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Use of Elemental Sulfur or Selenium in a Novel One-Pot Copper-Catalyzed Tandem Cyclization of Functionalized Ynamides Leading to Benzosultams

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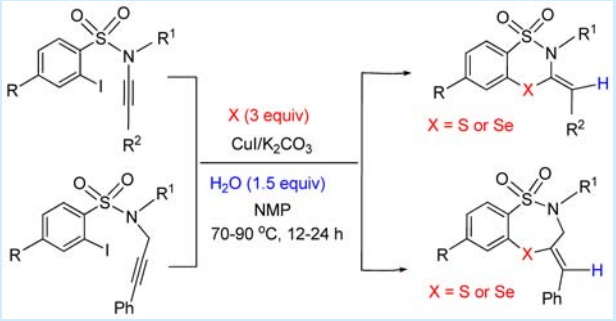
Supporting Information

ABSTRACT: A novel and efficient [Cu]-catalyzed one-pot regio- and stereospecific synthesis of benzo[1,4,2]dithiazine 1,1-dioxides and benzo[1,4,2]thiaselenazine 1,1-dioxides by cyclization of functionalized ynamides with elemental sulfur/selenium has been developed. Its generality is elegantly illustrated by extension to benzodithiazepines and benzothiaselenazepines. Involvement of water in the reaction is demonstrated by the incorporation of ^2D at the olefinic site by using D_2O in place of water. Selective oxidation at sulfur in benzo[1,4,2]dithiazine 1,1-dioxide by using *m*CPBA as the oxidizing agent is also described.



Ynamides have emerged as powerful synthons owing to their versatile ring-forming transformations.[1,2] In particular, transition metal catalyzed cyclization of ynamides is explored for the construction of diverse and novel nitrogen-containing heterocycles.[3,4] We have been interested in the reactions of sulfonamide-bearing ynamides (cf. Figure 1) with

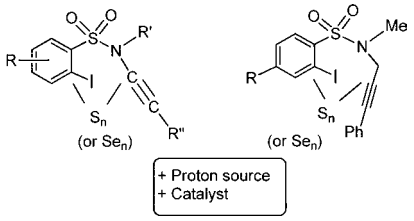
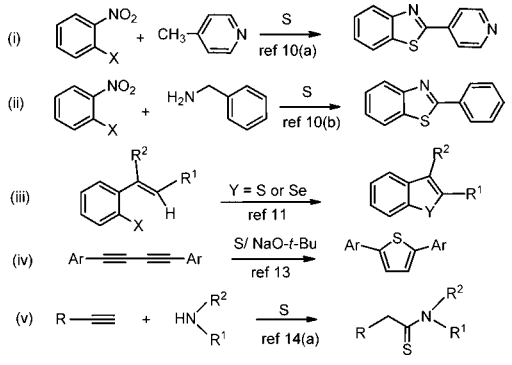


Figure 1. Possible reactivity of sulfonamide-containing ynamide or alkyne with sulfur/selenium.

sulfur, since the resulting benzosultams could be of significant pharmacological interest.[5−7] An extension to utilize selenium is also a worthwhile exercise since selenamides themselves could be medicinally useful.[8,9]

In the above context, it may be noted that elemental sulfur as a reactant to generate sulfur-based heterocycles or thioethers or thioketones is an economically attractive concept in organic synthesis. Several novel transformations that involve elemental sulfur have been reported recently,[10] and a few of them are illustrated in Scheme 1. In reactions (i)−(ii), generation of 2-heteroarylbenzothiazoles or arylbenzothiazoles is accomplished with 2-halonitroarene as the other common reactant; the nitro group is involved in an oxidation process involving a part of the sulfur reactant.[10a,b] Reaction (iii) can be construed as elimination of HX with concomitant insertion of sulfur/

