Photochemistry

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Visible-Light-Mediated [4+2] Cycloaddition of Styrenes: Synthesis of Tetralin Derivatives

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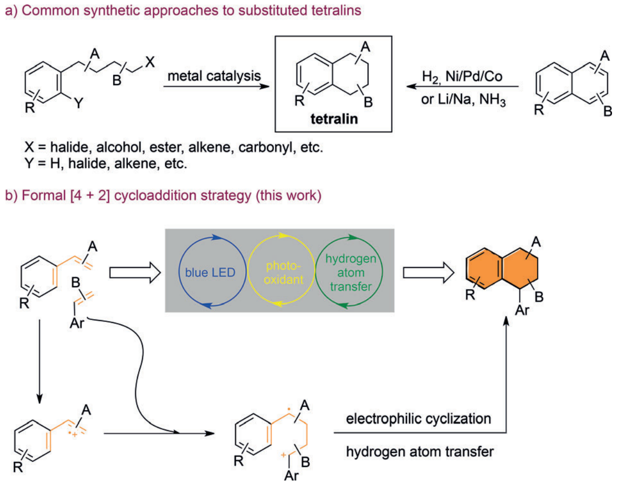
Abstract: *We report a formal [4+2] cycloaddition reaction of styrenes under visible-light catalysis. Two styrene molecules with different electronic or steric properties were found to react with each other in good yield and excellent chemo- and regioselectivity. This reaction provides direct access to polysubstituted tetralin scaffolds from readily available styrenes. Sophisticated tricyclic and tetracyclic tetralin analogues were prepared in high yield and up to 20/1 diasteroselectivity from cyclic substrates.*

Tetralin and its derivatives are prevalent structural motifs among natural products, pharmaceuticals, and agrochemicals.[1,2] Substituents along the tetrahydronaphthalene framework play a central role in controlling the biochemical properties of tetralins. As a result, considerable efforts[3] have been made to access this class of structures. Typically, tetralin systems are synthesized through metal-catalyzed cyclization reactions of aryl derivatives (Scheme 1 a).[4] A major drawback of this strategy is the need for pre-functionalization of the starting materials, which is often non-trivial. An alternative approach is the hydrogenation of naphthalene derivatives using H_2/transitional-metal catalysts[5] or Birch conditions[6] (Scheme 1 a). Step economy and differentiation between two fused benzene rings remain significant challenges. A strong demand remains for a mild, efficient, and atom-economic synthetic method for tetralins and their derivatives.

Over the past decade, photoredox catalysis using photosensitizers (PS) has introduced a new paradigm for olefin activation.[7,8] We recently established a number of transformations by means of styrene activation using the Fukuzumi acridinium as a single-electron photooxidation catalyst.[9,10] This family of organic photosensitizers are powerful oxidants in their singlet excited state under blue-LED radiation [$E^*_{red}(\text{Acr-Me}^+/\text{Acr-Me}^\bullet) = +2.18$ V].[7a,11] Employing this class of catalysts allows the photooxidation of styrenes to highly electrophilic cation radical species that can be captured by various nucleophiles.[12] Considering that the photooxidant is used in catalytic amounts, the remaining unoxidized styrene could also serve as an internal nucleophile to react with the cation radical intermediate. The resulting dimeric cation radical has two cyclization pathways: [2+2] to form cyclobutanes and [4+2] to form tetralin derivatives. We recently reported a [2+2] homodimerization of styrenes using an acridinium/naphthelene catalyst system.[13] Herein, we disclose our findings on the [4+2] cycloaddition of two different styrenes using a hydrogen atom transfer (HAT) cocatalyst to access tetralin derivatives (Scheme 1 b).



Scheme 1. Synthetic approaches to tetralins.

We made our initial discovery of the [4+2] cycloaddition of 4-methoxystyrene (product **3**, Table 1) by using PhSSPh as a HAT cocatalyst. In the absence of phenyl disulfide, the [2+2] cycloaddition (**2**, Table 1) was the only reaction observed. Although **2** remained the major product in acetonitrile, the chemoselectivity was reversed in dichloroethane. We hypothesized that the use of a nonpolar solvent would yield a shorter-lived cation radical that immediately undergoes electrophilic cyclization before reduction of the radical. The identity of the acridinium counterion had a minor effect on the yield. Mes-Acr-$PhBF_4$ (PS-B) delivered **3** in 77 % yield of isolated product (Table 1, entry 3). Similar yields were obtained for the corresponding perchlorate and chloride salts, both of which produced **2** as side product in approximately 10 % yield (Table 1, entries 2 and 4). No reaction occurred in the absence of blue light.

