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# ETHYNYLATION OF SALTS OF PHOSPHORUS THIOACIDS WITH

ETHYNYL BROMIDES IN THE PRESENCE OF CuC1

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The substituted S-ethynyl esters of thiophosphoric acids are of interest as potential insecticides and acaricides. Previously [1] we described a method for obtaining such esters, which consists in reacting magnesium bromoacetylides with dialkoxyphosphorylsulfenyl chlorides, but here the S-ethynyl thiophosphates are obtained in low yield.

We attempted to obtain the S-hexyne and ethylmercaptopropyne esters of diethylthiophosphoric acid by the alkynylation of potassium diethyl thiophosphate with the appropriate substituted ethynyl bromides, but only the starting reactants were isolated.

$$(EtO)_2P(S)OK + BrC \equiv CX - // \rightarrow (EtO)_2P(O)SC \equiv CX$$

where X = Bu,  $CH_2SEt$ .

It is known that many ethynylation reactions are catalyzed by metal chlorides. In this connection we studied the catalytic effect of cuprous chloride when ethynyl bromides are reacted with the salts of phosphorus monothioacids. It proved that the reaction of a potassium dialkyl thiophosphate with substituted ethynyl bromides can be run in the presence of equimolar amounts of CuCl in polar solvents with a 60-80% yield of the S-ethynyl esters (Table 1).

$$(RO)_{2}P(S)OK + Br - C \equiv C - X \xrightarrow{CuCl} (RO)_{2}P(O)SC \equiv C - X$$
(A)

where R = alky1 and X = alky1, alky1mercaptomethy1, alkoxymethy1, hydroxymethy1, acy1oxymethy1, and pheny1.

The reaction can only be run in polar solvents like alcohol, acetone, THF or MeCN. It does not go in less polar solvents like ether or benzene. The structure of the obtained compounds is confirmed by the IR spectra, which have absorption bands in the 1270 (P=0) and 2195-2210 cm<sup>-1</sup> (C=C) regions for all of the compounds (Table 2).

Compounds containing an OH group in the unsaturated radical, proved to be unstable and their structure, besides the IR spectra, was proved by converting them to the stable