Scheme 1. Selected Recent Examples of Sulfur Insertion Reactions



selenium to lead to benzothiophenes or benzoselenophenes, respectively.[11] In another report, benzoisothiazolones have been prepared by a Cu(II) mediated C−S/N−S bond formation using sulfur as a reactant.[12] Electron paramagnetic resonance (EPR) experiments revealed that the trisulfur radical anion ($S_3^{\bullet-}$) was involved in the formation of diarylthiophene shown in reaction (iv).[13] In the last three-component reaction (v), initial formation of $R^1R^2NS_7S^-$ is proposed.[14a] This anion reacts with the alkyne to form the final product, thioamide, in several steps. Singh and co-workers have also reported thioamide formation but, interestingly, by using arylacetic acid and sulfur.[14b] Another report utilizes two aliphatic amines and sulfur to produce thioamides.[14c] Elemental sulfur, terminal

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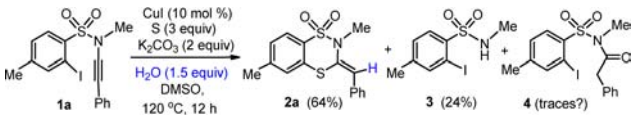
alkynes, and carbodiimides react in the presence of butyllithium to produce 2,3-dihydropyrimidinthiones.[14d] Yet another route utilizes amides and elemental sulfur in the presence of hydrochlorosilanes.[14e] An interesting ring expansion reaction of cyclopropanes using elemental sulfur has also been reported recently.[15] It is shown that trifluoromethylthiolation of terminal alkynes with elemental sulfur and CF_3SiMe_3 can be conducted readily.[16a] Trifluoromethylthiolation of α-bromoketones with sulfur and CF_3SiMe_3 is another significant reaction in this context.[16b]

In the last two reactions cited in Scheme 1, an alkyne is one of the reactants. In this context we felt that *N*-substituted alkynes (ynamides), in view of a highly polarized carbon−carbon triple bond directly attached to the nitrogen atom,[17] could be interesting substrates in reactions with sulfur or thiolates.[18] We report herein a simple and convenient synthesis of benzo[1,4,2]dithiazine 1,1-dioxides and benzo[1,4,2]-thiaselenazine 1,1-dioxides from functionalized ynamides and elemental sulfur or selenium with the aid of [Cu]-catalysis.[19] We also wish to highlight the fact that this type of selenium chemistry has hardly been explored earlier.[20] We also demonstrate that this methodology is extendable to other systems, as illustrated by the one-pot practical synthesis of benzodithiazepines and benzothiaselenazepines.

We started with the reaction between *N*-alkynyl 2-iodo-benzenesulfonamide **1a** and elemental sulfur (3 equiv) in the presence of CuI as a catalyst and K_2CO_3 as a base in DMSO using water (1.5 equiv) as the proton source at 120 °C for 12 h. This reaction afforded benzo[1,4,2]dithiazine 1,1-dioxide **2a** regio- and stereospecifically in 64% isolated yield along with 2-iodo-*N*,4-dimethylbenzenesulfonamide **3** (24%) (Scheme 2).

Scheme 2. [Cu]-Catalyzed Reaction of Ynamide 1a with Elemental Sulfur



The latter product arises from the hydrolysis of the ynamide. Hence it was required to minimize its formation in the optimization process. It should also be noted that, in **2a**, *extra hydrogen* has appeared at the olefinic site. Product **2a** may be construed as the one resulting from the reaction of hydrogen sulfide with **1a**, but in this apparently straightforward reaction, only a complex mixture of products was observed.