We next examined the feasibility of employing two different styrenes to obtain structurally more diverse [4+2]

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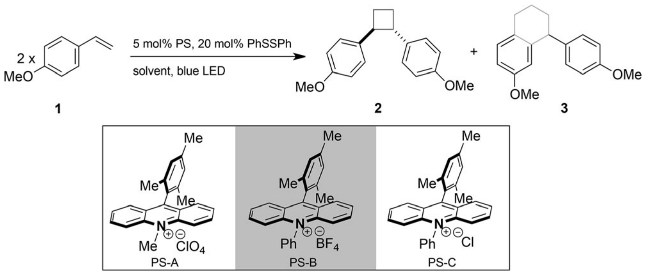
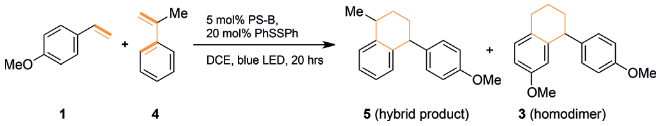
Table 1: Diverting the dimerization pathway from [2+2] to [4+2].[a]



Entry	Photosensitizer (PS)	Solvent	**2** [%][b]	**3** [%][b]
1	PS-A	ACN	64	14
2	PS-A	DCE	10	52
3	PS-B	DCE	< 5	77[c]
4	PS-C	DCE	8	56

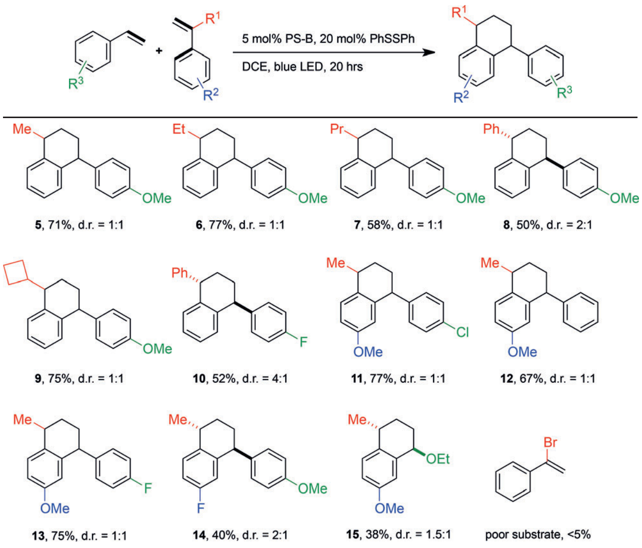
[a] Reaction conditions: **1** (0.2 mmol), PS (5 mol%), PhSSPh (20 mol%), solvent (2.0 mL), 20 hrs (two 15 W blue LEDs). [b] NMR yield. [c] Yield of isolated product.

cross cycloaddition products. Statistically, two different styrenes would yield three possible dimers. We envisioned that chemoselectivity might be accomplished by introducing electronic/steric bias. We decided to use a less oxidizable but more nucleophilic styrene to trap the cation radical from 4-methoxystyrene (**1**). α-Methylstyrene (**4**) has both a high redox potential (+1.91 V)[10b] and high nucleophilicity ($N = 2.35$–2.39, Mayr scale)[14] and is well-suited to test our proposal. We were pleased to find that **1** reacted smoothly with **4** to give the desired hybrid cycloadduct **5** in 29% yield and 1:1 d.r. (Scheme 2), along with a large amount of homodimer **3** (52% yield) as the major side product. Styrene **1** serves as dienophile in this transformation, thus suggesting a radical cyclization as opposed to Friedel–Crafts-type electrophilic ring closure. In order to minimize the homodimerization, we added **1** slowly into a stirring solution of **4** and catalysts. We expected that the transient radical cation of **1** would react with abundant **4** in the reaction vessel faster than with **1**, which would be present in very low concentrations. We were delighted to find that increasing the concentration of **4** from 0.1 M to 1.0 M and adding **1** slowly over 10 hours significantly improved the selectivity for cross cycloadduction over homodimerization. The yield of **5** was improved to 60% (d.r. = 1:1), with very little of homodimer **3** produced. Expanding the addition time of **1** to 20 hours further improved the yield of **5** (71%, d.r. = 1:1), while the use of PS-A and PS-C afforded slightly lower yields (42% and 48% respectively). Nevertheless, acrimidiniums proved critical for this reaction. Other photooxidants, such as Eosin-Y, $Ru(bpy)_3Cl_2$, $Ir(ppy)_3$, $[Ru(bpz)_3][PF_6]$, and $[Ru(bpm)_3]Cl_2$ all afforded very little product formation.



