MECHANISM OF THE REACTION OF CUPROUS DIALKYL THIOPHOSPHATES WITH PROPARGYL HALIDES

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In previous work [1], we showed that copper salts of dialkylthiophosphoric acids react with propargyl halides to form 0,0-dialkyl S-propargyl thiophosphates, which may also be obtained by the reaction of propargyl halides with the potassium salts of these acids

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 $HC \equiv CCH_{2}Hal + \frac{(C_{2}H_{5}O)_{2}PSOCu}{(C_{2}H_{5}O)_{2}PSOK} \rightarrow (C_{2}H_{5}O)_{2}P(O)SCH_{2}C \equiv CH$ Hal = Cl or Br.

In subsequent work [2], we showed, that, in contrast to the diethylthiophosphate anion in its potassium salt, the strongly coordinated diethylthiophosphate ligand in the copper salt does not possess nucleophilic properties and reacts with ordinary alkyl bromides. On the other hand, the covalently bound cuprous ion is capable of undergoing oxidation-reduction processes, which serve as a basis for the alkynylation of copper diethyl thiophosphates. Thus, EPR spectroscopy showed that the cuprous ions in dialkylphosphoric acid salts are readily oxidized by substituted ethynyl bromides to give cupric complexes with distorted octahedral structure [3], which are capable of converting to S-ethynyl thiophosphates

 $\begin{array}{l} (C_{2}H_{5}O)_{2}PSOCu + BrC \equiv CR \rightarrow (C_{2}H_{5}O)_{2}PSOCuBr + C \equiv CR \rightarrow \\ (C_{2}H_{5}O)_{2}P(O)SC \equiv CR + CuBr \end{array}$

Hence, we propose that the reaction of Cu(I) dialkyl thiophosphates with propargyl halides also involves an oxidation reduction step.

However, an alternative lies in a nucleophilic substitution in the reaction of propargyl halides with Cu(I) dialkyl thiophosphates.

In order to check these proposals, we took the EPR spectra of the reaction mixtures of various propargyl halides (Ia)-(Ie) with Cu(I) diethyl thiophosphate in toluene

 $\begin{array}{c} R & R \\ (C_2H_5O)_2PSOCu + Hal - C - C \equiv C - R' \rightarrow [?] \rightarrow (C_2H_5O)_2P(O)SC - C \equiv C - R' + CuHal \\ R & R \\ (Ia - e) & (IIa - e) \\ R = H, R' = H, Hal = Br (a); R = H, R' = C_3H_7, Hal = Br (b); R = CH_3, R' = H, \\ Hal = Cl (c); R = CH_3, R' = C_3H_7, Hal = Cl (d); R + R = (CH_2)_5, R' = H, Hal = Cl (e). \end{array}$

The physical constants for IIa, IIc, and IIe in this reaction corresponded to those described in our previous work [1] (see Experimental). Thiophosphates (IIb) and (IId) were synthesized by the reaction of cuprous diethyl thiophosphate with 1-bromo-2-hexyne and 2-chloro-2-methyl-3-heptyne, respectively. 2-Chloro-2-methyl-3-heptyne was obtained by the alkylation of 2-methyl-3-butyn-2-ol with propyl bromide in liquid ammonia in the presence of LiNH₂ and treatment of the intermediate, 2-methyl-3-heptyn-2-ol with concentrated hydrochloric acid

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TABLE 1. Magnetic Resonance Parameters of Cu(II) Complexes Arising in the Reaction of $(C_2H_5O)_2PSOCu$ with $R'C \equiv CCR_2Hal$ (Ia)-(Ie)

Compound	g T	៩ក្	^g a⊽	A∥, G
(Ia)	2,086	2,433	2,202	108,7
(Ib)	2,083	2,441	2,202	111.1
(Ic)	2,088	2,396	2,191	113.0
(Id)	2,118	2,395	2,210	114.0
(Ie)	2,086	2,408	2,193	100.0

 $HOC(CH_3)_2C \equiv CH \xrightarrow{C_3H_7Br} HOC(CH_3)_2C \equiv C - C_3H_7 \xrightarrow{conc.HCl} ClC(CH_3)_2C \equiv CC_3H_7$ (Id)

The reaction of halides (Ia)-(Ie) with Cu(I) diethyl thiophosphate gives paramagnetic cupric complexes. The EPR spectra of the reaction mixtures taken in glassy toluene solutions at 77 K have axial symmetry characteristic for tetragonal complexes with $d_{x^2-y^2}$ ground doublet state. We may assume that the square planar unit is given by the structure of the starting tetramer cluster [2], while the axial position is occupied by the ligand containing a triple bond. The magnetic resonance parameters obtained by analysis of these spectra are given in Table 1.

A general trend may be noted for a change in the values of g_{\parallel} and A_{\parallel} for (Ia)-(Id). The value for A_{\parallel} increases, while g_{\parallel} drops with increasing branching of the alkyl group in the propargyl halides. This finding indicates a strengthening of the bonds with the axial ligands and partial distortion of the square planar geometry to pyramidal [4].

