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Letter

Serendipitous Formation of Various Selenium Heterocycles Hidden in the Classical Synthesis of Selenophene

Patrycja Męcik, Bartłomiej Pigulski,* and Sławomir Szafert*

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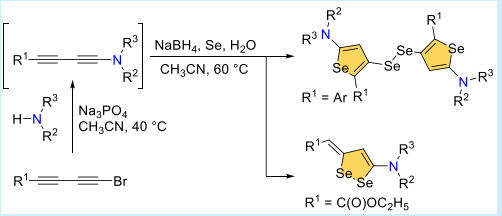
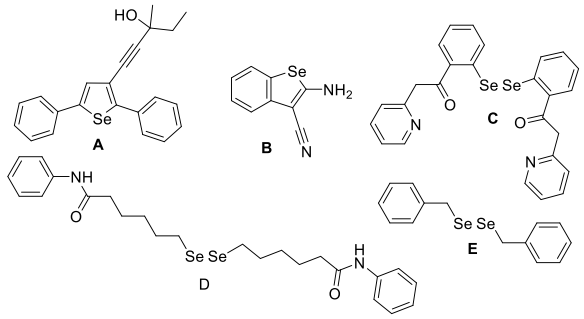
ABSTRACT: Synthesis of complex di(selenophen-3-yl)diselenides and 3-methylene-3*H*-1,2-diselenoles directly from 1-bromobutadiynes is described. The transformation is performed under conditions used before for the synthesis of simple selenophenes from butadiynes. The reaction is operationally straightforward, and complex products were obtained in high yields. Structures of the final products were unambiguously confirmed by the means of ^{77}Se NMR and single-crystal X-ray diffraction.



Swedish chemist Berzelius discovered the element selenium in 1817[1] and named it after the Greek goddess of the moon, Selene.[2] History of organoselenium chemistry might be dated to 1836, when the synthesis of diethylselenium was reported by Löwig.[3] Since then the chemistry of organoselenium compounds is gaining more attention due to the potential these compounds have as biologicaly active substances.[2] For instance, selenophenes are valued due to their antitumoral,[4] anticonvulsant[5] (Scheme 1A), and other

Scheme 1. Examples of Bioactive Selenophenes and Diselenides



medicinal applications. In addition to that, biologically active substances exhibiting hepatoprotective[6] or antiviral and antibacterial properties were reported (Scheme 1B).[7] For instance, diselenide C is a mimic of the glutathione peroxidase enzyme,[8] D is an antioxidant,[8a] and E is to possess chemopreventive properties (Scheme 1).[8b,9] It is worth noting that naturally occurring amino acid selenocysteine forms Se−Se bridges in natural and artificial selenoproteins.[10] Interestingly, currently only a very few examples of the synthesis of diselenide-bridged diselenophene have been reported due to synthetic difficulties.[11]

In view of the above, new synthetic protocols leading to substituted selenophenes and other selenium heterocycles are very interesting targets of research. Generally, selenophenes might be synthesized[12] by an addition of nucleophilic,[13] electrophilic,[14] or radical selenium reagents.[15] For instance, reaction of hexane-2,5-dione with phosphorus pentaselenide,[16] isomerization of (*Z*,*Z*)-1,4-bis(alkylseleno)-1,3-butadienes,[17] or reaction of butylselanyl propargyl alcohols with iodine[18] were reported. However, since a [1 + 4] annulation of selenides with conjugated 1,3-butadiynes is the most common method,[19] we decided to take advantage of our synthetic methodology for substituted thiophenes[20] and use the known 1-aminobutadiynes for the synthesis of new 2-aminoselenophenes. We adopted well-established literature conditions,[21] but surprisingly the use of such butadiynes led to different types of products than simple selenophenes. Here we report the unprecedented synthesis of di(selenophen-3-yl)diselenides and 3-methylene-3*H*-1,2-diselenoles from 1-aminobutadiynes, which were directly generated from 1-bromobutadiynes. Analogous reaction with the use of elemental tellurium under the same conditions gave the expected simple tellurophenes.