Scheme 2. A cross-cycloaddition reaction between 4-methoxystyrene and α-methylstyrene.

Table 2: Substrate scope with respect to the diene and dienophile.[a]

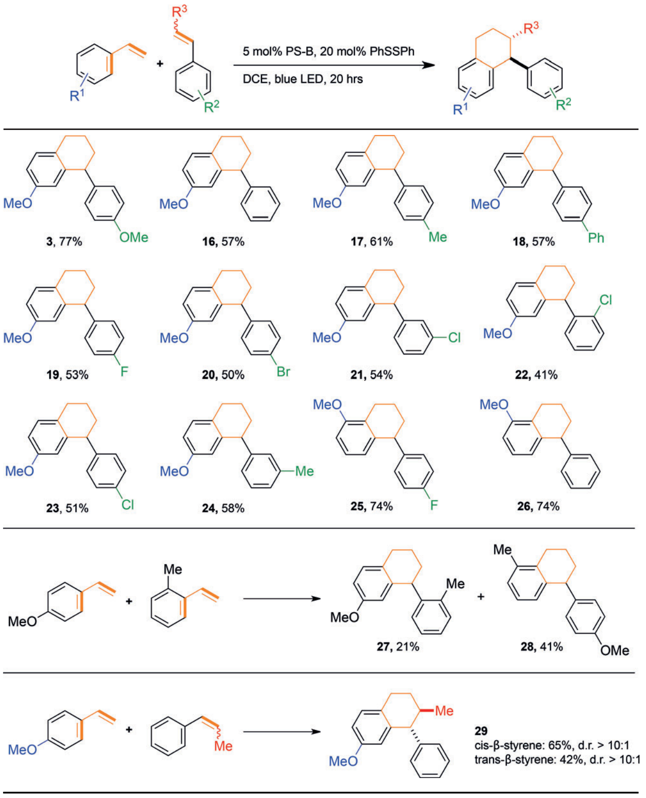


[a] Reactions were run on a 0.2 mmol scale. Yields of isolated product are shown.

With optimized reaction conditions in hand, we next examined the substrate scope with respect to the α-substituted styrenes as the 4π component (Table 2). Various alkyl groups were well tolerated. Polysubstituted tetralins were prepared in good to moderate yields. Little diastereoselectivity was observed for α-alkyl styrenes, thus indicating a stepwise cyclization process. 1,1-Diphenylethylene reacted more slowly with decreased yield, likely as a result of the attenuated nucleophilicity of this substrate. A moderate d.r. favoring the *trans* product was obtained for the reaction involving 1,1-diphenylethylene, likely due to steric influence during the HAT process (Table 2, products **8** and **10**). The scope with respect to the dienophile was also investigated. Styrenes with either electron-rich (e.g., MeO) or electron-poor (e.g., F) aryl substituents reacted with similar efficiency, however, a strong electron-withdrawing nitro substituent was not tolerated. In addition to styrenes, ethyl vinyl ether could also function as a 2π component for this reaction, giving the oxygenated tetralin product **15** in moderate yield.

