2. A. F. Gontar', E. N. Glotov, E. G. Bykhovskaya, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 1438 (1984).
3. Yu. V. Zeifman, V. V. Tyuleneva, P. A. Pleshkova, T. G. Kostyanovskii, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 2732 (1975).
4. M. Biffin, J. Miller, and D. Paul, in: S. Patai (editor), The Chemistry of the Azido Group, Wiley-Interscience, London (1971), p. 86.
5. W. D. Grow and C. Wentur, Tetrahedron Lett., 44, 4379 (1967).
6. W. R. Carpenter, "Evidence of overtone and combination bands in the spectra of organic azides," Appl. Spectrosc., 17, 70 (1963).
7. A. R. Bailey and R. E. Banks, J. Fluor. Chem., 24, 117 (1984).
8. A. F. Gontar', N. A. Til'kunova, E. G. Bykhovskaya, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 488 (1978).
9. R. A. Mitsch and P. H. Ogden, Chem. Commun., 59 (1967).

THE REACTIONS OF DIETHYLACETYL DITHIOPHOSPHITE WITH PROTON-DONOR NUCLEOPHILIC REAGENTS AND CHLORAL

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The mixed anhydrides of phosphorus and carboxylic acids are among the most convenient phosphorylating agents [1]. In our recent communication [2], we reported a synthesis based on amidodithiophosphites and carboxylic acid anhydrides to give new acyl dithiophosphites and described the reactions of these products with acyl halides and acids.

In the present work, we developed a convenient method for the preparation of dialkylacetyl dithiophosphites and studied the reactions of these compounds with protic nucleophilic reagents and chloral.

The mixed anhydride of ethylenedithiolphosphorous acid and CF_3CO_2H is obtained by heating 2-chloro-1,3,2-dithiaphospholane with CF_3CO_2K in pentane at reflux [3]. We have established that S,S-diethyl chlorodithiophosphite (I) reacts with CH_3CO_2Na in the presence of 15-crown-5 as a phase transfer catalyst in benzene at 20°C over 2 h to form S,S-diethyl acetyl dithiophosphite (II) in greater than 80% yield

$$\underset{(I)}{(EtS)_2PCl} + MeCOONa \xrightarrow[-NaCl]{15\text{-Crown-5}} \underset{(II)}{(EtS)_2POCOMe}$$

We should note that the reaction requires 48 h for completion in the absence of the crown ether and the yield of the final product is much lower.

The reactions of acyl phosphites with mercaptans have not been studied extensively. Under conditions excluding radical reactions, O,O-dialkylacyl phosphites do not react with mercaptans [4]. The reaction is carried out only in the presence of base and leads to the formation of dithiophosphates [5]

$$(RO)_2POCOMe + 2R'SH \xrightarrow{R''_3N} (RO)_2PSSR' + MeCOOH\cdot NR_3'' + R'H$$

Pyrocatechol-S-benzyl thiophosphite is obtained only by using sodium benzylmercaptide in the reaction with pyrocatecholacetyl phosphite [4].

Acyl dithiophosphites have not been studied relative to their reactions with mercaptans. In our previous work [6], we found that in contrast to the oxygen analogs, S,S-diethylacetyl dithiophosphite (II) readily phosphorylates ethyl and benzyl mercaptans in the absence of base at ∿20°C to form the corresponding trithiophosphites (IIIa) and (IIIb)

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$$\underset{(II)}{(EtS)_2POCOMe} + RSH \rightarrow \underset{(IIIa,\ b)}{(EtS)_2PSR} + MeCOOH$$

$$R = Et\ (a),\ PhCH_2\ (b).$$

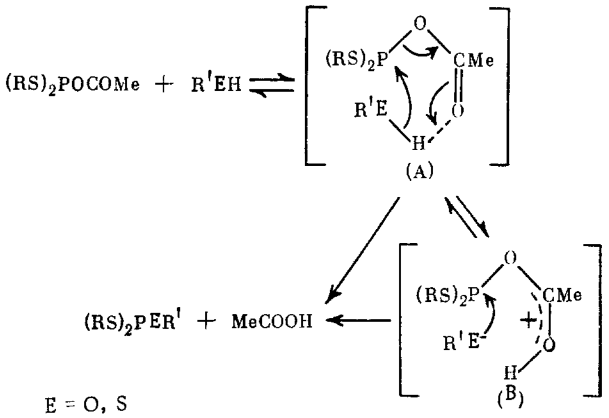
The products of the desulfurization of the mercaptans (tetrathiophosphates) were not detected in any case.

Dialkylacetyl dithiophosphites also readily phosphorylate aliphatic alcohols. For example, (II) reacts with methanol and n-butanol even at 0°C to form O-alkyl-S,S-diethyl dithiophosphites (IVa) and (IVb)

$$\underset{(II)}{(EtS)_2POCOMe} + ROH \rightarrow \underset{(IVa,\ b)}{(EtS)_2POR} + MeCOOH$$

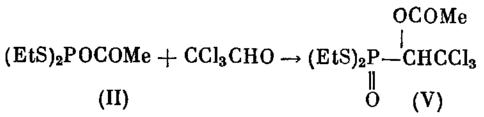
$$R = Me(a),\ Bu\ (b).$$

The experimental results for the reaction of dialkylacetyl dithiophosphites with alcohols and mercaptans taking into account the information available on the reaction of acyl dithiophosphites with acids [2] which proceeds as a substitution reaction with retention of the coordination of the phosphorus atom indicate that the phosphorylation of protic nucleophilic reagents starts with the formation a hydrogen-bonded intermediate complex (A), which undergoes synchronous decomposition or decomposes through an onium intermediate (B) by nucleophilic substitution of the acetoxyl group to give the corresponding thiophosphites



Dialkylacyl dithiophosphites have also not been studied relative to their reactions with carbonyl compounds, although the reaction of carbonyl compounds with the oxygen analogs has been studied in considerable detail [1].

