## Photocatalysis

## The Cleavage of a C–C Bond in Cyclobutylanilines by Visible-Light Photoredox Catalysis: Development of a [4+2] Annulation Method\*\*

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**Abstract:** We report the first example of an intermolecular [4+2] annulation of cyclobutylanilines with alkynes enabled by visible-light photocatalysis. Monocyclic and bicyclic cyclobutylanilines successfully undergo the annulation with terminal and internal alkynes to generate a wide variety of amine-substituted cyclohexenes including new hydrindan and decalin derivatives with good to excellent diastereoselectivity. The reaction is overall redox neutral with perfect atom economy.

he release of ring strain has often been exploited as a driving force to promote the cleavage of typically unreactive bonds such as carbon-carbon bonds.<sup>[1]</sup> This strategy has been successfully applied to the ring opening of cyclopropanes, which leads to the wide use of cyclopropanes in organic synthesis.<sup>[2]</sup> We recently reported visible-light-promoted [3+2] annulation reactions of cyclopropylanilines with various  $\pi$  bonds.<sup>[3]</sup> In these reactions, the cleavage of the cyclopropyl rings is promoted by photooxidation of the parent amine to the corresponding amine radical cation. Since the oxidation potentials of cyclopropylaniline and cyclobutylaniline were found to be similar,<sup>[4]</sup> we were intrigued by the possibility of using cyclobutylanilines in a similar manner in the annulation reactions. We were further encouraged by the fact that cyclobutane's strain energy is almost identical to that of cyclopropane.<sup>[5,6]</sup>

Still, the ring opening of cyclopropanes is generally much faster than that of cyclobutanes. Newcomb et al. reported that the rate constant for ring opening of a cyclobutylcarbinyl radical was  $1.5 \times 10^3$  s<sup>-1</sup> at 20 °C compared to  $7 \times 10^7$  s<sup>-1</sup> at 20 °C for ring opening of a cyclopropylcarbinyl radical.<sup>[7]</sup> Ingold et al. reported the rate constant for ring opening of the cyclobutyl-*n*-propylaminyl radical to be  $1.2 \times 10^5$  s<sup>-1</sup> at 25 °C whereas the rate constant was estimated to be greater than  $10^7$  s<sup>-1</sup> at 25 °C for ring opening of the cyclopropyl-*n*-propylaminyl radical (Scheme 1).<sup>[8]</sup> The proposed ring opening of the cyclobutylaniline radical cation was expected to be faster than the neutral aminyl radical,<sup>[9]</sup> which lent further credence to the proposed annulation reaction. Surprisingly, to

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Scheme 1. Proposed [4+2] annulation of cyclobutylaniline with alkyne.

the best of our knowledge, there have been no reports of using cyclobutylanilines in the tandem ring opening and annulation sequence to construct six-membered carbocycles. This is in contrast to the increasing use of other types of cyclobutanes in the tandem sequence.<sup>[10]</sup> Successful ring opening of these cyclobutanes usually relies on the decoration of the cyclobutyl ring with donor–acceptor<sup>[11]</sup> or ketone/hydroxy functionalities.<sup>[12]</sup> Herein we describe the successful development of the [4+2] annulation of cyclobutylanilines with alkynes by visible-light photoredox catalysis, which greatly broadens the use of cyclobutanes as a four-carbon synthon in organic synthesis. We hope that this method will add to the growing pool of synthetic methods based on photocatalysis.<sup>[13]</sup>

We chose 4-*tert*-butyl-*N*-cyclobutylaniline **1a** and phenylacetylene **2a** as the standard substrates to optimize the [4+2] annulation. After extensive screening (see the Supporting Information, SI), [Ir(dtbbpy)(ppy)<sub>2</sub>](PF<sub>6</sub>) **4a** in MeOH under

Table 1: Optimization of the reaction conditions.

