

MAY DITHIOPHOSPHORIC ACID PARTICIPATE IN THE SET PROCESS?

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*Recently we have developed a convenient method for the synthesis of S-thioacyl dithiophosphates **1**, excellent thioacylating reagents. When hydroxylamines with one bulky group or two substituents on the nitrogen atom are treated with S-thioacyl dithiophosphates **1** O-thioacyl hydroxylamines **3** are produced exclusively. What is more important, compounds **3** undergo interesting reaction with dithiophosphoric acid **4** yielding amine and acyl thiophosphoryl disulfide **5**. The disulfide **5** can be formed as a product of thiophilic attack of the dithiophosphate anion on the thiocarbonyl group in protonated O-thioacyl hydroxylamine **3**. On the other hand, it is well known that dithiophosphate anions easily undergo one electron oxidation. Hence the dithiophosphate anion can act as single electron donor and disulfide **5** can be formed as a product of the SET reaction. The influence of light and radical traps strongly suggests that the second possibility operates in the reaction in focus.*

Keywords: Hydroxylamines; SET; thioacylation; thiohydroxamic acids

We have recently discovered that easily available S-thioacyl dithiophosphates **1** are excellent thioacylating agents. Mixed anhydrides of type **1** chemoselectively thioacylate nitrogen or sulfur nucleophiles in the presence of hydroxyl groups. This property allowed us to obtain hydroxythioamides, hydroxydithioesters, or thiohydroxamic acids as well, from substrates nonprotected on oxygen atom.¹ Particularly interesting is the synthesis of thiohydroxamic acids **2** in the reaction of hydroxylamines with mixed anhydrides **1**. Thiohydroxamic acids are a very important class of compounds from the technological, theoretical,

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