Heteroatom Chemistry
Volume 18, Number 7, 2007

Reaction of Thio and Seleno Phosphoric Acid Derivatives with *O*-Thioacylated Hydroxylamine

Grzegorz Cholewinski,[1] Dariusz Witt,[1] Radosław Majewski,[2] Tadeusz Ossowski,[2] and Janusz Rachon[1]

[1]*Department of Organic Chemistry, Chemical Faculty, Gdansk University of Technology, Narutowicza 11/12, 80-952, Gdansk, Poland*

[2]*Department of Supramolecular Chemistry, Chemical Faculty, University of Gdansk, Sobieskiego 18/19, 80-852, Gdansk, Poland*

Received 18 October 2006; revised 19 November 2006

ABSTRACT: *The reactivity of thio and seleno analogs of phosphoric acid* **1b–f** *with O-thioacylhydroxylamine* **2** *was examined. The experimental evidence for the proposed mechanism involving an N—O bond cleavage and a single electron transfer process (SET) from phosphate anions was collected. The influence of phosphoric acids* **1** *structure and their oxidation potentials on the course of the reaction and products* **3, 4, 6, 7** *distribution was presented.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:767–773, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20368

INTRODUCTION

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

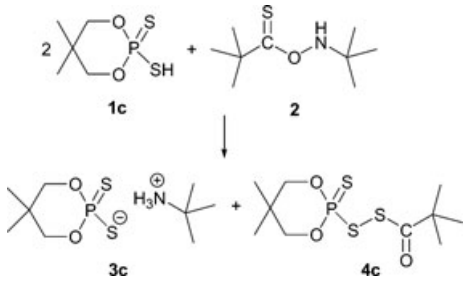
The influence of radical traps and light on the reaction strongly suggests the radical mechanism of the process. Moreover, considerable ability of dithiophosphate anions to one-electron oxidation [2] implied involvement of a single electron transfer process (SET) with dithiophosphate anion **5c** as a SET donor and radical scavenger as well (Scheme 2) [3].

On the other hand, in the chemical literature, it is presented that selenoles participate in the $S_{RN}1$ reaction as SET donors [4] as well. Taking into account the above facts, we decided to examine the reactivity of the whole range of thio- and seleno- selenophosphoric acid derivatives toward *O*-thioacylhydroxylamines. We also expected to find a correlation between the course of the reaction and oxidation potentials of thio- and seleno- phosphate anions under investigation.

RESULTS AND DISCUSSION

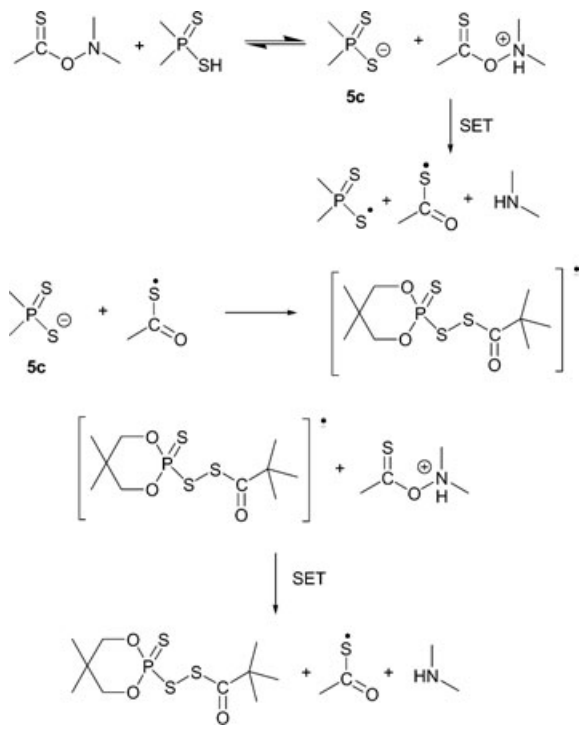
In the first series of experiments, *O*-thiopivaloyl-*N*-tert-butylhydroxylamine **2** was treated with 2 equivalents of phosphoric acid derivatives **1** (Scheme 3) in standard conditions (15 min, room temperature, $CHCl_3$ as a solvent). Thus, in the case of phosphoric acid **1a** (X, Y = O), the reaction did not occur and starting materials **1a**,**2** were quantitatively

Correspondence to: Janusz Rachon; e-mail: rachon@chem.pg.gda.pl.
Contract grant sponsor: Polish Ministry of Science and Higher Education.
Contract grant number: 1 T09A 064 30.

