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Review

Recent advances in the chemistry of selenium-containing heterocycles: Five-membered ring systems

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ABSTRACT

This review provides a comprehensive survey of the recent advances in the methods of construction of five membered ring systems containing selenium over the period from the year 2000 to the year 2015.

1. Introduction

Selenium is a micronutrient essential for mammals. It plays a crucial role in the mammalian defense system against oxidative stress, since it's essential for the activity of glutathione peroxidase (GPx). In addition, it's essential for the activity of various enzymes such as thioredoxin reductase, iodothyronine deiodinase, selenophosphate synthetase, and selenoprotein P [1–5].

Selenium chemistry is gaining increasing importance, since it was discovered by the Swedish chemist Berzelius, for nearly two decades. Accordingly, synthesis of organoselenium compounds continues to be a very active research area, due to their distinct chemical, physical and biological properties [6–10]. In fact, a variety of these compounds are well known for their antimicrobial, biocidal, anti-inflammatory, antioxidant, and free radical scavenging activities [11–23]. Their practical application in medicine for the treatment of tumors and cancers is a subject of current intense interest [24–34]. In material science, utilization of five-membered

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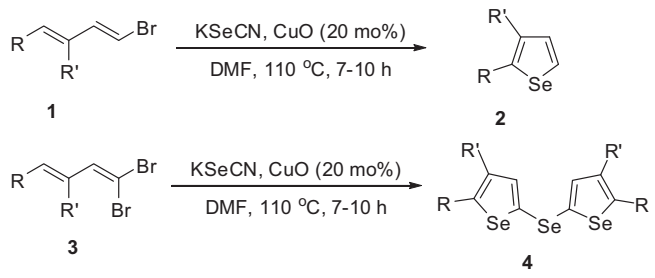
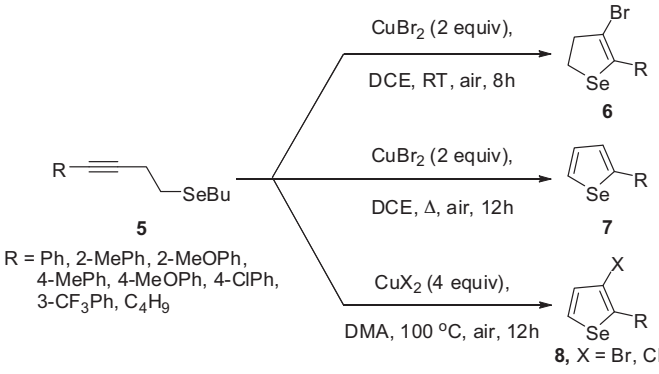


Scheme 1. CuO nanoparticles as catalyst for synthesis of selenophenes [42].



Scheme 2. Cyclization of homopropargyl selenides **5** into selenophenes **6–8** [43].

selenium-containing heterocycles in developing organic conductors, semiconductors and optoelectronics is another area of current interest [35–40]. Moreover, numerous organoselenium compounds are interesting fluorescent probes [41].

2. Selenophenes and their benzo-anulated analogues

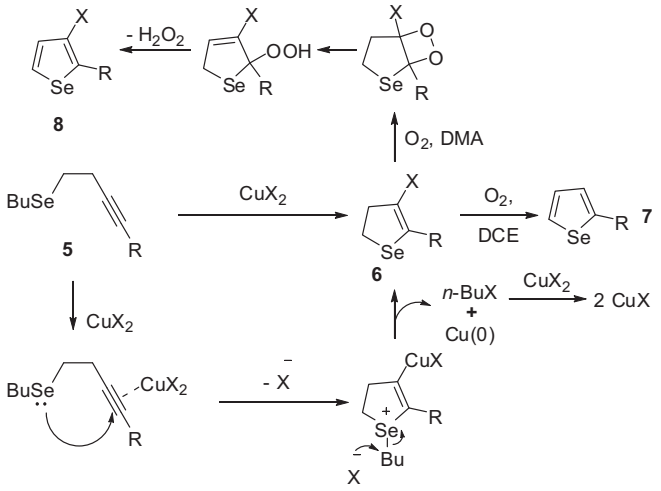
Recently, Ranu et al. developed a novel general approach for the construction of selenophenes **2** and selanyl selenophenes **4** through the reaction of KSeCN, as a selenium source, with 1,3-dienyl bromides **1** and 1,3-dienyl-gem-dibromides **3**, respectively. The reaction proceeds smoothly under CuO nanoparticles catalysis (Scheme 1) [42].

