INTERACTION OF THIOESTERS OF P(III) WITH OXYGEN

A. R. Burilov, Ya. A. Drozdova,
M. A. Pudovik, and A. N. Pudovik

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The compounds O,O-diethyl- and O,O-diisopropyl-S-benzylthiophosphite, 2-benzylthio-4,5-benzo-1,3,2-dioxaphospholane, diphenyl-S-benzylthiophosphinite, and S,S-dibenzylphenyldithiophosphonite were obtained. It was found that the thiophosphites enter into isomerization initiated by oxygen in the air; substitution together with isomerization is thereby observed in the case of thioesters of P(III) with the P—C bond. The interaction of thioesters of P(III) with oxygen is inhibited by spin traps.

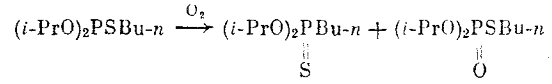
It is known that thioesters of P(III) acids isomerize to compounds of P(IV) thermally [1-5], by the action of alkyl halides [6], and by the action of trimethyliodosilane [7]. Thioesters with resonance-stabilized substituents at the sulfur atom, such as propargyl [4, 8], allyl [3, 9], and benzyl [9], already undergo isomerization at 20°C. The isomerization is also observed for thioesters with a cyclic grouping at the phosphorus atom [2, 10].

We have previously shown that some thiobenzyl esters of P(III) acids are thermally stable, but isomerize by the action of molecular oxygen [11]. The object of the present investigation was to obtain different thio derivatives of P(III) acids and investigate their behavior with oxygen.

The O,O-dialkyl-S-ethylthiophosphites were first obtained by A. E. Arbuzov and K. V. Nikonorov in 1948 by the reaction of diethyl- and dipropylchlorophosphites with EtSNa in ether [12]. When this method is reproduced, distillation gave a fraction for which the constants completely correspond with the literature values, but four signals occur in its ^{31}P NMR spectrum. Therefore, it is not possible to obtain thioesters of P(III) in the discrete form by the method described.

It is known that phosphorus trichloride and diphenylchlorophosphine [13] react with silylated mercaptans to form thioesters of P(III). We first investigated the reactions of diethyl- and diisopropylchlorophosphites and 2-chloro-4,5-benzo-1,3,2-dioxaphospholane with trimethylsilyl butyl- and trimethylsilyl benzyl sulfides.

The reaction of diisopropylchlorophosphite with trimethylsilyl butyl sulfide proceeds in an atmosphere of dry argon at 160°C with the distillation of trimethylchlorosilane, and leads to the formation of O,O-diisopropyl-S-butylthiophosphite (I) (δP 188 ppm). When the container with the substance is opened, the self-warming of the latter occurs, and the ^{31}P NMR spectrum shows a signal at 92 ppm corresponding to O,O-diisopropylbutylthiophosphonate (II). When dry oxygen is passed into the compound (II), an exothermal reaction proceeds to the end and leads to the formation of the mixture of the thiophosphonate (II) (δP 92 ppm) and the thiolphosphate (III) (δP 26 ppm).



$$(i\text{-PrO})_2PSBu\text{-}n \xrightarrow{O_2} (i\text{-PrO})_2\underset{\underset{S}{\|}}{P}Bu\text{-}n + (i\text{-PrO})_2\underset{\underset{O}{\|}}{P}SBu\text{-}n$$

(I) (II) (III)

The O,O-diisopropyl-S-butylthiophosphate (III) could not be isolated in the discrete form.

In contrast to trimethylsilyl butyl sulfide, the interaction of diethylchlorophosphite

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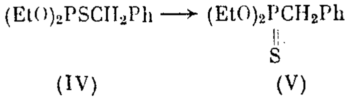
A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2127-2132, September, 1991. Original article submitted October 9, 1990.

with trimethylsilyl benzyl sulfide is accomplished at ~20°C with the formation of O,O-diethyl-S-benzylthiophosphite (IV).

$$(EtO)_2PCl + (CH_3)_3SiSCH_2Ph \longrightarrow \underset{(IV)}{(EtO)_2PSCH_2Ph}$$