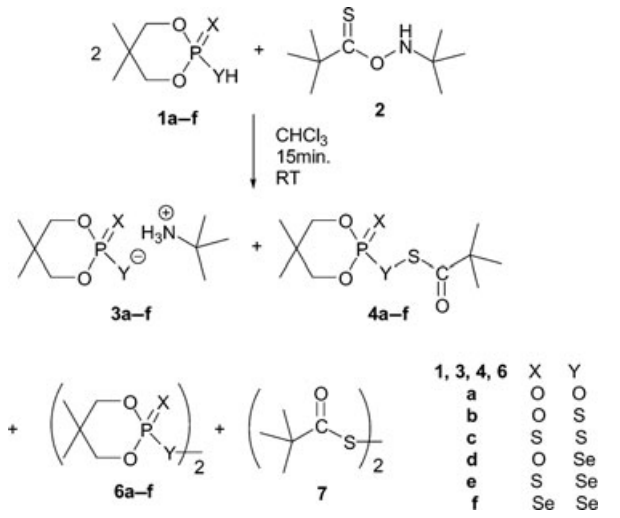


SCHEME 1 The reaction of 2 equivalents of dithiophosphoric acid **1c** with *O*-thioacylhydroxylamine **2**.

recovered from the reaction mixture (Table 1). However, monothiophosphoric acid **1b** (X = O, Y = S) gave, analogically to dithiophosphoric acid **1c** [1,3], ammonium monothiophosphate **3b** (^{31}P NMR, $\delta = 53.8$ ppm) and monothiophosphoric-acyl disulfide **4b** (^{31}P NMR, $\delta = 13.9$ ppm). On the other hand, monoselenophosphoric acid **1d** (X = O, Y = Se) produced, apart from expected tert-butylammonium monoselenophosphate **3d** (^{31}P NMR, $\delta = 44.6$ ppm, $^{1}J_{P-Se} = 745.3$ Hz), bis-(2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl) diselenide **6d** (^{31}P NMR, $\delta = 3.96$ ppm, $^{1}J_{P-Se} = 488.9$ Hz) and pivaloyl disulfide **7**. Similarly, selenothiophosphoric acid **1e** (X = S, Y = Se) leads to tert-butylammonium



SCHEME 2 Proposed mechanism for the reaction of dithiophosphoric acid with *O*-thioacylhydroxylamines.



SCHEME 3 The reaction of 2 equivalents of phosphoric acid derivatives **1** with *O*-thiopivaloyl-*N*-tert-butylhydroxylamine **2**.

selenophosphate **3e** (^{31}P NMR, $\delta = 98.5$ ppm, $^{1}J_{P-Se} = 739.1$ Hz) and bis-(2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl) diselenide (^{31}P NMR, $\delta = 67.2$ ppm, $^{1}J_{P-Se} = 471.3$ Hz) **6e** and pivaloyl disulfide **7**.

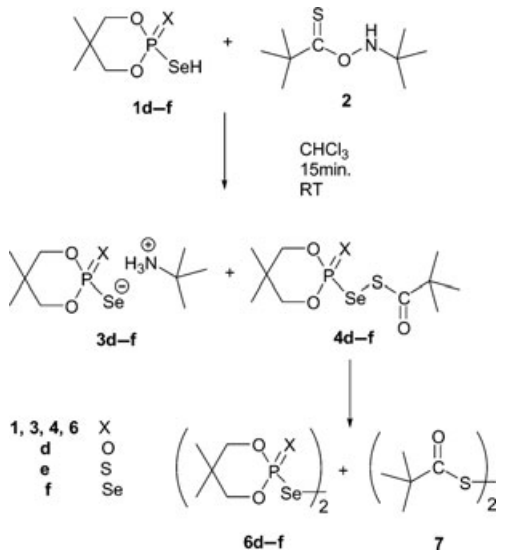
The question arises whether it is the same reaction course like in the case of mono- and dithiophosphoric acids **1b,c**. The first product should be (2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl)-*S*-pivaloyl selenosulfide **4d** or (2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl)-*S*-pivaloyl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

To prove this hypothesis, the reaction of monoselenophosphoric acid **1d** was monitored with the ^{31}P NMR technique (room temperature, $CDCl_3$ as a solvent). After several seconds, tert-butylammonium monoselenophosphate **3d** precipitated from the reaction mixture. After

TABLE 1 Products of Reaction of Phosphoric Acids **1** with *O*-Thiopivaloyl-*N*-tert-butylhydroxylamine **2**

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

[a]Based on ^{1}H NMR and ^{31}P NMR analysis of aqueous layer.
[b]see [3].



