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Formal insertion of selenoketenes into donor–acceptor cyclopropanes: mesomeric alkynylselenolates as key starting materials†

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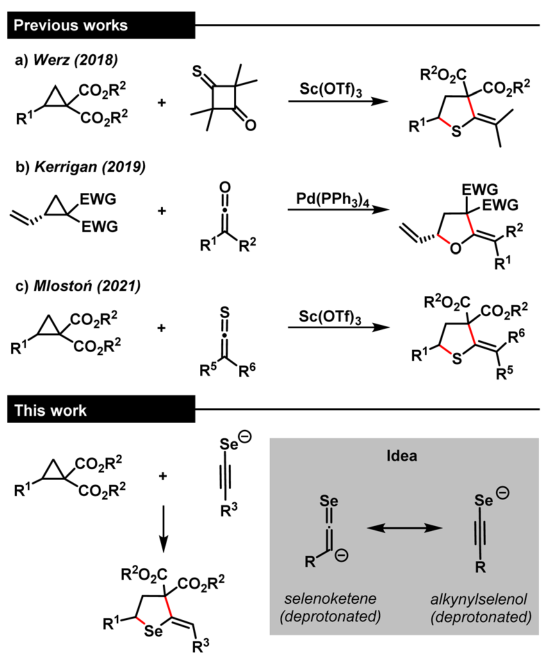
Donor–acceptor cyclopropanes (DACs) react with lithium alkynylselenolates in the presence of $In(OTf)_3$ to furnish tetrahydroselenophenes with exocyclic double bonds. The reaction can be regarded as a formal insertion of selenoketenes into the strained three-membered ring systems. Lithium alkynylselenolates are generated *in situ* from lithium acetylides and elemental selenium. The reactions afford tetrahydroselenophenes with a broad substrate scope and high yields (up to 95%).

Introduction

Donor–acceptor cyclopropanes (DACs) are well-established as useful three-carbon synthons.[1] The high ring strain of 115 kJ mol^{-1} and the polarization originating from the vicinally positioned donor and acceptor groups are the factors accounting for their versatile reactivity.[2] In addition to the intrinsic polarization, Lewis acids are able to polarize the C–C bond further by chelating to the corresponding acceptor moieties. The push–pull trigger caused by the electron-releasing donor moiety and the electron-withdrawing acceptor moiety enables the three-membered ring to behave as a masked 1,3-zwitterionic intermediate. Thus, these strained ring systems display various reactivities such as (3 + n)-cycloadditions,[3] rearrangements[4] and ring-opening reactions.[5] Highly functionalized, saturated or partially saturated four-, five-, six- or seven-membered rings are furnished by various (3 + n)-cycloaddition reactions of D–A cyclopropanes with π-systems such as carbonyls,[6] imines,[7] nitrosoarenes,[8] nitrones[9] and polarized hetero-2π-components.[10] However, cumulated π-systems have not been extensively explored as reaction partners with D–A cyclopropanes. In 2012, the Stolz group reported a (3 + 2)-cycloaddition of DACs with dipolarophiles such as isothiocyanates, carbodiimides and isocyanates to afford thioimidates, imidines and pyrrolidinones, respectively.[11] Shortly afterwards, in 2013, Wang and co-workers realized an intramolecular cycloaddition of DACs with an allene pendant on their aryl donor.[12] Werz *et al.* employed 3-thioxocyclobutanones as thioketene surrogates for the formal insertion of thioketenes, which are unstable under ambient conditions, into DACs (Scheme 1a).[13] This reaction provided a broad scope of tetrahydrothiophenes in a formal (3 + 2)-cycloaddition followed by a (2 + 2)-cycloreversion. In 2019, Kerrigan and co-workers explored the reactivity of ketenes with DACs, and observed that the reaction



Scheme 1 Previous work on the insertion of ketenes and thioketenes into DACs and our present work, with its basic idea of mesomerism between deprotonated selenoketene and deprotonated alkynylselenol.