The reaction protocol is shown in Scheme 2. First 1-aminobutadiynes **2** were generated from 1-bromobutadiynes **1** using our modified conditions.[20a] Electron-deficient butadiynes are needed here to facilitate a nucleophilic attack of a secondary amine. A crude reaction mixture was just passed through a short aluminum oxide plug, and 1-aminobutadiynes were reacted without further purification with the in situ generated sodium selenide (according to the literature

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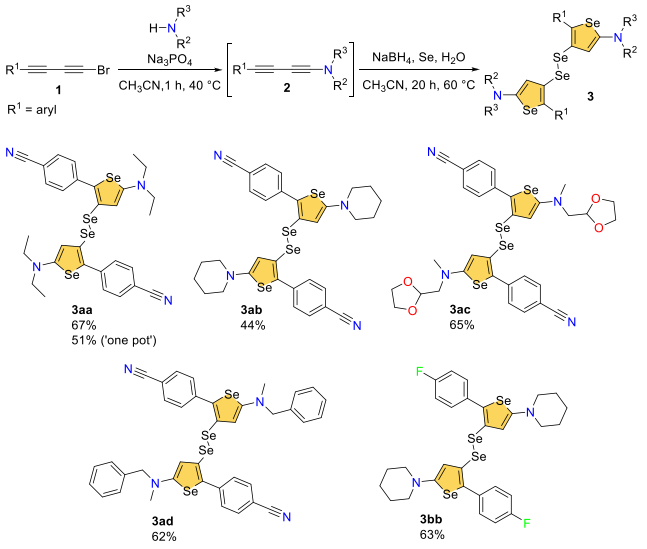
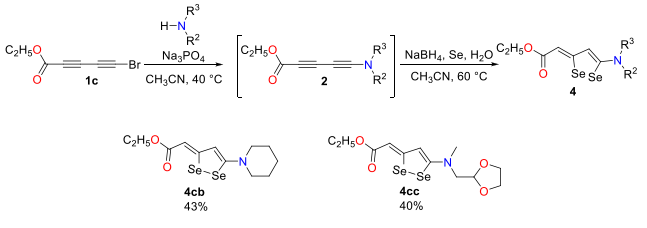
Scheme 2. Synthesis of Di(selenophen-3-yl)diselenides Directly from 1-Bromobutadiynes



procedure) that originally led to simple selenophenes.[21] The final step was performed in CH_3CN at 60 °C for 20 h. Surprisingly, even when strictly 1 equiv of selenium was used, mostly compounds **3** were observed as the main products of the reaction, but yields were much lower. Finally products **3aa**−**3bb** were isolated in good yields (44−67%) when 2.5 equiv of elemental selenium was used, and not even traces of the initially expected simple selenophenes were detected. Different secondary amines are tolerated under the reaction conditions, but the use of ketone or nitro functional groups on a phenyl ring leads to a mixture of partially reduced products. For compound **3aa** a "one-pot" procedure was tested as well. Sodium selenide solution was added directly to the reaction mixture after an amination step; however, the reaction yield dropped down from 67% to 51%. We also tested electron-rich 4-anisylbromobutadiyne, but no reaction was observed probably due to the more difficult nucleophilic attack of selenide during the second step (Scheme S1). It is worth noting that simple diphenyl-1,3-butadiyne gives only simple selenophene under the same reaction conditions, whereas dialkyl-1,3-butadiynes do not react at all (Scheme S1). This suggests that the presence of an amine group is crucial for the formation of these unusual products.

Interestingly, if the aryl group was replaced with a more electron-withdrawing ester group, then completely different products were observed (Scheme 3). Reactions were performed under exactly the same conditions, but new 3-methylene-3*H*-1,2-diselenoles **4cb** and **4cc** were isolated

Scheme 3. Synthesis of Diselenoles from 1-Bromobutadiynes



instead of di(selenophen-3-yl)diselenides. The final yields were rather good (43% and 40%, respectively), taking into account the complexity of the transformation. Further crystallographic studies confirmed the formation of *Z* isomer. Exactly the same type of selenium heterocycles is not known in the literature, and only the formation of some other diselenium heterocycles from butadiynes was reported using different reaction conditions.[22] However, similar structural motifs were reported as parts of bigger polycyclic systems.[23]

The structure of the newly synthesized organoselenium compounds was fully confirmed by ^1H, ^{13}C, and ^{77}Se NMR measurements and mass spectrometry. Particularly ^{77}Se NMR was a useful tool for such selenium heterocycles. It was easy to distinguish between two types of products, and a diselenide bridge was clearly visible. ^{77}Se NMR spectra of **3ac** and **4cc** are shown in Figure 1. Compound **3ac** gives two singlets at 444.9 ppm (diselenide bridge) and 611.2 ppm (selenophene), whereas heterocycle **4cc** gives two singlets at 388.1 and 668.4 ppm.

