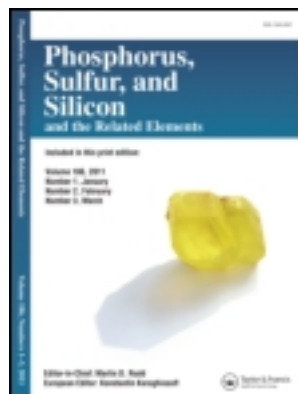


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### Synthesis of A New Class of Sulfurated and Selenated Silyl Heterocycles

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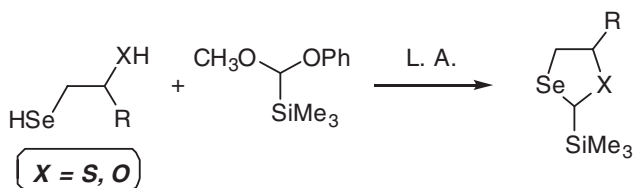
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## SYNTHESIS OF A NEW CLASS OF SULFURATED AND SELENATED SILYL HETEROCYCLES

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### GRAPHICAL ABSTRACT



**Abstract** 2-Trimethylsilyl-1,3-thiaselenolanes and 2-trimethylsilyl-1,3-oxaselenolanes can be accessed through the reaction of a silyl acetal with  $\beta$ -mercapto- and  $\beta$ -hydroxyselenols under Lewis acid conditions.

**Keywords** Selenoheterocycles; silyl acetal;  $\beta$ -functionalized selenols; lewis acid

## INTRODUCTION

Sulfur containing heterocycles have been extensively studied along the years for the important role played in many chemical and biochemical transformations. Our interest in the chemistry of both sulfur and silicon containing molecules led us to disclose a novel methodology for the synthesis and functionalization of 2-silyl five-membered sulfurated heterocycles.<sup>1</sup> We found that a convenient way to access such molecules was through the reaction of bromo(methoxy)methyl trimethylsilane with 1,2-dithiols,  $\beta$ -mercaptoalcohols, and  $\beta$ -mercaptoamines leading to the formation of silylated 1,3-dithiolanes,<sup>2</sup> 1,3-oxathiolanes,<sup>3</sup> and 1,3-thiazolidines,<sup>4</sup> respectively.

Besides thiaheterocycles, the related seleno-containing analogues are also interesting compounds, generally characterized by a relevant bioactivity. The chemistry of organoselenium derivatives in fact has recently attracted an increasing attention, due to the fact that several selenated molecules have been demonstrated as useful intermediates either from a synthetic and biologic point of view.<sup>5</sup> They are used in the synthesis of heterocyclic

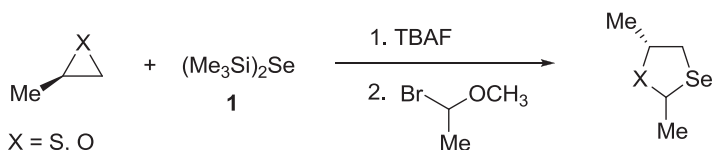
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compounds<sup>6</sup> or to obtain selenium containing cyclic structures.<sup>7</sup> Differently substituted 1,3-thiaselenolanes<sup>8</sup> and 1,3-oxaselenolanes<sup>9</sup> have been reported, but to the best of our knowledge no example appeared for the synthesis of silylated seleno-heterocycles.

