Trimethylsilyl Dithiophosphite with Acetaldehyde. To 8.0 g (0.033 mole) of S,S'-diethyl trimethylsilyl dithiophosphite was added with stirring 2.4 g (0.054 mole) of acetaldehyde and 3-5 drops of triethylamine. When the exothermic reaction had ceased, the mixture was evacuated. Molecular distillation of the residue gave 6.2 g (65.3%) of S,S'-diethyl 1-trimethylsilyloxyethyldithiophosphonite (VII) at a temperature of the spiral thermoelement of 80-100°C (0.02 mm), n_D^{20} 1.5008, d_4^{20} 1.0411. PMR spectrum (δ, ppm, J, Hz): 0.63 s (CH_3Si); 1.87 t (CH_3CS, $^3J_{HH}$ = 7.8); 1.88 d.d (CH_3CP, $^3J_{HH}$ = 7.0, $^3J_{HP}$ = 21.0); 2.93-3.67 m (CH_2S); 4.37-4.79 m (HCP). IR spectrum (ν, cm^{-1}): 1258 (CH_3Si); 1200 (PO); 648, 573, 545 (PSC). δP 70 ppm. Found, %: C 37.35; H 8.20; P 10.17; S 22.98; Si 9.17. $C_9H_{23}O_2PS_2Si$. Calculated, %: C 37.74; H 8.09; P 10.81; S 22.39; Si 9.80.

Reaction of S,S'-Diethyl Trimethylsilyl Dithiophosphite with Benzaldehyde. A mixture of 14.0 g (0.058 mole) of S,S-diethyl trimethylsilyl dithiophosphite and 6.1 g (0.058 mole) of benzaldehyde was treated with 3-5 drops of triethylamine, and the mixture heated for 2 h at 110°C. Fractionation gave 11.3 g (56.2%) of S,S'-diethyl 1-trimethylsilyloxybenzyldithiophosphonate (VIII), bp 140°C (0.06 mm), n_D^{20} 1.5401, d_4^{20} 1.1078. Found, %: C 48.33; H 6.71; P 8.76; S 18.02. $C_{14}H_{25}O_2PS_2Si$. Calculated, %: C 48.25; H 7.23; P 8.88; S 18.40.

Reaction of S,S'-Diethyl Trimethylsilyl Dithiophosphite with o-Nitrobenzaldehyde. To a solution of 3.3 g (0.022 mole) of o-nitrobenzaldehyde in 18 ml of benzene was added with stirring 5.3 g (0.22 mole) of S,S-diethyl trimethylsilyl dithiophosphite, followed by 3-5 drops of triethylamine. The reaction was slightly exothermic. The reaction mixture was evacuated at 10 mm to give 8.3 g of crude S,S'-diethyl 1-trimethylsilyloxy-o-nitrobenzyldithiophosphonate (IX). PMR spectrum (δ, ppm, J, Hz): 0.25 s (CH_3Si), 1.23 and 1.40 anisochron. two t (CH_3C, $^3J_{HH}$ = 7.5), 2.53-3.12 m (CH_2S), 6.47 d (HCP, $^2J_{HP}$ = 6.4), 7.33-8.07 m (C_6H_4). IR spectrum (ν, cm^{-1}): 1255 (CH_3Si); 1208 (P=O); 648, 560, 537 (PSC). δP 68 ppm. Found, %: C 42.12; H 5.95; P 8.11; Si 7.84. $C_{14}H_{24}NO_4PS_2Si$. Calculated, %: C 42.75; H 6.15; P 7.87; Si 7.14.

Hydrolysis of S,S-Diethyl 1-Trimethylsilyloxy-o-nitrobenzyldithiophosphonate (IX). A solution of 8.3 g of the phosphonate (IX), obtained in the preceding preparation, in 20 ml of diethyl ether was poured into a Petri dish, and allowed to stand in air. As the ether evaporated, the mixture crystallized. Recrystallization from acetone gave 4.0 g (58.8%) of S,S-diethyl 1-hydroxy-o-nitrobenzyldithiophosphonate (X), mp 113°C, δP 73 ppm (benzene) [2].

