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REACTION OF POTASSIUM DIALKYL THIOPHOSPHATES WITH ETHYNYL

BROMIDES IN THE PRESENCE OF CUPRIC CHLORIDE

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In our previous work [1], we described a method for the synthesis of S-ethynyl esters of dialkylthiophosphoric acids entailing the reaction of potassium or pyridinium salts of 0,0-dialkylthiophosphoric acids with ethynyl bromides in the presence of equimolar amounts of CuCl. We showed that CuCl and the dialkylthiophosphoric acid salt exchange anions, with the formation of the copper salt of this acid reacts with ethynyl bromide.

It was of interest to study the reactions of dialkylthiophosphoric acids with substituted ethynyl bromides in the presence of $CuCl_2$. For this purpose, we carried out the reaction of potassium diethynyl phosphate with phenylbromoacetylene in the presence of different amounts of $CuCl_2$

$$(EtO)_2 PSOK + BrC \equiv CPh \xrightarrow{CuCl_2} (EtO)_2 P(O)SC \equiv CPh$$
(1)

The reaction of equivalent amounts of these reagents gives 0,0-diethyl S-(phenylethynyl)thiophosphate (I). The yield of this product is reduced by a factor of almost 2 relative to the case of CuCl. Bis(diethoxyphosphoryl)disulfide (II) is isolated as a by-product. The reason for this low yield of ethynyl thiophosphate (I) is apparently related to the consumption of a portion of the $(EtO)_2P(S)OK$ in the formation of disulfide (II). Support for this hypothesis is found in the finding that $(EtO)_2PSOCu$ (III) and disulfide (II) were isolated upon the exchange of anions between diethyl thiophosphate and CuCl₂ taken in 2:1 ratio. Thus, this reaction may be represented as follows:

 $\begin{array}{l} 4(\mathrm{EtO})_{2}\mathrm{PSOK} + 2\mathrm{CuCl}_{2} \rightarrow [(\mathrm{EtO})_{2}\mathrm{P(O)S-l}_{2} + 2(\mathrm{EtO})_{2}\mathrm{PSOCu} + \\ & + 4\mathrm{KCl} \\ (\mathrm{III}) + \mathrm{BrC} \equiv \mathrm{CPh} \rightarrow (\mathrm{I}) + \mathrm{CuBr} \end{array}$

The reaction of $(EtO)_2 P(S)ONH_4$ with $Cu(OAc)_2$ gives $(EtO)_2 P(S)OCu$ [2]. Pesin and Khaletskii [2] proposed that the corresponding disulfide formed as a result of the oxidation of the diethyl thiophosphate salt should be another reaction product. In the present work, we have experimentally demonstrated the possibility of the formation of a disulfide in such reactions.

Hence, both the chloride ions in $CuCl_2$ are exchanged in the reaction of $(EtO)_2P(S)OK$ with this salt by diethoxyphosphorylmercapto groups to form $[(EtO)_2PSO]_2Cu$, which is unstable and decomposes to give disulfide (II) and copper salt (III)

$$4(\text{EtO})_2 \text{PSOK} + 2\text{CuCl}_2 \xrightarrow[-4K\text{CI}]{} 2 \, [(\text{EtO})_2 \text{PSO}]_2 \text{Cu} \rightarrow (\text{II}) + 2 \, (\text{III})$$

Another reaction scheme may be proposed for this reaction: anion exchange between $(EtO)_2P$ -(S)OK and CuCl₂ is accompanied by the formation of unstable $(EtO)_2PSOCuCl$ (IV), which rapidly

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 467-469, February, 1986. Original article submitted April 23, 1985. decomposes to give (II) and CuCl, which undergoes an exchange reaction with a second molecule of potassium diethyl thiophosphate to form (III)

$$2(\text{EtO})_{2}\text{PSOK} + 2\text{CuCl}_{2} \xrightarrow[-2\text{KCI}]{} 2(\text{EtO})_{2}\text{PSOCuCl} \rightarrow (\text{II}) + 2\text{CuCl}$$

$$(\text{IV})$$

$$2\text{CuCl} + 2(\text{EtO})_{2}\text{PSOK} \xrightarrow[-2\text{KCI}]{} 2(\text{III}) + 2\text{KCl}$$

Both these schemes are described by the same overall reaction, in which one CuCl₂ molecule is consumed by two potassium salt molecules.

In order to check our hypotheses, we carried out the reaction of $(EtO)_2 P(S)OK$ with $CuCl_2$ in 1:1 ratio. The slow addition of potassium diethyl thiophosphate to CuCl₂ led to the isolation of only disulfide (II) and CuCl from the reaction mixture. Thus, one chloride ion in CuCl₂ is exchanged by an ester group and unstable cuprichloride (IV) is formed.

Hence, the reaction of the potassium salts of dialkylthiophosphoric acids with substituted ethynyl bromides in the presence of CuCl₂ proceeds through the intermediate formation of the cuprous salts of these acids, which react with ethynyl bromide to form S-ethynyl thiophosphates.

EXPERIMENTAL

Reaction of $(EtO)_2P(S)$ with phenylbromoacetylene in the presence of equivalent amounts of CuCl₂. A sample of 1.35 g (0.01 mole) CuCl₂ was added to 4.16 g (0.02 mole) with (EtO)₂P(S)OK in 60 ml acetone. After 2 h, 1.81 g (0.01 mole) phenylbromoacetylene was added and the mixture was heated at reflux for 2 h. The solvent was evaporated and the residue was purified on a column packed with silica gel L 100/160 with 1:1 benzene-ether as the eluent to give 1 g (72%) 0,0-diethyl S-phenylethynyl thiophosphate with n_D^{20} 1.5620 [3] and 1.5 g (88%) disulfide (II) with nD²⁰ 1.4900 [4]. Found, %: C 28.1; H 5.9; P 17.9. C₈H₂₀O₆P₂S₂. Calculated, %: C 28.4; H 5.9; P 18.3.

Reaction of (EtO)₂P(S)OK with CuCl₂ in 2:1 ratio. A sample of 1.35 g (0.01 mole) CuCl₂ was added to 4.16 g (0.02 mole) (EtO)₂P(S)OK in 50 ml acetone and the mixture was stirred for 2 h at 20°C and 1 h at reflux. The precipitate was filtered off and the solvent was evaporated. The residue was purified on a column packed with silica gel L 100/160 using 1:1 benzene-ether as the eluent to give 1.8 g (78%) copper 0,0-diethyl thiophosphate, mp 100°C [2] and 1.5 g (88%) disulfide (II).

Reaction of (EtO)₂P(S)OK with CuCl₂ in 1:1 ratio. A sample of 2.08 g (0.01 mole) (EtO)₂P-(S)OK was added to 1.35 g (0.01 mole) $CuCl_2$ in 50 ml acetone and stirred for 2 h at 20°C and 1 h at reflux. The precipitate was filtered off, washed with water and then with 1% HCl and dried in vacuum to give 0.08 g (80%) CuCl. The filtrate was evaporated and the residue was purified on a column packed with silica gel L 100/160 using 1:1 benzene-ether as the eluent to give 0.85 g (51%) disulfide (II).

CONCLUSIONS

The reaction of potassium diethyl thiophosphate with phenylbromoacetylene in the presence of equivalent amounts of cupric chloride gives 0,0-diethyl S-phenylethynyl thiophosphate. The cuprous salt of diethylthiophosphate acid is formed as an intermediate which reacts with the ethynyl bromide.

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