In the same context, Cu-catalyzed cyclization of homopropargyl selenides **5** into 4-halo-2,3-dihydroselenophenes **6**, selenophenes **7**, and 3-haloselenophenes **8** was reported by Zeni and coworkers (Fig. 1) [43].

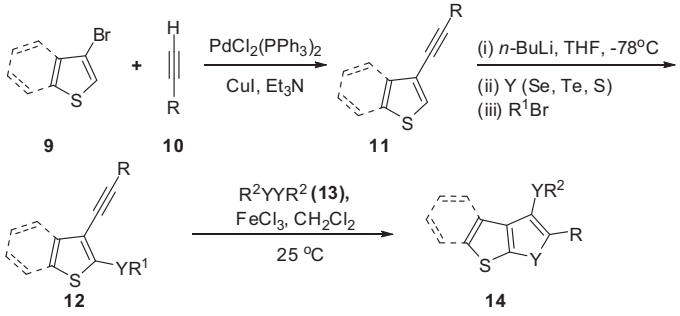
Cyclization of **5** in 1,2-dichloroethane (DCE) at room temperature in the presence of two equivalents of $CuBr_2$ afforded **6** in good yield. Performing the same cyclization at reflux gave preferably **7** along with **8a** as minor byproduct. However conducting the reaction in dimethylacetamide (DMA) at 100 °C gave **8a** exclusively; replacing $CuBr_2$ by $CuCl_2$ afforded the chloro-analogue **8b** (Scheme 2).

A proposed mechanism for these cyclization reactions is illustrated in Scheme 3.

In an extension to their previous work [19,20] on electrophilic cyclization of acetylenes into chalocogenophenes, Zeni et al. [44]



Scheme 3. A proposed mechanism for the formation of selenophenes **6–8**.



Scheme 4. $FeCl_3$ catalyzed cyclization of acetylenes into chalocogenophenes [44].

reported that 2-organochalcogen-3-alkynylthiophenes **12** undergoes clean intramolecular cyclization under the influence of $FeCl_3$-diorganyl dichalcogenides system, giving chalcogenophene[2,3-*d*]thiophene derivatives **14** in good yields (Scheme 4). The precursors of type **12** are achieved through the Sonogashira reaction [45–48], of 3-bromothiophenes **9** with terminal alkynes, followed by insertion of chalcogen and alkylation [49,50].

The optimum conditions for accessing **14** are: **12** (0.25 mmol), $FeCl_3$ (1.0 equiv.), diorganyl dichalcogenides **13** (1.0 equiv.) in CH_2Cl_2 (3 mL) at room temperature and under ambient atmosphere. Under these conditions a series of chalcogenophene[2,3-*d*]thiophene derivatives was prepared (Fig. 2).

In addition, the obtained chalcogenophenes **14** are readily transformed into more complex products through the palladium cross-coupling reaction with boronic acids or through the reaction of their lithium derivatives with aldehydes.

Previously, the same group studied the same cyclization reaction, exploring variety of substrates, electrophiles, and reaction conditions. A summary of their effort is depicted in Scheme 5 [51,52].

Furthermore, the heterocyclic products **15** and **18** undergo smooth palladium catalyzed cross-coupling reactions with

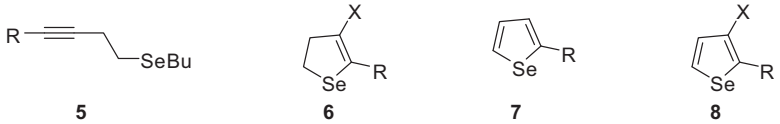


Fig. 1. Alkynylselenide **5** and Selenophene derivatives **6**, **7**, and **8**.