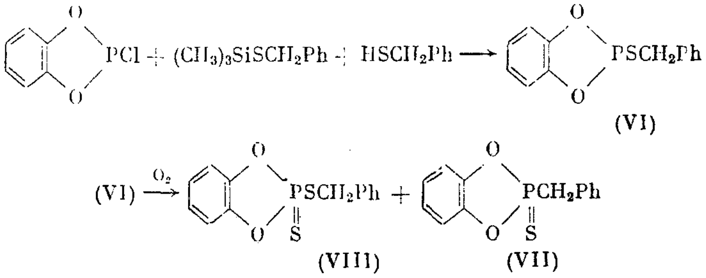
The ^{31}P NMR spectrum of the initial reaction mixture contains a single signal at 190 ppm, corresponding to the thiophosphite (IV). Compound (IV) is completely converted to O,O-diethylbenzylthiophosphonate (V) when the trimethylchlorosilane is removed without protection from the air, or with the passage of oxygen.



$$\underset{(IV)}{(EtO)_2PSCH_2Ph} \longrightarrow \underset{(V)}{(EtO)_2\underset{\underset{S}{\|}}{P}CH_2Ph}$$

The introduction of 2-chloro-4,5-benzo-1,3,2-dioxaphospholane into the reaction with trimethylsilyl benzyl sulfide also leads to 2-benzylthio-4,5-benzo-1,3,2-dioxaphospholane (VI) (δP 226 ppm). Compound (VI) proved to be even more sensitive to oxygen. When the container is opened only briefly, (VI) is completely converted to 2-benzyl-2-thioxo-4,5-benzo-1,3,2-dioxaphospholane (VII) (δP 118 ppm) with the impurity 2-benzylthio-2-thioxo-4,5-benzo-1,3,2-dioxaphospholane (VIII) (δP 110 ppm). The first of them was isolated; its structure was shown using ^1H and ^{31}P NMR spectroscopy. Compound (VIII) was not isolated in this reaction. Its structure was confirmed by the comparison with the ^{31}P NMR spectrum of the compound obtained by the addition of elemental sulfur to the thiophosphite (VI).

Having assumed that an admixture of mercaptan participates in the isomerization, we introduced the equimolar amount of benzyl mercaptan into the reaction presented above. The 2-chloro-4,5-benzo-1,3,2-dioxaphospholane interacts with trimethylsilyl benzyl sulfide in the presence of benzyl mercaptan with the formation of (VI) (δP 226 ppm). The passage of oxygen into the crude reaction mixture leads to the formation of the compound (VIII) as the main product; the corresponding thiophosphonate (VII) is only present in insignificant amount. Compound (VIII) was isolated in this reaction; its structure was shown using ^1H and ^{31}P NMR spectroscopy, elemental analysis, as well as the comparison of its physicochemical characteristics with the constants of the compound obtained by direct synthesis.



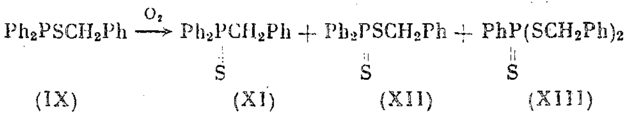
(VI)

(VIII)

(VII)

The interaction of diphenylchloro- and phenyldichlorophosphines with trimethylsilyl benzyl sulfide afforded diphenyl-S-benzylthiophosphinite (IX) and S,S-dibenzylphenyldithiophosphonite (X) with the corresponding δP values of 29 and 76 ppm.

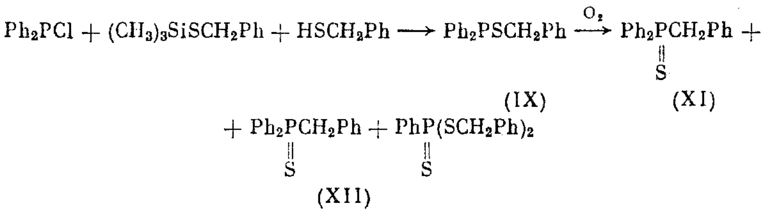
We previously showed that the product of the isomerization of diphenyl-S-benzylthiophosphinite (IX) is diphenylbenzylphosphine sulfide (XI) [11]. It was established in a more detailed investigation that the substitution products diphenyl-S-benzyldithiophosphinate (XII) and S,S-dibenzylphenyltrithiophosphonate (XIII) are formed together with (XI).