SCHEME 4 The reaction of 2 equivalents of selenophosphoric acid derivatives **1d–f** with *O*-thiopivaloyl-*N*-tert-butylhydroxylamine **2**.

filtration of the reaction mixture, the ^{31}P NMR spectrum was recorded immediately. One resonance signal ($\delta = 6.63$ ppm, $^{1}J_{P-Se} = 485.8$ Hz) was observed and was identified as bis-(2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl) diselenide **6d**. The ^{31}P NMR technique was repeated after 24 and 48 h and 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-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl) diselenide **6d** was very fast, or **4d** was not produced at all. Subsequently, we examined reaction of selenothiophosphoric acid **1e** with *O*-thiopivaloyl-*N*-tert-butylhydroxylamine **2** in a NMR tube. Tert-butylammonium selenothiophosphate **3e** was filtered, and a homogeneous solution of the reaction mixture was analyzed with the ^{31}P NMR technique. The only signal was detected at $\delta = 72.2$ ppm, $^{1}J_{P-Se} = 467.1$ Hz (adequate for a compound with a single P—Se bond), which could be assigned to (2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl)-*S*-pivaloyl selenosulfide **4e**. In the spectrum, performed after 24 h, the signal $\delta = 72.2$ ppm, $^{1}J_{P-Se} = 467.1$ Hz decreased and a new one appeared at $\delta = 68.2$ ppm, $^{1}J_{P-Se} = 478.7$ Hz, which we assigned to bis-(2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl) diselenide **6e** ($\delta = 67.2$ ppm, $^{1}J_{P-Se} = 471.3$ Hz). Moreover, the intensity of this new signal increased after 48 and 96 h. The compound with $\delta = 72.2$ ppm and $^{1}J_{P-Se} = 467.1$ Hz was isolated from the reaction mixture and was fully characterized by ^{1}H NMR, ^{13}C NMR, IR, and MS MALDI-TOF techniques. All of the above data confirmed formation of (2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl)-*S*-pivaloyl selenosulfide **4e**. Furthermore, the conversion of **4e** to **6e** was observed at the same time and conditions as in the crude reaction mixture of **1e** and **2**. The symmetrization process can be rationally explained by the Se—Se, S—S, and Se—S bond energy analysis [5]. Although the exact value of bonds energy can be slightly different for examined compounds, but it clearly showed that conversion of **4d–e** to **6d–e** and **7** is favored at least at about 15 kJ/mol and S—S bond formation is a driving force for that process.

All of the above observations supported the hypothesis presented in Scheme 4, where final products **6d,e** and **7** are formed as a result of symmetrization of intermediate **4d** or **4e**.

We also investigated the reaction of 2 equivalents of diselenophosphoric acid **1f** with *O*-thiopivaloyl–*N*-tert-butyl-hydroxylamine **2** (Scheme 4). Tert-butylammonium diselenophosphate **3f** (^{31}P NMR $\delta = 84.8$ ppm, $^{1}J_{P-Se} = 749.5$ Hz) was filtered and in the ^{31}P NMR spectrum of the homogeneous solution the one resonance signal was observed: $\delta = 70.6$ ppm, $^{1}J_{P-Se} = 485.8$ Hz, $^{1}J_{P-Se} = 956.0$ Hz, which could be assigned to 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 for 24 h, and ^{31}P NMR analysis indicated, apart from $\delta = 70.6$ ppm and $^{1}J_{P-Se} = 485.8$ and 956.0 Hz, numerous others signals. Since bis-(*O*,*O*-dialkylselenophosphoric) diselenides (>P(Se)—Se—)$_2$ are described as relatively stable compounds [6], we concluded that signal $\delta = 70.6$ ppm and $^{1}J_{P-Se} = 485.8$ and 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.