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outcome depended on the donor moiety and the employed reaction conditions. Palladium catalysis of vinyl cyclopropanes and ketenes furnished highly substituted tetrahydrofurans with an exocyclic double bond (Scheme 1b).[14] However, when the catalytic system was changed to $InBr_3$-$EtAlCl_2$, a dual Lewis acid system, exclusive formation of cyclopentanones was observed.[15] Recently, Mlostoń *et al.* successfully reacted sterically encumbered thioketenes with DACs to access the corresponding sulphur-containing heterocycles (Scheme 1c).[16]

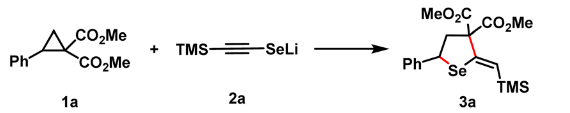
In view of these prior reports, we were keen to test whether a formal insertion of selenoketenes into DACs, to access similar selenium analogues, would be possible. Selenoketenes are highly labile species, much less stable than their oxygen and sulphur analogues,[17] but have been detected by flash-thermolysis and matrix-photolysis techniques.[18] In 1980, a stable selenoketene was synthesised *via* selena-Cope rearrangement of silyl ethynyl selenide with a bulky allyl residue, which provided extra stabilization of the expected selenoketene.[19] Such selenoketenes have been subjected to various addition and cycloaddition reactions.[20] Accordingly, we surmised that lithium alkynylselenolates, mesomeric forms of deprotonated selenoketenes, might be utilized for a formal insertion of selenoketenes into DACs to deliver tetrahydroselenophenes with an exocyclic double bond (Scheme 1, bottom).[21]

Results and discussion

We initiated the optimization of reaction conditions with the model cyclopropane **1a** and trimethylsilylacetylene. Lithium 2-(trimethylsilyl)ethynyl-1-selenolate **2a** was generated *in situ* from trimethylsilylacetylene, *n*BuLi and elemental selenium according to the literature procedure.[22] The solution of **1a** and various Lewis acids were added at 25 °C to the selenolate. Most of the commonly used Lewis acids such as $Sc(OTf)_3$, $Yb(OTf)_3$, $AlCl_3$, $Cu(OTf)_2$, $Sn(OTf)_2$, $Ni(OTf)_2$, $Y(OTf)_3$, $NiBr_2$ led to ring-opening of the DAC. Ring-closure to afford the desired five-membered ring containing selenium was observed only when $In(OTf)_3$, $Bi(OTf)_3$ or $Eu(OTf)_3$ were employed as Lewis acids (Table 1, entries 1–3), but at first only traces of the selenophene derivative were obtained. An increase in temperature to 50 °C showed an increase in yield of the product (entry 4). Increase in the catalyst loading to 50 mol% increased the product yield to 45% (entry 5). An increase in the temperature to 30 °C delivered **3a** in 51% yield (entry 6). Although heating the reaction mixture up to 40 °C gave a better yield of 64%, further heating to 50 °C negatively influenced the yield of the product (entry 8). Screening the stoichiometry of the reagents showed that a 1 : 2 ratio of DAC to selenolate is the best choice. It was observed that the product **3a** was formed in 87% yield when the catalyst loading was increased to 80 mol% (entry 9). The rationalization of high catalyst loading may be attributed to its dual role: activation of the DAC by chelation and π-complexation with the alkyne moiety.[23]

