THE REACTION OF SELENOPHOSPHORIC ACIDS WITH O-ACYLATED HYDROXYLOAMINE.

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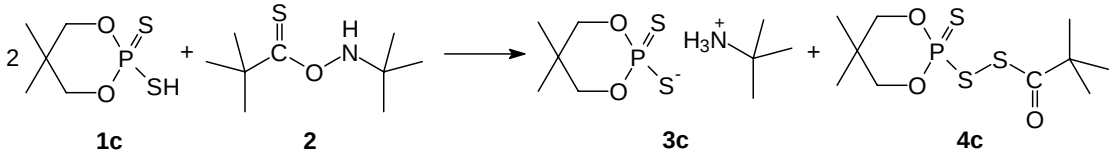
Introduction

The new reaction of dithiophosphoric acid **1c** with O-thioacylhydroxylamines **2**, which proceeds via N-O bond cleavage and lead to ammonium dithiophosphates **3c**, acyl thiophosphoryl disulphates **4c** has been recently described [1] (Scheme 1).



1c **2** **3c** **4c**

Scheme 1 The reaction of two equivalents of dithiophosphoric acid **1c** with O-thioacylhydroxylamines **2**.

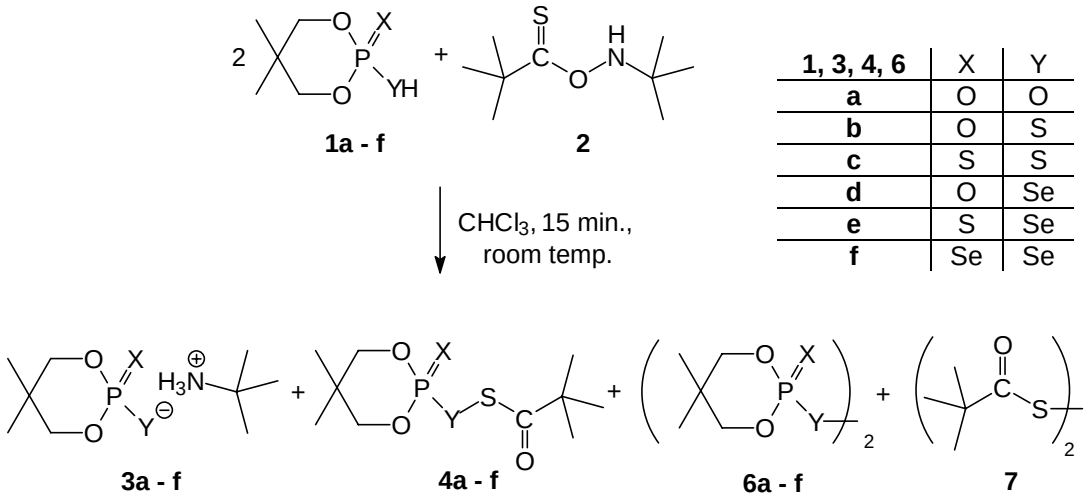
The influence of radical traps and light on the reaction strongly suggested the radical mechanism of the process. Moreover, considerable ability of dithiophosphate anions to one electron oxidation [2] implied involvement of a single electron transfer process (SET) with dithiophosphate anion >P(S)S$^-$ as SET donor and radical scavenger as well [3].

On the other hand, it is known very well, that selenoles participate in the $S_{RN}1$ reaction as a SET donors [4]. Taking above facts into account we decided to examine reactivity of selenophosphoric acid derivatives towards O-thioacylhydroxylamine and compare them with thiophosphoric and phosphoric acids ones. We also expected to find correlation between course of the reaction and oxidation potentials of phosphate anions **5** (see Table 2) under investigation.

Results and discussion

In the first series of experiments O-thiopivaloyl-N-tert-butylhydroxylamine **2** was treated with two equivalents of phosphoric acid derivatives **1** (Scheme 2) in standard conditions (15min., room temperature, $CHCl_3$ as a solvent). Thus, in the case of phosphoric acid **1a** (X, Y = O) the reaction did not occur and starting materials **1a, 2** were quantitatively recovered (Table 1). However, monothiophosphoric acid **1b** (X = O, Y = S) gave, analogically to dithiophosphoric acid **1c** [1,3], ammonium monothiophosphate **3b** (^{31}P NMR, δ = 53,8 ppm) and monothiophosphoric-acyl disulfide **4b** (^{31}P NMR, δ = 13,9 ppm). On the other hand, monoselenophosphoric acid **1d** (X = O, Y = Se) produced, apart from expected tert-butylammonium monoselenophosphate **3d** (^{31}P NMR, δ = 44,6 ppm, $^1J_{P\text{-}Se}$ = 745,3 Hz), symmetric bis-(2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl) diselenide **6d** (^{31}P NMR, δ = 3,96 ppm, $^1J_{P\text{-}Se}$ = 488,9 Hz) and pivaloyl disulfide **7**. Similarly, selenothiophosphoric acid **1e** (X = S, Y = Se) lead to tert-butylammonium selenophosphate **3e** (^{31}P NMR, δ = 98,5