$$\underset{(IX)}{Ph_2PSCH_2Ph} \xrightarrow{O_2} \underset{(XI)}{Ph_2\underset{\underset{S}{\|}}{P}CH_2Ph} + \underset{(XII)}{Ph_2\underset{\underset{S}{\|}}{P}SCH_2Ph} + \underset{(XIII)}{Ph\underset{\underset{S}{\|}}{P}(SCH_2Ph)_2}$$

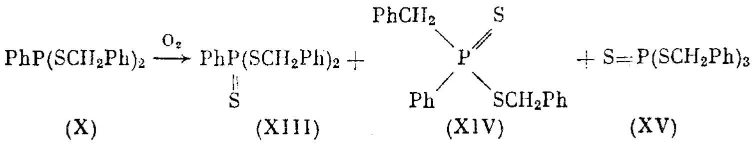
The compounds (XI)-(XIII) were isolated, and their structure was shown using ^1H and ^{31}P NMR spectra; the composition was confirmed by the data of elemental analysis. The structure of the compounds (XII) and (XIII) was also confirmed by the comparison of their characteristics with the physicochemical constants of the compounds obtained by the reaction of the compounds (IX) and (X) with elemental sulfur.

When the reaction of diphenyl-S-benzylthiophosphinite (IX) with oxygen is performed in the presence of an equimolar amount of benzyl mercaptan, the amount of the dithio and trithio derivatives increases, and the amount of the isomerization product decreases.

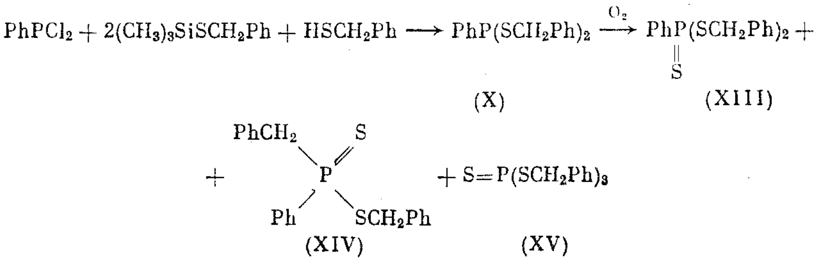


$$Ph_2PCl + (CH_3)_3SiSCH_2Ph + HSCH_2Ph \longrightarrow \underset{(IX)}{Ph_2PSCH_2Ph} \xrightarrow{O_2} \underset{(XI)}{Ph_2\underset{\underset{S}{\|}}{P}CH_2Ph} + Ph_2\underset{\underset{S}{\|}}{P}CH_2Ph + \underset{(XII)}{Ph\underset{\underset{S}{\|}}{P}(SCH_2Ph)_2}$$

An analogous series of experiments was performed with S,S-dibenzylphenyldithiophosphonite (X).



The compounds (XIII) and (XIV) were isolated; their structure was established using the ^1H and ^{31}P NMR spectra, and their composition was established using the data of the elemental analysis. Compound (XV) was not successfully isolated due to strong resinification. As is the case in the examples presented above, the introduction of benzyl mercaptan into the reaction of phenyldichlorophosphine with trimethylsilyl benzyl sulfide leads to a change in the composition of the mixture.



In order to explain the nature of the investigated conversions, initiated by the oxygen of the air, we introduced a 10% quantity of 4-methyl-2,6-di(tert-butyl)phenol or 2,4,6-trimethylphenol which are spin traps. When oxygen is passed through the S,S-dibenzylphenyldithiophosphonite (X) in the presence of substituted phenols, no change in the ^{31}P NMR spectrum (δP 76 ppm) occurs. These data indicate the radical nature of the processes studied. In our opinion, the oxygem may interact with the admixture of the mercaptan to form thiyl radicals [14], which commence the process of isomerization. The detailed stuydy of the interaction of thioesters of P(III) with oxygen is being conducted at the present time.

EXPERIMENTAL

The ^{31}P NMR spectra were registered on a non-serial NMR KGU-4 instrument (10.2 MHz) using the external standard 85% H_3PO_4. The ^1H NMR spectra were recorded on a "Varian T-60" spectrometer using TMS as the internal and external standard.