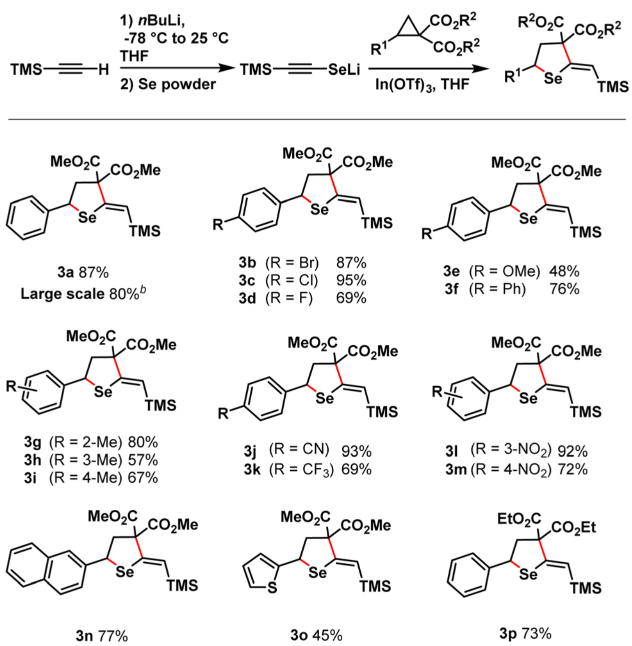
With the optimized reaction conditions in hand, the scope of this method using *in situ* generated lithium alkynylselenolate **2a** and variously substituted DACs was investigated (Scheme 2). Under the optimized reaction conditions, the reaction proceeded smoothly with halogen-bearing aryl cyclopropanes delivering the desired products **3b**–**3d** in good to excellent yields. The electron-rich cyclopropane with a methoxy group on the aryl donor gave the product **3e** in 48% yield. Notably, the cyclopropane with a biphenyl donor **1f** reacted with the corresponding selenolate to furnish the corresponding product **3f** in 76% yield. Aryl donors with *ortho*, *meta* and *para* methyl substituents **1g**–**1i** afforded the corresponding

Table 1 Optimization of the reaction conditions[a]



Entry	Lewis acid	Catalyst loading (mol%)	T (°C)	Yield[b] (%) 3a
1	$In(OTf)_3$	20	25	8
2	$Bi(OTf)_3$	20	25	4
3	$Eu(OTf)_3$	20	25	5
4	$In(OTf)_3$	20	50	19
5	$In(OTf)_3$	50	25	45
6	$In(OTf)_3$	50	30	51
7	$In(OTf)_3$	50	40	64
8	$In(OTf)_3$	50	50	33
9	$In(OTf)_3$	80	40	87

[a] Reaction conditions: **1a** (100 μmol), **2** (*in situ* generated), Lewis acid, solvent (0.05 M) under Ar for 18 h. [b] Yields refer to purified and isolated products.

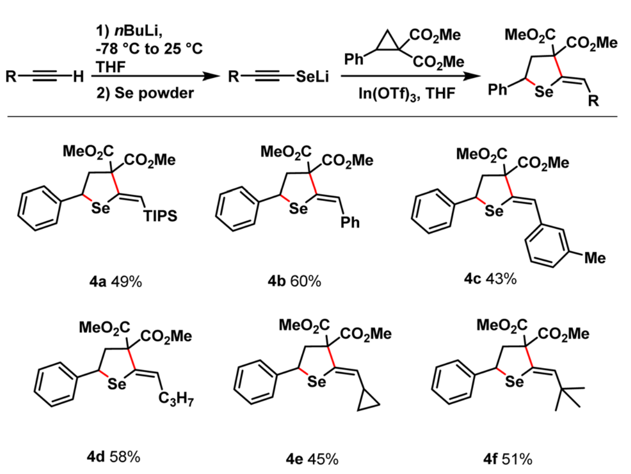


Scheme 2 Substrate scope with respect to DACs. [a] Reaction conditions: **1** (100 μmol), **2a** (200 μmol), $In(OTf)_3$ (80 mol%), THF (2 mL), at 40 °C under Ar for 18 h. Yields refer to purified and isolated products. [b] Large scale refers to 1 mmol of DAC.

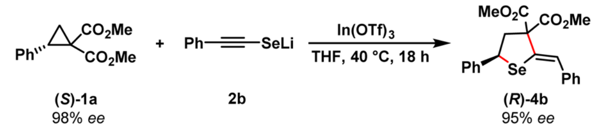
products **3g**–**3i** in yields up to 80%. Surprisingly, the electron-withdrawing cyano (–CN) substituent gave the product **3j** in excellent yield (93%); however, the trifluoromethyl (–CF_3) group negatively influenced the reactivity and furnished products **3k** in a moderate yield of 69%. The presence of an electron-withdrawing nitro (–NO_2) group at the *meta* and *para* position of the aryl donor yielded **3l** and **3m** in 92% and 72% yields, respectively. The naphthyl donor, an extended π-system, furnished the corresponding tetrahydroselenophene **3n** in 77% yield. The thienyl donor was found to be tolerated under the reaction conditions and afforded product **3o** in 45% yield. Ethyl esters as acceptor moieties delivered the corresponding product **3p** in 73% yield. Vinyl and alkyl moieties as donors did not yield the desired products.