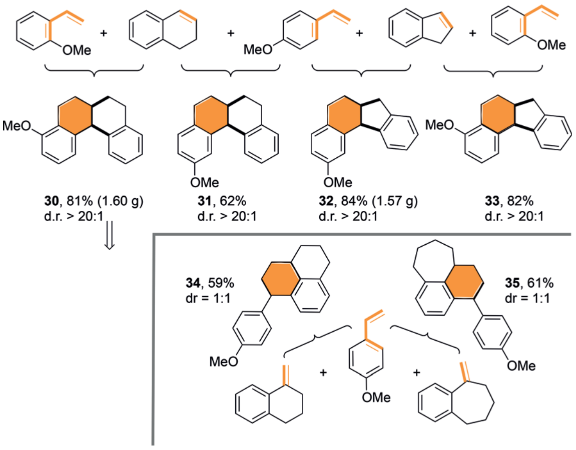
The [4+2] cycloaddition of two styrenes lacking an α-substituent would be significantly more challenging since both diene and dienophile are very similar sterically. In order to address the chemoselectivity issue, we choose styrene pairs that are electronically distinguishable. As exemplified in Table 3, a number of styrene pairs can be implemented in chemo- and regioselective tetralin formation reactions. *p*-Methoxystyrene (**1**) serves as an excellent cation radical precusor (diene) to react with a number of less electron-rich styrenes (dienophile). Unlike in cases involving α-substituted styrenes (Table 2), **1** always functions as the diene when reacting with other non-α-substituted styrenes (Table 3). Both electron-neutral and deficient styrenes are good reaction partners (dienophile) for **1**. When *o*-methylstyrene was

Table 3: Reactivity screening of terminal styrenes.



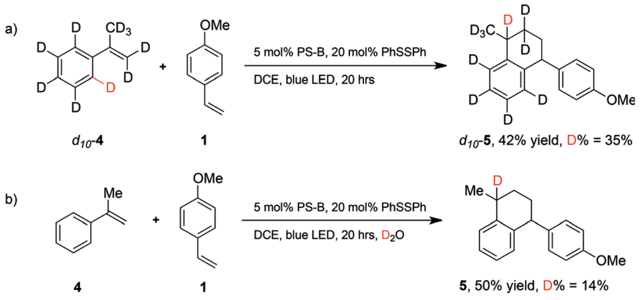
used as the dienophile, a mixture of two isomers (**27** and **28**) was isolated owing to competing cationic and radical cyclization pathways (see below). β-Methylstyrenes were good dienophiles for this transformation despite their low nucleophilicity, delivering trisubstituted tetralin products with excellent chemo-, regio-, and diastereoselectivity. It is worth noting that both *trans*- and *cis*-β-methylstyrenes yielded the same diastereomeric product **29**, with the *cis* alkene substrate delivering higher yields (65% vs. 42% yield). This result also confirms that the cyclization is stepwise and that bond rotation occurs during ring closure. Other electron-rich styrenes, such as *o*-methoxystyrene, are also competent dienes for this transformation. Strongly electron-deficient styrenes, such as *p*-nitrostyrene, failed to undergo the [4+2] cycloaddition reaction.

The synthetic application of this visible-light-promoted photoredox [4+2] cycloaddition of styrenes was further demonstrated in the one-step synthesis of several tetralin scaffolds with additional fused rings (Scheme 3). When indene was used as dienophile, a fused 6/6/5/6 ring system was obtained by using either *p*- or *o*-methoxystyrene as the 4π component. The structure and relative stereochemistry was confirmed by X-ray crystallography of product **30**. The corresponding 6/6/6/6 framework was accessed by using tetrahydronaphthalene as the dienophile. These reactions can be conveniently performed on a gram scale without compromising the yield, and the products were always isolated as single diastereomers. Additionally, exocyclic olefins also react with *p*-methoxystyrene to yield 6/6/6- and 6/6/7-fused tricyclic scaffolds. In this case, a 1:1 mixture of *cis* and *trans* isomers is generally obtained.



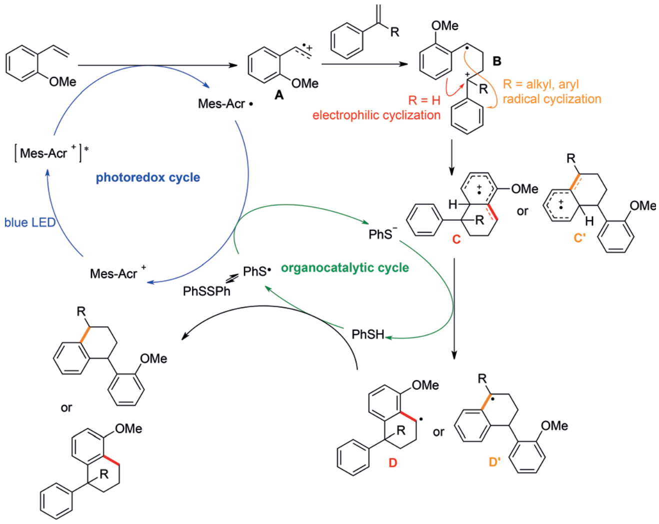
Scheme 3. Synthesis of fused polycyclic tetralins by using the [4+2] cycloaddition reaction.