We have shown that (II) reacts with chloral at 60-65°C to give S,S-diethyl-α-acetoxy-α-trichloromethyl dithiophosphonate (V). Migration of the acyl group occurs in this reaction



$$\underset{(II)}{(EtS)_2POCOMe} + CCl_3CHO \rightarrow \underset{\overset{\|}{O}}{(EtS)_2P}-\overset{\overset{OCOMe}{|}}{CHCCl_3}\quad (V)$$

The structure of dithiophosphate (V) was supported by ^1H and ^{31}P NMR spectroscopy and elemental analysis.

EXPERIMENTAL

The PMR spectra were taken on a Varian T-60 spectrometer relative to TMS in CCl_4. The ^{31}P NMR spectral data were obtained on a special YaMR-KGU-4 spectrometer at 10.2 MHz with 85% H_3PO_4 as the external standard. All the operations were carried out in a dry argon atmosphere.

S,S-Diethylacetyl Dithiophosphite (II). A mixture of 70 g chlorodithiophosphite (I) and 42 g finely ground anhydrous sodium acetate was stirred for 30 min in 100 ml benzene in the presence of 0.25 g 15-crown-5. The precipitate was filtered off and washed with benzene. The solvent was removed from the filtrate and the residue was fractionated to yield 64.8 g (82%) (II), bp 65-66°C (0.02 mm), n_D^{20} 1.5439, δP 178 ppm [2].

Reaction of (II) with Ethyl Mercaptan. A mixture of 5.0 g (II) and 1.23 g EtSH was maintained for 1 h at ∿20°C in an Arbuzov flask and then distilled to yield 3.34 g (66%) triethyl trithiophosphite, bp 85-86°C (0.08 mm), n_D^{20} 1.5670, δP 115 ppm [7]. Distillation of the liquid condensed in the trap give 1.2 g (84%) acetic acid, bp 118°C, n_D^{20} 1.3721 [8].

Reaction of (II) with Methanol and 1-Butanol. A sample of 0.64 g methanol was added dropwise to 2.5 g (II) cooled to 0°C and maintained at ∿20°C for 30 min to yield 1.93 g (89%) dithiophosphite (IVa), bp 54-55°C (0.06 mm), n_D^{20} 1.5414, δP 160 ppm [9]. The liquid-nitrogen trap gave 0.65 g (92%) acetic acid, bp 117-118°C, n_D^{20} 1.3717.

Analogously, 2.2 g (II) and 0.76 g 1-butanol gave 2.02 g (85%) dithiophosphite (IVb), bp 70-71°C (0.03 mm), n_D^{20} 1.5248 [9] and 0.54 g (87%) acetic acid, bp 118°C, n_D^{20} 1.3723.

S,S-Diethyl-α-acetoxy-α-trichloromethyl Dithiophosphonate (V). A mixture of 6.7 g (II) and 4.66 g chloral was heated in a sealed ampule at 60-65°C for 2 h. After this heating, the ^{31}P NMR spectrum of the reaction mixture showed a single signal with δP 59 ppm. Distillation gave 2.64 g (23%) (V), bp 115-117°C (0.02 mm), n_D^{20} 1.5512. PMR spectrum (δ, ppm): 1.42 t (H_3C, $^3J_{HH}$ 7.2 Hz), 2.23 s (H_3C), 2.97 m (H_2CS), 5.82 d (HC, $^3J_{HP} = 2.5$ Hz). P 59 ppm. Found: C 27.27; H 4.11; Cl 29.73; P 8.72%. Calculated for $C_8H_{14}Cl_3O_3PS_2$: C 26.71; H 3.89; Cl 29.59; P 8.63%.

CONCLUSIONS

1. Mercaptolysis and alcoholysis of S,S-diethylacetyl dithiophosphite proceed with replacement of the acetoxy group, leading to the corresponding thiophosphites and acetic acid.

2. S,S-Diethylacetyl dithiophosphite reacts with chloral to form S,S-diethyl-α-acetoxy-α-trichloromethyl dithiophosphonate.

LITERATURE CITED

1. É. E. Nifant'ev and I. V. Fursenko, Usp. Khim., 39, 2187 (1970).
2. O. G. Sinyashin, V. P. Kostin, É. S. Batyeva, and A. N. Pudovik, Zh. Obshch. Khim., 53, 502 (1983); O. G. Sinyashin, V. P. Kostin, É. S. Batyeva, A. N. Pudovik, and N. V. Ivasyuk, Zh. Obshch. Khim., 53, 1706 (1983).
3. I. V. Konovalova, V. F. Mironov, E. N. Ofitserov, and A. N. Pudovik, Zh. Obshch. Khim., 53, 690 (1983).
4. É. E. Nifant'ev and I. V. Fursenko, Vestn. Mosk. Univ., Ser. 2, Khim., 12, No. 2, 245 (1971).
5. E. K. Shlenkova and V. P. Evdakov, Zh. Obshch. Khim., 37, 898 (1967).
6. O. G. Sinyashin, V. P. Kostin, É. S. Batyeva, and A. N. Pudovik, Zh. Obshch. Khim., 52, 2701 (1982).
7. A. Lippert and E. E. Reid, J. Am. Chem. Soc., 60, 2370 (1938).
8. Short Chemist's Handbook [in Russian], Goskhimizdat, Moscow (1963), 176.
9. D. Minich, N. I. Rizpolozhenskii, and V. D. Akamsin, Izv. Akad. Nauk SSSR, Ser. Khim., 1792 (1968).