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(3 + 2)-Cycloaddition of Donor−Acceptor Cyclopropanes with Selenocyanate: Synthesis of Dihydroselenophenes and Selenophenes

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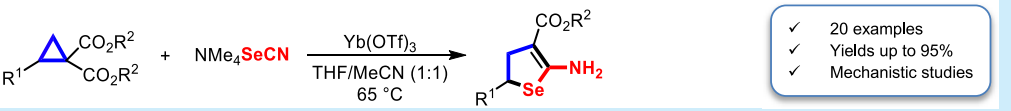
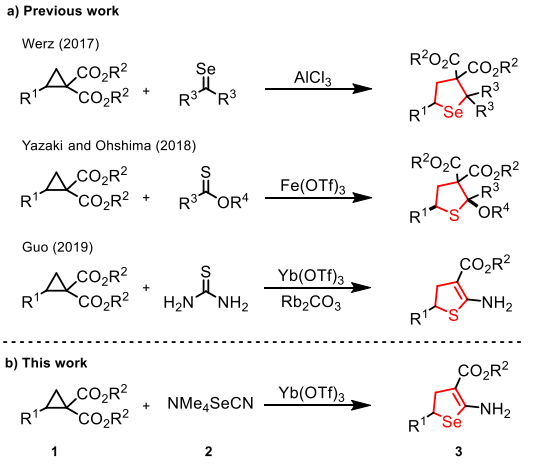


ABSTRACT: We present a Lewis-acid-catalyzed (3 + 2)-cycloaddition of donor−acceptor cyclopropanes and selenocyanate (as its tetramethylammonium salt) for the synthesis of dihydroselenophenes. The transformation proceeded with moderate to excellent yields and showed a high functional group tolerance. Further oxidation using DDQ delivered selenophenes.

Donor−acceptor (D−A) cyclopropanes, the smallest carbocyclic ring systems, have attracted the attention of synthetic chemists because of their versatility as masked 1,3-zwitterionic building blocks.[1] Pioneering reports by Wenkert and Reissig[2] on these highly strained molecules[3] date back to the late 1970s. Though the chemistry of D−A cyclopropanes had remained dormant for some decades, the area has seen a revival in the recent past, unlocking the synthetic utility of these interesting molecules. The "push effect" by the donor and the "pull effect" by the acceptor groups promote the lability of the bond that connects them, thus facilitating a wide variety of transformations including cycloadditions, rearrangements,[4] and ring-opening reactions.[5] Of these, the types most investigated are cycloadditions with various 1,2-, 1,3- and 1,4-dipoles including dienes,[6] carbonyls,[7] imines,[8] nitrones,[9] alkynes,[10] heterocumulenes,[11] and other dipolarophiles.[12] Although syntheses of oxygen- and nitrogen-containing heterocycles employing D−A cyclopropanes have been extensively studied, there are few routes to sulfur or selenium analogues. In 2012, the Stolz group demonstrated that a stoichiometric amount of $Sn(OTf)_2$ enabled the conversion of D−A cyclopropanes to thioimidates in the presence of isothiocyanate,[13] and tetrasubstituted thiophenes have been synthesized in two steps utilizing *trans*-2-aroyl-3-arylcyclopropane-1,1-dicarboxylates and in situ-generated mercaptoaldehyde.[14] In 2017, our group reported the synthesis of tetrahydrothio- and tetrahydroselenophenes in a (3 + 2)-cycloaddition of D−A cyclopropane with thio- and selenoketones, respectively.[15] Shortly after this, Yazaki and Ohshima were able to conduct a similar transformation with thionoesters.[16] Recently, Guo and co-workers reported the $Yb(OTf)_3$-catalyzed cycloaddition of D−A cyclopropanes with thiourea to provide dihydrothiophenes (Scheme 1a).[17]

Because the selenocyanate anion can be regarded as deaminated and deprotonated selenourea, we conjectured that selenocyanate might show a reaction with D−A cyclopropanes,

Scheme 1. Previous Work on the Formation of Sulfur/Selenium-Containing Heterocycles via D-A Cyclopropane Chemistry and Our Novel Route to Dihydroselenophenes



leading to dihydroselenophenes (Scheme 1b). These compounds might also be precursors for selenophenes, which have found prominent roles not only in optoelectronics,[18] luminescent materials,[19] and semiconductors[20] but also as antioxidants,[21] antinociceptives,[22] and anti-inflammatory agents.[23]

Selenophenes are usually synthesized from alkynes, dienes, and β-diketo compounds on treatment with elemental selenium

