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Brønsted Acid Catalysis in Visible-Light-Induced [2+2] Photocycloaddition Reactions of Enone Dithianes

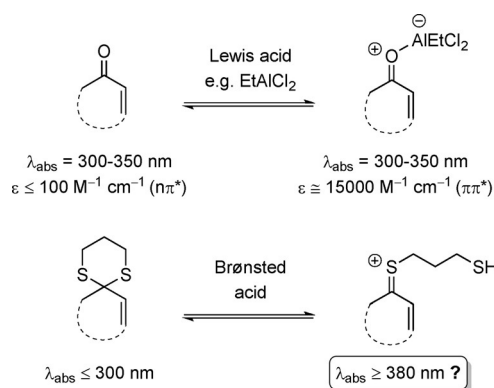
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In memory of Marcus Hübel

Abstract: 1,3-Dithiane-protected enones (enone dithianes) were found to undergo an intramolecular [2+2] photocycloaddition under visible-light irradiation ($\lambda = 405$ nm) in the presence of a Brønsted acid (7.5–10 mol %). Key to the success of the reaction is presumably the formation of colored thionium ions, which are intermediates of the catalytic cycle. Cyclobutanes were thus obtained in very good yields (78–90 %). It is also shown that the dithiane moiety can be reductively or oxidatively removed without affecting the photochemically constructed ring skeleton.

Among all photochemical reactions, the [2+2] photocycloaddition is undoubtedly of the greatest synthetic importance.^[1] This reaction enables the simultaneous construction of two C–C bonds and up to four stereogenic centers. In this regard, it parallels the thermal [4+2] cycloaddition, the Diels–Alder reaction, which allows for a similarly high increase in complexity. In the case of a [2+2] photocycloaddition, the newly formed ring is a strained four-membered ring (cyclobutane), which offers multiple options for further functionalization.^[2,3] The photochemically excitable component of a [2+2] photocycloaddition is frequently a cyclic α,β -unsaturated carbonyl compound, and its olefinic double bond can react with a suitable alkene either inter- or intramolecularly. Embedding the double bond in a cyclic compound avoids deactivation in the excited state by *E/Z* isomerization. Conjugation to the carbonyl group allows for direct long-wavelength excitation, for example, at $\lambda_{\text{abs}} = 300$ –350 nm with cycloalkenones (enones; Scheme 1).^[4]

We recently showed that the long-wavelength absorption of typical enones becomes more intense upon complexation by a Lewis acid.^[5] This observation is in agreement with earlier studies that reported on a similar behavior for coumarins and other α,β -unsaturated β -aryl-substituted car-



Scheme 1. Upon coordination of a Lewis acid to an enone, an onium ion is formed, which strongly absorbs at $\lambda_{\text{abs}} = 300$ –350 nm (top). Can a thionium ion that absorbs in the visible region ($\lambda_{\text{abs}} > 380$ nm) be formed upon protonation of a 1,3-dithiane (bottom)?

bonyl compounds.^[6] The reason for the intensity increase is a bathochromic shift of the strong short-wavelength $\pi\pi^*$ absorption.^[5c] As a consequence of the high absorption cross-sections of such Lewis acid/enone complexes, [2+2] photocycloaddition reactions can be rendered enantioselective in the presence of a chiral Lewis acid.^[5,7,8]

When searching for substrates that exhibit a negligible long-wavelength absorption but would potentially show a strong bathochromic shift upon activation by an acid, we tested enones upon transformation of their carbonyl groups into 1,3-dithianes (enone dithianes). The putative thionium ions that were expected to be formed upon protonation could potentially be excited in the visible region ($\lambda_{\text{abs}} > 380$ nm),^[9] and would thus be suited to undergo a Brønsted acid catalyzed [2+2] photocycloaddition (Scheme 1). Possible background reactions should be completely avoided. We now report initial results of our studies.