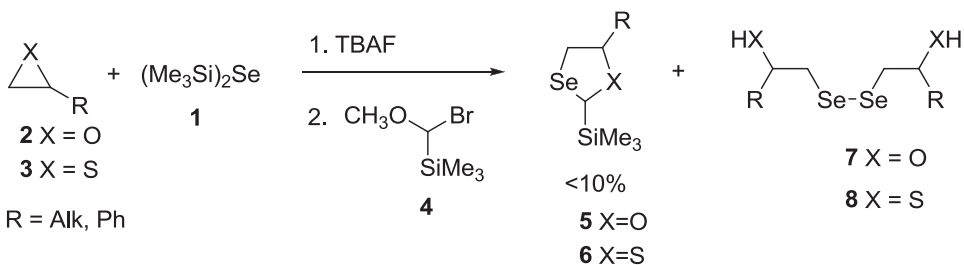
## RESULTS AND DISCUSSION

Our long dated interest in the chemistry of organosilanes led us to describe a convenient method to access 1,3-thiaselenolanes and 1,3-oxaselenolanes through the reaction of bis(trimethylsilyl)selenide (HMDSS) **1** and episulfides or epoxides, under TBAF catalysis,<sup>10</sup> followed by the treatment of the *in situ* generated 1-bromo-1-methoxyethane (Scheme 1).



Scheme 1

With the aim to obtain the silylated heterocycles, epoxides **2** and episulfides **3** were reacted under similar conditions, this time in the presence of bromo(methoxy)methyl trimethylsilane **4** and TBAF, but the desired silyl seleno-heterocycles **5**, **6** were formed in very poor yields, and the corresponding  $\beta$ -substituted diselenides **7**, **8** were the major products isolated (Scheme 2).



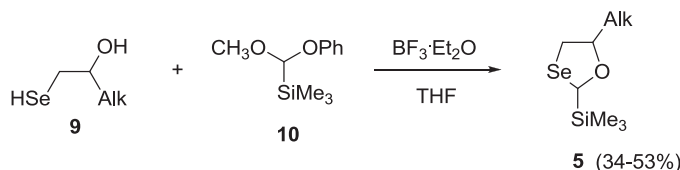
Scheme 2

This result could be ascribed to the presence of TBAF, which can induce the desilylation of the bromo derivative **4**, thus decreasing its reactivity.

Thus, taking advantage of our recent findings on the synthesis of  $\beta$ -functionalized selenols,<sup>11</sup>  $\beta$ -hydroxyselenols **9** (obtained through the reaction of epoxides and HMDSS under strictly controlled conditions) were reacted with bromo(methoxy)methyl silane **4**, but no formation of the desired silyl-oxaselenolanes **5** was observed. A similar result was obtained when  $\beta$ -mercaptoselenols were treated with **4**, no trace of the silylated 1,3-thiaselenolanes **6** was isolated. In both cases, a complex mixture of products was evidenced.

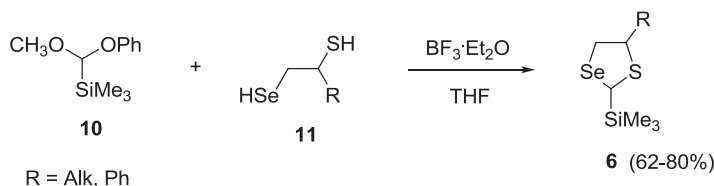
Thus, we thought to perform the reaction under different conditions to minimize deleterious processes and we reasoned that a silyl acetal could behave as a good precursor for the reaction with selenols.

Then, methoxy(phenoxy)methyl trimethylsilane **10**, obtained from **4** and phenol, was treated with selenols **9** in the presence of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ . Under these conditions the wanted 5-substituted-2-silyl-1,3-oxaselenolanes **5** could be obtained as ca. 2:1 mixture of isomers, depending on the nature of the substituent (Scheme 3).



Scheme 3

This reactivity can be efficiently extended to  $\beta$ -mercaptoselenols **11**, leading this time to differently substituted 2-silyl-1,3-thiaselenolanes **6** as mixture of *cis* and *trans* diastereoisomers (Scheme 4).



Scheme 4

The so obtained silyl-1,3-thiaselenolanes were usually isolated in higher yield with respect to the oxygenated analogues, thus evidencing that the heteroatom could play a crucial role in this kind of reactions.

In conclusion, this procedure discloses a novel and mild access to this new class of selenated silyl-heterocycles, whose functionalization with electrophiles is now under investigation.

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