

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

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**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).

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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<sub>RN</sub>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<sub>3</sub> 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