Reproduction of the Method of the Synthesis of O,O-Diethyl-S-ethylthiophosphite [12]. Diethylchlorophosphite (15.65 g, 0.1 mole) in 150 ml of ether was mixed with 8.4 g (0.1

mole) of freshly prepared sodium ethyl mercaptide in 150 ml of ether. The residue was allowed to settle for 1 day. The pure ether layer was poured off. To the residue were added 150 ml of abs. ether and the mixture was decanted. The ether was removed in vacuo using a water-jet pump, and the residue was fractionated. The fraction separated had the bp 73-76°C (9 mm), d_4^{20} 1.0218, and n_D^{20} 1.4600. The ^{31}P NMR spectrum (δ, ppm) was as follows: 190, 88, 26, and 9 ($^2J_{PH}$ = 760 Hz) (cf. [12]). The fraction had the bp 75-77°C (10 mm), d_4^{20} 1.0213, and the n_D^{20} 1.4592.

Interaction of Diorganylchlorophosphites with Trimethylsilyl Organyl Sulfides (General Method). The reaction mixture consisting of 0.1 mole of the diorganylchlorophosphite and 0.1 mole of the trimethylsilyl organyl sulfide was maintained for 1 day at ~20°C (in the case of trimethylsilyl butyl sulfide, heating was performed at 160-180°C with the distillation of trimethylchlorosilane) in an atmosphere of dry argon. The resulting thioester was either fractionated or utilized in the crude form.

O,O-Diisopropyl-S-butylthiophosphite (I). This compound was obtained by the general method from 8.1 g (0.05 mole) of diisopropylchlorophosphite and 8.53 g (0.05 mole) of trimethylsilyl butyl sulfide. It had the yield 9.16 g (77%), the bp 61-64°C (0.015 mm), d_4^0 0.9585, and n_D^{20} 1.4540. The ^{1}H NMR spectrum in the capillary (δ, ppm) was as follows: 1.12-1.70 m ($CH_3-CH_2-CH_2$), 1.40 d [$(C\underline{H}_3)_2CH$, $^3J_{HH}$ = 7 Hz], 2.7 m ($-C\underline{H}_2-S-P-$, $^3J_{PH}$ = 9 Hz), and 4.9 m ($-P-O-C\underline{H}-$). The ^{31}P NMR spectrum (δ, ppm) was as follows: 188. Found: P 13.13%. $C_{10}H_{23}O_2PS$. Calculated: P 13.03%.

Interaction of (I) with Oxygen. Oxygen was bubbled through the compound (I) for 0.5 h. The ^{31}P NMR spectrum (δ, ppm) was as follows: 92 and 26. Fractionation yielded O,O-diisopropylbutylthiophosphonate (II). It had the yield 1.80 g (15%), the bp 67-70°C (0.015 mm), d_4^{20} 0.9877, and the n_D^{20} 1.4501. The ^{31}P NMR spectrum (δ, ppm) was as follows: 92. Found: P 12.95%. $C_{10}H_{23}O_2PS$. Calculated: P 13.03%. The O,O-diisopropyl-S-butylthiophosphate (III) was not successfully isolated.

O,O-Diethyl-S-benzylthiophosphite (IV). This compound was obtained by the general method from 3 g (0.02 mole) of diethylchlorophosphite and 3.75 g (0.02 mole) of trimethylsilyl benzyl sulfide. The ^{31}P NMR spectrum (δ, ppm) was as follows: 190. Fractionation without protection from the oxygen of the air led to the isolation of O,O-diethylbenzylthiophosphonate (V). It had the yield 4.15 g (85%), the bp 108-110°C (0.04 mm), d_4^{20} 1.0748, and the n_D^{20} 1.5204. The ^{1}H NMR spectrum (CCl_4, δ, ppm; J, Hz) was as follows: 1.2 t ($C\underline{H}_3$, J_{HH} = 7), 3.2 d ($-P-C\underline{H}_2-$, $^2J_{PH}$ = 18), 3.88, 4.00 d.q ($C\underline{H}_2-O-P-$, $^3J_{PH}$ = 10), and 7.1 s ($C_6\underline{H}_5$). The ^{31}P NMR spectrum (δ, ppm) was as follows: 92. Found: C 53.85, H 7.13, P 13.01, and S 13.03%. $C_{11}H_{17}O_2PS$. Calculated: C 54.09, H 6.97, P 12.70, and S 13.11%.

