ESTERS OF TRIVALENT PHOSPHORUS THIOACIDS

COMMUNICATION 15. REACTION OF ESTERS OF THIOPHOSPHONOUS CHLORIDES AND THIOPHOSPHOROUS DICHLORIDES WITH PROPARGYL ALCOHOL AND PROPARGYL MERCAPTAN

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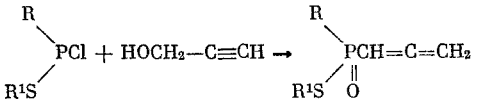
UDC 542.91:547.1'118

Previously it was shown that the reaction of S-alkyl dichlorothiophosphites, S,S-dialkylchlorodithiophosphites and S-alkyl alkylchlorothiophosphonites with allyl alcohol leads to the formation of trivalent phosphorus thioacid derivatives, whereas the dihalophosphines, S-alkyl dichlorophosphites and S,S-dialkyl chlorodithiophosphites react with allyl mercaptan to give pentavalent phosphorus derivatives [1]. We continued to study the reactions of the chlorides of trivalent phosphorus thioacids with unsaturated alcohols and mercaptans. In the present communication we report the data that were obtained in studying the reactions of the S-alkyl alkyl(aryl)chlorothiophosphonites and S-alkyl dichlorothiophosphites with propargyl alcohol, and also the reactions of the S-alkyl alkylchlorothiophosphonites and ethyldichlorophosphine with propargyl mercaptan.

The reactions of acetylenic alcohols with the chlorides of phosphorus acids, devoid of sulfur, have been studied in considerable detail [2-6]. As a rule, pentavalent derivatives, containing the allene grouping, are formed as a result of these reactions. However, in some cases a further prototropic isomerization takes place, with the formation of the acetylenic isomer [2, 3].

The reaction of S-alkyl alkyl(aryl)chlorothiophosphonites with propargyl alcohol in the presence of a base leads to the formation of S-alkyl alkyl(phenyl)allenylthiophosphinates as the main product.



$R = C_2H_5, C_6H_5$; $R^1 = Alk$

The reactions of S-ethyl ethylchlorothiophosphonite and S-propyl ethylchlorothiophosphonite with propargyl alcohol lead to the formation of only the allene isomers. The IR spectra of the obtained compounds have the absorption band of the P = O group in the 1200 cm^{-1} region and a split band with maxima in the vicinity of 1940 and 1960 cm^{-1}, which can be assigned to the absorption of the allene grouping [6]. The ^{31}P NMR spectra have a signal in the −48 ppm region, which testifies to the formation of only one isomer. A mixture of the allene and acetylenic isomers is formed in the reactions of S-butyl ethylchlorothiophosphonite and S-isobutyl phenylchlorothiophosphonite. Besides the absorption band in the 1940-1960 cm^{-1} region, the IR spectra of the crude products of these reactions have a weak band at 2200 cm^{-1}, which corresponds to the vibrations of the C = C bond in disubstituted acetylenes [7]. We were unable to separate the mixed isomers by distillation. Prototropic isomerization occurs when the mixed isomers are heated with a catalytic amount of Na alcoholate, as a result of which the S-alkyl ethyl(phenyl)-1-propynylthiophosphinates were obtained. In the IR spectra of the isomerized products the 2200 cm^{-1} band becomes intense, while the band in the 1940-1960 cm^{-1} region almost vanishes. S-Propyl ethylallenylthiophosphinate when heated with Na alcoholate is converted to S-propyl ethyl-1-propynylthiophosphinate. In the ^{31}P NMR spectrum of the isomerization product of S-propyl ethylallenylthiophosphinate the signal in the −48 ppm region disappears

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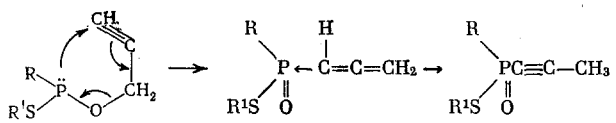
completely and a signal appears at −18 ppm, which is associated with the formation of the acetylenic isomer. The isomerization of the allene isomers to the acetylenic isomers can be depicted by the scheme that was proposed for the reaction of diethyl chlorophosphite with propargyl alcohol [2].



In the first step, which proceeds through a five-center transition state, the S-alkyl ethyl(phenyl)-2-propynylthiophosphonites are rearranged to S-alkyl ethyl(phenyl)allenylthiophosphinates, while the latter, undergoing isomeric transformation of the prototropic type, lead to the formation of S-alkyl ethyl(phenyl)-1-propynylthiophosphinates. The S-alkyl dichlorothiophosphites react with propargyl alcohol in the same manner as the alkyl(aryl)dichlorophosphines [4] to give S-alkyl(phenyl) allenylchlorothiophosphonates. The stability of the allene structure in these compounds is associated with the presence of the acid chloride atom [5]. The reaction of S-ethyl dichlorothiophosphite with 2 M of propargyl alcohol leads to the formation of O-2-propynyl S-ethyl allenylthiophosphonate. The IR spectrum of the compound has intense absorption bands with maxima at 1940, 1960, 2125, and 3210, 3290 cm^{-1}, which confirms the presence of the allene and acetylenic bonds.

