Phosphorus, Sulfur, and Silicon and the Related Elements

Synthesis of A New Class of Sulfurated and Selenated Silyl Heterocycles

Antonella Capperucci, Damiano Tanini, Alessandro Degl’Innocenti

Dipartimento di Chimica “Ugo Schiff”, Università di Firenze, Via della Lastruccia, 13 - I-50019, Sesto Fiorentino, Italy

Accepted author version posted online: 17 Sep 2012. Published online: 29 May 2013.

To cite this article: Antonella Capperucci, Damiano Tanini & Alessandro Degl’Innocenti (2013): Synthesis of A New Class of Sulfurated and Selenated Silyl Heterocycles, Phosphorus, Sulfur, and Silicon and the Related Elements, 188:4, 437-440

To link to this article: http://dx.doi.org/10.1080/10426507.2012.727518

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.
SYNTHESIS OF A NEW CLASS OF SULFURATED AND SELENATED SILYL HETEROCYCLES

Antonella Capperucci, Damiano Tanini, and Alessandro Degl’Innocenti
Dipartimento di Chimica “Ugo Schiff”, Università di Firenze, Via della Lastruccia, 13 - I-50019, Sesto Fiorentino, Italy

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 β-mercapto- and β-hydroxyselenols under Lewis acid conditions.

Keywords Selenoheterocycles; silyl acetal; β-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.\(^1\) We found that a convenient way to access such molecules was through the reaction of bromo(methoxy)methyl trimethylsilane with 1,2-dithiols, β-mercaptoalcohols, and β-mercaptoamines leading to the formation of silylated 1,3-dithiolanes,\(^2\) 1,3-oxathiolanes,\(^3\) and 1,3-thiazolidines,\(^4\) 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.\(^5\) They are used in the synthesis of heterocyclic
compounds or to obtain selenium containing cyclic structures. Differently substituted 1,3-thiaselenolanes and 1,3-oxaselenolanes 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) and episulfides or epoxides, under TBAF catalysis, 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 and episulfides were reacted under similar conditions, this time in the presence of bromo(methoxy)methyl trimethylsilane and TBAF, but the desired silyl seleno-heterocycles, were formed in very poor yields, and the corresponding β-substituted diselenides 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, thus decreasing its reactivity.

Thus, taking advantage of our recent findings on the synthesis of β-functionalized selenols, β-hydroxyselenols (obtained through the reaction of epoxides and HMDSS under strictly controlled conditions) were reacted with bromo(methoxy)methyl silane, but no formation of the desired silyl-oxaselenolanes was observed. A similar result was obtained when β-mercaptoselenols were treated with 4, no trace of the silylated 1,3-thiaselenolanes 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 BF\textsubscript{3} \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).

```
\begin{center}
\begin{tikzpicture}
  \node (A) at (0,0) [draw] {\text{CH}_3\text{O} \text{OPh}};
  \node (B) at (1,0) [draw] {\text{SiMe}_3};
  \node (C) at (0,-1) [draw] {\text{HSe} \text{OH}};
  \node (D) at (1,-1) [draw] {\text{SiMe}_3};
  \draw (A) -- (B);
  \draw (B) -- (D);
  \draw (A) -- (C);
  \draw (C) -- (D);
  \node at (0.5,0.5) {\text{Alk}};
  \node at (0.5,-0.5) {\text{Alk}};
  \node at (1.5,0) {\text{Alk}};
  \node at (1.5,-1) {\text{Alk}};
  \draw (A) -- (B);
  \draw (B) -- (D);
  \draw (A) -- (C);
  \draw (C) -- (D);
  \node at (0.5,0.5) {\text{Alk}};
  \node at (0.5,-0.5) {\text{Alk}};
  \node at (1.5,0) {\text{Alk}};
  \node at (1.5,-1) {\text{Alk}};
 \end{tikzpicture}
\end{center}
```

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).

```
\begin{center}
\begin{tikzpicture}
  \node (A) at (0,0) [draw] {\text{CH}_3\text{O} \text{OPh}};
  \node (B) at (1,0) [draw] {\text{SiMe}_3};
  \node (C) at (0,-1) [draw] {\text{HSe} \text{OH}};
  \node (D) at (1,-1) [draw] {\text{SiMe}_3};
  \draw (A) -- (B);
  \draw (B) -- (D);
  \draw (A) -- (C);
  \draw (C) -- (D);
  \node at (0.5,0.5) {\text{R}};
  \node at (0.5,-0.5) {\text{R}};
  \node at (1.5,0) {\text{R}};
  \node at (1.5,-1) {\text{R}};
  \draw (A) -- (B);
  \draw (B) -- (D);
  \draw (A) -- (C);
  \draw (C) -- (D);
  \node at (0.5,0.5) {\text{R}};
  \node at (0.5,-0.5) {\text{R}};
  \node at (1.5,0) {\text{R}};
  \node at (1.5,-1) {\text{R}};
 \end{tikzpicture}
\end{center}
```

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.

REFERENCES