2-Benzylthio-4,5-benzo-1,3,2-dioxaphospholane (VI). This compound was obtained by the general method from 10 g (0.06 mole) of 2-chloro-4,5-benzo-1,3,2-dioxaphospholane and 11.2 g (0.06 mole) of trimethylsilyl benzyl sulfide. The ^{31}P NMR spectrum (δ, ppm) was as follows: 226. Trimethylchlorosilane was removed in vacuo using a water-jet pump without protection from the oxygen of the air. The ^{31}P NMR spectrum (δ, ppm) was as follows: 118 and 110. Fractionation led to the isolation of 2-benzyl-2-thioxo-4,5-benzo-1,3,2-dioxaphospholane (VII), which was crystallized after 1 day. It was recrystallized from CCl_4. It had the yield 10.2 g (65%), the bp 139-143°C (0.04 mm), and the mp 62°C. The ^{1}H NMR spectrum (CCl_4, δ, ppm) was as follows: 3.80 d ($P-C\underline{H}_2-$, $^2J_{PH}$ = 17 Hz) and 6.97 s ($C_6\underline{H}_5$). The ^{31}P NMR spectrum (δ, ppm) was as follows: 118. Found: C 59.26, H 4.23, and P 11.88%. $C_{13}H_{11}O_2PS$. Calculated: C 59.54, H 4.20, and P 11.83%.

The 2-benzylthio-2-thioxo-4,5-benzo-1,3,2-dioxaphospholane (VIII) could not be isolated in the discrete form.

2-Benzylthio-2-thioxo-4,5-benzo-1,3,2-dioxaphospholane (VIII). To (VI), obtained by the general method from 5 g (0.03 mole) of 2-chloro-4,5-benzo-1,3,2-dioxaphospholane and 5.62 g (0.03 mole) of trimethylsilyl benzyl sulfide, was added 0.92 g (0.03 mole) of elemental sulfur; the reaction mass was maintained at 160°C for 4 h. Crystals of (VIII) were precipitated after the removal of the trimethylchlorosilane. They were washed with hexane and recrystallized from ether. It had the yield 7.49 g (85%) and the mp 67°C. The ^{1}H NMR spectrum (CCl_4, δ, ppm) was as follows: 4.1 d ($-P-S-C\underline{H}_2-$, $^3J_{PH}$ = 17 Hz), 6.9 s ($C_6\underline{H}_4$), and 7.13 s ($C_6\underline{H}_5$). The ^{31}P NMR spectrum (δ, ppm) was as follows: 110. Found: C 52.79, H 3.64, and P 10.55%. $C_{13}H_{11}O_2PS_2$. Calculated: C 53.06, H 3.74, and P 10.54%.

Interaction of (VI) with Oxygen in the Presence of Benzyl Mercaptan. Into the mixture consisting of 5 g (0.03 mole) of 2-chloro-4,5-benzo-1,3,2-dioxaphospholane, 5.62 g (0.03 mole) of trimethylsilyl benzyl sulfide, and 3.55 g (0.03 mole) of benzyl mercaptan was bubbled oxygen until the cessation of the warming was achieved. The ^{31}P NMR spectrum (δ, ppm) was as follows: 110 and 118. The mixture was crystallized after some time. The yield of 6.73 g (80%) of 2-benzylthio-2-thioxo-4,5-benzo-1,3,2-dioxaphospholane (VIII) with the mp 67°C was obtained. The ^{31}P NMR spectrum (δ, ppm) was as follows: 110.

Diphenyl-S-benzylthiophosphinite (IX). This compound was obtained by the general method from 5 g (0.02 mole) of diphenylchlorophosphine and 4.44 g (0.02 mole) of trimethylsilyl benzyl sulfide. The trimethylchlorosilane was removed in vacuo using a water-jet pump in a stream of dry argon. The residue was characterized in the crude form. It had the d_4^{20} 1.1529 and the n_D^{20} 1.6361. The ^{1}H NMR spectrum in a capillary (δ, ppm) was as follows: 3.50 d ($-P-S-C\underline{H}_2-$, $^3J_{PH}$ = 10 Hz), 6.73 m ($C_6\underline{H}_5-P-$), and 7.12 m ($C_6\underline{H}_5CH_2$). The ^{31}P NMR spectrum (δ, ppm) was as follows: 28. Found: C 74.49, H 5.23, and P 10.03%. $C_{19}H_{17}PS$. Calculated: C 74.03, H 5.52, and P 10.06%.