In a first set of experiments, the UV/Vis spectra of cyclic *S,S*-acetals derived from 3-(4-pentenyl)-cyclohex-2-enone were recorded. As expected, no significant absorption was observed at wavelengths of $\lambda \geq 300$ nm. The spectrum of dithiane **1a**^[10] is depicted as a representative example in Figure 1 (dotted line). Upon addition of bis(trifluoromethanesulfonyl)imide Tf₂NH (Tf = trifluoromethanesulfonyl) as a Brønsted acid, the solution of **1a** turned yellow, and a strong long-wavelength absorption with a maximum at $\lambda_{\text{abs}} = 356$ nm was observed that stretched into the visible region. The absorbance reached saturation after addition of 12.5 equiv of the Brønsted acid. Assuming full conversion of the dithiane, the value for the molar decadic absorption coefficient ϵ was calculated as 23900 M⁻¹ cm⁻¹.

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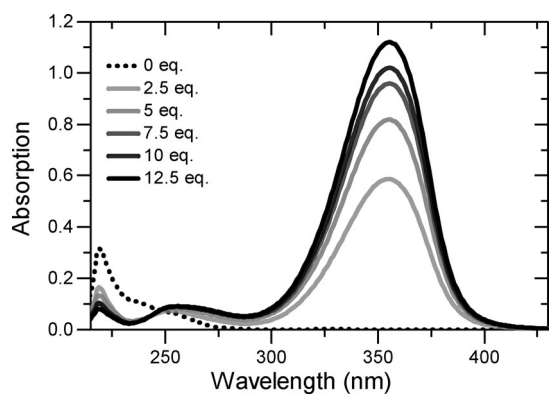
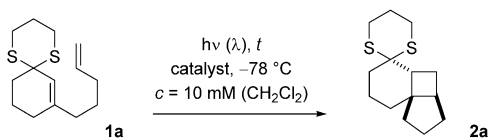


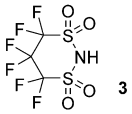
Figure 1. UV/Vis spectrum of compound **1a** in CH_2Cl_2 as the solvent ($c=0.5$ mM) without Brønsted acid (.....) and after addition of various equivalents of Tf_2NH (—).

As the absorption of the putative thionium ion partially lies in the visible region, it was attempted to induce a reaction with light of $\lambda \geq 380$ nm in the presence of a catalytic amount of a Brønsted acid. To this end, light emitting diodes (LEDs) were employed as the light source, which exhibit a sharp emission band.^[11] To our delight, at $\lambda=398$ nm, 1,3-dithiane **1a** was indeed converted into product **2a** in an intramolecular [2+2] photocycloaddition upon addition of 10 mol % Tf_2NH (Table 1, entry 1). The dithiane turned out to be clearly superior to the corresponding 1,3-dithiolane, which did not undergo a reaction under the same reaction conditions.^[12]

When testing further acids, the strong Brønsted acids HOTf (entry 2), $\text{C}_6\text{F}_5\text{CHTf}_2$ (entry 5), and imide **3** (entry 6)

Table 1: Optimization of the reaction conditions for the Brønsted acid catalyzed [2+2] photocycloaddition of 1,3-dithiane **1a** to cyclobutane **2a**.



Entry	Catalyst ^[a]	Loading [mol %]	λ [nm]	t ^[b] [h]	Yield ^[c] [%]
1	Tf_2NH	10	398	2.5	88
2	HOTf	10	398	3.0	81
3	CSA	10	398	26.0	— ^[d]
4	$\text{B}(\text{C}_6\text{F}_5)_3$	10	398	22.0	44
5	$\text{C}_6\text{F}_5\text{CHTf}_2$	10	398	5.5	86
6		10	398	1.5	86
7	3	10	— ^[e]	3.5	— ^[d]
8	3	7.5	398	3.5	86
9	3	7.5	405	3.5	85 ^[f]

[a] All reactions were performed on 0.1 mmol scale with an LED lamp (7 W power output, emission at the indicated wavelength)^[11] as the light source.^[13] Cooling bath: acetone/dry ice. [b] Irradiation time. [c] Yield of isolated product. [d] No reaction. The starting material was recovered. [e] Without irradiation. [f] The reaction was successfully performed under almost identical conditions ($c=20$ mM, 16 h, 10 W, 93 % yield) on a larger scale (1.6 mmol).

were found to perform well while a weaker acid (camphor-sulfonic acid, CSA; entry 3) and the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ (entry 4) delivered unsatisfactory results. The absence of a reaction with CSA correlates with the fact that there was no long-wavelength absorption to be detected in the UV/Vis spectrum of **1a** even upon addition of 40 equivalents of this acid (see the Supporting Information).

