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One-pot assembling of selenazolines from elemental selenium, alkenes and acetonitrile

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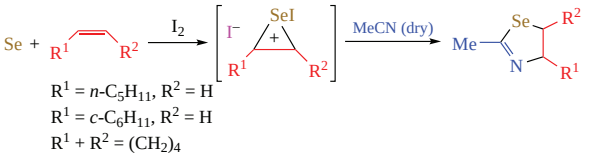
A new method for assembling 1,3-selenazolines by the iodine-mediated reaction of the simplest building blocks such as elemental selenium, alkenes and acetonitrile has been discovered. A proposed mechanism includes the addition of the intermediate selenium iodides to alkene with subsequent solvent interception by the formed seleniranium ion.

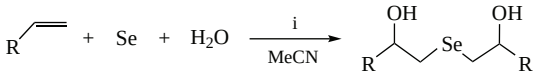


Keywords: selenium, organoselenium compounds, alkenes, acetonitrile, iodine assistance, solvent interception, 1,3-selenazolines.

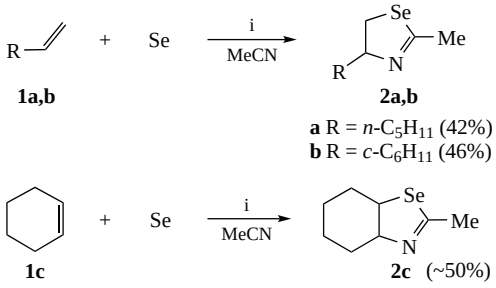
An ongoing interest in developing new methods for the synthesis of five-membered Se,N-containing heterocycles including 1,3-selenazoles and 1,3-selenazolines is due to different types of biological activity demonstrated by these compounds.[1] As a rule, the construction of selenazoline heterocycle is performed in several steps or with the application of hardly accessible selenium sources, *e.g.* highly toxic selenoureas and their analogues,[2] β-azido diselenides,[3] or selenoamides[4] (see Online Supplementary Materials, Scheme S1). To the best of our knowledge, the only approach utilizing elemental selenium is its reaction with *N*-acyloxazolidinones, which, in turn, have to be synthesized by acylation of oxazolidinones.[5]

Recently, we have first reported the synthesis of β-hydroxy selenides *via* the iodine-assisted reaction of elemental selenium with alkenes in aqueous acetonitrile (Scheme 1).[6] The proposed mechanism includes the formation of selenium iodides, elusive intermediates detected only by NMR,[7] or their selenium iodine cations with counterions of strong acids.[8]

Herein, we report on an unexpected change of the reaction course by carrying out the iodine-assisted transformation of



Scheme 1 *Reagents and conditions*: i, MeCN/H_2O (7 : 1 v/v), I_2 (1 equiv.), room temperature, 40 h.



Scheme 2 *Reagents and conditions*: i, MeCN (dry), I_2 (1 equiv.), room temperature, 24 h.

elemental selenium with alkenes in nonaqueous acetonitrile (Scheme 2).

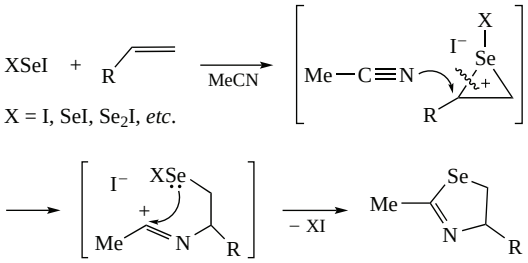
The reaction of equimolar amounts of finely ground selenium and iodine with twofold excess of alkene proceeds under mild conditions (room temperature, no catalyst) and represents a novel method for assembling 1,3-selenazoline skeleton from the simplest building blocks such as elemental selenium, alkene and acetonitrile (the solvent) in one preparative step. The isolated yields of 2-methyl-1,3-selenazolines **2a**,**b** after column chromatography relative to the consumed selenium (71 and 62%, respectively) are 42 and 46%. The fused bicyclic product **2c** (the yield estimated by NMR is ~50% at 48% conversion of selenium taken) is less stable and cannot be isolated by column chromatography. Its structure was proved by ^{1}H, ^{13}C, ^{77}Se NMR spectroscopy and HRMS of the crude material. Note, that the {^{77}Se–^{1}H} 2D NMR spectra of compounds **2a**,**b** show cross peaks of Se atom with diastereotopic protons of the endocyclic methylene group (^2J) and the 2-methyl group (^3J), but not with the 4-CH proton (see Online Supplementary Materials).†

A tentative mechanism includes oxidation of elemental selenium with iodine to produce reactive intermediates [XSeI] which would add to alkenes to form seleniranium cations (Scheme 3). The latter are attacked by the molecule of acetonitrile as an N-nucleophile at the substituted carbon atom with the ring opening and subsequent ring closure.

The proposed mechanism nicely explains the observed difference between the reaction courses in aqueous and dry acetonitrile (see Schemes 1 and 2). In aqueous acetonitrile, the

† *General procedure for the preparation of 1,3-selenazolines* **2a**–**c**. To a mixture of finely ground elemental selenium (0.158 g, 2 mmol) and iodine (0.508 g, 2 mmol), hept-1-ene (0.392 g, 4 mmol) and dry acetonitrile were added, and this was stirred at room temperature for 24 h. Then, saturated $Na_2S_2O_3$ solution (4 ml) and chloroform (10 ml) were added, the unreacted selenium (0.06 g, conversion 71%) was filtered off. The filtrate was diluted with water (15 ml) and extracted with chloroform (2 × 10 ml), solvent was removed in vacuum, the residue was purified on a silica column with CCl_4 and $CHCl_3$ as successive eluents to give compound **2a** (0.130 g, 42% to the converted selenium).

Compounds **2b** and **2c** were prepared in a similar way. For details, see Online Supplementary Materials.



Scheme 3

acting nucleophile is the water molecule whose O-nucleophilicity is increased due to hydrogen bonding with the nitrogen atom of acetonitrile.[9] The N-nucleophilicity of pure acetonitrile is much higher than that of acetonitrile in the presence of water[10] allowing it to react as an N-nucleophile.

The use of other nitriles was unsuccessful: no products could be isolated from the reactions in butyronitrile or benzonitrile. This result is consistent with the earlier results on solvent interception in oxidative amidation, where the reaction in nitriles other than acetonitrile either did not afford the products of solvent interception,[11] or showed lower yields.[12]

To summarize, we have discovered a new method for assembling 1,3-selenazolines from the simplest components such as elemental selenium and alkenes with interception of the molecule of the solvent MeCN by carrying out the process in dry acetonitrile. The use of non-aqueous solvent is crucial, as it changes the reaction route by increasing the nucleophilicity of the solvent relative to that in the presence of water and allowing it to act as an N-nucleophile.

The spectral data were obtained using the equipment of the Baikal Analytical Center for collective use of Siberian Branch of the Russian Academy of Sciences. We thank Dr. A. V. Kuzmin for HRMS measurements, and Dr. S. V. Zinchenko for recording {^{77}Se–^{1}H} 2D NMR spectra.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.05.035.

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