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Lewis-Acid-Catalyzed (3 + 2)-Cycloadditions of Donor-Acceptor Cyclopropanes with Thioketenes

Grzegorz Mloston,^{*[a]} Mateusz Kowalczyk,^[a] André U. Augustin,^[b] Peter G. Jones,^[c] and Daniel B. Werz^{*[b]}*In memory of Professor Dr. Klaus Hafner.*

The reactivity of donor-acceptor (D-A) cyclopropanes towards thioketenes was investigated. In a (3 + 2)-cycloaddition using Sc(OTf)₃ as a Lewis acidic catalyst, the corresponding exocyclic thioenol ethers (2-methylidene tetrahydrothiophenes) were formed in moderate to good yields. Unsymmetrical thioketenes provided *E/Z* mixtures at the double bond, with the *Z* isomer being preferred.

Donor-acceptor (D-A) cyclopropanes have become one of the most important building blocks for three-carbon units. Although initial and fundamental work was performed in the 1980s by the groups of Wenkert and Reissig,^[1] a wide range of novel reactions exploiting these polarized strained systems have been developed since the beginning of the 21st century.^[2] The thermodynamic driving force is the strain energy of the three-membered ring, amounting to *ca.* 115 kJ/mol. Nevertheless, without substitution by donor and acceptor groups the activation barrier to opening the cyclopropane ring would be much too high.^[3] This special polarizing substitution pattern has set the basis not only for the development of ring-enlargement^[4] and cycloaddition^[5] reactions of D-A cyclopropanes, but also for their ring-opening 1,3-bisfunctionalization.^[6] The intrinsic polarization can be further increased by adding Lewis acids as catalysts, which chelate the two ester groups,

thus removing even more electron density from the bond to be broken.^[7] π -Systems such as olefins, alkynes, aldehydes,^[8] imines,^[9] nitroso compounds^[10] and thiocarbonyls^[11] have readily engaged in (3 + 2)-cycloaddition reactions with D-A cyclopropanes. Furthermore, α,β -unsaturated thioketones (thiochalcones) reacted smoothly with D-A cyclopropanes yielding seven-membered tetrahydrothiopynes as perfectly stable products of a unique (4 + 3)-cycloaddition.^[12]

Less is known about related cycloaddition reactions using cumulated π -systems. In 2012, isocyanates, isothiocyanates and carbodiimides were reacted with D-A cyclopropanes by the Stolz group.^[13] Allenes have also been used as the parent carbon-based cumulative systems, in an intramolecular fashion.^[14] Based on our initial work on cycloadditions with thioketones,^[12,15] our group designed a reaction in which four-membered thioketones, derived from sterically crowded 2,2,4,4-tetramethylcyclobutane-1,3-dione, were exploited as surrogates for the formal thioketene (3 + 2)-cycloadditions (Scheme 1).^[16] However, in-depth mechanistic investigations have demonstrated that no thioketene is formed, but that the reaction proceeds via a spirocyclic intermediate that undergoes a (2 + 2)-cycloreversion of the cyclobutanone ring, catalyzed by Lewis acids. Very recently, the Kerrigan group has designed a Lewis-acid-catalyzed insertion of ketenes into D-A cyclopropanes. Depending on the type of donor and the reaction conditions, different reaction outcomes were observed. With vinyl groups as donor, exocyclic enol ethers were obtained under Pd catalysis whereas InBr₃ as Lewis acid led to the (3 + 2)-cycloaddition of the two carbon atoms of the ketene, allowing a facile and elegant access to cyclopentanones (Scheme 1).^[17]

In contrast to thioketones, which have demonstrated great utility in the construction of various sulfur-containing heterocycles,^[18] thioketenes have not been investigated as thoroughly. Their limited use in modern organic synthesis results mainly from their instability under ambient conditions. In addition, there are only a limited number of efficient procedures for a straightforward access to differently substituted representatives. It is well established that enhanced thermodynamic stability of the monomeric form of a thioketene can be achieved only by the introduction of electron-withdrawing perfluoroalkyl groups or by steric shielding of the heterocumulenic C=C=S bonds as in (*tert*-butyl)*iso*-propyl thioketene or 2,2,6,6-tetramethylcyclohexylidene thioketene. With these representatives, some (3 + 2)-cycloadditions were successfully performed with thioketenes as the reactive C=S