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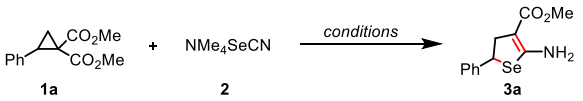
or other selenium sources.[24] However, routes to partially saturated dihydroselenophenes are scarce in the literature.[25]

To test our notion that such a (3 + 2)-cycloaddition reaction of selenocyanate and a D−A cyclopropane might be feasible, we started by using cyclopropane **1a** as a model compound. As suitable selenocyanate sources, NH_4SeCN, KSeCN, NBu_4SeCN, and NMe_4SeCN were chosen. The initial experiments were performed by mixing cyclopropane **1a** and tetramethylammonium selenocyanate in THF for 12 h at 25 °C with various Lewis acids such as $AlCl_3$, MgI_2, $TiCl_4$, and $Sc(OTf)_3$; however, no reaction was observed (Table 1, entries 1−4). With $Yb(OTf)_3$ (20 mol %), the desired product was formed in 21% yield (entry 5). The investigations with cyclopropane **1a** and NH_4SeCN were unsuccessful because of the tendency of NH_4SeCN to decompose to elemental selenium. Thereafter, KSeCN was chosen as the selenocyanate source (entry not shown in Table 1). KSeCN together with 18-crown-6 was envisioned as providing a more "naked" and thus more nucleophilic selenocyanate, facilitating the desired reaction, yet in fact, it exhibited poor reactivity with D−A cyclopropanes. Under the same reaction conditions, NBu_4SeCN gave the desired product in 9% yield (entry not shown in Table 1). An increase in temperature to 65 °C using NMe_4SeCN increased the product yield from 21 to 35% (entry 6). A change of the solvent to acetonitrile, in which the salt is much better soluble than in THF, proved to be unsuccessful when 20 mol % of the Lewis acid was used (entry 7). Increasing the amount of Lewis acid to 30 mol % afforded the product in 22% yield (entry 8). Additionally, we observed a sharp increase in the yield with increasing catalyst loading. An exploration of various solvents showed that a 1:1 mixture of THF and acetonitrile proved to be the best choice and furnished **3a** in 6 h in 91% yield (entries 9 and 10).

Table 1. Optimization of the Reaction Conditions[a]

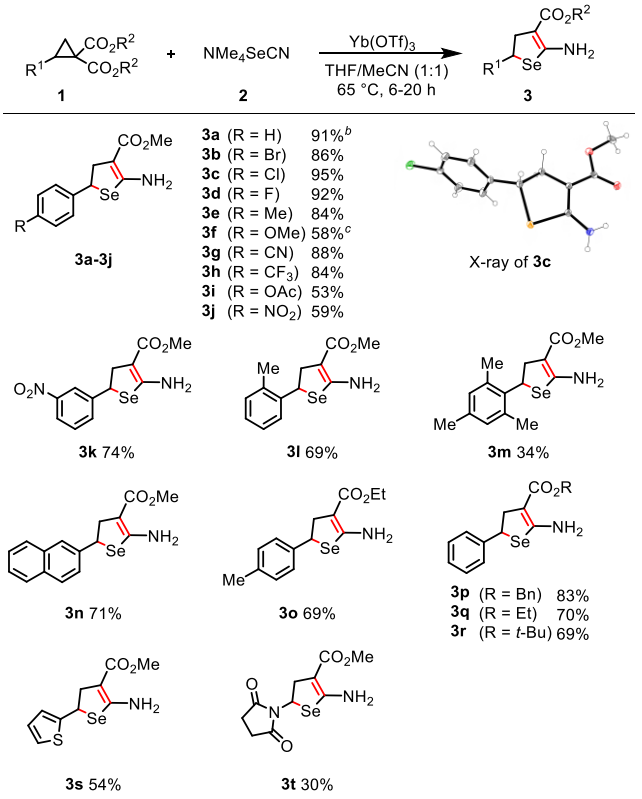


entry	Lewis acid	solvent	T (°C)	yield of **3a**[b] (%)
1	$AlCl_3$	THF	25	0
2	MgI_2	THF	25	0
3	$TiCl_4$	THF	25	0
4	$Sc(OTf)_3$	THF	25	0
5	$Yb(OTf)_3$	THF	25	21
6	$Yb(OTf)_3$	THF	65	35
7	$Yb(OTf)_3$	MeCN	65	0
8	$Yb(OTf)_3$[c]	MeCN	65	22
9	$Yb(OTf)_3$[d]	THF/MeCN[e]	65	52[f]
10	$Yb(OTf)_3$[g]	THF/MeCN[e]	65	91[f]

[a]Reaction conditions: **1a** (100 μmol), **2** (250 μmol), Lewis acid (20 mol %), solvent (1 mL), under Ar, 12 h. [b]Yields refer to purified and isolated products. [c]30 mol % of $Yb(OTf)_3$. [d]30 mol % of Lewis acid was used. [e]The ratio of the solvent system is 1:1. [f]The reaction was stirred for 6 h. [g]60 mol % of Lewis acid was used.