It was then unambiguously established that the reaction was indeed light-induced (entry 7). As imide **3** exhibited the strongest rate acceleration, the catalyst loading was lowered for this acid. Even at a loading of 7.5 mol %, the reaction was complete after 3.5 hours (entry 8), and it was possible to apply light of a longer wavelength ($\lambda=405$ nm) without a deterioration in yield (entry 9). These conditions were subsequently employed for the reaction of other dithianes **1** (Table 2).

The δ -dimethylated analogue **1b** of enone dithiane **1a** reacted as smoothly as the parent compound (entry 1). Compound **1c**, which is dimethylated in the side chain, was somewhat less reactive, and a longer irradiation time and a higher catalyst loading were required to guarantee full conversion (entry 2). The reaction of dithiane **1d** to the highly strained cyclobutene **2d** is a remarkable transformation that proceeded in very high yield (entry 3). With cyclopentenone dithiane **1e**, it was already observed by visual inspection that the bathochromic shift that occurs upon Brønsted acid addition^[14] is not very extensive, and the reaction was therefore conducted at $\lambda=366$ nm (entry 4). The reactions of the chiral substrates **1f–1i** were again conducted under visible-light irradiation ($\lambda=405$ nm), and the yields were very high in all cases (entries 5–8).

As anticipated, a stereogenic center in δ -position led to poor facial differentiation, and product **2f** was isolated as a mixture of diastereomers (d.r.=diastereomeric ratio; entry 5). The asymmetric induction by a stereogenic center in γ -position, however, is excellent, and product **2g** (entry 6), as well as product **2h** (entry 7), was formed in diastereomerically pure form. Owing to 1,3-allylic strain,^[15] the [2+2] photocycloaddition of substrate **1i** also proceeded with high facial diastereoselectivity (entry 8). In most instances, the relative configurations were unambiguously assigned by one- and two-dimensional NMR spectroscopy and NOESY experiments (see the Supporting Information). For product **2g**, however, a crystal structure was required to determine the relative configuration beyond any doubt (Figure 2). The configuration of product **2h** was assigned in analogy to that of **2g**.

It is well established that dithiane moieties can be removed reductively or oxidatively,^[16] and with the tricyclic products **2** of the [2+2] photocycloadditions, the cleavage also proceeded without any complications. The reductive desulfurization^[17] was exemplarily performed with product **2b** and delivered the volatile hydrocarbon **4**^[18] in 75 % yield (Scheme 2). Upon treatment of product **2a** with [bis(trifluoroacetoxy)iodo]benzene,^[19] ketone **5** was obtained in 84 % yield. The cleavage can also be used to generate the respective ketones without isolation of the intermediate dithiane photoproducts. In the case of substrate **1j**, for example, it turned out to be impossible to separate product **2j** from minor impurities. Consequently, the dithiane moiety was

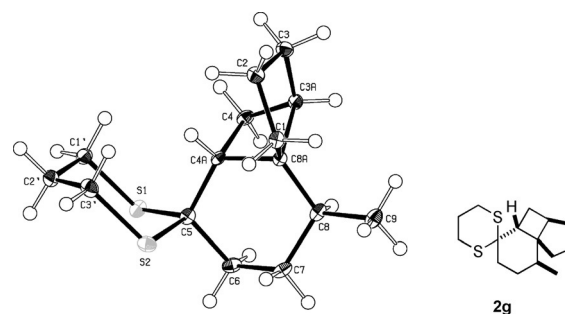
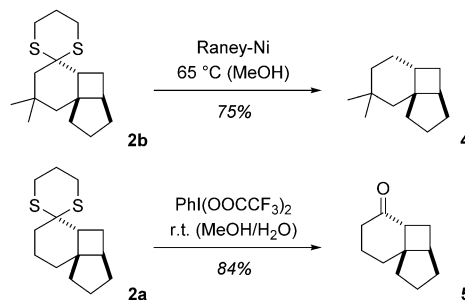
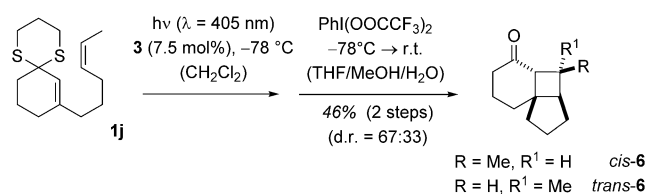
Table 2: Brønsted acid catalyzed [2+2] photocycloaddition of various dithianes **1**^[10] under visible-light irradiation.

