REACTION OF THIODIACETONE ALCOHOL WITH CHLORIDES OF TRIVALENT PHOSPHORUS ACIDS

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As a continuation of studying the reactions of β -keto alcohols with phosphorus-containing compounds we reacted thiodiacetone alcohol with some trivalent phosphorus acid chlorides. When diethylchlorophosphine and the chlorides of alkylthioalkylphosphonous acids were reacted in the presence of Et₃N we isolated S- α , α -dimethyl- γ -ketobutyl diethylthiophosphinite and the S-alkyl-S- α , α -dimethyl- γ -ketobutyl alkyldithiophosphonites

$$R = R' = C_2H_6 (I); R = C_2H_5, R' = C_2H_5S (II); R = C_2H_5, R' = C_4H_9S (III)$$

The structure of the obtained compounds was confirmed by the elemental analysis data, and also by the IR ($\nu_{C=O}$ 1720 cm⁻¹, absence of $\nu_{P=O}$) and ³¹P NMR [δ_{31P} -16 ppm for (I) and -92 ppm for (II) and (III)] spectral data. In addition, the presence of P(III) in (I) was confirmed by the addition of sulfur

 $(C_2H_5)_2PSC(CH_3)_2CH_2COCH_3 + S \rightarrow (C_2H_5)_2P(S)SC(CH_3)_2CH_2COCH_3$

As a result, thiodiacetone alcohol reacts with the chlorides of P(III) acids in the presence of a base in the same manner as diacetone alcohol [1, 2], with the formation of tricoordinated phosphorus derivatives.

The dichlorides of P(III) acids react with diacetone alcohol in the presence of a base to give the 2-substituted oxa-3-phospholanols [3]. The reaction of thiodiacetone alcohol with ethyl dichlorophosphite in the presence of Et_3N also gives the corresponding 2-ethoxy-2-thio-3,5,5-trimethyl-1,2-thia-3-phospholanol lanol



According to the scheme given in [3], the formation of phosphite (V) could be expected in the first step. The IR and ³¹P NMR spectroscopy data confirm the presence of (V). The IR spectrum of the undistilled reaction product has an intense absorption band at 1720 cm⁻¹, while the ³¹P NMR spectrum contains a single signal at -150 ppm (for compounds of type (RS)₂POR' δ_{31P} -153-162 ppm). The undistilled reaction product has the characteristic odor of a phosphite. Mesityl oxide is cleaved when (V) is distilled, and phospholanol (VI) is formed. The structure of (VI) is confirmed by the elemental analysis data, and

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TABLE	1
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Com- pound	Formula Yield,	Vield Wa	Bp, °C (p, mm of Hg)	d ²⁰ 4	n_D^{20}	Found/calculated				
						MR	C, %	н, %	.P, %	s, %
(1)	(C2H5)2PSC(CH3)2CH2COCH3	50,0	63-64(0,006)	0,9633	1,5090	$rac{68,20}{66,77}$	54,17 54,51	9,64 9,60	$\frac{14,11}{14,05}$	$ \frac{14,52}{14,55} $
· (II)	$C_{2}H_{5}$ $PSC(CH_{3})_{2}CH_{2}COCH_{3}$ $C_{2}H_{5}S$	59,0	86(0,01)	1,0680	1,5420	$\frac{74,38}{74,90}$	<u> </u>	—	$\frac{12,30}{12,30}$	$\frac{25,36}{25,42}$
(111)	C2H5 PSC(CH3)2CH2COCH3	40,0	98(0,01)	1,0657	1,5530	$\frac{79,99}{79,52}$	·	-	$\frac{12,01}{11,62}$	$\tfrac{23,69}{24,07}$
(IV)	$ \begin{array}{c} C_4H_9S \\ (C_2H_5)_2PSC(CH_3)_2CH_2COCH_3 \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	69,5	103—104(0,006)	1,0811	1,5470	$\frac{74,03}{73,64}$	47,07 47,59	$\frac{8,28}{8,38}$	$\frac{12,22}{12,27}$	$\tfrac{25,75}{25,41}$
(VI)	$\begin{array}{c c} S & -C(CH_3)_2 \\ \hline C_2H_5OP & \\ \parallel \\ C & -CH_2 \end{array}$	40,0	88—89(0,006)	1,1562	1,5435	$\frac{65,57}{64,85}$	$\frac{40,40}{39,98}$	6,99 7,13	$\frac{12,64}{12,89}$	$\frac{27,05}{26,71}$
(VII)	$ \begin{array}{c c} S \\ CH_3 \\ O-C-CH_3 \\ C_6H_5P \\ S \\ C-CH \end{array} $	85,3	115(0,02) Mp 69°	_					$\frac{12,57}{12,99}$	<u>13,10</u> 13,45
	CH ₃ CH ₃									

also by the IR (absence of $\nu_{C=O}$ at 1720 cm⁻¹, and the appearance of $\nu_{OH-bonded}$ at 3450 cm⁻¹) and ³¹P NMR (δ_{31P} -130 ppm) spectral data.