With the optimized reaction conditions in hand, we probed the generality of this method using tetramethylammonium selenocyanate (**2**) and variously substituted D−A cyclopropanes. The reaction proceeded smoothly with several *p*-substituted aryl cyclopropanes under the optimized reaction conditions, providing the desired products **3a**−**3j** in good to excellent yields (Scheme 2). Single-crystal X-ray analysis of

Scheme 2. (3 + 2)-Cycloaddition Reaction with Respect to Different D−A Cyclopropanes[a]



[a]Reaction conditions: **1** (100 μmol), **2** (250 μmol), $Yb(OTf)_3$ (60 mol %), THF/MeCN (1:1) (2 mL), at 65 °C under Ar, 6−20 h; yields refer to purified and isolated products. [b]Large scale: 71% yield for 1.5 mmol of starting material. [c]The reaction was run for 4 h at 25 °C.

compounds **3a** and **3c** unambiguously confirmed the structure of the product. Cyclopropane **1f** was completely consumed in 4 h at 25 °C to deliver the corresponding product in 58% yield, consistent with its high reactivity. Notably, cyclopropane **1k** underwent smooth transformation under the standard conditions to give product **3k** in 74% yield. More steric bulk, with the *o*-methyl substituent on the phenyl donor, afforded product **3l** in 69% yield. However, the mesityl variant **3m** showed a strong decrease in the yield to 34%. The naphthyl group with an extended π system furnished the corresponding dihydroselenophene **3n** in 71% yield. Different ester groups, such as benzyl, ethyl, and *tert*-butyl esters, as acceptor moieties were found to be tolerant under reaction conditions and provided very good yields (**3p**−**3r**). Heterocyclic donors such as thienyl and succinimide moieties delivered the corresponding product in 54 and 30% yield, respectively (**3s**, **3t**).

To demonstrate the utility of the dihydroselenophene moiety, products **3** were oxidized to selenophenes. DDQ proved to be the agent of choice. We tried various solvents such as DCM, DCE, and toluene; however, the best results were obtained in benzene (Scheme 3). All selenophenes **4** were obtained in good to excellent yields. The structure of **4a** was confirmed by X-ray crystallography. Unfortunately, a combination of the two reactions (cycloaddition and oxidation) in one pot did not provide the selenophenes.

To shed light on the reaction mechanism for the dihydroselenophene formation, we performed several experi-

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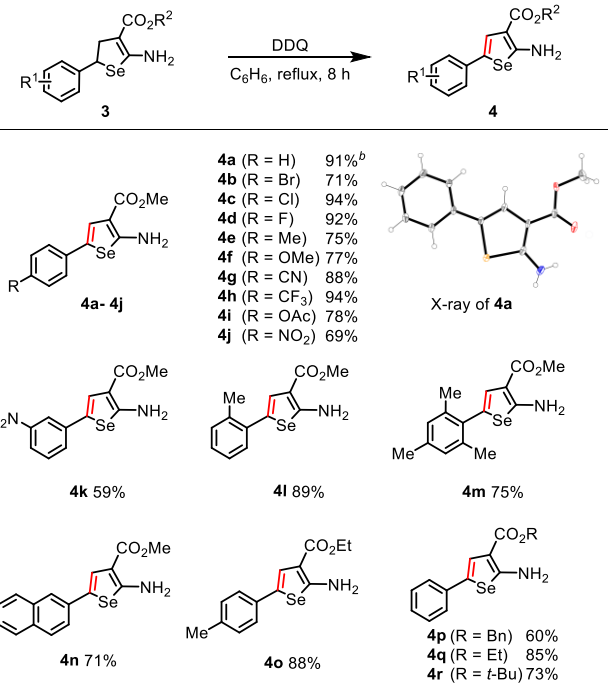
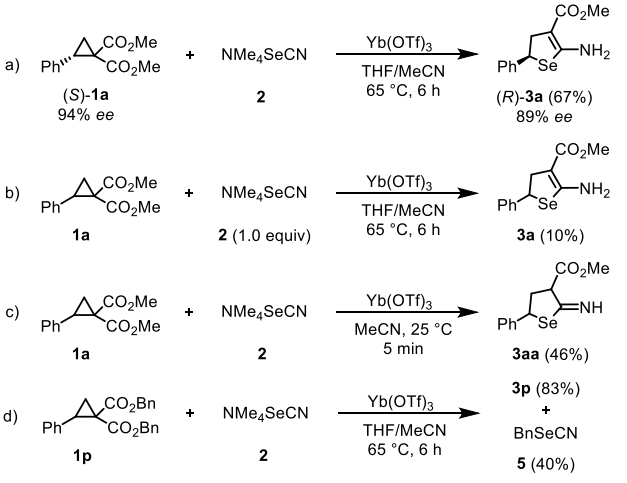
Scheme 3. Oxidation of Dihydroselenophenes to Selenophenes[a]



