2-oxobutyl radicals occurs in decane and acetonitrile. A singlet radical pair of trichloromethyl and 2-oxobutyl radicals is formed in CCl_4. Both these mechanisms occur in $CHCl_3$.

2. 3-Oxobutyltrimethyltin coordinates with the solvent in CCl_4 and $CDCl_3$.

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REACTIONS OF COPPER SALTS OF DIALKYLTHIOPHOSPHORIC ACIDS WITH PROPARGYL HALIDES

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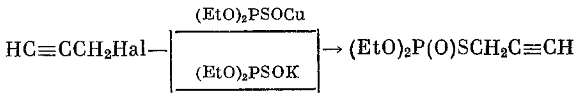
We have reported a significant difference in the chemical properties of cuprous and potassium dialkylmonothiophosphates: The copper salts readily react with ethynyl bromides $BrC\equiv CX$ to form the corresponding S-ethynyl thiophosphates but do not undergo the analogous reactions with alkyl bromides, while the potassium salts do not react with ethynyl bromides but readily react with alkyl bromides [1].

In the present work, we studied the reactions of cuprous dialkylthiophosphates with several propargyl halides. In contrast to haloalkanes, these compounds readily react with cuprous dialkylmonothiophosphates. Thus, cuprous diethylthiophosphate reacts with propargyl bromide and chloride to give diethyl-S-propargyl thiophosphate in 80-90% yield. This product was also obtained from potassium diethylthiophosphate and propargyl bromide:

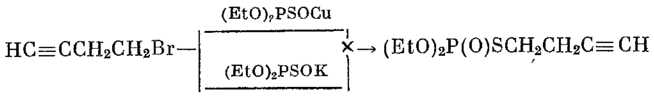


$$HC\equiv CCH_2Hal-\left|\begin{array}{c}(EtO)_2PSOCu\\ \hline (EtO)_2PSOK\end{array}\right|\rightarrow (EtO)_2P(O)SCH_2C\equiv CH$$

Hal = Cl, Br.

This reaction proceeds both in polar solvents such as ethanol and acetone and in nonpolar solvents such as ether and benzene.

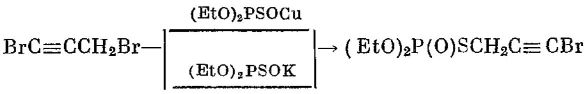
It is interesting that 1-bromo-3-butyne reacts only with potassium diethylthiophosphate



$$HC\equiv CCH_2CH_2Br-\left|\begin{array}{c}(EtO)_2PSOCu\\ \hline (EtO)_2PSOK\end{array}\right|\overset{\times}{\rightarrow} (EtO)_2P(O)SCH_2CH_2C\equiv CH$$

In our previous work [1], we showed that cuprous diethylthiophosphate reacts with 1,4-dibromo-1-butyne at the ethynyl bromine atom to form O,O-diethyl-S(ω-bromobut-1-ynyl) thiophosphate, while potassium diethylthiophosphate reacts at the alkyl bromine atom to form, O,O-diethyl-S-(ω-bromobut-3-ynyl) thiophosphate.

It was of interest to study the reaction of these salts with 1,3-dibromopropyne which has one ethynyl bromine atom and one propargyl bromine atom. Cuprous and potassium diethylmonothiophosphates replace the propargyl bromine atom to form O,O-diethyl-S-(3-bromoprop-2-ynyl) thiophospate in 70% yield in both cases.



$$BrC\equiv CCH_2Br-\left|\begin{array}{c}(EtO)_2PSOCu\\ \hline (EtO)_2PSOK\end{array}\right|\rightarrow (EtO)_2P(O)SCH_2C\equiv CBr$$

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1181-1183, May, 1985. Original article submitted May 30, 1984.