Entry	Substrate ^[a]	<i>t</i> ^[b] [h]	Product	Yield ^[c] [%]
1		5		80 ^[d]
2		22		78 ^[e]
3		24		86 ^[e]
4		21		78 ^[d,f]
5		24		90 ^[e,g]
6		21		89 ^[e,h]
7		24		79 ^[e,h]
8		6		85 ^[d,i]

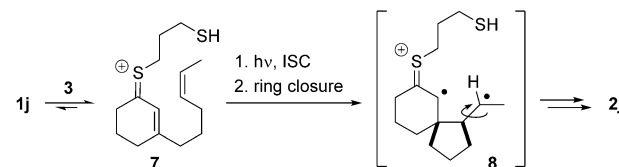
[a] All reactions were performed on 0.1 mmol scale with an LED lamp (7 W power output, $\lambda = 405$ nm)^[11] as the light source.^[13] Cooling bath: acetone/dry ice. [b] Irradiation time. [c] Yield of isolated product. [d] Catalyst (7.5 mol%). [e] Catalyst (10 mol%). [f] Irradiation at $\lambda = 366$ nm. [g] 60:40 d.r. [h] $\geq 95/5$ d.r. [i] 90:10 d.r.

removed oxidatively, and the pure product **6** was isolated as a mixture of the two diastereomers *cis*-**6** and *trans*-**6** (Scheme 3).

The [2+2] photocycloaddition of the *Z*-configured substrate **1j** proceeded in a stereo-unspecific fashion, that is, without retention of the double-bond configuration. The ratio of the two diastereomeric cyclobutanes was already deter-

**Figure 2.** Confirmation of the relative configuration of product **2g** by crystal-structure analysis.**Scheme 2.** Reductive (**2b**→**4**) and oxidative (**2a**→**5**) removal of the dithiane moiety in the products **2** of the [2+2] photocycloaddition.**Scheme 3.** Combination of the [2+2] photocycloaddition with oxidative cleavage of the dithiane group to obtain ketones **6** directly from substrate **1j**.

mined prior to cleavage of the dithiane group to be 67:33 by GC analysis. This finding supports the notion that the reaction proceeds via triplet 1,4-diradical **8**,^[20] in which free rotation about the indicated single bond is feasible (Scheme 4). As illustrated for substrate **1j**, the excitation thus proceeds via thionium ion **7**, which undergoes ring closure to intermediate **8** upon intersystem crossing (ISC). The strong absorption of the thionium ion (Figure 1) indicates that a $\pi\pi^*$ singlet state (S_1) is populated upon excitation.^[21]

**Scheme 4.** Proposed mechanism for the Brønsted acid catalyzed [2+2] photocycloaddition, exemplarily shown for substrate **1j**.

The configuration of the C=S double bond in **7** remains unclear but the sensitivity of the reaction towards steric hindrance at the terminal end of the olefinic double bond provides circumstantial evidence for the depicted *Z* configuration. The dithiane group also points towards the cyclobutane ring in the reaction products (see Figure 2), which indicates that the carbon chain at the sulfur atom is somewhat biased towards this orientation.

In conclusion, we have shown for the first time that derivatives of cyclic enones can undergo a [2+2] photocycloaddition under visible-light irradiation. The resulting dithianes **2** offer several options for chemical functionalization. The most important result of this study, however, seems to be the fact that catalytic amounts of a Brønsted acid are sufficient to render an otherwise photochemically inaccessible reaction pathway viable. We are convinced that the strategy of catalytic chromophore activation will enable further transformations to be performed with visible light that have thus far only been possible upon UV irradiation. Moreover, the use of chiral 1,3-dithianes^[22] or chiral Brønsted acids^[23] might allow to achieve enantioselectivity with methods that cannot be applied to the classic [2+2] photocycloaddition of enones.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: Brønsted acids · cycloaddition · diastereoselectivity · enones · homogenous catalysis · photochemistry

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