<sup>t</sup> Bu	$Ph = \frac{[lr(dtbbp)]}{additi}$ $Ph = \frac{[lr(dtbbp)]}{additi}$	v)(ppy) <sub>2</sub> ve, solv sible ligt	]PF <sub>6</sub> ( <b>4a</b> ) vent, nt	<sup>1</sup> Bu Ph
Entry <sup>[a]</sup>	Conditions	<i>t</i> [h]	Conv. of <b>1 a</b> [%] <sup>[b]</sup>	Yield of <b>3 a</b> [%] <sup>[b]</sup>
1	<b>4a</b> (2 mol%), MeOH	12	100	97 (90) <sup>[c]</sup>
2	<b>4a</b> (2 mol%), MeOH, air	16	100	42
3	without <b>4a</b> , MeOH	16	7	3
4	<b>4a</b> (2 mol%), MeOH, light bulb off	16	10	7
5 <sup>[d]</sup>	<b>4a</b> (2 mol%), MeOH	12	70	68
6 <sup>[e]</sup>	<b>4a</b> (2 mol%), MeOH	12	29	27

[a] Reaction conditions: 1a (0.2 mmol, 0.1  $\mbox{m}$  in degassed solvent), 2a (1 mmol), irradiation with two 18 W LED light bulbs at room temperature. [b] Yield determined by GC analysis using dodecane as an internal standard unless noted otherwise. [c] Yields of isolated products are shown. [d] One 18 W LED light, reaction tube in a 55 °C water bath. [e] One 18 W LED light. dtbbpy=4,4'-di-*tert*-butyl-2,2'-bipyridine, ppy=2phenylpyridine. irradiation with two 18 W LEDs was identified as the optimal conditions, providing the desired product 3a in 97% yield as determined by gas chromatography (GC; 90% yield of the isolated product; Table 1, entry 1). Conducting the experiment without degassing the reaction mixture led to a significant decrease in the yield (entry 2; see SI). Two control studies showed that omitting either the photocatalyst or light produced a negligible amount of 3a (entries 3 and 4). The beneficial effect of using two LED lights could be due to an increased exposure to light and to raising the reaction temperature. An internal temperature of 55 °C was measured with two bulbs whereas 25°C was recorded with only one bulb. To further probe this phenomenon, we performed a temperature control study in which the test tube was placed in a 55°C water bath with one LED light (entry 5). Though the yield was not as high as when two LED lights were used, the product 3a was detected in 68% yield. This improvement, in comparison to using one LED light at room temperature (entry 6), suggests that higher temperature and photon output are both beneficial to the reaction.

We next examined the scope of cyclobutylaniline derivatives with phenylacetylene **2a** as annulation partner under optimized conditions (Table 2). Cyclobutylanilines were readily prepared by the Buchwald–Hartwig amination of cyclobutylamine with aryl halides.<sup>[14]</sup> The annulation reaction generally tolerated both electron-withdrawing (e.g.,  $CF_3$  and CN) and electron-donating substituents (e.g., OMe, Ph, and

**Table 2:** [4+2] Annulation of phenylacetylene (**2 a**) with monocyclic cyclobutylanilines.

,	R	[Ir(dtbbpy)(ppy) <sub>2</sub> ]PF <sub>6</sub> MeOH, visible light	R-C	Ph
Entry <sup>[a]</sup>	Substrate	Product	<i>t</i> [h]	Yield [%] <sup>[b]</sup>
1	1 <b>b</b> , R=H	3b Ph	12	76
2	<b>1c</b> , $R = 4-CF_3$	F <sub>3</sub> C 3c	24	79
3	<b>1 d</b> , R=4-OMe	MeO 3d H Ph	18	27
4	<b>1</b> e, R=2-CN	3e H Ph	20	84
5	<b>1</b> f, R=2-phenyl	3f Ph Ph Ph	20	78
6	<b>1 g</b> , R=2- <sup><i>i</i></sup> Pr	3g Ph	24	73
7	1 h,	3h Ph	12	87
8	1i,	3i Ph	14	76
9	1j, 🖓		18	83

alkyl) on the aryl ring. The low yield of **3d** (entry **3**) was due to the low solubility of **1d** in MeOH. Use of a cosolvent, such as DMF, helped to solubilize **1d** but failed to improve the yield. Steric hindrance was also well tolerated as *ortho* substituents with various sizes (**1e–1g**) showed little effect on the reaction. Moreover, it is worth noting that heterocycles can be easily incorporated into the annulation products. The cyclobutylanilines (**1i** and **1j**) substituted by a pyridyl group at the 2- or 3-position underwent the annulation reaction uneventfully, affording the desired products (**3i** and **3j**) in good yields.