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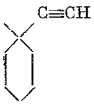
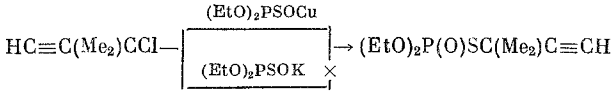
TABLE 1. S-Proparagyl Esters of Diethylthiophosphoric Acid $(EtO)_2P(O)SR$ Obtained from Proparagyl Halides and Cuprous Diethylthiophosphate

R	Yield, %	d_4^{20}	n_D^{20}	Chemical formula	Found/ calculated, %	
					P	S
$-CH_2C\equiv CH$	80	–	1,4805 *	–	–	–
$-C(Me)_2C\equiv CH$	80	1,0834	1,4784	$C_8H_{17}O_3PS$	12,86 13,14	13,67 13,56
	70	1,1251	1,5110	$C_{12}H_{21}O_3PS$	11,35 11,23	11,55 11,61
$-CH_2C\equiv CBr$	70	1,4485	1,5180	$C_7H_{12}BrO_3PS$	10,49 10,80	11,15 11,14

*For a sample obtained by convergent synthesis, n_D^{20} 1.4800.

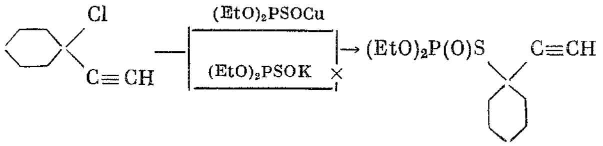
The reaction of dibromo-1-propyne with the copper salt proceeds in acetone and benzene, while the reaction with the potassium salt proceeds only in acetone. The products were identified according to the physicochemical constants (see the Experimental section), and their IR and PMR spectra. In both cases, the IR spectra show bands at 1265 cm^{-1} (νPO) and 2220 cm^{-1} ($\nu C\equiv C$), while the PMR spectra have a signal at 2.95 ppm (CH_2S). In addition, the treatment of diethyl-S-(3-bromoprop-2-ynyl) thiophosphate with trimethylamine in ether does not give the corresponding ammonium salt; only the starting thiophosphate was isolated after permitting the mixture to stand for many days. Such low chemical activity of the bromine atom indicates its position at the acetylenic bond and not at the methylene group. Thus, the bromine atom at C-3 in 1,3-dibromopropyne reacts more readily in the exchange reaction with the K and Cu salts of diethylmonothiophosphoric acid.

Sterically hindered tert-butyl bromide and cyclohexyl bromide were found not to form the corresponding S-alkyl dialkylthiophosphates with potassium dialkylthiophosphates. It was of interest to study sterically hindered propargyl halides in their reactions with the Cu and K salts of these acids. 1-Chloro-1,1-dimethyl-2-propyne does not react with potassium diethylthiophosphate but readily reacts with cuprous diethylthiophosphate to form the corresponding O,O-diethyl-S-(1,1-diemthylprop-2-ynyl) thiophosphate in 80% yield.



$$HC\equiv C(Me_2)CCl-\xrightarrow[(EtO)_2PSOK\ \times]{(EtO)_2PSOCu}(EtO)_2P(O)SC(Me_2)C\equiv CH$$

Sterically hindered 1-chloro-1-ethynylcyclohexane reacts similarly to give a 70% yield of O,O-diethyl-S-(1-ethynylcyclohexyl) thiophosphate



The IR spectra of the products have bands at 1265 cm^{-1} (νPO) and 2120 cm^{-1} ($\nu C\equiv C$). The reaction of cuprous diethylthiophosphate with sterically hindered propargyl halides permits us to prepare previously unknown sterically hindered thiopropargyl esters of dialkylthiophosphoric acids.

EXPERIMENTAL

General Method for the Reactions of Propargyl Halides with Cuprous Diethylthiophosphate. A sample of 0.045 mole propargyl halide was added to 0.044 mole cuprous diethylthiophosphate in 20 ml benzene or acetone and stirred for 0.5 h at 20°C and then for 0.5 h at reflux. The precipitate was filtered off and the solvent was evaporated. The residue was purified on a column packed with L 100/160 silica gel using 2:1 benzene—ether as the eluant. The physical constants and yields are given in Table 1.

