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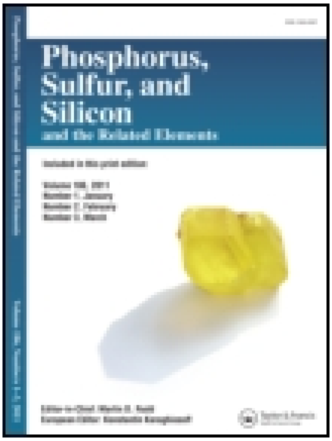

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Selenosilanes Mediated Stereoselective Synthesis of Polyfunctionalized Organic Molecules

Alessandro Degl'Innocenti [a] , Antonella Capperucci [a] , Giulio Castagnoli [a] , Irene Malesci [a] , Caterina Tiberi [a] & Brunella Innocenti [a]
[a] Università di Firenze, Dipartimento di Chimica Organica and HBL , Sesto Fiorentino, Italy

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Selenosilanes Mediated Stereoselective Synthesis of Polyfunctionalized Organic Molecules

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Università di Firenze, Dipartimento di Chimica Organica and HBL, Sesto Fiorentino, Italy

Bis(trimethylsilyl)selenide (HMDSS) acts as an efficient reagent in the TBAF catalyzed reaction with different substituted epoxides, episulfides, and aziridines, leading to β-functionalized diselenides in a highly regio- and stereoselective way. When using α-bromo alkyl ethers as trapping agent, 1,3-oxaselenolanes and 1,3-thiaselenolanes can be isolated, while 1,3-selenazolidines could be obtained through reduction of β-amino diselenides followed by in situ treatment with different aldehydes.

Keywords Silyl-selenide; epoxides; episulfides; aziridines; selenoheterocycles

INTRODUCTION

The chemistry of organoselenium compounds is of great interest both from the synthetic and biologic point of view.[1] Selenated reagents are in fact used either as useful intermediates in the synthesis of heterocyclic compounds[2] or in the synthesis of selenium containing cyclic structures.[3] Although a number of synthetic processes based on selenium chemistry have been reported along the years, little is known about methodologies based on the reactivity of selenosilanes.

Our long dated interest in the chemical behavior of bis(trimethylsilyl)sulfide (HMDST), led us to elucidate its efficiency as a useful reagent in the delivery of sulfur functionalities, such as the generation of a variety of thiocarbonyl compounds.[4] More recently we reported the TBAF catalyzed reaction of a range of substituted epoxides with HMDST, that smoothly afforded a direct and simple

Address correspondence to Alessandro Degl'Innocenti, Università di Firenze, Dipartimento di Chimica Organica and HBL, Via della Lastruccia 13, 50019 Sesto Fiorentino, Italy. E-mail: alessandro.deglinnocenti@unifi.it

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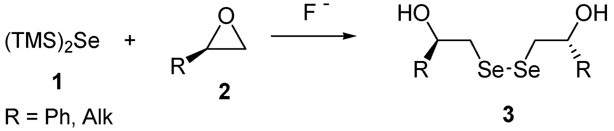
access to β-mercaptoalcohols in a highly regio- and stereoselective way.[5]

On the other hand, the chemistry of the corresponding selenium derivative, bis(trimethylsilyl)selenide (HMDSS, TMS-Se-TMS)[6] has received much less attention, despite the relevance that organoselenium compounds have actually gained. To the best of our knowledge, only few reports dealing with the reactivity of silyl selenides with heterocyclic rings have been reported. In particular, reactions of phenylseleno(trimethylsilane) towards tetrahydrofurans[7] and epoxides,[8] under Lewis acid (ZnI_2) or basic conditions (n-BuLi) were described. Lewis acid catalyzed reaction of epoxides with the related $PhSeSnBu_3$ has also been reported.[9] On the contrary, a large number of papers concerning the reactivity of diselenides and different selenium anions with epoxides have been described in the literature.[10]

RESULTS AND DISCUSSION

In this letter we want to report on our recent findings on the reactivity of hexamethyldisilaselenane (HMDSS) **1** with epoxides **2** that affords a highly regioselective ring opening of these small membered heterocyclic rings under TBAF catalysis (Scheme 1).



SCHEME 1

Several attempts to isolate the β-hydroxy silyl selenide (or selenol) intermediates were unsuccessful, and the corresponding β-hydroxy diselenides **3** were always obtained. The reaction proved quite general, occurring with aliphatic and aromatic substituents on the epoxide. When enantiopure oxiranes are reacted, optically active β-hydroxy diselenides were regioselectively formed. The described reactivity is not limited to epoxides, but may be conveniently extended to other ring strained heterocycles, such as episulfides **4** and *N*-tosyl-aziridines **5**, leading to a convenient access to several β-mercapto diselenides **6** and β-amino diselenides **7**, respectively (Scheme 2).

Attack generally occurs at the less hindered position to provide ring-opening products. With the aim to gain evidence for the formation of the transient β-functionalized silyl selenides, the reaction of three-membered heterocycles with HMDSS was run in the presence of an

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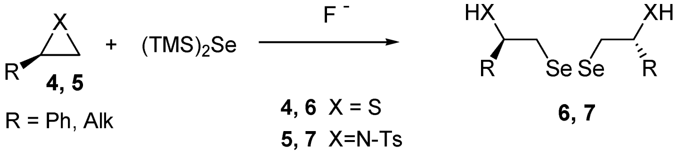
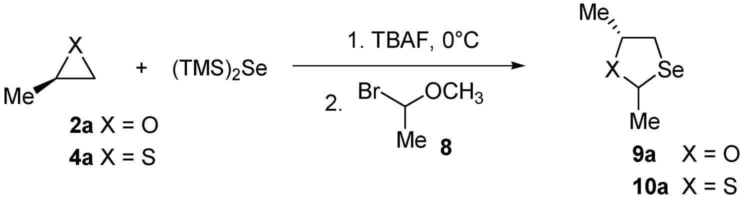


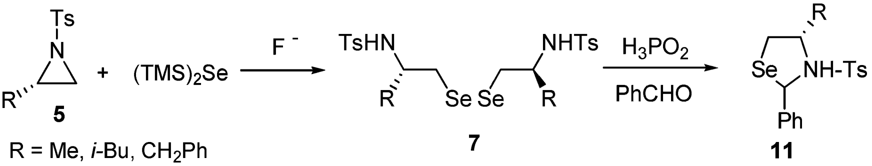
SCHEME 2

aldehyde under TBAF catalysis, but no evidence of the formation of the desired pentaatomic heterocycles was detected. Nevertheless, when 2-methyloxirane **2a** and 2-methylthiirane **4a** were treated with HMDSS in the presence of the more reactive 1-bromo-1-methoxyethane **8**,[11] the expected 1,3-oxaselenolane **9a** and 1,3-thiaselenolane **10a** were obtained (Scheme 3), arising from the in situ trapping of the β-hydroxy silyl selenide intermediate by the bromo derivative, with a d.r. of 94:6 and 70:30, respectively.



SCHEME 3

In these conditions, 1,3-selenazolidines were unfortunately obtained in very poor yield (ca. 10%). Thus, taking advantage of the possible reduction of diselenides in acidic medium by hypophosphorous acid,[12] β-amino diselenides **7** were reacted with H_3PO_2 and in situ treated with benzaldehyde (Scheme 4). Under these conditions, the reaction afforded the desired 1,3-selenazolidines **11** in good yields, with the formation of different *N*-tosyl-2-phenyl-4-substituted heterocycles, as a mixture of *cis* and *trans* diastereoisomers.



SCHEME 4

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