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Abstract

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O- and S-Alkylation of the Dialkyl Thiophosphate Anion by Triethyloxonium Borofluoride

It is known that alkali-metal and ammonium salts of phosphorus monothio acids possess the dual reactivity typical of ambident ions. Alkylation of these salts with alkyl halides ($^{1-5}$) and alkyl esters of mineral acids (^{6}) proceeds at sulfur, with formation of thiol phosphates (thiolphosphinates), for example:

$$(RO)_2P(S)ONa + R'X \rightarrow (RO)_2P(O)SR' + NaX.$$

Acylation of these salts with acid halides (^{2,4,7}) and acid halide anhydrides of phosphorus acids (^{2,8}) proceeds predominantly at oxygen, with formation of thionic acid anhydrides, for example:

$$(RO)_2P(S)ONa + CH_3COCl \rightarrow (RO)_2P(S)OCOCH_3 + NaCl.$$

Only two publications contain indications of O-alkylation of salts of phosphorus monothio acids; however, both are of low reliability. Hoffmann and Moore (^{9}) write that, upon alkylation of the dimethylanilinium salt of O-ethylmethylthiophosphinic acid with β-chlorodiethyl sulfide, along with the main product—O-ethyl-S-β-ethylmercaptoethylmethylthiophosphinate (the thiol isomer)—up to 8% of the thiono isomer is also formed. The latter was not isolated in pure form, and the authors judged its admixture to the thiol isomer from changes in the molecular refraction, IR, and NMR spectra of the mixture in comparison with the pure substance. Cadogan (^{10}), studying the pyrolysis of the 1,1,4,4-tetraethylpiperazinium salt of diethylthiophosphoric acid, established by gas-liquid chromatography the presence among the reaction products of about 1% triethyl thionophosphate, which, in the author' s opinion, is formed as a result of O-alkylation of the ambident anion by the piperazinium cation, and this reaction pathway accompanies S-alkylation and other pathways of pyrolysis to a significant extent.

If one proceeds from the ideas of A. N. Nesmeyanov and M. I. Kabachnik (^{11}) concerning the factors influencing reactions of metallic derivatives of tautomeric substances, then it should have been expected that O-alkylation of salts of phosphorus monothio acids would be observed when using the most electrophilic alkylating agents, capable of alkylating ambident ions at the most electronegative atom of the system.

We studied the alkylation of sodium diethylthiophosphate with triethyloxonium borofluoride and established that the reaction proceeds with formation of two isomeric triethylthiophosphates:

$$(C_2H_5O)_2P(S)\overset{\ominus}{O}Na^{\oplus}+(C_2H_5)_3\overset{\oplus}{O}\,BF_4{}^{\ominus} \rightarrow (C_2H_5O)_2P(O)(SC_2H_5)+(C_2H_5O)_3PS+(C_2H_5)_2O+NaBF_4.$$

The reaction was carried out in chloroform medium with equimolar ratios of the components. A solution of the borofluoride in chloroform was added dropwise with stirring to a solution of the salt; during this, the temperature of the reaction mixture rose from room temperature to 34–38°. The reaction products were then heated at 45–50°; the sodium borofluoride formed was filtered off (yield 96.4%), and the filtrate, after removal of the solvent, was used-

was monitored by thin-layer chromatography and then fractionated.

Chromatography of the reaction mixture on silica gel with 10% water (eluant hexane–acetone, 4 : 1) (12) gave two spots, corresponding in R_f value to triethyl thionophosphate ($R_f = 0.64$; for a sample of the authentic preparation $R_f = 0.63$) and triethyl thiolphosphate ($R_f = 0.30$; R_f of the authentic preparation 0.30).

On fractionation, triethyl thionophosphate was obtained in 4.5% yield, b.p. 86-87° at 8 mm (column ∼ 12 theoretical plates), n_D^{20} 1.4481, d_4^{20} 1.0746.

$C_6H_{15}O_3PS$. Found %: C 36.5; 36.4; H 7.7; 7.7; P 15.5; 15.4; S 16.1; 16.1.
Calculated %: C 36.4; H 7.6; P 15.6; S 16.2.

MR_D found 49.39, calculated 49.40. Lit.: b.p. 105-105.5° at 20 mm; n_D^{20} 1.4500, d_4^{20} 1.0768 (3); b.p. 88.5° at 8 mm, n_D^{20} 1.4480, d_4^{20} 1.0756 (13); and triethyl thiolphosphate was obtained in 61.7% yield: b.p. 105-106° at 8 mm; n_D^{20} 1.4584, d_4^{20} 1.1095.

