CHEMISTRY
A EUROPEAN JOURNAL

COMMUNICATION

DOI: 10.1002/chem.201300766

Shedding Light on Organocatalysis—Light-Assisted Asymmetric Ion-Pair Catalysis for the Enantioselective Hydrogenation of Pyrylium Ions

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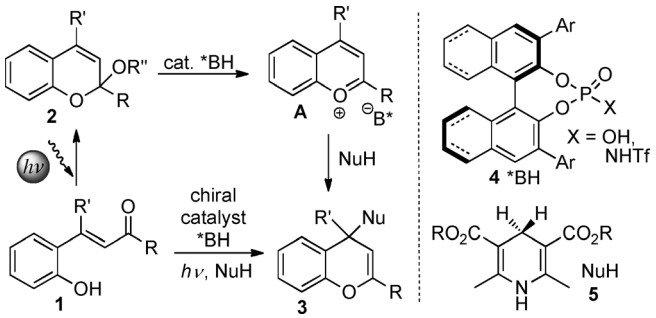
The use of dual catalytic methods, in which two or more catalysts are employed in one-pot procedures, is becoming an increasingly important tool for sustainable chemistry. In this regard considerable progress has been achieved in the development of asymmetric domino reactions[1] in which different metal, bio, or organo catalysts have been employed, in a combined and synergistic fashion, to provide optically active products from achiral substrates. However, the use of benzopyrylium ions in asymmetric catalysis is rare[2] although the corresponding chromanes are privileged structural motifs of natural products and bioactive agents, which exhibit antioxidant, antifungal, antiviral, cytotoxic, and anti-inflammatory activities.[3] Thus, it is desirable to develop improved methodologies for the preparation of chiral chromanes, which could potentially lead to bioactive products with enhanced pharmacological features. Based on our experience in Brønsted acid catalysis and the activation of allylic alcohols and hemiaminals, we decided to examine the use of chromene acetals **2** for the generation of reactive pyrylium ion intermediates (Scheme 1). The Brønsted acid[4,5] catalyzed protonation and subsequent elimination was anticipated to result in the formation of an intermediary chiral ion pair **A** consisting of a benzopyrylium ion and a chiral acid anion.[6] The subsequent enantioselective nucleophilic addition at the 4-position of benzopyrylium ion would give the desired 4*H*-chromenes. So far, no catalytic asymmetric reaction with an intermediate of type **A**, comprising a pyrylium ion and a chiral counter anion, has been reported. Thus, the successful development of this Brønsted acid catalyzed process would not only be the first example of such a reaction, but more importantly would open new avenues in asymmetric anion-pair catalysis.[7]



Scheme 1. First asymmetric Brønsted acid catalyzed hydrogenation of benzopyrylium ions.

In order to validate our proposal, we examined the enantioselective Brønsted acid catalyzed hydrogenation of benzopyrylium ions[8] by employing Hantzsch ester[9] as the nucleophile. Initial experiments were conducted with readily available and generally stable chromene acetals **2** (R″ = Me or Et, see Scheme 1). To our delight, the Brønsted acid catalyzed reduction proceeded well and the desired 4*H*-chromenes were obtained with good yields. However, generally better reactivities and significantly better selectivities were obtained if 2*H*-chromen-2-ols (R″ = H) were applied. Unfortunately, 2*H*-chromen-2-ols are less stable and purification can be difficult. Therefore, we decided to examine enones **1** as precursors for the in situ generation of pyrylium ions. Enones **1** are stable and easily prepared from commercially available starting materials. Furthermore, they undergo photocyclization to form the 2*H*-chromen-2-ols **2**,[10] which in the presence of the Brønsted acid could directly yield the chiral ion pairs **A**, crucial intermediates for the asymmetric hydrogenation.