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		Yield, %				Found, %			Calculated, %			
R	х	•	Б	d420	$n_D^{20}$	С	н	Р	Empirical formula	С	н	р
Et The same » » » Me The same » Pr The same	CH <sub>2</sub> SEt Bu CH <sub>2</sub> SBu CH <sub>2</sub> OEt CH <sub>2</sub> OEt CH <sub>2</sub> OBu CH <sub>2</sub> OC(O)Me Ph CH <sub>2</sub> SEt Bu CH <sub>2</sub> OEt CH <sub>2</sub> OC(O)Me CH <sub>2</sub> OC(O)Me Ph	$70 \\ 76 \\ 81 \\ 85 \\ \\ 79 \\ 71 \\ 75 \\ 78 \\ 73 \\ 75 \\ 82 \\ 82 \\ 75 \\ 82 \\ 82 \\ 82 \\ 82 \\ 81 \\ 81 \\ 81 \\ 81$	-68 60 -75 70 -70 	$\begin{array}{c} 1,1648\\ 1,0758\\ 1,1925\\ 1,1482\\ 1,1281\\ 1,1082\\ 1,2190\\ 1,1940\\ 1,3365\\ 1,1175\\ 1,0575\\ 1,3091\\ 1,1860\\ 1,1575\\ \end{array}$	$\begin{array}{c} 1,4980 \\ 1,4705 \\ 1,5155 \\ 1,4820 \\ 1,4810 \\ 1,4859 \\ 1,5640 \\ 1,5430 \\ 1,4845 \\ 1,4940 \\ 1,4989 \\ 1,4904 \\ 1,5370 \end{array}$	39,8 47,8 44,7 42,7 45,3 46,4 40,3 53,4 36,4 43,8 37,3 36,4 44,6,8 37,3 36,4 44,6,8 37,3 36,8 36,8 37,3 36,8 44,6 56,8	6,8 7,4 6,8 7,4 5,6 5,6 5,6 6,1 4,6 6,4	$\begin{array}{c} 11,7\\12,2\\10,9\\12,1\\10,9\\10,6\\10,7\\11,0\\12,8\\13,4\\13,4\\13,7\\12,4\\11,3\\10,5\\\end{array}$	$\begin{array}{c} C_9H_{17}O_3PS_2\\ C_{10}H_{19}O_3PS\\ C_{11}H_{21}O_3PS_2\\ C_9H_{17}O_1PS\\ C_{11}H_{21}O_4PS\\ C_{13}H_{25}O_4PS\\ C_{29}H_{15}O_3PS\\ C_{29}H_{15}O_3PS\\ C_{2}H_{15}O_3PS\\ C_{2}H_{15}O_3PS\\ C_{2}H_{15}O_3PS\\ C_{2}H_{15}O_3PS\\ C_{2}H_{15}O_3PS\\ C_{2}H_{15}O_3PS\\ C_{2}H_{15}O_3PS\\ C_{2}H_{15}O_3PS\\ C_{2}H_{15}O_3PS\\ C_{11}H_{19}O_3PS\\ C_{14}H_{19}O_3PS\end{array}$	$\begin{array}{r} 40,3\\48,0\\44,6\\42,8\\45,3\\47,1\\40,6\\53,3\\36,1\\43,3\\37,5\\35,3\\44,8\\56,4\end{array}$	<b>6,</b> 36 <b>7</b> , 6, <b>7</b> , <b>7</b> , 5, 5, 6, 6, <b>4</b> <b>8</b> , 6, 4 <b>6</b> , <b>7</b> , <b>7</b> , <b>5</b> , 5, 5, 6, <b>8</b> , <b>6</b> , <b>4</b> <b>6</b> , <b>4</b> , <b>4</b>	<b>11,6</b> <b>12,4</b> <b>10,5</b> <b>12,3</b> <b>11,6</b> <b>11,0</b> <b>11,6</b> <b>11,5</b> <b>12,9</b> <b>13,9</b> <b>13,8</b> <b>13,9</b> <b>13,8</b> <b>13,0</b> <b>10,6</b> <b>10,4</b>

TABLE ]	L. S-E	thyny1	Esters	of	Thiophosp	horic	Acid	.s
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\*Cf. [1].

TABLE 2. Vibration Frequencies of P=O and C=C Groups in IR Spectra (EtO)<sub>2</sub>P(O)SC=CX

والمستعدية والمتناف المتحج والمتحج والمتحج والمتحد		
x	vP=0	vC≡C
Ph CH <sub>2</sub> OA]k CH <sub>2</sub> SA]k Bu SH <sub>2</sub> OC(O)Me	1270 1270 1270 1270 1270 1270	2180 2195 2205 2210 2210

TABLE 3. Reactivity of XC=CBr When Reacted with  $(RO)_2P(S)OK$  in the Presence of CuCl

R	x	Т., °С	Time, min*	R	x	T., °C	Time, min*
Et The same » »	CH <sub>2</sub> OC(O)Me CH <sub>2</sub> OH Bu CH <sub>2</sub> SEt CH <sub>2</sub> OEt	20 20 40 40 40	15 20 60 80 80	Me same »	CH <sub>2</sub> OC(O)Me Bu CH <sub>2</sub> SEt CH <sub>2</sub> OEt	40 40 40 40	30 60 80 100

\*The times were determined by the disappearance of the ethynyl bromide from the reaction medium. The checking was done using TLC on Silufol UV-254.

0,0-dialky1-S-( $\gamma$ -acetoxypropargy1) thiophosphates by treatment with acety1 chloride.

 $(EtO)_2P(O)SC \equiv CCH_2OH + MeC(O)CI \rightarrow (EtO)_2PSC \equiv CCH_2OCMe$ 

0,0-Diethyl-S-( $\gamma$ -acetoxypropargyl) thiophosphate was also obtained by counter synthesis from potassium 0,0-diethyl thiophosphate and acetoxypropargyl bromide. The S-ethynyl esters of thiophosphoric acids can also be obtained by treating a mixture of the dialkylthiophosphoric acid, pyridine, and CuCl with an equimolar amount of the substituted ethynyl bromide.

$$(RO)_2 P(S)OH + Br - C \equiv C - X \xrightarrow{Py, CaCl} (RO)_2 P(O)SC \equiv C - X$$
 (B)

where R = Et, Pr; X = Pb,  $CH_2OPr$ .