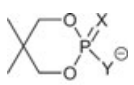
In the next set of experiments, the radical mechanism of the reaction was examined. Thiophenols are known to be free-radical traps [3]. Hence, to prove the hypothesis that the SET process is involved in the reaction under investigation, we performed the reactions of 2 equivalents of (i) monothiophosphoric acid **1b** and (ii) selenothiophosphoric acid **1e** with *O*-thiopivaloyl-*N*-tert-butyl-hydroxylamine **2** in the presence of 2,6-dimethylthiophenol. After 30 min, the reaction mixtures were quenched with triethylamine and were analyzed with the ^{31}P NMR technique. The only products were triethylammonium monothiophosphate (^{31}P NMR, $\delta = 54.4$ ppm) and triethylammonium selenothiophosphate (^{31}P NMR,

$\delta = 97.7$ ppm, $^1J_{P-Se} = 740.1$ Hz). These experiments showed that 2,6-dimethylthiophenol prevented 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 undergo reaction with the N—O bond cleavage in hydroxylamine, required a rational explanation. The results of our experiments strongly suggest that the SET process was involved in the mechanism of the reaction under discussion. Thus, the first stage is a single electron transfer process from phosphate anion to protonated *O*-thioacylated hydroxylamine (Scheme 2). In other words, the course of the reaction should depend on oxidation potentials of phosphate anions and its sulfur and selenium analogs **5**. To verify this hypothesis, we measured oxidation potentials of thio- and seleno- phosphate anions **5** by the cyclic voltammetry technique. The results are summarized in Table 2.

Data presented in the Table 2 show that irreversible oxidation potentials of phosphate anions **5** decrease with an increase in the atomic mass of chalcogens X,Y dramatically. The oxidation potential of phosphate anion **5a** was more than 2.0 V, besides the measured range. It means that phosphate anion **5a** is a very poor SET donor and does not react with *O*-thioacylated hydroxylamine. In contrast to that monothiophosphate anion **5b** ($E_p = 0.8$ V), dithiophosphate anion **5c** ($E_p = 0.56$ V), monoselenophosphate anion **5d** ($E_p = 0.42$ V), selenothiophosphate anion **5e** ($E_p = 0.23$ V), and diselenophosphate anion **5f** ($E_p = 0.24$ V) participated in the reaction and the total conversion of the substrates **1b–f, 2** was observed. 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.

TABLE 2 Oxidation Potentials E_p of Phosphate Anions **5**



5a–f

	X	*Y*	E_p *(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

CONCLUSION

Sulfur and selenium analogs of phosphoric acids **1b–f** reacted with *O*-thioacylated hydroxylamine **2** with the N—O bond cleavage. The course and products of the reaction depended on the structure of used phosphoric acid derivatives.

Monothiophosphate anion **5b** possesses low-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**. In addition, in the case of selenothiophosphoric acid**1e**, subsequent conversion of selenosulfide **4e** to symmetric diselenide **6e** and pivaloyl disulfide **7** was observed.

EXPERIMENTAL

All reactions of phosphoric acids derivatives **1a–f** with *O*-thiopivaloyl-*N*-tert-butylhydroxylamine **2** were carried out under argon atmosphere in dry chloroform. All solvents were dried and were distilled by the standard procedure. Melting points are uncorrected. NMR spectra were recorded on a Varian Gemini 500 MHz (*J* values are given in Hz); IR spectra were measured on a Bruker IFS66 (liquids from NaCl film and solids from KBr tablet); MS (EI) spectra were recorded on a Maspec II system (II32/99D9) and MS (Maldi-TOF) on Bruker BIFLEX 3 mass spectrometer. The products were characterized by comparing their physical data with those of known samples or by their spectral data.

All electrochemical measurements were performed for potassium phosphates **5a–f** (0.001 M) in the solution of 0.1 M TBAP (tetrabutylammonium perchlorate) in acetonitrile. Working electrode was made from 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 (EcoChemie, Holland) electroanalytical system. Prior to the cyclic voltametry (CV) experiment, solution was purged with argon for at least 15 min and the gas atmosphere was then maintained over the solution during the course of experiment.

O-thiopivaloyl-*N*-tert-butylhydroxylamine **2** was prepared according to the known procedure [7].

Potassium salt of 2-hydroxy-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinan **5a** (4.06 g, 85%) was prepared from 2-chloro-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinan [8] (4.32 g) and potassium

hydroxide, on the basis of modified synthesis of sodium salt of 2-hydroxy-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan [9]. ^{31}P NMR (202 MHz, D_2O; 85% H_3PO_4) $\delta = 2.38$; ^{1}H NMR (500 MHz; D_2O; Me_4Si) $\delta = 0.85$ (6H, s, $(CH_3)_2CH_2O$), 3.77 (4H, d, $J_{H-P} = 11.7$, $(CH_3)_2CH_2O$).

Literature data [10] for triethylammonium salt: ^{31}P NMR (202 MHz, D_2O; 85% H_3PO_4) $\delta = 3.8$.