Thus, the reaction of Cu(I) diethyl thiophosphate with propargyl halides entails oxidation of cuprous to cupric ions and the formation of intermediate paramagnetic Cu(II) complexes, which are stable at low temperature. Under the conditions of the alkynylation reaction by the copper salt, when the reaction temperature is 20-60°C, such Cu(II) complexes are apparently unstable and are reduced to the thermodynamically stable Cu(I) complexes. This gives S-propargyl esters of diethylthiophosphoric acid (IIa)-(IIe) in 60-80% yield and CuHal in 80-90% yield

$$\begin{array}{c} R & R \\ (C_{2}H_{5}O)_{2}PSOCu + Hal - C = C - R' \rightarrow (C_{2}H_{5}O)_{2}PSOCu Hal C - C \equiv C - R' \rightarrow R' \\ R & R \\ \rightarrow (C_{2}H_{5}O)_{2}P(O) - S - C = C - R' + Cu Hal \\ R \end{array}$$

In previous work [1], we showed that (Ia) reacts with both the potassium and cuprous salt of diethylthiophosphoric acid, while sterically hindered propargyl halides (Ic) and (Ie) react only with the cuprous salt of this acid. In the present work, we found that (Ib) also reacts both with the potassium and cuprous salt of diethylthiophosphoric acid, while (Id) reacts only with cuprous diethyl thiophosphate. The starting reagents were isolated in experiments with (Id) and diethyl thiophosphate under analogous conditions.

Thus, halides (Ia) and (Ib) are capable of forming S-propargyl thiophosphates by two pathways differing in mechanism. One pathway involves an S_N2 reaction with potassium diethyl thiophosphate, while the second involves an oxidation-reduction reaction with cuprous diethyl thiophosphate. The first pathway for the preparation of S-propargyl esters of dialkylphosphoric acids is apparently impossible for halides (Ic)-(Ie) as a consequence of unfavorable steric factors. As shown above, such factors do not affect the reaction of these halides with Cu(I) diethyl thiophosphate, which proceeds by an oxidation-reduction mechanism.

EXPERIMENTAL

The EPR spectra were taken in the 3 cm range on a Varian E-12 spectrometer. The starting reagents were mixed in a reaction flask and then the reaction mixture was transferred to EPR tubes. <u>1,1-Dimethyl-2-hexynol.</u> A sample of 22.4 g (0.25 mole) 1,1,-dimethyl-2-propynol was added over 40 min to a solution of LiNH₂ derived from 4 g lithium in 600 ml NH₃. After 30 min, 30.75 g (0.25 mole) propyl bromide was added to the reaction mixture. Ammonia was evaporated after 1 h and 110 ml ice water was added to the residue. The product was extracted with ether and dried over sodium sulfate. The solvent was evaporated and the residue was distilled in vacuum to give 20 g (63.5%) 1,1-dimethyl-2-hexynol, bp 76-78°C (40 mm), $d_4^{20} = 0.8544$, n_D^{20} 1.4250; MR_{exp} 38.8, MR_{calc} 38.6. Found: C 75.9; H 11.1%. Calculated for C₈H₁₄O: C 76.2; H 11.1%.

<u>2-Chloro-2-methyl-3-heptyne (Id).</u> A sample of 12.6 g (0.1 mole) 1,1-dimethyl-2-hexynol was added with stirring over 0.5 h to 57 ml conc. HCl at 0°C. After 1 h, 11.2 g CaCl₂ was added to the reaction mixture and stirring was continued until an upper dark layer appeared. This layer was separated, dried over CaCl₂, and distilled to give 8.1 g (56%) (Id), bp 50°C (10 mm), d_4^{20} 0.9048, n_D^{20} 1.4480; MR_{exp} 42.3, MR_{calc} 42.0. Found: C 66.4; H 9.1; Cl 24.6%. Calculated for C₈H₁₃Cl: C 66.4; H 9.0; Cl 24.6%,

<u>0,0 Diethyl S-(1,1-dimethyl-2-hexynyl)thiophosphate (IId)</u>. A sample of 1.6 g (0.011 mole) 2-chloro-2-methyl-3-heptyne was added to 2.33 g (0.01 mole) Cu(I) diethyl thiophosphate in 100 ml toluene at 20°C and then heated for 2 h at 50°C. The CuCl precipitate (80%) was separated and the solvent was evaporated. The residue was extracted with hexane. The extract was evaporated and purified by chromatography on a column packed with L100/140 silica gel using 9:1 benzene-ether as the eluent to give 1.3 g (47%) (IId), d_4^{20} 1.0395, n_D^{20} 1.4900; MR_{exp} 75.4, MR_{calc} 75.2. Found: C 52.4; H 8.4; P 10.7; S 11.4%. Calculated for $C_{12}H_{23}O_3PS$: C 51.8; H 8.3; P 11.1; S 11.5%.

0,0-Diethyl S-(1,1-dimethyl-2-propynyl)thiophosphate (IIc) was obtained analogously in 52% yield, np²⁰ 1.4780 (1.4784 [1]).

<u>O,O-Diethyl S-(1-ethynylcyclohexyl)</u> thiophosphate (IIe) was obtained analogously in 55% yield, n_D^{20} 1.5112 (1.5110 [1]).

<u>O,O-Diethyl S-propargyl thiophosphate</u> was obtained analogously in 80% yield, nD^{20} 1.4806 (1.4800 [1]).

CONCLUSIONS

The reaction of propargyl halides with Cu(I) diethyl thiophosphate proceeds through intermediate paramagnetic Cu(II) complexes, which are unstable under ordinary conditions. These complexes decompose with the formation of S-propargyl esters of diethylthiophosphoric acid and cuprous halide.

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