The generality of the proposed methodology was then evaluated using different selenolate precursors **2** (Scheme 3). These were generated from the corresponding terminal alkynes and elemental selenium and reacted with cyclopropane **1a.** Under the optimized conditions, alkynes with a more sterically encumbered terminus such as the triisopropylsilyl (TIPS) group underwent smooth transformation and furnished the product **4a** in 49% yield. The lithium alkynylselenolate generated from phenylacetylene afforded the corresponding product **4b** in 60% yield. The presence of a *meta*-methyl group on the phenylacetylene lowered the yield of corresponding product **4c** to 43% yield. Changing to the aliphatic pentyne as the selenolate precursor delivered the corresponding tetrahydroselenophene **4d** in 58% yield. Utilising cyclopropyl acetylene as precursor furnished the product **4e** in 45% yield. *tert*-Butylacetylene was found to be tolerated under the reaction conditions and afforded the product **4f** in 51% yield.

To shine a light on the reaction mechanism, the stereochemical course of the reaction using enantioenriched cyclopropane **(*S*)-1a** (98% ee) was explored. It was found that the product **4b** was formed in 79% yield with 95% ee (Scheme 4). The reaction was observed to proceed with high stereospecificity, with only



Scheme 3 Substrate scope with respect to various alkynes. Reaction conditions: **1a** (100 μmol), **2** (200 μmol), $In(OTf)_3$ (80 mol%), THF (2 mL), at 40 °C under Ar for 18 h. Yields refer to purified and isolated products.

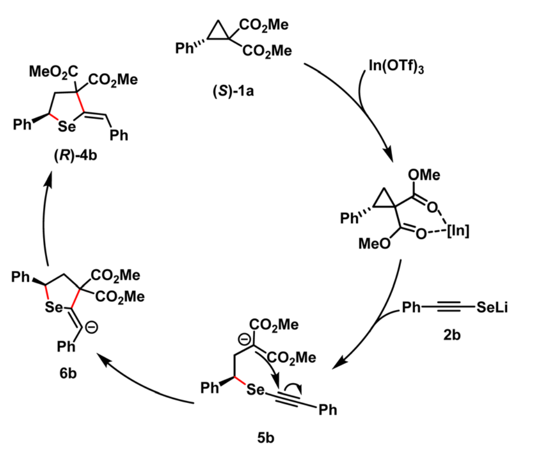


Scheme 4 Stereospecificity experiment.

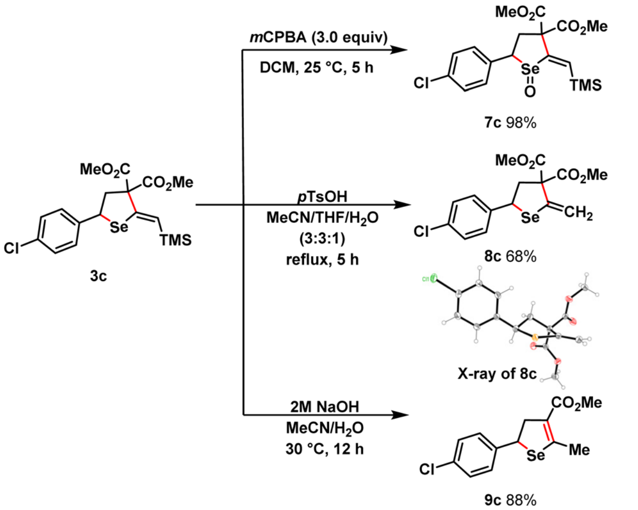
a slight erosion of enantiopurity. This clearly rules out the likelihood of an S_N1 pathway, in which a racemic mixture would have been observed. This prompted us to conclude that the initial attack is an S_N2-like ring-opening of the highly strained ring system by *in situ* generated alkynylselenolate **2b**, followed by a ring-closure to obtain **(*R*)-4b** with an inverted stereochemistry.