A potassium salt of 2-hydroxy-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan **5b** was obtained by following the procedure described for dithiophosphoric acid salts [11]. Potassium (8.78 g, 225 mmol) was dissolved in methanol (400 mL, 0°C), then solution was saturated with H_2S (30 min). Later, 2-chloro-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinan [8] (19.93 g, 108 mmol) was added with stirring and the reaction mixture was kept overnight at room temperature. Suspension was filtered and was evaporated under reduced pressure. The crude product was washed with diethyl ether (200 mL), crystallized from methanol–diethyl ether, and filtered through a short pad of silica gel (eluent: acetone/methanol 5:1). Evaporation of solvents gave potassium salt **5b** (1.57 g, 7%) as a white solid. ^{31}P NMR (202 MHz, D_2O; 85% H_3PO_4) $\delta = 52.4$; ^{1}H NMR (500 MHz; D_2O; Me_4Si) $\delta = 0.86$ (6 H, s, $(CH_3)_2CH_2O$); 3.77 (4H, d, $J_{H-P} = 11.7$, $(CH_3)_2CH_2O$).

Literature data for methyltriethylammonium salt of 2-hydroxy-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan [12]: ^{31}P NMR (CH_2Cl_2) $\delta = 49.9$.

A potassium salt of 2-sulfanyl-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan **5c** was obtained by adding potassium hydroxide (2.6 mmol) in water (10 mL) to a solution of 5,5-dimethyl-2-sulfanyl-2-thioxo-1,3,2-dioxaphosphorinan [13] (0.52 g, 2.6 mmol) in acetone (10 mL). After 15 min, solvents were evaporated, residue was dissolved in acetone and was filtered through a short pad of silica gel. The solvent was removed, and pure potassium dithiophosphate **5c** (0.57 g, 93%) was obtained as a white solid. ^{31}P NMR (202 MHz, D_2O; 85% H_3PO_4) $\delta = 110.2$.

A potassium salt of 2-oxo-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinan **5d** (4.14 g, 62%) was prepared via reduction of 2-chloro-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinan (4.61 g, 25 mmol) with potassium (1.95 g, 50 mmol) followed by selenation in liquid ammonia [14].

A potassium salt of 2-seleno-2-sulfanyl-5,5-dimethyl-1,3,2-dioxaphosphorinan **5e** was obtained by following the procedure described for dithiophosphoric acid salts [11]. Potassium (1.72 g, 44 mmol) was dissolved in methanol (100 mL, 0°C), then solution was saturated with H_2S (30 min). Later, 2-chloro-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinan [15] (4.95 g, 20 mmol) was added and the reaction mixture was stirred for 1 h at room temperature. Suspension was filtered and was evaporated under reduced pressure. The residue was washed with diethyl ether (200 mL). Subsequently, the crude product was dissolved in hot acetone (600 mL), filtered, and the solvent was removed under reduced pressure. Potassium selenothiophosphate **5e** (4.81 g, 85%) was obtained as a white solid. ^{31}P NMR (202 MHz, D_2O; 85% H_3PO_4) $\delta = 98.6$, $J_{P-Se} = 739$.

A potassium salt of 2-seleno-2-selenyl-5,5-dimethyl-1,3,2-dioxaphosphorinan **5f** (3.11 g, 25%) was prepared from 2-chloro-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinan [8] (9.19 g), analogically to potassium monoselenophosphate **5d** [14]. The crude product can by purified by crystallization from acetone–CH_2Cl_2 or column chromatography (eluent: acetone/CH_2Cl_2 1:2). IR (KBr) $\nu = 574$ (P=Se) cm^{-1}; ^{31}P NMR (202 MHz, aceton-d_6, 85% H_3PO_4) $\delta = 87.5$, $J_{P-Se} = 792$.

The structure of **5f** was confirmed by reaction with methyl iodide in THF. Appropriate Se-methyl ester, 2-selenomethyl-2-selenono-5,5-dimethyl-1,3,2-dioxaphosphorinane (75 mg, 62%), was isolated and was compared with the literature data [16] mp 90–91°C (from benzene-petroleum ether); IR (KBr) $\nu = 560$ (P=Se) cm^{-1}; ^{31}P NMR (202 MHz, D_2O; 85% H_3PO_4) $\delta = 80.9$, $J_{P-Se} = 470$, $J_{P-Se} = 936$. Lit. [16]: mp 91°C (from benzene-petroleum ether); ^{31}P NMR (24.3 MHz, dioxane, 85% H_3PO_4) $\delta = 79.4$, $J_{P-Se} = 469$, $J_{P-Se} = 945$.