$C_6H_{15}O_3PS$. Found %: C 36.0; 36.1; H 7.7; 7.7; P 15.2; 15.3; S 16.2; 15.9.
Calculated %: C 36.4; H 7.6; P 15.6; S 16.2.

MR_D found 48.79; calculated 49.10. Lit.: b.p. 122.5-123° at 20 mm; n_D^{20} 1.4578, d_4^{20} 1.1067 (3); b.p. 61-62° at 2.5 mm; n_D^{20} 1.4582, d_4^{20} 1.1080 (5).

The isolated isomers on chromatograms on silica gel each gave only one spot with R_f, respectively, 0.63 and 0.30. The distillation residue (8.2% of the weight of the starting substances) was a black viscous mass containing some amount of triethyl thiolphosphate (according to thin-layer chromatography).

The IR spectra* of the isomers were completely identical with the spectra of the corresponding authentic preparations of triethyl thiono- and triethyl thiolphosphates. Since isolation of the isomers (especially triethyl thionophosphate) in pure form is associated with appreciable losses, the IR spectrum of the reaction mixture was recorded to determine the yield (after removal of sodium borofluoride, solvent, and distillation of the reaction mixture in vacuo). The spectrum of the mixture obtained was compared with the IR spectra of pure preparations containing 3, 10, and 20% of the thiono isomer. On the basis of these data (intensity of the band at 830 cm^{-1}) the ratio of isomers in the mixture was calculated; it proved to be 1 : 9. The corresponding yields were 8% of the thiono and 72% of the thiol isomers. This approximately coincides with the data obtained on fractionation.

It may be assumed that in reality, as a result of alkylation, the thiono isomer is formed in somewhat higher yield, since it should isomerize under the action of triethyloxonium borofluoride to the thiol isomer (14). Indeed, on heating equimolar amounts of triethyl thionophosphate with triethyloxonium borofluoride in chloroform solution at 50°, the thiono isomer disappears and triethyl thiolphosphate is formed (cf. (14)):

$$(C_2H_5O)_3PS+(C_2H_5)_3O^{\oplus}BF_4^{\ominus} \rightarrow (C_2H_5O)_2P(O)(SC_2H_5)+(C_2H_5)_2O\cdot BF_3+C_2H_5F.$$

However, catalytic isomerization under the action of borofluoride is not observed. Study of the competing reaction of alkylation of sodium diethyl thiophosphate and triethyl thionophosphate with an insufficient amount of triethyloxonium borofluoride (0.05 mole each) showed, however, that alkylation of the salt proceeds faster than isomerization of triethyl thionophosphate.

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* The IR spectra were recorded on a UR-10 instrument by L. B. Sinyavina, for which the authors are deeply grateful.

Thus, alkylation of sodium diethyl dithiophosphate with triethyloxonium borofluoride proceeds with the formation of two isomers: O- and S-derivatives.

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REFERENCES

1. E. J. Hoegberg, J. T. Cassaday, *J. Am. Chem. Soc.*, **73**, 557 (1951).
2. G. Schrader, *Die Entwicklung neuer Insektizide auf Grundlage organischer Fluor- und Phosphorverbindungen*, 2. Auflage, Weinheim, 1952, p. 76.
3. M. I. Kabachnik, T. A. Mastryukova, ZhOKh, **25**, 1924 (1955).
4. M. I. Kabachnik, T. A. Mastryukova et al., ZhOKh, **26**, 2228 (1956).
5. T. A. Mastryukova, T. B. Sakharova, M. I. Kabachnik, ZhOKh, **34**, 94 (1964).
6. G. Hilgetag, H. Teichmann, *J. prakt. Chem.*, (4) **8**, 121 (1959).
7. M. I. Kabachnik, T. A. Mastryukova et al., ZhOKh, **26**, 120 (1956).
8. J. Michalski, M. Mikolajczyk, A. Ratajczak, *Chem. and Ind.*, **1962**, No. 18, 819.
9. F. W. Hoffmann, T. R. Moore, *J. Am. Chem. Soc.*, **80**, 1150 (1958).
10. J. I. G. Cadogan, *J. Chem. Soc.*, **1962**, 18.
11. A. N. Nesmeyanov, M. I. Kabachnik, ZhOKh, **25**, 41 (1955).
12. T. A. Mastryukova, T. B. Sakharova, M. I. Kabachnik, *Izv. AN SSSR, OKhN*, **1963**, 2211.
13. B. A. Arbuzov, V. S. Vinogradova, *Izv. AN SSSR, OKhN*, **1947**, 459.
14. H. Teichmann, G. Hilgetag, *Ber.*, **96**, 1454 (1963).

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