Optimization [Supporting Information, Table S1] of the conditions was carried out to obtain a better yield of **2a**. Unlike DMSO, other polar solvents such as DMF and PEG-400 gave only a moderate yield. Use of water itself as a solvent led to the undesired water addition product, 2-iodo-4,*N*-dimethyl-*N*-phenylacetylbenzenesulfonamide **4**[19a] in 46% yield in addition to the desired product **2a** (32%). Solvents such as toluene, diethyl carbonate, and ethanol did not give **2a**. Satisfyingly, NMP as a solvent led to the formation of **2a** in 72% yield along with **3** in 16% isolated yield (Table S1, entry 8). To our delight, the yield of the product was enhanced to 90% by a decrease in temperature to 70 °C (Table S1, entry 10). However, a further decrease in temperature to room temperature decreased the yield of the desired product. Thus, it is revealed that temperature has a great impact on the cyclization reaction. A decrease in the yield of the product (42%) was observed in the absence of water (entry 12). Thus, most probably, water is participating in the reaction. The yield of the product was reduced to 72% by using 5 mol % of CuI. Notably, in the absence of the CuI catalyst, we did not observe the formation of **2a**. Increasing the [Cu]-catalyst loading to 20 mol % did not enhance the yield of the product. It is noteworthy that a decrease in the amount of sulfur to 2 equiv decreased the yield of the product (Table S1, entry 16). Other copper sources such as CuBr, $CuSO_4{\cdot}5H_2O$, etc. did not improve the yield. On the other hand, a sulfur source such as $Na_2S{\cdot}9H_2O$ gave undesired products **3** and **4** with only trace amounts of product **2a**. Anhydrous Na_2S and $Na_2S_2O_3{\cdot}5H_2O$ were ineffective (Table S1, entry 20). H_2S gas as a sulfur source gave a complex reaction mixture with only a trace amount of **2a**. In the absence of K_2CO_3, we observed only **3** and **4** (Table S1, entry 21). Thus, the best conditions are CuI (10 mol %), sulfur (3 equiv; i.e., 3/8 S_8), water (1.5 equiv), and K_2CO_3 (2 equiv) with NMP as a solvent at 70 °C for 12 h. For the corresponding selenium compounds (e.g., **5a**), a higher temperature (90 °C) and longer time (20 h) were required for optimum yields [cf. Table S2, Supporting Information].

We then explored the substrate scope of this [Cu]-catalyzed one-pot reaction by employing various *N*-alkynyl 2-iodo-benzenesulfonamides with elemental sulfur and selenium. The products, benzo[1,4,2]dithiazine 1,1-dioxide derivatives **2a−l** and benzo[1,4,2]thiaselenazine 1,1-dioxide derivatives **5a−h**, were isolated in good to excellent yields (Scheme 3). The selenium compounds were also characterized by ^{77}Se NMR. The structures of compounds **2i** and **5a** as confirmed by X-ray crystallography are shown in Figure 2.[21] By changing the substituents on either the sulfonyl attached benzene ring or on the nitrogen atom we did not observe any significant change in the product yields. Furthermore, there was no pronounced effect on the product yields by changing the alkyne substituent R^2. Indeed, the reaction using triisopropylsilyl substituted ynamide **1j** afforded the desired product **2j** in 82% yield (cf Scheme 2). Even the bulky 4-biphenyl substituted ynamide **1h** gave the product **2h** in 72% yield. *N*-Alkynyl 2-bromo-benzenesulfonamide **1m** did not react, suggesting that the iodo-substituent is essential for this cyclization reaction. The method described in this report is indeed versatile for the synthesis of 1,4,2-benzodithiazines 1,1-dioxides or 1,4,2-benzo-thiaselenazine 1,1-dioxides.

A perusal of the above reaction indicates that it need not be restricted to just sulfonamides leading to six-membered rings. Pleasingly, we realized that it can be extended to the formation of the seven-membered ring systems via 2-iodo-*N*-methyl/phenyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamides (**6−8**). Thus, the reaction of **6−8** with elemental sulfur or selenium readily afforded the desired seven-membered benzosultams, benzodithiazepines (**9**, **11**, and **13**), and benzothiaselenazepines (**10**, **12**, and **14**), regio- and stereospecifically in excellent yields (Scheme 4). The structure of compound **9** was confirmed by X-ray crystallography (Figure 2).