The reaction of alkyl(aryl)dichlorophosphines with diacetone alcohol in the absence of a base leads to the phospholene [4]. The reaction of thiodiacetone alcohol with phenyldichlorophosphine also gives the corresponding 2-phenyl-2-thio-1,2-oxa-3,3,5-trimethyl-4-phospholene (VII)



The constants and IR spectrum of (VII) coincide with the constants and IR spectrum of the phospholene that was obtained as described in [5].

EXPERIMENTAL METHOD

The properties and constants of the obtained compounds are given in Table 1.

<u>Thiodiacetone Alcohol.</u> With stirring, into a mixture of 409 g of mesityl oxide, 40 g of Et_3N , and 200 ml of absolute ether at -65 to -70°C was passed dry H_2S , the needed amount of which was determined gravimetrically. After the absorption of 162 g of H_2S (20 g excess) the cooled mixture was charged into an autoclave and allowed to stand overnight. The next day the mixture was heated in the autoclave for 2 h at 50°, and then distilled. We obtained 361 g (64.5%) of thiodiacetone alcohol with bp 55-56° (12 mm) (cf. [7]).

<u>S- α , α -Dimethyl- γ -ketobutyl Diethylthiophosphinite (I)</u>. With stirring, to an ether solution of 20.7 g of thiodiacetone alcohol and 17 g of Et₃N in a CO₂ stream, at -10 to -15°, was added 19.5 g of diethyl-chlorophosphine in drops. The precipitate was filtered, the ether was evaporated, and the residue was fractionally distilled. We obtained 18 g (50%) of (I) with bp 63-64° (0.006 mm); d₄²⁰ 0.9633; n_D²⁰ 1.5090. Found: C 54.17; H 9.64; P 14.11; S 14.52%; MR 68.20. C₁₀H₂₁OPS. Calculated: C 54.51; H 9.60; P 14.05; S 14.55%; MR 66.77.

Compounds (II) and (III) were obtained in a similar manner.

Addition of Sulfur to $S-\alpha, \alpha$ -Dimethyl- γ -ketobutyl Diethylthiophosphinite. To 5 g of (I) was added 0.74 g of powdered sulfur. The temperature rose spontaneously to 103°. After fractional distillation we

obtained 4 g (69.5%) of S- α , α -dimethyl- γ -ketobutyl diethyldithiophosphinate (IV) with bp 103-104° (0.006 mm); d₄²⁰ 1.0811; n_D²⁰ 1.5470. Found: C 47.07; H 8.28; P 12.22; S 25.75%; MR 74.03. C₁₀H₂₁OPS₂. Calculated: C 47.59; H 8.38; P 12.27; S 25.41%; MR 73.64.

Reaction of Thiodiacetone Alcohol with Ethyl Dichlorophosphite. To an ether solution of 22.7 g of thiodiacetone alcohol and 18.5 g of Et₃N at -10° was added 12.65 g of ethyl dichlorophosphite in drops. The precipitate was filtered, the ether was evaporated in vacuo, and the residue was fractionally distilled. We obtained 8.2 g (40%) of 2-ethoxy-2-thio-3,5,5-trimethyl-1,2-thia-3-phospholanol (VI) with bp 88-89° (0.006 mm); d_4^{20} 1.1562; n_D^{20} 1.5435. Found: C 40.40; H 6.90; P 12.64; S 27.05%; MR 65.67. $C_8H_{17}O_2$ -PS₂. Calculated: C 39.98; H 7.13; P 12.84; S 26.71%; MR 64.85. Besides (VI), we isolated 7 g (81%) of mesityl oxide with bp 126-128°; d_4^{20} 0.8662; n_D^{20} 1.4420.

<u>2-Phenyl-2-thio-1,2-oxa-3,3,5-trimethyl-4-phospholene (VII)</u>. To 17.9 g of phenyldichlorophosphine in 20 ml of CH_2Cl_2 was added in drops 13.2 g of thiodiacetone alcohol at a temperature not exceeding 35°. Then the mixture was refluxed for 30 min and distilled. We obtained 20.3 g (85.3%) of (VII) with bp 115° (0.02 mm); mp 69° (cf. [5]). Found: P 12.57; S 13.10%. $C_{12}H_{15}OPS$. Calculated: P 12.99; S 13.45%.

CONCLUSIONS

1. Thiodiacetone alcohol reacts with the monochlorides of trivalent phosphorus acids in the presence of a base to give tricoordinated phosphorus derivatives. 2-Ethoxy-2-thio-3,5,5-trimethyl-1,2-thia-3-phospholanol is formed in the case of ethyl dichlorophosphite.

2. The reaction of thiodiacetone alcohol with phenyldichlorophosphine in the absence of a base gives 2-phenyl-2-thio-1,2-oxa-3,3,5-trimethyl-4-phospholene.

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