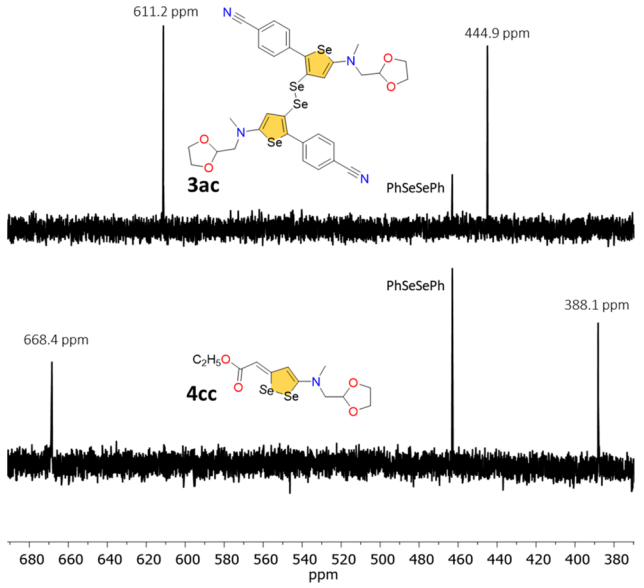


Figure 1. ^{77}Se NMR spectra of **3ac** and **3cc** (114 MHz, 300 K, $CDCl_3$; PhSeSePh as an external standard).

Single crystals of **3aa**, **3ab**, and **4cb** suitable for X-ray single crystal experiments were obtained by slow evaporation of their CH_2Cl_2/*n*-hexane solutions. All three compounds crystallize in a monoclinic system, space group $P2_1/c$, with $Z = 4$. Molecular structures of **3aa**, **3ab**, and **4cb** are shown in Figure 2 and unambiguously confirm their identity postulated from the NMR experiments. The Se−Se bond lengths in **3aa** (2.349(2) Å) and **3ab** (2.316(1) Å) are slightly longer than those for bisphenyldiselenide (2.285 Å).[24] Interestingly, the length of the Se−Se bond in the new heterocycle **4cb** is rather similar (2.372(1) Å).

Next, we tested analogous conditions with the use of elemental tellurium instead of selenium (Scheme 4). However, the expected simple tellurophenes **5ab**−**5ae** were isolated in 36−74% yields instead of more complex heterocycles. This might be attributed to the lower stability of the Te−Te bond when compared to the Se−Se bond,[25] and thus only tellurophenes were observed after the reaction. The selenium derivatives were stored in a freezer and showed no visual

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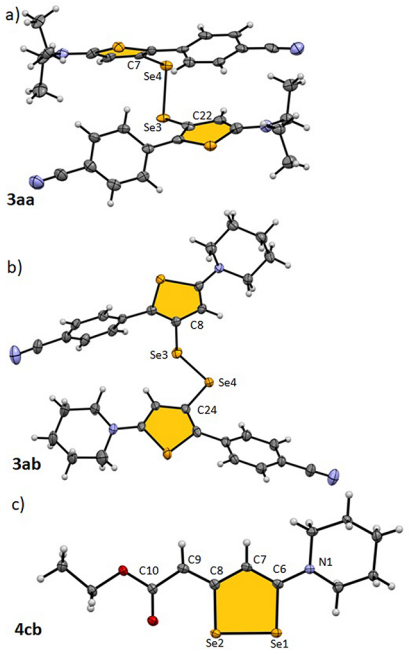
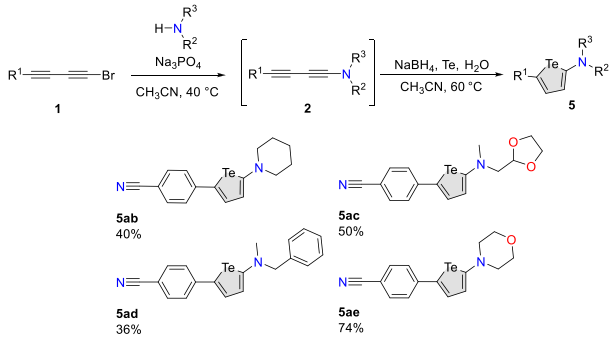