Reaction of S,S-Diethyl Trimethylsilyl Dithiophosphite with Chloral. To 5.0 g (0.02 mole) of S,S-diethyl trimethylsilyl dithiophosphite was added dropwise, with stirring and cooling to 0°C, 3.0 g (0.02 mole) of chloral. There was obtained 8.0 g (100%) of crude S,S-diethyl 1-trimethylsilyloxy-2,2,2-trichloroethyldithiophosphonate (XII), n_D^{20} 1.5291. PMR spectrum (δ, ppm, J, Hz): 0.72 s (CH_3Si), 1.78 and 1.82 anisochron. two t (CH_3, $^3J_{HH}$ = 7.0), 3.40 d. q (CH_2, $^3J_{HP}$ = 7.0), 4.93 d (HCP, $^2J_{HP}$ = 2.0). IR spectrum (ν, cm^{-1}): 1255 (CH_3Si); 1208 (P=O); 648, 550, 510 (PSC). δP 64 ppm. Found, %: C 27.46; H 5.29; Cl 28.78; P 7.95; Si 7.17. $C_9H_{20}Cl_3O_2PS_2Si$. Calculated, %: C 27.73; H 5.17; Cl 27.28; P 7.95; Si 7.21.

Hydrolysis of S,S-Diethyl 1-Trimethylsilyloxy-2,2,2-trichloroethyldithiophosphonate (XII). A solution of 0.92 g (0.002 mole) of the phosphonate (XII) in 10 ml of diethyl ether was poured into a Petri dish. As the ether evaporated, crystals were formed. Recrystallization from chloroform gave 0.6 g (80.0%) of S,S-diethyl 1-hydroxy-2,2,2-trichloroethyldithiophosphonate (XI), mp 101-111°C, δP 69 ppm [2].

Reaction of S,S-Diethyl Trimethylsilyl Dithiophosphite with Benzalaniline. To 15.0 g (0.062 mole) of S,S-diethyl trimethylsilyl dithiophosphite was added 11.2 g (0.062 mole) of benzalaniline dissolved in 20 ml of benzene, followed by the dropwise addition of 1.1 ml (0.062 mole) of water. An exothermic reaction occurred, with separation of a crystalline solid. The solvent was partly removed under reduced pressure, and the solid was filtered off and recrystallized from alcohol to give 15.5 g (71.5%) of S,S-diethyl 1-(N-phenylamino)-benzyldithiophosphonate (XIII), mp 89°C. PMR spectrum (CD_3OD, δ, ppm, J, Hz): 1.17 and 1.20 anisochron. two t (CH_3, $^3J_{HH}$ = 7.5), 2.37-3.03 m (CH_2S), 5.08 d (CH, $^2J_{HP}$ = 15.0), 6.53-7.73 m (C_6H_5). IR spectrum (ν, cm^{-1}): 3320 (NH); 1500, 1520, 1580, 1600 (C_6H_5); 1190 (P=O); 525, 540, 555, 575 (PSC). δP 66 ppm. Found, %: C 49.22; H 6.74; N 5.98; P 10.62. $C_{12}H_{20}NOPS_2$. Calculated, %: C 49.83; H 6.92; N 5.95; P 10.73.

Similarly, from 1.4 g (0.005 mole) of S,S-diethyl trimethylsilyldithiophosphite, 1.0 g (0.005 mole) of benzalaniline, and 0.27 g (0.005 mole) of ethanol there was obtained 1.8 g (91.3%) of the phosphonate (XIII), mp 89-90°C, the spectral properties of which were the same as a sample from the preceding experiment.

Reaction of S,S-Diethyl Trimethylsilyl Dithiophosphite with o-Nitrobenzal-o-chloroaniline. To 5.0 g (0.02 mole) of S,S-diethyl trimethylsilyl dithiophosphite was added a solution of 5.4 g (0.02 mole) of o-nitrobenzal-o-chloroaniline in 10 ml of benzene, followed by 0.37 ml of water. The reaction was exothermic. On the following day, the crystals which had separated were filtered off and recrystallized from ethanol to give 5.9 g (66.4%) of bright yellow crystals of S,S-diethyl 1-(N-o-chloroanilino)-p-nitrobenzylphosphonate (XIV), mp 100°C. PMR spectrum (C_6D_6, δ, ppm, J, Hz): 0.97 t (CH_3, $^3J_{HH}$ = 7.0), 2.27-2.93 m (CH_2S), 5.40 d.d (CH, $^2J_{HP}$ = 12.0, $^3J_{HH}$ = 10.0), 6.37-7.90 m (Ar). IR spectrum (ν, cm^{-1}): 3350 (NH); 1500, 1595 (Ar); 1212 (P=O); 520, 550 (PSC). δP 69 ppm. Found, %: C 48.53; H 4.77; N 6.63; P 7.59; S 15.43. $C_{17}H_{20}ClN_2O_3PS_2$. Calculated, %: C 47.39; H 4.67; N 6.50; P 7.20; S 14.87.