From the outset we were aware that several problems needed to be addressed in order to perform such an unprecedented photocyclization–hydrogenation sequence: 1) the Brønsted acid catalyzed transfer hydrogenation of enones **1** with Hantzsch dihydropyridine **5** as hydride source has been reported.[11a] This reaction would lead to the undesired saturated ketones, which undergo acid-catalyzed cyclization to the chroman-2-ols. The subsequent acid-catalyzed water elimination would result in our desired product **3**. However, the enantioselectivity determining step would be the initial asymmetric reduction of the enone **1**, which to date has not been possible with chiral Brønsted acids; 2) the light driven reduction of electron-deficient alkenes by photoexcited dihydropyridines, including Hantzsch ester has been stud-

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[+] Determination of the absolute configuration.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201300766.

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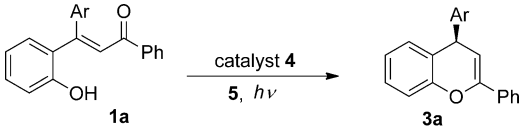
ied.[11b] This reaction may also occur through a photoinduced electron-transfer mechanism[11c] and would result in the racemic saturated ketones, which would ultimately give *rac*-**3**. Furthermore, the chroman-2-ol could also be reduced by the photoactivated Hantzsch ester yielding *rac*-**3**; 3) the photooxidation and photocatalytic production of hydrogen from Hantzsch esters **5** has been well established and could lead to the undesired decomposition of the hydride donor; 4) next to their use as antioxidants, benzopyrylium cations have been shown to be excellent electron acceptors, which are involved in charge-transfer reactions. They can also act as a source of free radicals, which could lead to undesired side reactions.[11d]

Given the above considerations we performed several test reactions (Table 1). First, we started with the Brønsted acid catalyzed reduction of chalcone **1a** (R and R′ = Ph) employing the Hantzsch ester **5** as the hydride source. Pleasingly, no reduction was observed when the reaction was performed in aromatic solvents at room temperature. Additionally, no direct acid-catalyzed cyclization of **1a** to **2a** occurred. However, **1a** was smoothly reacted to the desired 2*H*-chromen-2-ols **2** when the photocyclization was performed in toluene, setting the stage for exploring the photo assisted Brønsted acid catalyzed transfer hydrogenation. Initial reactions were carried out with different dihydropyridines **5a–e** and BINOL-derived phosphoric acid diester **4a**, which had proven to be a good catalyst in organocatalytic hydrogenations of *N*-heterocycles. To our delight, not only was the product **3a** formed, but enantioselectivities of up to 18% enantiomeric excess (*ee*) were obtained if dihydropyridine **5d** was applied (Table 1, entry 4).

Table 1. Optimization of the Brønsted acid catalyzed photocyclization reduction reaction.[a]



4a: Ar = [H8]-2-napthyl
4b: Ar = [H8]-1-napthyl
4c: Ar = [H8]-3,5-$(CF_3)_2$-C_6H_3
4d: Ar = [H8]-9-phenanthryl
4e: Ar = [H8]-4-F-C_6H_4
4f: Ar = [H8]-2,4,6-$(i\text{Pr})_3C_6H_2$
4g: Ar = 2,4,6-$(i\text{Pr})_3C_6H_2$

5a: R = ethyl
5b: R = isopropyl
5c: R = *tert*-butyl
5d: R = allyl
5e: R = benzyl

	T [°C]	4	5	Yield [%][d]	*ee* [%][e]
1	RT	**4a**	**5a**	57	9
2	RT	**4a**	**5b**	55	17
3	RT	**4a**	**5c**	41	8
4	RT	**4a**	**5d**	70	18
5	RT	**4a**	**5e**	67	racemic
6	RT	**4b**	**5d**	50	8
7	RT	**4c**	**5d**	83	racemic
8	RT	**4d**	**5d**	77	racemic
9	RT	**4e**	**5d**	87	22
10	RT	**4f**	**5d**	97	73
11[b]	RT	**4g**	**5d**	91	21
12	RT	**4f**	**5d**	92	34
13	RT	–	**5d**	3	–
14	−20	**4f**	**5d**	69	94
15[b]	−20	**4f**	**5d**	84	55
16[c]	−20	**4f**	**5d**	89	80
17	−45	**4f**	**5d**	42	94