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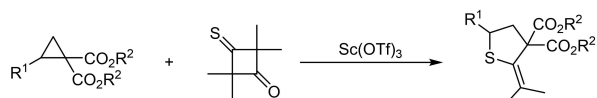
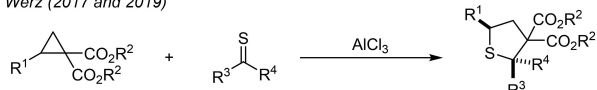
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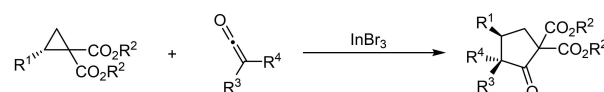
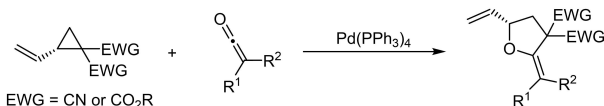
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Previous Work

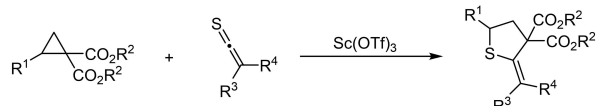
Werz (2017 and 2019)



Kerrigan (2019)



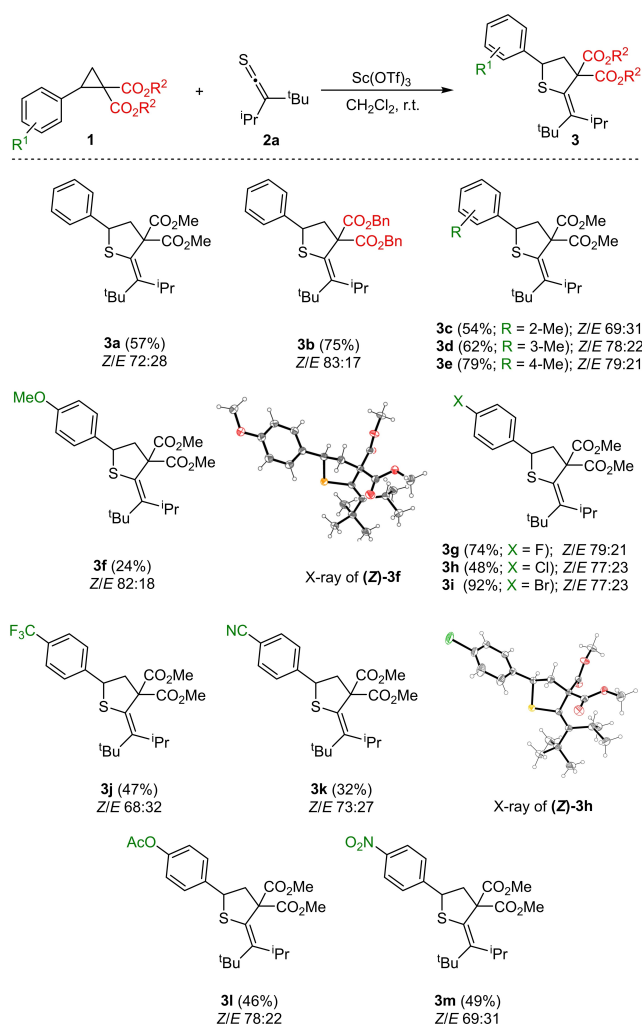
This Work



Scheme 1. Previous work of our group and the Kerrigan group demonstrating the insertion of thioketones and ketenes, and our present work.