In order to explain the plausible catalytic cycle, we have done the following control experiments under our standard conditions. Thus, the reaction of elemental sulfur with phenyl iodide **I** afforded the product **II** (Scheme 5a). A similar observation has already been made by Zhou and co-workers.[22] In contrast, the reaction between sulfur and ynamide **III** leads to a complex reaction mixture (Scheme 5b). The reaction of ynamide **1a** with elemental sulfur in the D_2O and NMP (1:3) mixture delivers compound **2a′** (Scheme 5c). Formation of this

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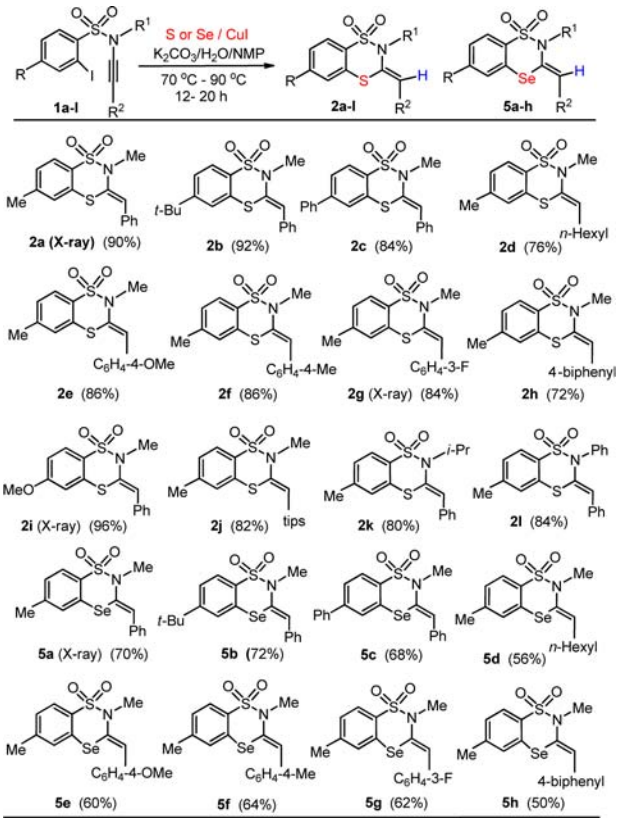
Scheme 3. Synthesis of Benzo[1,4,2]dithiazine 1,1-Dioxides (2a–l) and Benzo[1,4,2]thiaselenazine 1,1-Dioxides (5a–h) from *N*-Alkynyl 2-Iodo-benzene Sulfonamides[a]



[a]Conditions: **1** (0.24 mmol), sulfur [0.09 mmol as S_8]/selenium [0.09 mmol as Se_8], CuI (10 mol %), K_2CO_3 (0.48 mmol), and H_2O (0.36 mmol) in NMP (1 mL) at 70 °C (for S)/90 °C (for Se) for 12 h (for S)/20 h (for Se). Isolated yields after column chromatography are given in parentheses.

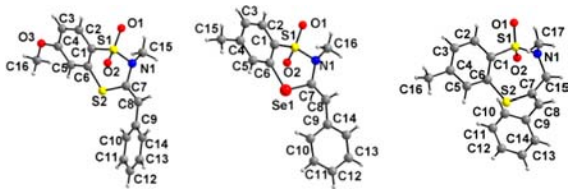
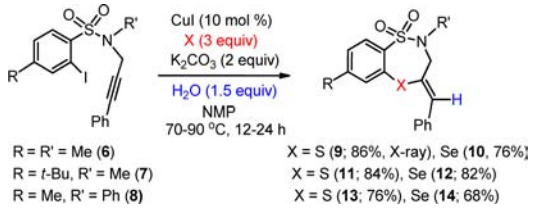


Figure 2. X-ray structures of compounds **2i** (left), **5a** (middle), and **9** (right).