[a] Reactions were performed with chalcone **1a** at 0.06 M concentration, dihydropyridines **5** (1.3 equiv), and **4** (5 mol%). The solution was irradiated for 1 h at room temperature or for 12 h at −20 °C. Irradiation was carried out in a Rayonet reactor at 300 nm or with a TQ 150 high pressure mercury lamp, $\lambda \geq 300$ nm. [b] Reactions performed with preformed 2,4-diphenyl-2*H*-chromen-2-ol. [c] Addition of 3 Å MS. [d] Yield of isolated product after column chromatography. [e] Enantiomeric excess was determined by HPLC on a chiral stationary phase.

In order to increase the enantioselectivity, several BINOL derived phosphoric acids and the corresponding triflylamides were evaluated. From all catalysts tested, **4f** was the best and yielded 97% of the desired chiral 4*H*-chromene **3a** with 73% *ee* (Table 1, entry 10). Interestingly, performing the reaction with 2,4-diphenyl-2*H*-chromen-2-ol (**2a**) resulted in reduced enantiomeric excess (Table 1, entry 11). All *N*-triflylphosphoramides resulted in lower enantioselection. In order to ascertain that the light-driven reduction by photoexcited dihydropyridines had not occurred we performed a reaction without catalyst under otherwise identical conditions. Fortunately, no considerable product formation was observed (Table 1, entry 13). However, at higher light intensity and with prolonged reaction times this reaction occurs leading to considerable loss in enantioselectivity. The presence of oxygen results in the photodecomposition of the dihydropyridine. In order to further improve the enantioselectivity, the reaction was performed at lower temperatures. Pleasingly, decreasing the reaction temperature to −20 °C improved the enantioselectivity significantly and the product was isolated in 69% yield and with an excellent enantiomeric excess of 94% *ee* (Table 1, entry 14).

Further optimization, including the addition of molecular sieves for trapping any water produced, performing the reaction in different solvents[12] or using lower temperatures did not improve the results. With the optimal reaction conditions in hand the scope of the asymmetric Brønsted acid catalyzed photocyclization–reduction sequence was explored (Table 2).

In general a range of chalcone derivatives **1** with various substitution patterns could be applied and the 4*H*-chromene derivatives **3a–o** were isolated in good to excellent yields and enantioselectivities (Table 2, entries 1–15). It is worth mentioning that the newly developed protocol is not only the first example of a catalytic asymmetric reduction of pyrylium ions, but also the first example in which 4*H*-chromenes are obtained in organocatalytic enantioselective fashion.

In order to shed light on the reaction mechanism of this new light driven Brønsted acid catalyzed hydrogenation of benzopyrylium ions, we performed a series of experiments. In addition to the overall transformation (1→3), we also examined the individual cyclization (1→2) and hydrogenation (2→3) steps of the reaction sequence as our experiments indicated a more complex mechanistic scenario (Figure 1). Under the optimal reaction conditions 1) the phosphoric

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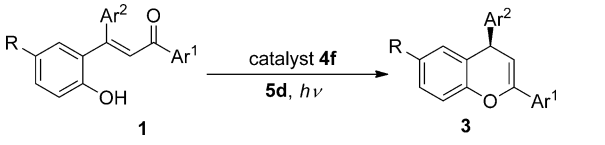
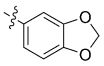
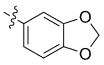
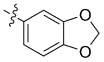
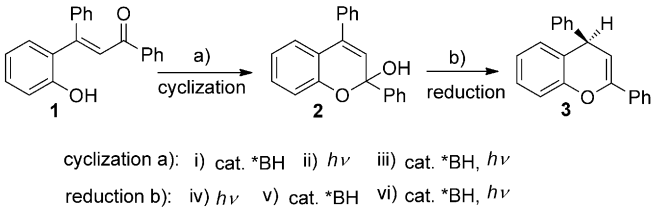
Table 2. Scope of the new photocyclization–reduction cascade.[a]