Interaction of (IX) with Oxygen. Into the compound (IX), obtained by the general method from 5 g (0.02 mole) of diphenylchlorophosphine and 4.44 g (0.02 mole) of trimethylsilyl benzyl sulfide, was bubbled oxygen for 1 h. When the mixture was left to stand for 1 day, crystals corresponding to diphenylbenzylphosphine sulfide (XI) were precipitated. The crystals were separated and recrystallized from isopropanol. The yield was 3.96 g (65%), and the mp was 161°C. The ^{1}H NMR spectrum (DMSO-d_6, δ, ppm) was as follows: 4.1 d ($-P-C\underline{H}_2-$, $^2J_{PH}$ = 14 Hz), 7.05 s ($C_6\underline{H}_5P$), and 7.45 m ($C_6\underline{H}_5CH_2$). The ^{31}P NMR spectrum (DMF, δ, ppm) was as follows: 42. Found: C 74.15, H 5.23, and P 9.85%. $C_{19}H_{17}PS$. Calculated: C 74.03, H 5.52, and P 10.06%. The residue was fractionated in vacuo using an oil pump. The fraction with the bp 200-205°C (0.02 mm) corresponds to diphenyl-S-benzyldithiophosphinate (XII). The yield was 0.95 g (14%); the product had the n_D^{20} 1.6771. The ^{1}H NMR spectrum (CCl_4, δ, ppm) was as follows: 4.04 d ($-P-S-C\underline{H}_2-$, $^3J_{PH}$ = 13 Hz), 7.00 m ($C_6\underline{H}_5P$), and 7.20 m ($C_6\underline{H}_5CH_2$). The ^{31}P NMR spectrum (δ, ppm) was as follows: 65. Found: C 66.60, H 5.01, P 9.01, and S 19.07%. $C_{19}H_{17}PS_2$. Calculated: C 67.05, H 5.00, P 9.11, and S 18.82%. The fraction with the bp 232-242°C (0.02 mm) corresponds to S,S-dibenzylphenyltrithiophosphonate (XIII). The yield was 0.4 g (5%), and the n_D^{20} was 1.6829. The ^{1}H NMR spectrum (CCl_4, δ, ppm) was as follows: 4.03 d ($-P-S-C\underline{H}_2-$, $^3J_{PH}$ = 13 Hz), 7.10 s ($C_6\underline{H}_5P$), and 7.20 m ($C_6\underline{H}_5CH_2$). The ^{31}P NMR spectrum (δ, ppm) was as follows: 83. Found: C 61.56, H 4.59, P 8.77, and S 24.74%. $C_{20}H_{19}PS_3$. Calculated: C 61.91, H 4.90, P 8.02, and S 24.87%.

Diphenyl-S-benzyldithiophosphinate (XII). Dipehnyl-S-benzylthiophosphinite (IX) (5.59 g, 0.02 mole), obtained by the general method from 5 g (0.02 mole) of diphenylchlorophosphine and 4.44 g (0.02 mole) of trimethylsilyl benzyl sulfide, and 0.58 g (0.02 mole) of elemental sulfur were mixed. The reaction was accompanied by strong warming up. The mixture was kept for 1 h. Fractionation in vacuo using an oil pump led to the isolation of diphenyl-S-benzyldithiophosphinate (XII). The yield was 4.76 g (70%); the product had the bp 200-3203°C (0.02 mm), and the n_D^{20} 1.6761. The ^{31}P NMR spectrum (δ, ppm) was as follows: 65.

S,S-Dibenzylphenyltrithiophosphonate (XIII). S,S-Dibenzylphenyldithiophosphonite (X) (5.93 g, 0.016 mole), obtained by the general method from 3 g (0.016 mole) of phenyldichlorophosphine and 6.56 g (0.032 mole) of trimethylsilyl benzyl sulfide, was mixed with 0.53 g (0.016 mole) of elemental sulfur. The reaction mixture was kept for 1 h at 100°C. Fractionation in vacuo using an oil pump led to the isolation of S,S-dibenzylphenyltrithiophosphonate (XIII). It had the yield of 4 g (65%), the bp 237-242°C (0.02 mm), and the n_D^{20} 1.6850. The ^{31}P NMR spectrum (δ, ppm) was as follows: 83.

