



Direct synthesis of fused 1,2,5-selenadiazoles from 1,2,5-thiadiazoles



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ABSTRACT

A short and convenient synthesis of fused 1,2,5-selenadiazoles from the corresponding 1,2,5-thiadiazoles and selenium dioxide has been developed.

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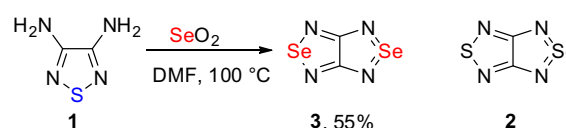
Compounds containing the 1,2,5-selenadiazole moiety have attracted significant attention in various fields of fundamental and applied chemistry, biomedicine, and technology. Recent interest in 1,2,5-selenadiazole derivatives, especially fused with aromatic and/or heterocyclic rings, is due to their potential applications as building blocks in the design and synthesis of organic light emitters, solar cells, electric conductors, molecular magnets, as well as agrochemicals and pharmaceuticals for preventive and therapeutic medical treatment.^{1–3}

The most common method for the preparation of 1,2,5-selenadiazoles is via the reaction of *vicinal* diamines with selenium-containing reagents, often with cheap and easy-to-use selenium dioxide (SeO₂).^{1–3} Although this protocol is well elaborated for benzo-fused 1,2,5-selenadiazoles, that is, 2,1,3-benzoselenadiazoles, there is still lack of methods for the synthesis of heterocycle-fused derivatives, particularly aza-heterocycles. The sulfur congeners of selenadiazoles, that is, 1,2,5-thiadiazoles, are much more readily available, and methods for their preparation are numerous.^{1a,4} Benzo-fused 1,2,5-thiadiazoles, that is, 2,1,3-benzothiadiazoles, can serve as starting materials for the corresponding selenadiazoles in two-step syntheses including their reduction to 1,2-benzenediamines followed by treatment with SeO₂ or, rarely,

selenium tetrachloride (SeCl₄).^{1a,5–10} The approach covers both hydrocarbon^{5–9} and fluorocarbon¹⁰ analogues.^{1a}

We have studied the reaction between 3,4-diamino-1,2,5-thiadiazole (**1**) and SeO₂ in the hope for improved access to known [1,2,5]selenadiazolo[3,4-*c*][1,2,5]thiadiazole (**2**)¹¹ and found that by heating at 100 °C in dimethylformamide (DMF), [1,2,5]selenadiazolo[3,4-*c*][1,2,5]selenadiazole (**3**) was formed in moderate yield (Scheme 1). Previously, compound **3** was only observed as a very minor side product in the synthesis of **2** from diamine **1** and SeCl₄.¹¹

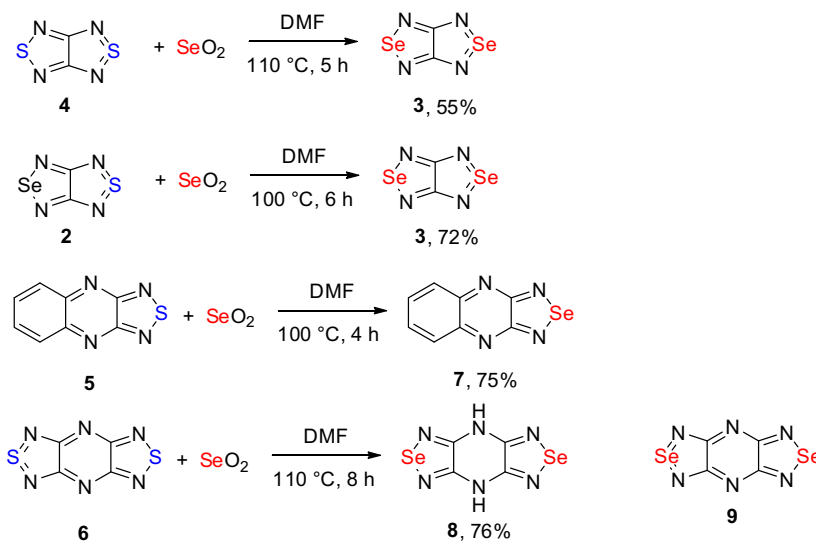
The main feature of the found transformation is that two processes occur in the same pot: formation of a 1,2,5-selenadiazole ring via condensation of a *vic*-diamine with SeO₂, and exchange of the sulfur atom in the 1,2,5-thiadiazole ring with a selenium atom. The conversion of 1,2,5-thiadiazoles into 1,2,5-selenadiazoles has, to the best of our knowledge, not been reported. In this



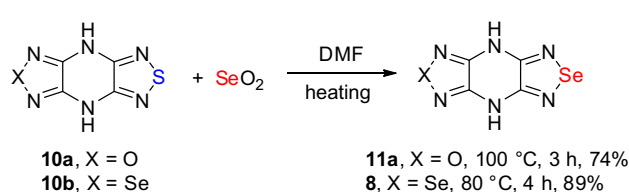
Scheme 1. Synthesis of [1,2,5]selenadiazolo[3,4-*c*][1,2,5]selenadiazole (**3**) from 3,4-diamino-1,2,5-thiadiazole (**1**).