	3	R	Ar[1]	Ar[2]	Yield [%][b]	*ee* [%][c]
1	**3a**	H	Ph	Ph	69	94
2	**3b**	H	Ph	4-MePh	74	92
3	**3c**	H	Ph	4-*t*BuPh	98	90
4	**3d**	H	Ph		61	92
5	**3e**	H	Ph	4-FPh	56	91
6	**3f**	H	Ph	4-ClPh	75	89
7	**3g**	H	Ph	3-BrPh	50	88
8	**3h**	OMe	Ph	Ph	95	91
9	**3i**	Me	Ph	Ph	76	80
10	**3j**	H	3-MePh	Ph	72	86
11	**3k**	H	4-MePh	Ph	90	92
12	**3l**	H	4-MePh	4-ClPh	76	87
13	**3m**	H	4-PentPh	4-ClPh	82	81
14	**3n**	H	4-PentPh		80	83
15	**3o**	H	3-MePh		93	80

[a] Reactions were performed with chalcone **1** at 0.06 M concentration in toluene, dihydropyridine **5d** (1.3 equiv), and **4f** (5 mol%). The solution was irradiated with a TQ 150 high pressure mercury lamp for 12–48 h under argon. [b] Yield of isolated product after column chromatography. [c] Enantiomeric excess was determined by HPLC on a chiral stationary phase.



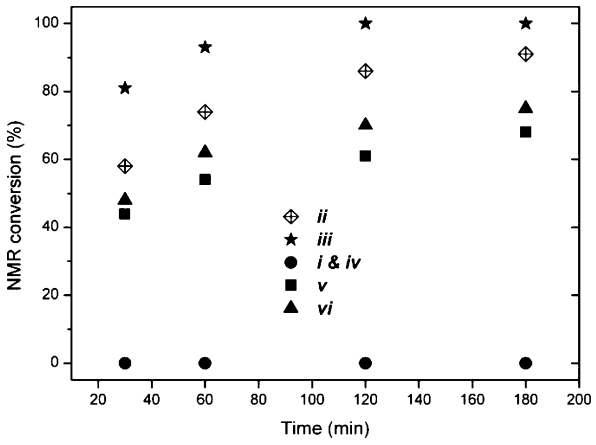
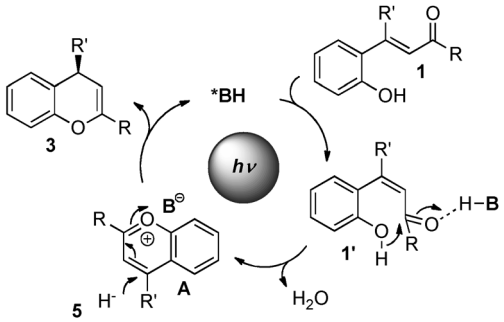


Figure 1. Influence of light and Brønsted acid on the individual steps of the reaction sequence.

acid is not sufficiently active to catalyze the cyclization (1→2); 2) as expected the cyclization proceeds under irradiation; 3) irradiation in the presence of the Brønsted acid leads to significant rate enhancement, clearly demonstrating its involvement in the cyclization event; 4) as also evident from the overall reaction (Table 1, entry 13) no reduction takes place under irradiation conditions alone; 5) the Brønsted acid is crucial for the benzopyrylium-ion formation,[13,14] which allows the subsequent hydrogenation to proceed; 6) surprisingly, the Brønsted acid catalyzed hydrogenation is enhanced by light irradiation. Although it is known that light can positively influence metal-catalyzed transformations this effect has, to our knowledge, never been reported for asymmetric Brønsted acid catalysis.