Interaction of (IX) with Oxygen in the Presence of Benzyl Mercaptan. Into the mixture consisting of 2 g (0.009 mole) of diphenylchlorophosphine, 1.78 g (0.009 mole) of trimethylsilyl benzyl sulfide, and 1.12 g (0.009 mole) of benzyl mercaptan was bubbled oxygen until the cessation of the warming was achieved. Crystals corresponing to (XI) were precipitated after the mixture was allowed to stand for 1 day. The yield was 0.69 g (25%); the mp was 161°C. The ^{31}P NMR spectrum (DMF, δ, ppm) was as follows: 42. Fractionation in vacuo using an oil pump led to the isolation of two fractions. The fraction with the bp 200-205°C (0.02 mm) and the n_D^{20} 1.6771 corresponded to (XII). Its ^{31}P NMR spectrum had δ 65 ppm. The fraction with the bp 237-240°C (0.02 mm) and the n_D^{20} 1.6835 corresponds to (XIII). The ^{31}P NMR spectrum had δ 83 ppm.

S,S-Dibenzylphenyldithiophosphonite (X). This compound was obtained by the general method from 3 g (0.016 mole) of phenyldichlorophosphine and 6.56 g (0.032 mole) of trimethylsilyl benzyl sulfide. The removal of the trimethylchlorosilane led to the precipitation of crystals corresponding to (X), having the mp 65°C. The ^{1}H NMR spectrum (C_6H_6, δ, ppm) was as follows: 3.70 and 3.78 d.d (—P—S—CH$_2$—, $^3J_{PH}$ = 10 Hz). The ^{31}P NMR spectrum (C_6H_6, δ, ppm) was as follows: 76. Found: C 67.98, H 5.43, and P 8.76%. $C_{20}H_{19}PS_2$. Calculated: C 67.80, H 5.37, and P 8.76%.

Interaction of (X) with Oxygen. Into the compound (X), obtained by the general method from 3 g (0.016 mole) of phenyldichlorophosphine and 6.56 g (0.032 mole) of trimethylsilyl benzyl sulfide, was bubbled oxygen until the cessation of the warming was achieved. Fractionation led to the isolation of a fraction with the bp 200-202°C (0.02 mm) corresponding to benzylphenyl-S-benzyldithiophosphinate (XIV). The yield was 2.5 g (50%), and the n_D^{20} was 1.6488. The ^{1}H NMR spectrum (CCl_4, δ, ppm) was as follows: 3.43 d (—P—C$\underline{H}_2$—, $^2J_{PH}$ = 14 Hz), 3.86, 4.04 d.d (—P—S—C$\underline{H}_2$—, $^3J_{PH}$ = 13 Hz), 6.97 m ($C_6\underline{H}_5P$), and 7.10 m ($C_6\underline{H}_5CH_2$). The ^{31}P NMR spectrum (δ, ppm) was as follows: 68. Found: P 8.54 and S 17.95%. $C_{20}H_{19}PS_2$. Calculated: P 8.76 and S 18.08%. The fraction with the bp 235-240°C (0.02 mm) and the n_D^{20} 1.6845 corresponds to (XIII). The yield was 0.74 g (12%). The ^{31}P NMR spectrum (δ, ppm) was as follows: 83. The compound (XV) was not isolated; it had the δP 95 ppm.

Interaction of (X) with Oxygen in the Presence of Benzyl Mercaptan. Into the mixture consisting of 5 g (0.03 mole) of phenyldichlorophosphine, 10.93 g (0.06 mole) of trimethylsilyl benzyl sulfide, and 3.46 g (0.03 mole) of benzyl mercaptan was passed oxygen until the cessation of the warming was achieved. Fractionation in vacuo using an oil pump led to the isolation of S,S-dibenzylphenyltrithiophosphonate (XIII). The product had the yield 3.47 g (30%), the bp 235-240°C (0.02 mm), and the n_D^{20} 1.6829. The ^{31}P NMR spectrum had the δ 83 ppm. Benzylphenyl-S-benzyldithiophosphinate (XIV) had the yield 0.5 g (5%), the bp 200-202°C (0.2 mm), and the n_D^{20} 1.6479. The ^{31}P NMR spectrum had the δ 68 ppm. The compound (XV) (δP 95 ppm) was not isolated.

LITERATURE CITED

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