When compared to the alcohols, the acetylenic mercaptans have been studied to a lesser degree in the reactions with trivalent phosphorus chlorides. As is known [8, 9], these reactions lead to the formation of the thiono derivatives of pentavalent phosphorus acids. We obtained the S-alkyl ethylallenyldithiophosphinates by the reaction of S-alkyl ethylchlorothiophosphonites with propargyl mercaptan. The structure of the obtained compounds was confirmed by the data of the IR and ^{31}P NMR spectra, and also by the elemental analysis data. The IR spectra of the obtained compounds have the absorption band of the allene grouping with maxima at 1940 and 1960 cm^{-1} [6]. The absorption band in the 600-700 cm^{-1} region can be associated with P = S [7]. The ^{31}P NMR spectra have one signal in the −64 ppm region, which corresponds to compounds with a similar structure [10].

The reaction of ethyldichlorophosphine with propargyl mercaptan in the absence of a base leads to the formation of the pentavalent derivative, namely ethylallenylchlorothionophosphine.

EXPERIMENTAL METHOD

S-Ethyl Ethylallenylthiophosphinate (I). To 21 g of S-ethyl ethylchlorothiophosphonite in 400 ml of ether at −10°C was added 13.5 g of triethylamine, and then 7.8 g of propargyl alcohol was added in drops. After 12 h the precipitate was filtered, the ether was removed in vacuo, and the residue was distilled. The distillation gave 16 g (67.8%) of (I), bp 75° (0.006 mm); n_D^{20} 1.5410; d_4^{20} 1.0881, δ_{31P} −48 ppm. Found: P 17.89; S 18.54%; MR 50.89. $C_7H_{13}OPS$. Calculated: P 17.58; S 18.19%; MR 50.53.

S-Propyl Ethylallenylthiophosphinate (II). In a similar manner, from 22 g of S-propyl ethylchlorothiophosphonite, 13 g of triethylamine and 7.2 g of propargyl alcohol we obtained 17.2 g (70.2%) of (II), bp 81° (0.01 mm); n_D^{20} 1.5360; d_4^{20} 1.0686; δ_{31P} −48 ppm. Found: P 16.41; S 17.16%; MR 55.50. $C_8H_{15}OPS$. Calculated: P 16.28; S 16.85%; MR 55.25.

S-Propyl Ethyl-1-propynylthiophosphinate (III). A mixture of 10 g of (II) and several drops of a saturated Na ethylate solution was heated at 80-90° for 1 h. Distillation gave 7.8 g (78%) of (III), bp 76° (0.01 mm); n_D^{20} 1.5190; d_4^{20} 1.0580; δ_{31P} −18 ppm. Found: P 16.47; S 16.90%; MR 54.56. $C_8H_{15}OPS$. Calculated: P 16.28; S 16.85%; MR 54.08.

S-Butyl Ethyl-1-propynylthiophosphinate (IV). To 15 g of S-butyl ethylchlorothiophosphonite in 300 ml of ether at −10° was added 8.2 g of triethylamine, and then 4.6 g of propargyl alcohol was added in drops. After 12 h the precipitate was filtered, the ether was removed in vacuo, and the residue was heated with several drops of a saturated Na ethylate solution at 80-90° for 1 h. Distillation gave 12.7 g (76.5%) of (IV), bp 86° (0.01 mm); n_D^{20} 1.5130; d_4^{20} 1.0423. Found: P 15.32; S 15.75%; MR 58.88. $C_9H_{17}OPS$. Calculated: P 15.18; S 15.67%; MR 58.70.

S-Isobutyl Phenyl-1-propynylthiophosphinate (V). In a similar manner, from 34 g of S-isobutyl phenylchlorothiophosphonite, 14.8 g of triethylamine and 8.2 g of propargyl alcohol we obtained 24.3 g (66%) of (V), bp 125° (0.008 mm); n_D^{20} 1.5530; d_4^{20} 1.0818. Found: P 12.29; S 12.36%; MR 74.62. $C_{13}H_{17}OPS$. Calculated: P 12.24; S 12.68%; MR 74.52.