Preliminary isotope-labeling experiments were carried out. Partial deuterium incorporation was observed at one of the benzylic carbon atoms of the product when using fully deuterated α-methylstyrene (Scheme 4a). The incomplete deuterium labeling suggests that the HAT process is not entirely intramolecular. In order to confirm this, D_2O was introduced to the reaction and the product was found to possess 14% deuterium at the same carbon atom (Scheme 4b). This result indicates that intramolecular hydrogen transfer might be slow and a compensating process from other hydrogen sources in the reaction system is also operative.



Scheme 4. Isotope-labeling experiments.

Based on these results and our previous studies on the hydrofunctionalization of styrenes, we propose a polar radical crossover cycloaddition (PRCC) reaction mechanism (Scheme 5). Under blue-light irradiation, the acridinium catalyst oxidizes the more electron-rich styrene through photoinduced electron transfer (PET) to give the acridine radical (Mes-Acr$^\bullet$) and cation radical **A**. Reoxidation of Mes-Acr$^\bullet$ by a phenylthiyl radical, generated by homolytic cleavage of the cocatalyst PhSSPh, completes the photoredox catalytic cycle. Intermediate **A** reacts with another styrene to yield radical cation **B**. In the presence of an electron-relay catalyst, **B** preferentially undergoes four-membered-ring formation to give the formal [2+2] product. In the presence



Scheme 5. Proposed mechanism.

of PhSSPh in a non-polar solvent, the [4+2] pathway is accelerated. Depending on the relative reactivity of its radical and cation centers, **B** can undergo two types of cyclization: electrophilic cyclization or radical cyclization. For non-α-substituted dienophiles, cationic cyclization is more favorable. When the dienophile bears an α-substituent, its cation center is more stable and less reactive and the corresponding radical cyclization pathway becomes predominant. Nevertheless, intermediates **C** and **C′** from the two cyclization pathways share the same 6-carbon,5-electron conjugated cation radical character. Subsequent deprotonation and hydrogen atom transfer, promoted by thiophenolate and thiophenol, effects rearomatization.

In summary, we developed a straightforward synthetic approach to substituted tetralins from readily available styrenes using visible-light-promoted organocatalysis. A formal Diels–Alder cycloaddition between two styrenes is catalyzed by acridinium salts under irradiation by blue LED light. A disulfide cocatalyst was found to be essential to divert the chemoselectivity of the styrene/styrene cycloaddition from [2+2] to [4+2]. This method exhibits remarkable chemo-, regio-, and stereoselectivity between the several possible cyclization pathways between two styrenes. Multi-substituted tetralin derivatives were prepared in one step in good to moderate yields under mild reaction conditions. Preliminary mechanistic studies suggests two possible cyclization pathways, electrophilic or radical, which are controlled by the substrates.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: cycloaddition · organocatalysis · photoredox chemistry · radical reactions · tetralin

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Communications

Photochemistry

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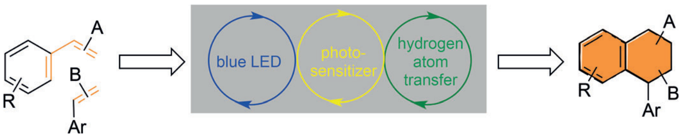
Visible-Light-Mediated [4+2] Cycloaddition of Styrenes: Synthesis of Tetralin Derivatives



Circle of light: A formal [4+2] cycloaddition reaction of styrenes under visible-light catalysis was developed. Two styrene molecules with different electronic or steric properties were found to react with each other in good yield and excellent chemo- and regioselectivity. This reaction provides direct access to polysubstituted tetralin scaffolds from readily available styrenes.