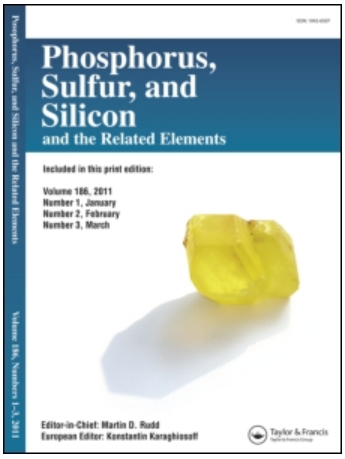

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Selenium Catalyzed Synthesis of Cyclic Thionecarbamates from Hydroxyisocyanides and Sulfur

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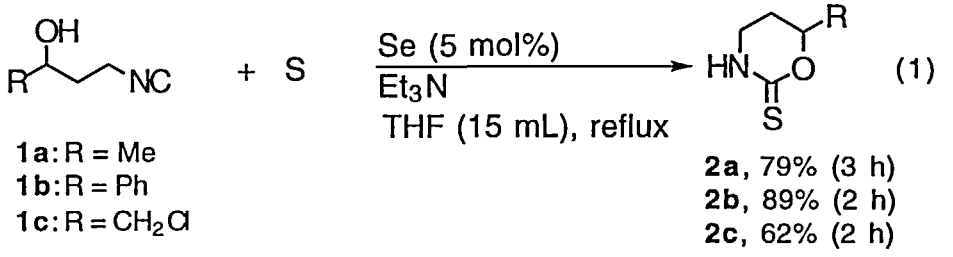
Abstracts 1,3-Oxazine-2-thiones were prepared from 3-hydroxyisocyanides and sulfur in the presence of catalytic amounts of selenium.

KEY WORDS: 1,3-oxazine-2-thione, 1,3-oxazine-2-selone, Se-S exchange

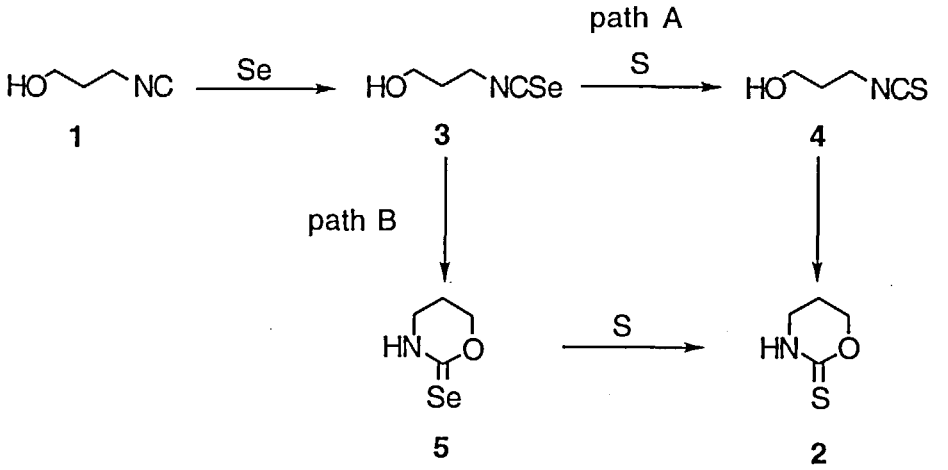
Cyclic thionecarbamates were usually prepared by the reaction of aminoalcohols with carbon disulfide or thiophosgen.[1] Recently, we have found that selenium[2] and tellurium[3] possess high catalytic activities for the formation of isothiocyanates from isocyanides and sulfur. These successful results led us to examine selenium catalyzed synthesis of cyclic thionecarbamates from hydroxyisocyanides and sulfur.

Treatment of 3-hydroxybutylisocyanide (**1a**, 2.5 mmol) with sulfur (3 mmol) in the presence of selenium (0.125 mmol, 5 mol% based on **1a**) and Et_3N (3 mmol) in refluxing THF for 3 h resulted in the formation of the corresponding 1,3-oxazine-2-thione **2a** in 79% yield (eq 1). Isocyanides **1b** and **1c** gave 1,3-oxazine-2-thiones **2b** and **2c** in 89% and 62% yields, respectively, under similar conditions.



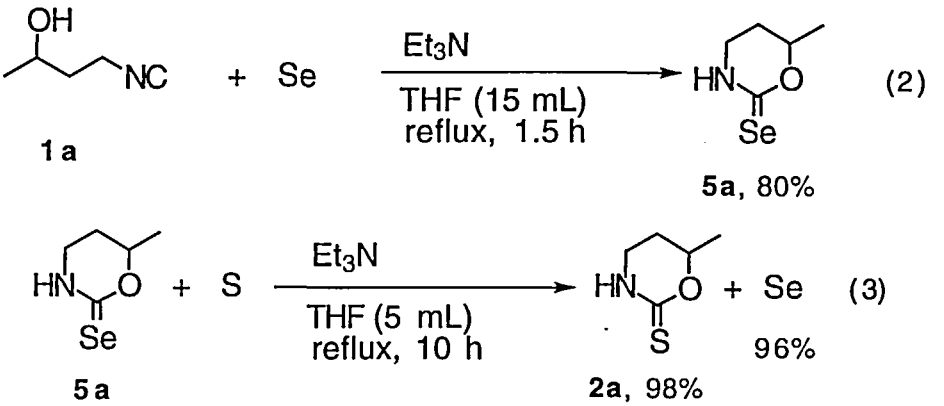
Plausible reaction paths are shown in Scheme 1. Hydroxyisocyanide **1** reacts with selenium to give isoselenocyanate **3**. Product **2** may be formed *via* Se-S exchange of **3** leading to isothiocyanate **4** followed by cyclization (path A) or cyclization of **3** giving

1,3-oxazine-2-selone **5** and the subsequent Se-S exchange (path B).



SCHEME 1. Plausible Reaction Paths

In order to test the possibility of path B, isocyanides **1a** (2.5 mmol) was treated with slightly excess amounts of selenium (3 mmol) in the presence of Et_3N (3 mmol) in refluxing THF for 1.5 h. After usual workup, 1,3-oxazine-2-selone **5a** was obtained in 80% yield (eq 2). However, the reaction of **5a** (2 mmol) with sulfur (2 mmol) in the presence of Et_3N (2 mmol) in refluxing THF was slow (eq 3), indicating that path B may not be a major process.



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