S-Ethyl Allenylchlorothiophosphonate (VI). To 25.4 g of ethyl dichlorothiophosphite in 500 ml of ether at −10° was added 15.2 g of triethylamine, and then 8.4 g of propargyl alcohol was added in drops. After 12 h the precipitate was filtered, the solvent was removed, and the residue was fractionally distilled. We isolated 19.8 g (69.5%) of (VI), bp 74° (0.06 mm); n_D^{20} 1.5540; d_4^{20} 1.2683. Found: P 17.02; Cl 19.08%; MR 46.05. C_5H_8ClOPS. Calculated: P 16.98; Cl 19.44%; MR 46.01.

S-Butyl Allenylchlorothiophosphonate (VII). In a similar manner, from 34 g of butyl dichlorothiophosphite, 18.2 g of triethylamine and 10 g of propargyl alcohol we obtained 27.1 g (72%) of (VII), bp 87° (0.06 mm); n_D^{20} 1.5350; d_4^{20} 1.1911. Found: P 15.03; Cl 16.69%; MR 55.07. $C_7H_{12}ClOPS$. Calculated: P 14.71; Cl 16.84%; MR 55.25.

S-Phenyl Allenylchlorothiophosphonate (VIII). From 30 g of phenyl dichlorothiophosphite, 15 g of triethylamine and 8.3 g of propargyl alcohol we obtained 11.8 g (35.7%) of (VIII), bp 107° (0.04 mm); n_D^{20} 1.6100; d_4^{20} 1.3221. Found: P 13.45; Cl 15.63%; MR 60.48. C_9H_8ClOPS. Calculated: P 13.44; Cl 15.37%; MR 60.88.

O-2-Propynyl S-Ethyl Allenylthiophosphonate (IX). To 32.6 g of ethyl dichlorothiophosphite in 500 ml of ether at −10° was added 40.5 g of triethylamine in drops, and then 22.4 g of propargyl alcohol was added in drops. After 12 h the precipitate was filtered, and the ether was removed in vacuo. Distillation gave 20.3 g (50.2%) of (IX), bp 93° (0.006 mm); n_D^{20} 1.5380; d_4^{20} 1.1592. Found: P 15.28; C 47.11; S 16.03%; MR 54.55. $C_8H_{11}O_2PS$. Calculated: P 15.33; C 47.48; S 15.85%; MR 54.27.

S-Propyl Ethylallenyldithiophosphinate (X). To 17 g of S-propyl ethylchlorothiophosphonite in 300 ml of ether at −10° was added 10.1 g of triethylamine, and then 7.2 g of propargyl mercaptan was added in drops. After 5 h the precipitate was filtered, and the ether was removed in vacuo. Distillation gave 6.5 g (31.5%) of (X), bp 81° (0.01 mm); n_D^{20} 1.5720; d_4^{20} 1.0779; δ_{31P} −64 ppm. Found: P 14.83; S 31.08%; MR 62.96. $C_8H_{15}PS_2$. Calculated: P 15.02; S 31.08%; MR 62.64.

S-Butyl Ethylallenyldithiophosphinate (XI). In a similar manner, from 13 g of S-butyl ethylchlorothiophosphonite, 7.2 g of triethylamine and 5 g of propargyl mercaptan we obtained 5.4 g (34.8%) of (XI), bp 85° (0.015 mm); n_D^{20} 1.5520; d_4^{20} 1.0403; δ_{31P} −64 ppm. Found: P 14.29; S 29.20%; MR 67.66. $C_9H_{17}PS_2$. Calculated: P 14.07; S 29.12%; MR 67.26.

Ethylallenylchlorothionophosphine (XII). To 19 g of ethyldichlorophosphine in 20 ml of CH_2Cl_2 was added 10.4 g of propargyl mercaptan in drops, and the mixture was heated for 15 min and then distilled. We obtained 9 g (37.4%) of (XII), bp 55° (0.015 mm); n_D^{20} 1.5790; d_4^{20} 1.2435; δ_{31P} −82 ppm. Found: P 18.64; Cl 20.96; S 19.36%; MR 44.52. C_5H_8ClPS. Calculated: P 18.59; Cl 21.30; S 19.24%; MR 45.18.

The IR spectra were taken on a UR-10 spectrometer. The ^{31}P NMR spectra were taken on a KGU-4 NMR spectrometer (10.2 MHz).

CONCLUSIONS

1. The reaction of S-alkyl alkyl(aryl)chlorothiophosphonites with propargyl alcohol or with propargyl mercaptan in the presence of a base leads to the formation of S-alkyl alkyl(aryl)allenylthio(dithio)phosphinates, which when heated with a sodium alcoholate are converted to S-alkyl alkyl(aryl)-1-propynylthiophosphinates.

2. Alkyl(aryl)dichlorothiophosphites react with propargyl alcohol to give S-alkyl(aryl)allenylchlorothiophosphonates, while the reaction of ethyldichlorophosphine with propargyl mercaptan leads to the formation of ethylallenylchlorothionophosphine.

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