ppm, $^{1}J_{P\text{-}Se}$ = 739,1 Hz) and bis-(2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl) diselenide (^{31}P NMR, δ = 67,2 ppm, $^{1}J_{P\text{-}Se}$ = 471,3 Hz) **6e** and pivaloyl disulphide **7**.



1, 3, 4, 6	X	Y
a	O	O
b	O	S
c	S	S
d	O	Se
e	S	Se
f	Se	Se

Scheme 2 The reaction of two equivalents of phosphoric acid derivatives **1** with O-thiopivaloyl-N-tert-butylhydroxylamine **2**

Table 1. Products of reaction of phosphoric acids **1** with O-thiopivaloyl-N-tert-butylhydroxylamine **2**.

	X	Y	Yield %			
			3	**4**	**6**	**7**
a	O	O	0	0	0	0
b	O	S	100	81	0	0
c	S	S	99 [3]	92 [3]	0	0
d	O	Se	100	0	49	70
e	S	Se	100	0	83	84
f	Se	Se	100	0	0	38

The question arose: is it the same reaction like in the case of mono – and dithiophosphoric acids **1b**, **1c** ? The first product should be (2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl)-S-pivaloyl selenosulfide **4d** or (2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl)-S-pivaloyl selenosulfide **4e** which could symmetrize to diselenide **6d,e** and pivaloyl disulphide **7** respectively.

To prove this hypothesis the reaction of monoselenophosphoric acid **1d** was monitored with ^{31}P NMR technique (room temperature, $CDCl_3$ as a solvent). The tert-butylammonium monoselenophosphate **3d** precipitated from the reaction mixture after several seconds. After filtration the ^{31}P NMR spectrum was recorded immediately. There was one resonance signal: δ = 6,63 ppm, $^{1}J_{P\text{-}Se}$ = 485,8 Hz observed and identified as bis-(2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl) diselenide **6d**. The ^{31}P NMR repeated after 24h, 48h did not indicate any further changes. It could mean that symmetrization of (2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl)-S-pivaloyl selenosulfide **4d** to bis-(2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl) diselenide **6d** was very fast or **4d** was not obtained at all. Subsequently, we examined reaction of selenothiophosphoric acid **1e** with O-thiopivaloyl-N-tert-butylhydroxylamine **2** in NMR tube. Tert-butylammonium selenothiophosphate **3e** was

filtered off and filtrate analyzed with ^{31}P NMR technique. The only signal was δ = 72,2 ppm, $^{1}J_{P\text{-}Se}$ = 467,1 Hz (adequate for a compound with single P-Se bond) which could be assigned to (2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl)-S-pivaloyl selenosulfide **4e**. On the spectrum performed after 24h the signal δ = 72,2 ppm, $^{1}J_{P\text{-}Se}$ = 467,1 Hz decreased and the new one appeared: δ = 68,2 ppm, $^{1}J_{P\text{-}Se}$ = 478,7 Hz and assigned as bis-(2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl) diselenide **6e** (δ = 67,2 ppm, $^{1}J_{P\text{-}Se}$ = 471,3 Hz). Moreover, intensity of this new signal increased after 48h and 96h. The compound with δ = 72,2 ppm, $^{1}J_{P\text{-}Se}$ = 467,1 Hz was isolated from the reaction mixture and fully characterized by ^{1}H NMR, ^{13}C NMR, IR, MALDI-TOF-MS. All above data confirmed formation of (2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl)-S-pivaloyl selenosulphide **4e**. Furthermore, the conversion of **4e** to **6e** was observed in the same time and conditions as in the crude reaction mixture of **1e** and **2**.

These observations supported hypothesis where final products **6d,e** and **7** are formed as the result of symmetrization of intermediate **4d** or **4e**.

We also investigated reaction of two equivalents of diselenophosphoric acid **1f** with O-thiopivaloyl–N-tert-butyl-hydroxylamine **2**. Tert-butylammonium diselenophosphate **3f** (^{31}P NMR δ = 84,8 ppm, $^{1}J_{P\text{-}Se}$ = 749,5 Hz) was filtered off and on the ^{31}P NMR spectrum the one resonance signal was observed: δ = 70,6 ppm, $^{1}J_{P\text{-}Se}$ = 485,8 Hz, $^{1}J_{P\text{-}Se}$ = 956,0 Hz, which could be assigned as the most likely structures: (2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl)-S-pivaloyl selenosulfide **4f** or bis-(2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl) diselenide **6f**.

