

On the Reaction of Bis(phosphothioyl)disulfanes with Hydroxamic Acids, Part I: Ionic versus Radical Reaction Pathways

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ABSTRACT: Among sodium *N*-alkyl-4-chlorobenzo-hydroxamates treated with bis(phosphothioyl)disulfanes $>P(S)SSP(S)<$ (where $>P(S)$ is phosphorothioyl, phosphonothioyl, and phosphinothioyl), only the *N*-methyl one yields quantitatively the respective *O*-phosphothioyl derivatives exhibiting complete inversion of configuration at phosphorus in a reaction whose products are inert toward dithiophosphate arising in the reaction. For branched *N*-alkyl benzo-hydroxamates, products of a SET process predominated. The mechanism of the title reaction is discussed. © 2008 Wiley Periodicals, Inc. *Heteroatom Chem* 19:271–282, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20423

INTRODUCTION

Disulfanes **1** have found wide practical application and are involved in some important technical processes. They are used as stabilizers for polymer compositions [1], vulcanization accelerators [2], antioxidant and antiwear additives in engine lubricant oil additives [3], and as highly effective sulfurizing agents [4] in organic synthesis. Some of them are physiologically active compounds with both insecticidal and fungicidal activity [5]. Phostex—a mixture of bis(dialkoxyphosphinethioyl)disulfanes—is

the only one representative of disulfanes **1** among commercial organophosphorus pesticides in use.

Chemical properties of bis(phosphothioyl)disulfanes **1** are not nearly as well documented as those of other phosphothioyl derivatives, but it is known that in **1**, like in other phosphorus pseudohalogenes, the reactive disulfane unit exhibits strong sulfur cationoid properties. The S–S bond is readily cleft by nucleophiles [6] and metal species [7] with formation of stable dithioacid anion or its metal complexes, respectively. Amines, cyanide, and organometallic compounds react in this manner. It should be emphasized that this mechanism is not exclusive. In situ generated dithioacid anion or an external nucleophile can dealkylate the disulfane when an alkoxy group is attached to the phosphorus. Thus, primary amines are able to dealkylate both methoxy- and isopropoxy-substituted disulfanes **1**.

There is still a pressing need to develop effective methods for detoxification of neurotoxic organophosphorus compounds. The reaction with supernucleophiles is one of the most frequently studied. For the first time, it was found that benzohydroxamic acids accelerate the hydrolysis of diisopropyl fluorophosphates (DFP) and isopropyl methylphosphonofluoridate (sarin) by the factor of 100 and even more at higher pH [8]. Also other phosphoric acid derivatives (mainly esters) hydrolysis mediated by hydroxamate **2** was investigated except for bis(phosphothioyl)disulfanes **1**. It was postulated that the corresponding *O*-phosphorylated hydroxamic acids are the primary products of hydroxamate-catalyzed hydrolysis, but they were never detected or isolated from aqueous media [9].

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