dipolarophiles.^[19] The most extensively explored bis-(trifluoromethyl)thioketene reacted smoothly with such 1,3-dipoles as aryl azides,^[20] diazomethane, nitrile oxides, and nitrones^[21] yielding the desired cycloadducts. Sterically crowded thioketenes were studied in reaction with diazomethanes such as 2-diazopropane and di(*tert*-butyl)diazomethane, yielding 2-alkylidene-1,3,4-thiadiazolines.^[22] The formation of a (3 + 2)-cycloadduct at the C=S bond was also observed in the reaction of (*tert*-butyl)*iso*-propyl thioketene with 2-phenyl-(3-(dimethylamino))-2-methyl-2*H*-azirine.^[23]

Based on our previous investigations in donor-acceptor cyclopropane chemistry, we attempted to engage sterically stabilized thioketenes in reactions with D-A cyclopropanes. Because Sc(OTf)₃ proved to be a good choice as Lewis acid for such insertion reactions, we started our studies with this catalyst. As starting point we used the phenyl-substituted derivative **1a** (R¹ = H) and (*tert*-butyl)*iso*-propyl thioketene **2a**. A first experiment in dichloromethane at room temperature afforded the desired product in 57% yield as a diastereomeric mixture of *Z/E* isomers in a ratio of 72:28 (Scheme 2). With these encouraging results in hand, we immediately used benzyl esters as acceptor groups, leading to the product in 75% yield and a slightly better *Z/E* ratio of 83:17. Substitution of the phenyl unit by methyl groups gave the respective products **3c–3e** in similar yields and selectivity. Also, halogen substituents in *para*-position were well tolerated, leading to thioenol ethers **3g–3i**. X-ray structure analysis of the Cl-substituted derivative **3h**^[24] confirmed the anticipated structure with the sterically bulkier *t*-butyl group *trans* to the carbon bearing the two ester



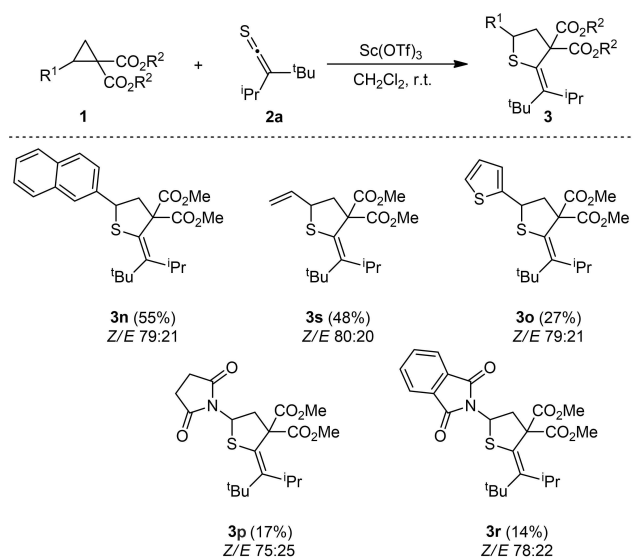
Scheme 2. (3 + 2)-Cycloaddition of various D-A cyclopropanes **1** with thioketene **2a**. Reaction conditions: **1** (100 μmol), **2a** (120 μmol), Sc(OTf)₃ (10 mol%), CH₂Cl₂ (1.0 mL), rt. Yields refer to the purified and isolated *Z/E* mixtures *dr* = *Z*:*E*.

functionalities. In contrast to many previous studies, the very electron-rich donor *para*-methoxyphenyl did not lead to good yields; only 24% of the respective thioenol ether **3f** was obtained. This structure was also confirmed by single crystal X-ray crystal structure analysis (Scheme 2).^[24] Other *para*-substituted phenyl groups as donors, such as trifluoromethyl, cyano, nitro and acetoxy, yielded the anticipated products in moderate yields and selectivity with the less sterically hindered *Z* isomers as the major ones.