The sample of this reaction mixture was kept at room temperature 24 h and ^{31}P NMR analysis indicated, apart from δ = 70,6 ppm, $^{1}J_{P\text{-}Se}$ = 485,8 Hz, $^{1}J_{P\text{-}Se}$ = 956,0 Hz, numerous others signals. Since bis-(O,O-dialkylselenophosphoric) diselenides (>P(Se)-Se-)$_2$ are described as a relatively stable compounds [5] we concluded, that signal δ = 70,6 ppm, $^{1}J_{P\text{-}Se}$ = 485,8 Hz, $^{1}J_{P\text{-}Se}$ = 956,0 Hz is from (2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl)-S-pivaloyl selenosulfide **6f** which is not stable and undergoes decomposition.

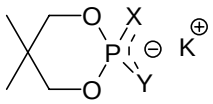
In the next set of experiments the radical mechanism of the reaction was examined. Thiophenols are known to be free radical traps [3]. Hence, to proof the hypothesis that SET process is involved, we performed the reactions of two equivalents of i) monothiophosphoric acid **1b** and ii) selenothiophosphoric acid **1e** with O-thiopivaloyl–N-tert-butyl-hydroxylamine **2** in the presence of one equivalent of 2,6-dimethylthiophenol.

After 30 min. the reaction mixtures were quenched with triethylamine [3] and analyzed with ^{31}P NMR. The only products were: triethylammonium monothiophosphate (^{31}P NMR δ = 54,4 ppm) and triethylammonium selenothiophosphate (^{31}P NMR δ = 97,7 ppm, $^{1}J_{P\text{-}Se}$ = 740,1 Hz) respectively. These experiments showed, that 2,6-dimethylthiophenol prevents the formation of monothiophosphoric-acyl disulfide **4b** or (2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl)-S-pivaloyl selenosulfide **4e** in the above reaction mixtures.

The fact, that phosphoric acid **1a** did not react with O-thiopivaloyl-N-tert-butylhydroxylamine **2** in contrast to its sulfur and selenium analogs **1b-f**, which underwent reaction of the N-O bond cleavage in hydroxylamine, required rational explanation. The results of our experiments strongly suggested, that SET process is involved in the mechanism of the reaction under discussion. Thus, the first stage is single electron transfer process from phosphate anion to protonated O-acylated

hydroxylamine [3] . In other words, the course of the reaction should depend on oxidation potentials of phosphate anion and its sulfur and selenium analogs **5**. To verify this hypothesis we measured oxidation potentials of phosphate anions **5** by cyclic voltamperometry technique. The results are summarized in Table 2.

Table 2. Redox potentials of phosphate anions **5**.



5a - f

	X	Y	E [V] **5**
a	O	O	above 2.0
b	O	S	0.8
c	S	S	0.56
d	O	Se	0.42
e	S	Se	0.23
f	Se	Se	0.24

The all measurements were performed for potassium salts of **5a-f** (0.001 M) in the solution of 0.1 M TBAP (tetrabutylammonium perchlorate) in acetonitrile. Working electrode; glassy carbon (3 mm diameter), counter electrode was a platinum wire, and as a reference electrode was used a saturated calomel electrode (SCE). All measurements were made on Autolab 30 electroanalytical system.

Data presented in the Table 2 show, that oxidation potentials of phosphate anions **5** decrease with increasing of the atomic mass of chalcogen X, Y dramatically. The electrochemical measurements indicated, that replacement of at least one oxygen atom for sulfur or selenium in phosphoric acid **1** molecule decreased the oxidation potential of anions **5** and improved their ability as a SET donor.

Conclusions

Sulfur and selenium analogs of phosphoric acids **1b-f** reacted with O-acylated hydroxylamine **2** with N-O bond cleavage. The course and products of the reaction depended on structure of used phosphoric acid derivatives. Monothiophosphate anion **5b** possesses low enough oxidation potential and can participate in the reaction as a SET donor, analogically to dithiophosphoric acid **1c** [1,3]. They lead to tert-butylammonium thiophosphates **3b,c** and disulfides **4b,c**. Additionally, in the case of selenothiophosphoric **1e** acid subsequent conversion of selenosulfide **4e** to symmetric diselenide **6e** and pivaloyl disulfide **7** was observed.

Literature

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