Figure 2. (a) Molecular structure of **3aa**, selected distances: C7−Se4 = 1.908(10) Å, Se3−Se4 = 2.349(2) Å, Se3−C22 = 1.909(10) Å, C7−Se4−Se3−C22 torsional angle = −72.2°. (b) Molecular structure of **3ab**, selected distances: C8−Se3 = 1.920(6) Å, Se3−Se4 = 2.316(1) Å, Se4−C24 = 1.927(6) Å, C8−Se3−Se4−C24 torsional angle = 97.2°. (c) Molecular structure of **4cb**, selected distances: C6−C7 = 1.381(5) Å, C7−C8 = 1.421(5) Å, C8−C9 = 1.370(5) Å, C9−C10 = 1.434(5) Å, C6−Se1 = 1.904(4) Å, Se1−Se2 = 2.372(1) Å, Se2−C8 = 1.908(4) Å; thermal ellipsoids set at 50% probability.

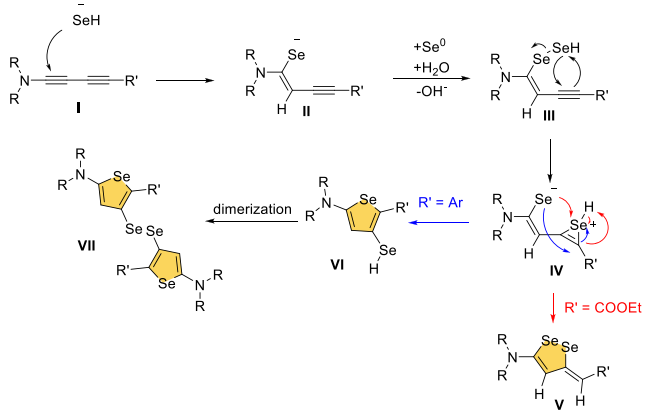
Scheme 4. Synthesis of 2-Aminotellurophenes from 1-Bromobutadiynes



degradation over the course of several months. Tellurophene also did not degrade under such conditions; however, at room temperature they decompose to black metallic solids over the course of several weeks.

Consequently, a possible mechanism explaining the formation of the unusual selenium products was postulated (Scheme 5). The first step is a well-documented nucleophilic attack of in situ-generated selenide SeH^- on butadiyne **I** leading to hydroselenation and formation of enyne **II**.[19c] Since the formation of diselenides was reported even under reductive conditions[26] we propose a formation of biselenide **III** and its further transformation to selenirenium ion **IV**.[27] This might explain why an electron-donating amine substituent is needed for the reaction. Compound **IV** might next undergo an internal nucleophilic attack of Se^- on Se^+ and rearrangement to

Scheme 5. Proposed Reaction Mechanism



heterocycle **V** when R′ = C(O)OEt. When R′ = Ar then a nucleophilic attack to a carbon atom is more likely, and finally selenophene **VI** is formed, which undergoes further dimerization to **VII**. Since the Te−Te bond is less stable than the Se−Se bond[24] the formation of ditelluride is less possible, and thus only "classical" tellurophenes are observed.

In summary, we have discovered an efficient method for the synthesis of di(selenophen-3-yl)diselenides and 3-methylene-3*H*-1,2-diselenoles directly from 1-bromobutadiynes. This approach is particularly interesting because it shows a selective formation of complex selenium heterocycles from simple substrates. Most importantly, this transformation may be used for the synthesis of new organoselenium compounds with pharmaceutical potential.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c04275.

Experimental procedures, characterization of all new compounds, copies of ^1H, ^{13}C, and ^{77}Se NMR spectra of all new compounds, details of X-ray diffraction experiments (PDF)

Accession Codes

CCDC 2016100, 2016101 and 2016102 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

Bartłomiej Pigulski − *Faculty of Chemistry, University of Wrocław, 50-383 Wrocław, Poland;* orcid.org/0000-0002-9925-2878; Email: bartlomiej.pigulski@chem.uni.wroc.pl

Sławomir Szafert − *Faculty of Chemistry, University of Wrocław, 50-383 Wrocław, Poland;* orcid.org/0000-0002-0570-8847; Email: slawomir.szafert@chem.uni.wroc.pl

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Author

Patrycja Męcik − *Faculty of Chemistry, University of Wrocław, 50-383 Wrocław, Poland*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c04275

Notes

The authors declare no competing financial interest.

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