Reaction of Phosphoric Acid Derivatives **1a–f** *with O-Thiopivaloyl-N-tert-butylhydroxylamine* **2**

General Procedure. A mixture of 2 mmol potassium phosphate **5a–f** and 2 mmol of TFA (trifluoroacetic acid) in 2 mL of $CHCl_3$ was added to 1 mmol of *O*-thiopivaloyl-*N*-tert-butylhydroxylamine **2** in 1 mL of $CHCl_3$. The reaction mixture was stirred for 15 min at room temperature and was washed with water. Then, an aqueous layer containing potassium trifluoroacetate and unreacted phosphoric acid derivative **1a** or tert-butylammonium phosphate **3b–f** was separated. After evaporation of solvent, the residue was analyzed with ^{1}H and ^{31}P NMR techniques. The organic layer was dried over anhydrous $MgSO_4$, filtered, evaporated under reduced pressure, and the unreacted substrate **2** or products **4b**, **6d**, **6e**, and **7** were isolated by column chromatography on silica gel. The results are summarized in Table 1.

An aqueous layer containing phosphoric acid derivative **1a** and potassium trifluoroacetate was

obtained. ^{31}P NMR (202 MHz; D_2O; 85% H_3PO_4) $\delta = 2.70$ ^{1}H NMR (500 MHz; D_2O; Me_4Si) $\delta = 0.83$ (6H, s, $(CH_3)_2CH_2O$); 3.78 (4H, d, $J_{H-P} = 11.7$, $(CH_3)_2CH_2O$).

Tert-butylammonium monothiophosphate **3b**. ^{31}P NMR (202 MHz; D_2O; 85% H_3PO_4) $\delta = 53.8$; ^{1}H NMR (500 MHz; D_2O; Me_4Si) $\delta = 0.83$ (3H$_a$, s, $(CH_3)_2CH_2O$); 1.18 (3H$_e$, s, $(CH_3)_2CH_2O$); 1.46 (9H, s, $C(CH_3)_3$); 3.68 (2H$_a$, dd, $J_{H_a-H_e} = 10.7$, $J_{H_a-P} = 24.4$, $(CH_3)_2CH_2O$); 4.26 (2H$_e$, dd, $J_{H_e-H_a} = 10.7$, $J_{H_e-P} = 3.91$, $(CH_3)_2CH_2O$).

Tert-butylammonium monoselenophosphate **3d**. ^{31}P NMR (202 MHz; D_2O; 85% H_3PO_4) $\delta = 44.6$, $J_{P-Se} = 745.3$; ^{1}H NMR (500 MHz; D_2O; Me_4Si) $\delta = 0.74$ (3H$_a$, s, $(CH_3)_2CH_2O$), 1.02 (3H$_e$, s, $(CH_3)_2CH_2O$), 1.23 (9H, s, $C(CH_3)_3$), 3.64 (2H$_a$, dd, $J_{H_a-H_e} = 11.2$, $J_{H_a-P} = 23.5$, $(CH_3)_2CH_2O$), 3.99 (2H$_e$, dd, $J_{H_e-H_a} = 10.7$, $J_{H_e-P} = 5.9$, $(CH_3)_2CH_2O$).

Tert-butylammonium selenothiophosphate **3e**. ^{31}P NMR (202 MHz; D_2O; 85% H_3PO_4) $\delta = 98.5$, $J_{P-Se} = 739.1$; ^{1}H NMR (500 MHz; D_2O; Me_4Si) $\delta = 0.85$ (3H$_a$, s, $(CH_3)_2CH_2O$), 0.98 (3H$_e$, s, $(CH_3)_2CH_2O$), 1.26 (9H, s, $C(CH_3)_3$), 3.79 (2H$_a$, dd, $J_{H_a-H_e} = 11.2$, $J_{H_a-P} = 20.0$, $(CH_3)_2CH_2O$). 4.00 (2H$_e$, dd, $J_{H_e-H_a} = 11.2$, $J_{H_e-P} = 1.2$, $(CH_3)_2CH_2O$).