It is known that reductive dimerization occurs [2] when CuCl is reacted with substituted ethynyl bromides and diacetylenes are formed. It proved that, parallel with the main ethynylation reaction, dimerization occurs with the formation of the corresponding diynes, whose yield is 10-20%:

$$X - C \equiv C - Br + 2CuCl \rightarrow X - C \equiv$$
  
= C - C \equiv C - X + 2CuClBr

where X = Bu, Ph.

It is not excluded that similar diynes can also be formed from the reaction products, and specifically the S-ethynyl esters of thiophosphoric acids, in which the dialkoxyphosphorylmercapto group can function as a pseudohalogen. The yield of the thioesters decreases with increase in the reaction time, while the yield of the diyne increases. It should be mentioned that the ease with which the salts of thiophosphoric acids are ethynylated in the presence of CuCl depends both on the polarity of the solvent and on the nature of the X substituent found at the acetylenic bond (Table 3).

In their effect on the ease of alkynylation the X substituents can be arranged in the following order:  $CH_2OCOMe > CH_2OH > Bu > CH_2SEt > CH_2OEt$ .

Thus, from Table 3 it can be seen that the acetoxy- and hydroxymethylethynyl bromides react with potassium diethyl thiophosphate at ~20° in 15 and 20 min, whereas the reaction with 1-bromohexyne and ethylmercaptopropynyl bromide at 40° is ended in 60 and 80 min respectively. The bromoalkynes react with somewhat greater difficulty with potassium dimethyl thiophosphate.

#### EXPERIMENTAL

<u>S-Ethynyl Esters of Thiophosphoric Acids.</u> a) To 0.02 mole of potassium 0,0-diethyl thiophosphate in 30 ml of alcohol were added 0.02 mole of CuCl and 0.02 mole of the appropriate ethynyl bromide. The temperature and reaction time are indicated in Table 3. The precipitate was filtered, the solvent was evaporated, and the residue was separated by chromatography on a column packed with silica gel L 100/160 (eluant = 1:1:1 benzene-ether-hexane).

b) To 0.03 mole of the dialkylthiophosphoric acid in 25 ml of alcohol were added 0.02 mole of pyridine, 0.02 mole of CuCl, and 0.02 mole of the ethynyl bromide. The mixture was heated for 2 h at 40° and then worked up the same as before. The constants and yields of the obtained compounds are given in Table 1.

<u>0,0-Diethyl-S-( $\gamma$ -acetoxypropargyl)</u> Thiophosphate. A mixture of 4.48 g (0.02 mole) of potassium 0,0-diethyl thiophosphate, 98 g (0.02 mole) of CuCl, and 2.7 g (0.02 mole) of 1-hydroxy-3-bromo-3-propyne was stirred for 20 min at 20°, the precipitate was filtered, the solvent was evaporated, and the residue was added to a mixture of 1.1 g (0.014 mole) of AcCl and 1.1 g (0.014 mole) of pyridine in 50 ml of abs. ether at ~0°. The reaction mixture was kept for 0.5 h at 0°, then for 0.5 h at the boil, and worked up the same as described above. We obtained 2.6 g (50% when based on K diethyl thiophosphate) of 0,0-diethyl-S-( $\gamma$ -acetoxypropargyl) thiophosphate,  $n_D^{20} = 1.4850$ . Infrared spectrum ( $\nu$ , cm<sup>-1</sup>): 2210 (C=C) and 1750 (C=0).

# CONCLUSION

1. A method was developed for the alkynylation of the salts of thiophosphoric acids by alkynyl bromides in the presence of CuCl.

2. The ease of reaction depends on the nature of the substituent attached to the acetylenic bond of the alkynyl bromide.

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