A plausible mechanism for the transformation of DACs to tetrahydroselenophenes is proposed in Scheme 5. $In(OTf)_3$ activates the strained three-membered ring **(*S*)-1a** by coordinating to the acceptor moieties. This depletes the electron density from the C–C bond between the donor-substituted and the acceptor-substituted carbon atoms of the cyclopropane, thereby weakening it. The nucleophilic selenolate **2b** undergoes an S_N2-like ring-opening of the highly strained system, leading to open-chain intermediate **5b**. The emerging malonate attacks the electrophilic carbon next to selenium in a 5-*exo-dig* fashion to obtain **6b.** Protonation furnishes product **(*R*)-4b**. Because of the bulky dicarboxylate moiety, the final step takes place in a highly selective manner; only one of the two possible double bond isomers is formed.

Finally, we demonstrated the utility of the proposed methodology by subjecting tetrahydroselenophene **3c** to several further transformations (Scheme 6). Notably, oxidation of **3c** using 3.0 equivalents of *m*CPBA delivered selenoxide **7c** in 98% yield as a single diastereoisomer; the double bond was not effected by oxidation. Desilylation of **3c** under acidic conditions using *p*TsOH delivered the corresponding product **8c** in 68% yield. The structure of **8c** was unambiguously confirmed by single crystal X-ray analysis. Decarboxylation and concomitant desilylation of **3c** using NaOH furnished dihydroselenophene **9c** in 88% yield.



Scheme 5 Proposed mechanism.



Scheme 6 Follow-up reactions.

Conclusions

In summary, we have demonstrated a simple and efficient strategy for the construction of tetrahydroselenophenes starting from D–A cyclopropanes and alkynylselenolates. Alkynylselenolates can be regarded as mesomeric forms of deprotonated selenoketenes. This transformation thus represents the formal insertion of a selenoketene into the three-membered ring. The method was found to be general, and an extensive substrate scope with high functional group tolerance was realized. Various tetrahydroselenophene derivatives were obtained in good to excellent yields. The concept of exploiting such masked (and previously neglected) mesomerism might pave the way to other types of formal cycloaddition reactions with unusual or unstable cumulated π-systems.

Experiments

General procedure for the synthesis of tetrahydroselenophene 3

A flame-dried, argon-filled microwave tube was charged with alkyne (2.2 equiv.) in THF (0.1 M) at 0 °C. The solution was cooled to −78 °C. To this solution was added *n*BuLi (2.0 equiv.). The reaction was stirred for 1 h and slowly warmed to 25 °C. Elemental grey selenium (2.2 equiv.) was then added in one portion. Further stirring led to dissolution of the selenium, whereby the solution changed colour from black to pale yellow, furnishing **2**.

A solution of cyclopropane diester **1** (100 µmol, 1.0 equiv.) and $In(OTf)_3$ (80 µmol, 0.8 equiv.) dissolved in THF (0.1 M) were added to the *in situ* generated **2** under an argon atmosphere. The solution was stirred at 40 °C (oil bath) until TLC analysis showed full conversion of cyclopropane **1**. The reaction tube was allowed to cool to the room temperature. EtOAc (10 mL) was added, and the reaction mixture was then washed with saturated $NaHCO_3$ solution and extracted with EtOAc (3 × 20 mL). The organic layers were combined and dried over Na_2SO_4. The solvent was evaporated under reduced pressure. The crude product **3** was purified by silica gel column chromatography.

Author contributions

A. J. conducted the experiments, analysed the data and wrote the draft. P. G. J. determined the crystal structure of compound **8c** and assisted with manuscript preparation. D. B. W. supervised the work and finalised the manuscript.

Conflicts of interest

There are no conflicts to declare.

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