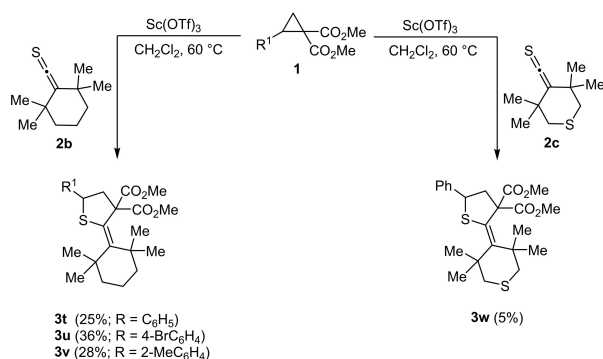
Furthermore, we tested other non-phenyl substituents as donors. For example, a naphthyl unit worked well and furnished the desired product in 55% yield. Decreasing the size of the π-system to just a vinyl group also allowed a successful transformation, affording compound **3s**. With the very electron-rich thienyl moiety the product was only obtained in 27% yield. With the classical Waser cyclopropanes,^[25] bearing succinimide and phthalimide as donors, rather poor yields of only 17% and 14%, respectively, were obtained. In all cases diastereomeric

mixtures in a ratio of 3:1 to 4:1, with a strong preference for the *Z* isomer, were obtained (Scheme 3).

As already mentioned, the number of thioketenes that are easily accessible is rather limited. Thus, only two other thioketenes **2b** and **2c** were used for our study. They are based on six-membered rings with steric shielding in the α,α' -positions by geminal methyl groups. They differ in the presence of an endocyclic sulfur atom in **2c**, whereas **2b** is based on a native hydrocarbon ring system. Three different cyclopropanes were converted. In contrast to the more flexible thioketene **2a** the reaction temperature had to be raised to 60 °C to reach conversion, conducted in these cases in a vial equipped with screw cap. Under these conditions, using dichloromethane as solvent, the desired thioenol ethers **3t**, **3u** and **3v** were obtained in yields ranging from 25–36%. We connect the poorer yields with the higher steric crowding in comparison to



Scheme 3. (3 + 2)-Cycloaddition of various D-A cyclopropanes **1** (bearing non-phenyl substituents) with thioketene **2a**. Reaction conditions: **1** (100 μ mol), **2a** (120 μ mol), Sc(OTf)₃ (10 mol%), CH₂Cl₂ (1.0 mL), rt. Yields refer to the purified and isolated *Z/E* mixtures *dr* = *Z*:*E*.



Scheme 4. (3 + 2)-Cycloaddition of D-A cyclopropanes **1** with sterically highly shielded thioketenes **2b** and **2c**. Reaction conditions: **1** (100 μ mol), **2** (120 μ mol), Sc(OTf)₃ (10 mol%), CH₂Cl₂ (1.0 mL), 60 °C. Yields refer to the purified and isolated product.

thioketene **2a**. The transformation of **1a** with thioketene **2c** led to only 5% of the respective product **3w** (Scheme 4). Because of the longer S–C bonds compared to C–C, the thioketene moiety is even less accessible than in **2b**. It is noteworthy that the exocyclic double bonds in compounds **3t–3w** are sterically highly shielded.

In summary, we report (3 + 2)-cycloadditions of thioketenes with donor-acceptor cyclopropanes. Scandium triflate (Sc(OTf)₃) was used as Lewis acid to facilitate the transformation. For (*tert*-butyl)*iso*-propyl thioketene, room temperature was sufficient, whereas for the more sterically encumbered derivatives a temperature of 60 °C was necessary. In the case of (*tert*-butyl)*iso*-propyl thioketene, isomeric mixtures with respect to the configuration of the semi-cyclic double bond were obtained, with a strong preference for the *Z* isomer. This method nicely complements the recently discovered reactions of donor-acceptor cyclopropanes for efficient (3 + 2)-cycloadditions performed with thioketones and ketenes.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Cycloaddition · D-A cyclopropanes · Lewis acids · Sulfur heterocycles · Thioketenes

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