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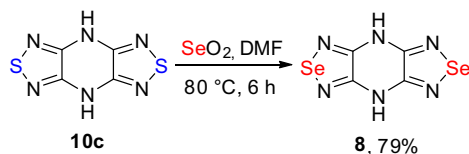
E-mail address: orakitin@ioc.ac.ru (O.A. Rakitin).



Scheme 2. Synthesis of 1,2,5-selenadiazoles from the corresponding thiadiazoles.



Scheme 3. Synthesis of 4*H*,8*H*-[1,2,5]oxa- (**11a**) and seleno- (**8**) diazolo[3,4-*b*][1,2,5]selenadiazolo[3,4-*e*]pyrazines from thiadiazoles **10**.



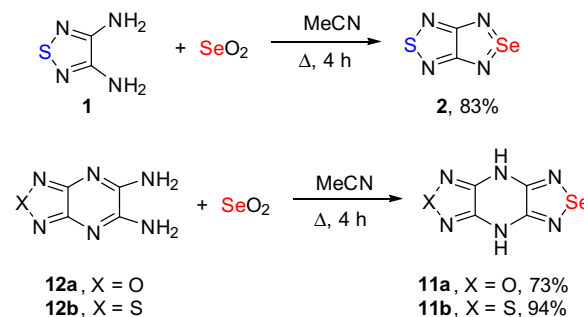
Scheme 4. Synthesis of 4*H*,8*H*-bis[1,2,5]selenadiazolo[3,4-*b*:3',4'-*e*]pyrazine **8** from the corresponding bisthiadiazole **10c**.

Letter we report the synthesis of fused 1,2,5-selenadiazoles from the corresponding thiadiazoles and SeO_2 .

In an attempt to develop general direct syntheses of 1,2,5-selenadiazoles from thiadiazoles, the latter were reacted with SeO_2 . Treatment of 1,2,5-thiadiazoles fused with electron-acceptor heterocycles, such as 1,2,5-thiadiazole (**4**), 1,2,5-selenadiazole (**2**), quinoxaline (**5**), and thiadiazolopyrazine (**6**), with SeO_2 in different organic solvents (chloroform, benzene, THF, ethanol, 1,4-dioxane) under reflux gave no reaction, and the starting compounds were recovered in almost quantitative yield. In contrast, the reaction of thiadiazoles with SeO_2 in DMF started at 80–100 °C. After prolonged heating at these temperatures, the corresponding mono- (**7**) and bis-1,2,5-selenadiazoles (**3**, **8**) were obtained in good yields (**Scheme 2**).

The formation of 4*H*,8*H*-bis[1,2,5]selenadiazolo[3,4-*b*:3',4'-*e*]pyrazine **8** instead of the expected bis-selenadiazolo-pyrazine **9** can be explained by reduction of **9** with the water liberated by decomposition of SeO_2 in DMF.

4*H*,8*H*-[1,2,5]Oxadiazolo[3,4-*b*][1,2,5]thiadiazolo[3,4-*e*]pyrazine (**10a**) and its Se congener (**10b**) reacted with SeO_2 similarly to



Scheme 5. Synthesis of fused 1,2,5-selenadiazoles from vicinal diamines.

afford selenadiazoles **11a** and **8** in high yields (**Scheme 3**). The isolation of compound **11a** indicates that the 1,2,5-oxadiazole ring remains unchanged under the reaction conditions favorable for transformation of the 1,2,5-thiadiazole ring into a selenadiazole.

In the case of 4*H*,8*H*-bis[1,2,5]thiadiazolo[3,4-*b*:3',4'-*e*]pyrazine **10c**, two sulfur atoms were exchanged for selenium atoms, as with the other bis-thiadiazoles, **4** and **6**. These findings indicate that in DMF the reaction cannot be stopped after substitution of only one sulfur atom (**Schemes 2** and **4**).

With the aim of obtaining unsymmetrical mono-selenadiazoles, the reactions between heteroaromatic vicinal diamines with SeO_2 were studied. Further investigation of the reaction between diamino thiadiazole **1** and SeO_2 showed that the transformation can be stopped at selenadiazolo-thiadiazole **2** by using acetonitrile as the solvent. Heating the reaction mixture for four hours at reflux led to bicycle **2** in high yield. We extended this reaction to other vicinal diamines, for example, [1,2,5]oxadiazolo[3,4-*b*]pyrazine-5,6-diamine **12a** and its S congener **12b**. Fused unsymmetrical selenadiazoles **11a,b** were obtained in moderate to high yields on reaction with SeO_2 in MeCN (**Scheme 5**).

We attempted to extend this reaction to other benzo-fused and monocyclic 1,2,5-thiadiazoles. It was found that substituted 2,1,3-benzothiadiazoles and the uncondensed 1,2,5-thiadiazoles shown in **Figure 1** did not react with SeO_2 in different organic solvents under forcing conditions (refluxing in chloroform, benzene, THF, ethanol, 1,4-dioxane, or heating in DMF or DMSO at 100 °C for 10 h).

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