Tert-butylammonium diselenophosphate **3f**. ^{31}P NMR (202 MHz; D_2O; 85% H_3PO_4) $\delta = 84.8$, $J_{P-Se} = 749.6$; ^{1}H NMR (500 MHz; D_2O; Me_4Si) $\delta = 0.91$ (6H, s, $(CH_3)_2CH_2O$); 1.25 (9H, s, $C(CH_3)_3$), 3.87 (4H, d, $J_{H-P} = 15.6$, $(CH_3)_2CH_2O$).

S-Pivaloyl (5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yl) disulfide **4b**. (Eluent: $CHCl_3$); mp 73–75°C; IR (KBr) $\nu = 1728$ (C=O), 1290 (P=O), 1005, 1054 (P–O–C) cm^{-1}; ^{31}P NMR (202 MHz; $CDCl_3$; 85% H_3PO_4) $\delta = 13.9$; ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) $\delta = 0.94$ (3H$_a$, s, $(CH_3)_2CH_2O$), 1.31 (3H$_e$, s, $(CH_3)_2CH_2O$), 1.32 (9H, s, $C(CH_3)_3$), 3.91 (4H$_a$, dd, $J_{H_a-H_e} = 11.2$, $J_{H_a-P} = 25.4$, $(CH_3)_2CH_2O$), 4.42 (4H$_e$, d, $J_{H_e-H_a} = 11.0$, $(CH_3)_2CH_2O$); ^{13}C NMR (126 MHz; $CDCl_3$; Me_4Si) $\delta = 20.2$, 21.8, 27.1, 32.4 (d, $J_{P-C} = 6.9$), 47.2, 78.8 (d, $J_{P-C} = 6.9$), 201.5; HR-EI-MS: $m/z = 298.0449$ ($C_{10}H_{19}O_4PS_2$ requires 298.0462).

S-Pivaloyl (5,5-dimethyl-2-seleno-1,3,2-dioxaphosphorinan-2-yl) selenosulfide **4f**. ^{31}P NMR (202 MHz; $CDCl_3$; 85% H_3PO_4) $\delta = 70.6$, $J_{P-Se} = 485.8$ Hz, $J_{P-Se} = 956.0$.

Bis-(2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl)diselenide **6d**. (Eluent: $CHCl_3$/ethyl acetate 1:1); mp 125–127°C; ^{31}P NMR (202 MHz; $CDCl_3$; 85% H_3PO_4) $\delta = 3.96$, $J_{P-Se} = 488.9$. Lit. [14]: mp 134–137°C (from methylene chloride-petroleum ether); ^{31}P NMR (202 MHz; $CDCl_3$; 85% H_3PO_4) $\delta = 4.69$, $J_{P-Se} = 497$.

Bis-(2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl) diselenide **6e**. (Eluent: $CHCl_3$/ethyl acetate 1:1); mp 123–125°C; ^{31}P NMR (202 MHz; $CDCl_3$; 85% H_3PO_4) $\delta = 67.2$, $J_{P-Se} = 471.3$. Lit. [17]: mp 128–130°C, ^{31}P NMR (24.3 MHz; benzene; 85% H_3PO_4) $\delta = 63.9$, $J_{P-Se} = 478$.

Pivaloyl disulfide **7**. (Eluent: $CHCl_3$/hexane 1:2); ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) $\delta = 1.37$ (18H, s, $C(CH_3)_3$). Lit. [18]: ^{1}H NMR (200.132 MHz; $CDCl_3$; Me_4Si) $\delta = 1.37$ (18H, s, $C(CH_3)_3$).

Monitoring of the Reaction of Monoselenophosphoric Acid Derivative **1b**, *Selenothiophosphoric Acid Derivative* **1e**, *Diselenophosphoric Acid Derivative* **1f** *with O-Thiopivaloyl-N-tert-butylhydroxylamine* **2** *in NMR Scale*

General Procedure. The mixture of 0.2 mmol potassium selenophosphate **1d–f** and 0.2 mmol TFA (trifluoroacetic acid) in 0.5 mL $CDCl_3$ was added to 0.1 mmol *O*-thiopivaloyl-*N*-tert-butylhydroxylamine **2** in 0.25 mL $CDCl_3$. Tert-butylammonium selenophosphate **3d–f** and potassium trifluoroacetate were filtered and ^{31}P NMR (202 MHz; $CDCl_3$; 85% H_3PO_4) spectrum recorded. Intensities of the signals are given in parentheses.

Monitoring of the reaction of monoselenophosphoric acid derivative **1d** *with O-thiopivaloyl-N-tert-butylhydroxylamine* **2** *with ^{31}P NMR technique at room temperature.* After 5 min: 24 h, 48 h; ^{31}P NMR $\delta = 6.63$, $J_{P-Se} = 485.8$, **6d**, (100%).