[a]Reaction conditions: **3** (100 μmol), DDQ (100 μmol), C_6H_6 (2 mL), under Ar, 8 h; yields refer to purified and isolated products. [b]Large scale: 73% for 1 mmol of **3a**.

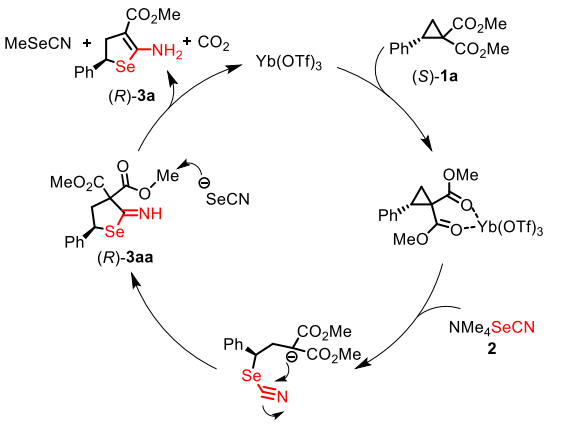
ments. First, we wished to establish whether the initial attack of the selenocyanate takes place via an S_N2-like mechanism. Therefore, we used enantiomerically (94% ee) enriched D−A cyclopropane (Scheme 4a). As shown by HPLC measurements,

Scheme 4. Control Experiments with Respect to the Mechanism



a slight loss of enantiomeric purity was found for the product (89% ee). However, no racemic mixture was obtained. Thus, we assume that the initial attack proceeds via an S_N2-like mechanism, but because of the large amount of Lewis acid, a significant background reaction converting one enantiomer of the cyclopropane to the other takes place. Second, we wished to understand why more than 2 equiv of selenocyanate is required. As shown in Scheme 4b, 1 equiv delivered the desired product in only 10% yield. Full conversion up to a yield of 91% was only found with more than 2 equiv (Scheme 4b). The intermediate of the potential mechanism, imino dicarboxylate **3aa**, was isolated in 46% yield when the reaction was carried out for 5 min at room temperature. When we performed the same reaction with D−A cyclopropane **1p**, bearing benzyl ester groups, we were able to isolate 40% of BnSeCN **5** as side product. Thus, we assume that the selenocyanate has a dual role: it serves as a reagent to incorporate the selenium, but its second crucial role is to cleave one of the ester moieties by acting as a nucleophile; therefore, 2 equiv is required. Taking these considerations into account, we propose the following mechanism (Scheme 5). $Yb(OTf)_3$

Scheme 5. Proposed Mechanism



coordinates to the acceptor moieties in the D−A cyclopropane. The activated ring allows a nucleophilic attack of the selenocyanate in an S_N2-like fashion, opening the highly strained cyclic system. The emerging malonate attacks the carbon of the nitrile, leading to a kinetically favored five-membered ring system. Excess selenocyanate in the reaction medium attacks the alkyl moiety of the ester, setting the stage for decarboxylation, followed by formation of dihydroselenophene.

In conclusion, we have demonstrated an attractive and efficient strategy for the construction of dihydroselenophenes by Lewis-acid-catalyzed (3 + 2)-cycloaddition reaction of donor−acceptor cyclopropanes and selenocyanate (as its tetramethylammonium salt). Numerous functional groups are tolerated. The emerging dihydroselenophenes were easily oxidized by DDQ to selenophenes. The special substitution pattern might be interesting for applications in materials chemistry. Current studies using thiocyanates are underway and will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c03329.

Detailed experimental procedures and analytical data, ^1H and ^{13}C spectra for all new compounds, and details on mechanistic experiments (PDF)

Accession Codes

CCDC 2034505−2034507 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 Cam-

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Notes

The authors declare no competing financial interest.

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