The IR spectra of all the compounds with a terminal acetylenic bond have bands at 1265 cm^{-1} (νPO) and 2110-2120 cm^{-1} (νC≡C). The bands for the H—C stretching vibrations are markedly broadened and shifted toward lower frequencies and have pronounced doublet nature (3300 and 3235 cm^{-1}). The low-frequency band apparently should be assigned to an intermolecular P O... H—C≡ hydrogen bond.

Reaction of Propargyl Bromide with Potassium Diethylthiophosphate. A mixture of 2.09 g (0.01 mole) potassium diethylthiophosphate and 1.19 g (0.01 mole) propargyl bromide in 30 ml acetone was heated at refleux for 1 h and the precipitate was filtered off. The solvent was evaporated and the residue was distilled in vacuum to yield O,O-diethyl-S-propargyl thiophosphate in 80% yield, bp 65°C (0.6 mm), n_D^{20} 1.4800 [2].

Reaction of 1,3-Dibromopropyne with Potassium Diethylthiophosphate. A sample of 1 g (0.045 mole) dibromopropyne was added to 0.92 g (0.044 mole) potassium diethylthiophosphate in 20 ml acetone, stirred for 20 min at 20°C, and then heated at reflux for 0.5 h. The precipitate was filtered off and the filtrate was evaporated. The residue was subjected to chromatography on a column packed with L 100/160 silica gel using 2 1 benzene—ether as the eluent to yield 0.88 g (70%) O,O-diethyl-S-(3-bromoprop-2-ynyl) thiophospate, n_D^{20} 1.5810. The IR spectrum corresponds to that of a sample of O,O-diethyl-S-(3-bromoprop-2-ynyl) thiophosphate obtained from cuprous diethylthiophosphate.

Reaction of 1-Bromo-3-butyne with Potassium Diethylthiophosphate. A mixture of 2.09 g (0.01 mole) potassium diethylthiophosphate and 1.33 g (0.01 mole) 1-bromo-3-butyne was heated at reflux for 4 h in acetone or ethanol. The precipitate was filtered off and the solvent was evaporated. The residue was subjected to chromatography on a column packed with L100/160 silica gel using 1:1 benzene—ether as eluent to yield 1.7 g (80%) O,O-diethyl-S-(but-3-ynyl) thiophosphate, d_4^{20} 1.1020, n_D^{20} 1.4760. Found: C 42.96; H 6.82; P 14.20; S 14.41%; MR 56.80. Calculated for $C_8H_{15}O_3PS$: C 42.43; H 6.82; P 14.08; S 14.51%; MR 56.70.

Reaction of 1-Bromo-3-butyne with Cuprous Diethylthiophosphate. A mixture of 2.33 g cuprous diethylthiophosphate and 1.33 g (0.01 mole) 1-bromo-3-butyne was heated for 10 h at reflux in acetone. A precipitate was not formed. The solution yielded 2.2 g (95%) cuprous diethylthiophosphate.

Reaction of 1-Chloro-1,1-dimethyl-2-propyne and 1-Chloro-1-ethynylcyclohexane with Potassium Diethylthiophosphate. A sample of 0.95 g (0.01 mole) 1-chloro-1,1-dimethyl-2-propyne or 1.33 g (0.01 mole) 1-chloro-1-ethynylcyclohexane was added to 2.09 g (0.01 mole) potassium diethylthiophosphate in 30 ml acetone and the mixture was heated at reflux for 6 h. A precipitate was not formed. A sample of 1.98 g (95%) potassium diethylthiophosphate was isolated from the solution.

CONCLUSIONS

1. Copper salts of dialkylthiophosphoric acids react with propargyl halides to form O,O-dialkyl-S-propargyl thiophosphates.

2. Sterically hindered propargyl halides readily react with cuprous dialkylthiophosphates but do not react with the analogous potassium salts.

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