S,S-Diethyl Dithiophosphite. To 10.0 g (0.04 mole) of S,S-diethyl trimethylsilyl dithiophosphite, frozen in liquid nitrogen, was added 0.75 ml (0.04 mole) of water. The temperature of the reaction mixture was gradually brought to ~20°C with constant stirring. Volatile products were removed under a vacuum of 0.02 mm. The residue contained S,S-diethyl dithiophosphite (XVI) (for spectral data, see text). According to the ^{31}P NMR spectrum, the diethyl dithiophosphite had decomposed after 3-4 h.

Similarly, from 5.0 g (0.02 mole) of S,S-diethyl trimethylsilyl dithiophosphite and 1.25 g (0.02 mole) of 2-propanol there was obtained diethyl dithiophosphite (XVI), δP 28 ppm, J_{PH} 632 Hz.

S,S-Diisopropyl Dithiophosphite. To 10.0 g (0.037 mole) of S,S-diisopropyl trimethylsilyl dithiophosphite, frozen in liquid nitrogen, was added 0.67 ml (0.037 mole) of water. The temperature of the mixture was gradually brought to 20°C with stirring. The mixture separated into layers. The lower layer was separated, and evacuated at 0.02 mm. The residue was S,S-diisopropyl dithiophosphite (XVII), δP 27 ppm, J_{PH} = 632 Hz). According to its ^{31}P NMR spectrum (XVII) had decomposed by the following day.

Reaction of S,S-Diethyl Trimethylsilyl Dithiophosphite with Ethanol. A mixture of 10.0 g (0.04 mole) of S,S-diethyl trimethylsilyl dithiophosphite and 5.7 g (0.12 mole) of ethanol was fractionated to give 3.6 g (81.8%) of diethylphosphorous acid, bp 70°C (10 mm), n_D^{20} 1.4090, δP 8 ppm, J_{PH} = 680 Hz [15].

Reaction of S,S-Diethyl Dithiophosphite with Chloral. To 5.0 g (0.02 mole) of S,S-diethyl trimethylsilyldithiophosphite, cooled to the temperature of liquid nitrogen, was added dropwise 0.4 g (0.02 mole) of water. The temperature of the mixture was gradually raised to 20°C. The ^{31}P NMR signal of the mixture had δP 28 ppm, J_{PH} = 632 Hz. The mixture was cooled in liquid nitrogen, and treated with 3.0 g (0.02 mole) of chloral. The mixture then crystallized, and was recrystallized from chloroform to give 4.9 g (74.3%) of S,S-diethyl 1-hydroxy-2,2,2-trichloroethyldithiophosphonate (XI), mp 110°C, δP 69 ppm [2].

Reaction of S,S-Diethyl Dithiophosphite and S,S-Diisopropyl Dithiophosphite with Benzalaniline. a) To 6.0 g (0.025 mole) of S,S-diethyl trimethylsilyl dithiophosphite was added dropwise with cooling 0.45 ml (0.025 mole) of water. The mixture was evacuated (0.02 mm), the residue containing S,S-diethyl dithiophosphite, δP 28 ppm. Benzalaniline (4.5 g, 0.025 mole) in 10 ml of benzene was added, and after one day the solvent was partially removed, whereupon the solution crystallized. Recrystallization from ethanol gave 4.1 g (57.3%) of the phosphonate (XIII), mp 90°C.

b) Similarly, from 19.0 g (0.07 mole) of S,S-diisopropyl trimethylsilyldithiophosphite, 1.3 ml (0.07 mole) of water, and 12.8 g (0.07 mole) of benzalaniline there was obtained 21 g (78.4%) of S,S-diisopropyl 1-(N-phenylamino)benzyldithiophosphonate (XV), mp 123°C, δP 63 ppm (acetonitrile). PMR spectrum (CD_3OD, δ, ppm, J, Hz): 1.15 and 1.27 anisochron. two d (CH_3, $^3J_{HH}$ = 7.0). IR spectrum (ν, cm^{-1}): 3290 (NH); 1505, 1595 (C_6H_5); 1205 (P=O); 520, 550, 565, 578 (PSC). Found, %: C 59.93; H 6.77; N 3.78; S 16.70. $C_{19}H_{26}NOPS_2$. Calculated, %: C 60.15; H 6.86; N 3.69; S 16.88.

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