An unexpected consequence of the above is that both light and the Brønsted acid are involved in both of the individual steps of the cyclization–reduction sequence. Furthermore, we were unable to detect the chiral benzopyrylium/phosphate ion pair in any of the experiments we performed. This indicates that it is the formation of the ion pair that is the rate-determining step in the cyclization–hydrogenation sequence.

Based on the above experiments we propose that the first step of the catalytic cycle involves a light induced and Brønsted acid catalyzed photoisomerization of **1** to **1′**. The subsequent Brønsted acid catalyzed cyclization with elimination of water leads to the highly reactive chiral ion pair **A** consisting of a pyrylium cation and the chiral phosphate anion. Hydride transfer from the dihydropyridine **5** provides the chromene **3** and the regenerated Brønsted acid catalyst (Scheme 2). Although it is apparent that the Brønsted acid



Scheme 2. First asymmetric Brønsted acid catalyzed hydrogenation of benzopyrilium ions.

is engaged in each step of the catalytic cycle, we currently have no proof for the additional effect played by light in the reduction step and whether irradiation accelerates the water elimination, the hydride transfer, or both elimination and hydride transfer.

In summary, we have developed a new light driven[15] asymmetric ion-pair catalysis procedure for performing an enantioselective hydrogenation of pyrylium ions. The newly developed dual and combined photo-assisted Brønsted acid catalyzed procedure has broad scope and allows, for the first

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time, access to valuable 4*H*-chromenes in good yields and with excellent enantioselectivities. The reaction sequence consists of a dual light and Brønsted acid mediated isomerization–cyclization reaction to yield chroman-2-ol intermediates. The subsequent Brønsted acid catalyzed elimination of water leads to an unprecedented intermediary chiral ion pair consisting of a benzopyrylium ion and a chiral phosphate anion. The following organo-hydride addition, exclusively occurring in the 4-position, provides the desired enantioenriched 4*H*-chromenes.[16]

Detailed mechanistic investigations demonstrate an unexpected synergistic effect as both light and the Brønsted acid catalyst are involved in both the cyclization and transfer hydrogenation events. In addition, the enantiodifferentiating fluorescence quenching has not been observed for BINOL-phosphoric acid derivatives, which make their use in light driven catalysis promising.[17] From a synthetic view, the present approach is particularly attractive as it utilises readily available chalcones and avoids the preparation of rather sensitive and unstable chroman-2-ol intermediates. Thus, we are confident that the concept of asymmetric pyrylium ion pair catalysis, in which the chiral information is efficiently transferred from the Brønsted acid anion to the product, will find broad application.

Acknowledgements

We thank the DFG for financial support. C.-C. H acknowledges DAAD and H.-H. Liao acknowledges Taiwan Ministry of Education for doctoral fellowships. We thank Dr. Michael Muratore for providing chiral catalyst.

Keywords: asymmetric catalysis · benzopyrane · chiral ion pair · oxocarbenium ion · reduction

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Received: December 3, 2013
Revised: February 26, 2013
Published online: ■■ ▮▮, 0000

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Organocatalysis

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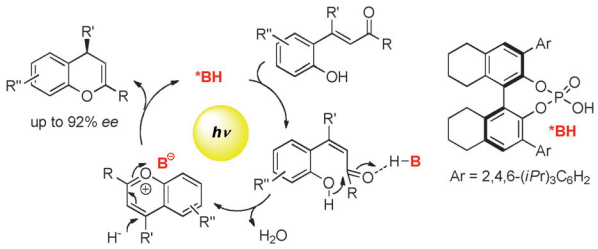
Shedding Light on Organocatalysis—Light-Assisted Asymmetric Ion-Pair Catalysis for the Enantioselective Hydrogenation of Pyrylium Ions



A new light-driven asymmetric ion-pair catalysis procedure for the metal-free enantioselective hydrogenation of in situ generated pyrylium ions from readily available chalcones was developed (see scheme). The photo-assisted Brønsted acid catalyzed procedure has broad scope and allows, for the first time, access to valuable 4*H*-chromenes in good yields and with excellent enantioselectivities.

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