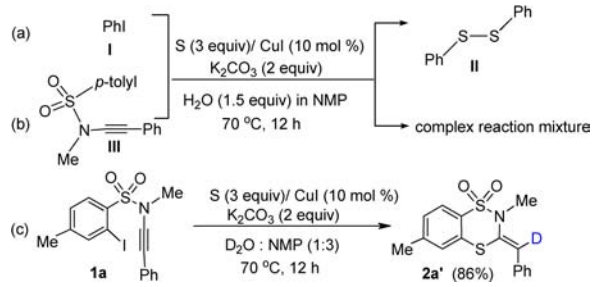
Scheme 4. Formation of Benzodithiazepines (9, 11, and 13) and Benzothiaselenazepines (10, 12, and 14)



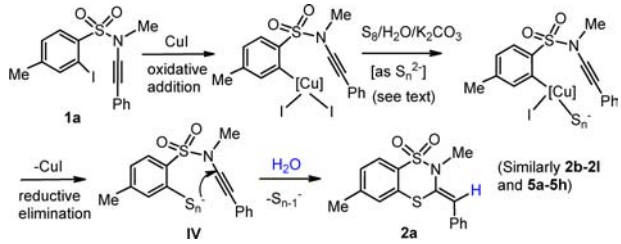
deuterated compound clearly indicates the crucial role of water during the course of the cyclization process as a proton source.

A plausible pathway for the formation of **2a** based on the control experiments and earlier literature is shown in Scheme 6.[23] Oxidative addition of **1a** to CuI occurs initially,[24] followed

Scheme 5. Control Experiments



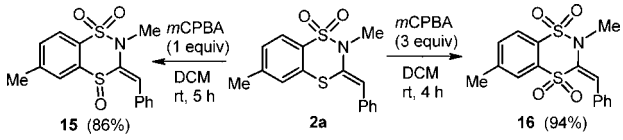
Scheme 6. Proposed Pathway for the Formation of 2a



by the attack of sulfur (as possibly S_n^{2-})/water/base and subsequent reductive elimination of CuI leading to intermediate **IV**. It is known that elemental sulfur disproportionates in the presence of a base to an oligosulfide anion and sulfite.[23] Intermediate **IV** undergoes cyclization followed by abstraction of a proton (source: water) to give product **2a**. The fact that we could isolate the deuterated compound **2a′** (cf. Scheme 5c) is consistent with the intervention of water in this cyclization. The regiospecific attack of sulfur on the carbon N−C≡C carbon is consistent with that observed in hydrothiolation of ynamides.[18b,c]

It may be noted that, in benzo[1,4,2]dithiazine 1,1-dioxide **2a**, one sulfur is in the +6 oxidation state and the other in the +2 oxidation state. We felt that the variability/utility of such systems will be better if we oxidize the low-valent sulfur. Selective oxidation reactions are of significant interest in the pharmaceutical industry.[25] Fortunately, oxidation of benzo[1,4,2]dithiazine 1,1-dioxide **2a** with *m*CPBA (1equiv) in dichloromethane (1 mL) preferentially gives benzo[1,4,2]-dithiazine 1,1,4-trioxide **15** in 86% yield. Increasing the amount of *m*CPBA (3 equiv) results in the formation of benzo[1,4,2]-dithiazine 1,1,4,4-tetraoxide **16** in 94% yield (Scheme 7).

Scheme 7. Selective Oxidation of Compound 2a



In conclusion, a simple and efficient one-pot protocol for the regio- and stereospecific synthesis of benzo[1,4,2]dithiazine 1,1-dioxides **2a–l** and benzo[1,4,2]thiaselenazine 1,1-dioxides **5a–h** by [Cu]-catalyzed cyclization of functionalized ynamides using elemental sulfur or selenium is developed. Involvement of water in this reaction is proven by deuterium labeling experiments. Selective oxidation of **2a** by *m*CPBA is accomplished. This methodology is extended to benzodithiazepines/benzothiaselenazepines **9–14** illustrating its utility.

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■ ASSOCIATED CONTENT

Supporting Information

Experimental details; optimization Tables S1−S2; X-ray crystallographic data (cif file; CCDC Nos. 1062368−1062372); ORTEPS of **2a**, **2g**, **2i**, **5a**, and **9**; $^{1}H/^{13}C$ NMR/^{77}Se spectra. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01287.

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Notes

The authors declare no competing financial interest.

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(21) The structures of compounds **2a** and **2g** were also determined (Figures S1−S2), but the quality of data was only moderate.

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