Monitoring of the reaction of selenothiophosphoric acid derivative **1e** *with O-thiopivaloyl-N-tert-butylhydroxylamine* **2** *with ^{31}P NMR technique at room temperature.* 5 min: ^{31}P NMR $\delta = 72.2$, $J_{P-Se} = 467.1$, **4e**, (100%). 24 h: ^{31}P NMR $\delta = 72.2$, $J_{P-Se} = 467.1$, **4e**, (82%); $\delta = 67.2$, $J_{P-Se} = 471.3$, **6e**, (18%). 48 h: ^{31}P NMR $\delta = 72.2$, $J_{P-Se} = 467.1$, **4e**, (60%); $\delta = 67.2$, $J_{P-Se} = 471.3$, **6e**, (35%). 96 h: ^{31}P NMR $\delta = 72.2$, $J_{P-Se} = 467.1$, **4e**, (45%); $\delta = 67.2$ $J_{P-Se} = 471.3$, **6e**, (42%).

S-Pivaloyl (5,5-dimethyl-2-thiono-1,3,2-dioxaphosphorinan-2-yl) Selenosulfide **4e**. It was isolated from the reaction mixture. IR (film) $\nu = 1668$ (C=O), 1043, 994 (P–O–C), 661 (P=S) cm^{-1}; ^{31}P NMR (202 MHz; $CDCl_3$; 85% H_3PO_4) $\delta = 72.2$, $J_{P-Se} = 467.1$; ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) $\delta = 0.98$ (3H$_a$, s, $(CH_3)_2CH_2O$), 1.27 (3H$_e$, s, $(CH_3)_2CH_2O$), 1.34 (9H, s, $C(CH_3)_3$), 3.98 (4H$_a$, dd, $J_{H_a-H_e} = 11.2$, $J_{H_a-P} = 23.4$, $(CH_3)_2CH_2O$), 4.32 (4H$_e$, dd, $J_{H_e-H_a} = 10.7$, $J_{H_e-P} = 6.8$,

$(CH_3)_2CH_2O$); ^{13}C NMR (126 MHz; $CDCl_3$; Me_4Si) $\delta = 21.2$, 22.5, 27.9, 32.8 (d, $J_{P-C} = 7.3$), 47.4, 78.8 (d, $J_{P-C} = 9.2$), 200.6. LR-MALDI-TOF $m/z = 385.9$ ($C_{10}H_{19}O_3PS_2$ ^{80}Se + Na requires 386.3).

Monitoring of the reaction of diselenophosphoric acid derivative **1f** *with O-thiopivaloyl-N-tert-butylhydroxylamine* **2** *with ^{31}P NMR (202 MHz; $CDCl_3$; 85% H_3PO_4) technique at room temperature.* 5 min: ^{31}P NMR $\delta = 70.6$, $J_{P-Se} = 485.8$, $J_{P-Se} = 956.0$, **4f**, (100%). 24 h: ^{31}P NMR $\delta = 70.6$, $J_{P-Se} = 485.8$, $J_{P-Se} = 956.0$, **4f**, (23%), decomposition was observed.

Reaction of Monothiophosphoric Acid Derivative **1b** *and Selenothiophosphoric Acid Derivative* **1e** *with O-Thiopivaloyl-N-tert-butylhydroxylamine* **2** *in the Presence of 2,6-Dimethylthiophenol*

The mixture of 0.2 mmol potassium monothiophosphate **5b** or potassium selenothiophosphate **5e**, 0.2 mmol TFA (trifluoroacetic acid), and 0.1 mmol 2,6-dimethylthiophenol in 0.5 mL $CDCl_3$ was added to 0.1 mmol *O*-thiopivaloyl-*N*-tert-butylhydroxylamine **2** in 0.25 mL $CDCl_3$. The reaction mixture was stirred for 30 min at room temperature. Then, triethylamine (1 mmol) was added and ^{31}P NMR spectrum was recorded. In the both cases, only one resonance signal appeared from respective phosphate anion: monothiophosphate ^{31}P NMR (202 MHz; $CDCl_3$; 85% H_3PO_4) $\delta = 54.4$; selenothiophosphate ^{31}P NMR (202 MHz; $CDCl_3$; 85% H_3PO_4) $\delta = 97.7$, $J_{P-Se} = 740.1$.

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