Encouraged by the success in the initial scope studies, we turned our attention to the generality of alkynes (Table 3). The reactivity pattern displayed by alkynes in the annulation reaction generally resembles that in the intermolecular addition of nonpolar nucleophilic alkyl radicals to alkynes.<sup>[15]</sup> Terminal alkynes substituted with a functional group that is capable of stabilizing the incipient vinyl radical, were found to be viable annulation partners. The list of functional groups includes quite diverse groups such as naphthyl (**2b**), 1,3-benzodioxole (**2c**), methyl ester (**2d**), and thiophene (**2e**). The annulation of these alkynes with several cyclobutylani-

Table 3: Scope of alkynes in the [4+2] annulation.

R-		+ $R^1 = R^2 = \frac{[lr(dt)]}{2b-h}$	bbpy)(ppy)₂]PF <sub>6</sub> R-€ MeOH, <i>v</i> isible light	ر ۲ ۶	$R^2$
Entry <sup>[a]</sup>	Substrate	Alkyne	Product	<i>t</i> [h]	Yield [%] <sup>[b]</sup>
1	1a	2b	NH 'Bu 5a	16	71
2 <sup>[c]</sup>	la	0 2c	'Bu 5b	16	57
3	1j	2 b	NH NH Sc	16	72
4	1f	MeO 2d	Ph VH OMe 5d	14	42
5	la	رتا 2e	NH S 'Bu 5e	12	66
6	la	2f	NH 'Bu	14	61
7	1h	CF <sub>3</sub> 2g	NH 5g CF <sub>3</sub>	24	42
8	1c	OEt 2h	Ph Ph 5h	12	92

[a] Reaction conditions: substrate (0.2 mmol, 0.1 м in degassed MeOH), 2a (1 mmol), 4a (2 mol%), irradiation with two 18 W LED light bulbs. [b] Yield of the isolated product.



lines showed complete regioselectivity, affording a range of six-membered carbocycles in good yields. A notable side reaction occurred when less hindered cyclobutylanilines were used in conjunction with methyl propiolate 2d. 1,4-Addition of cyclobutylaniline 1k to 2d completely suppressed the desired [4+2] annulation reaction.<sup>[16]</sup> An ortho substituent on the Naryl ring (e.g., 1f) was required to inhibit the side reaction. Typically, internal alkynes are less reactive than terminal alkynes in the intermolecular addition of carbon radicals to alkynes due to steric hindrance.<sup>[15]</sup> Internal alkynes were unsuccessful in the annulation with cyclopropylanilines.[3b,c] Surprisingly, divergent reactivity emerged between cyclopropylanilines and cyclobutylanilines with respect to this class of alkynes. Several internal alkynes (2 f-h) successfully underwent the annulation reaction with cyclobutylanilines under complete regiocontrol. A limitation of utilizing internal alkynes is that at least one of the two substituents must be capable of stabilizing the vinyl radical. The regiochemistry of the annulation products (5 f-h) was assigned based on 2D NMR spectroscopy. The structure of the annulation product (5 h) was further confirmed by X-ray crystallography (see SI).<sup>[17]</sup> The regioselectivity can be rationalized based on the substituent's ability to stabilize the incipient vinyl radical.

Bicyclo[4.3.0]nonane (hydrindan) and bicyclo-[4.4.0]decane (decalin) are two common structural motifs in small organic molecules. Yet, only a handful of methods such as the Diels–Alder reaction<sup>[18]</sup> and the Robinson annulation<sup>[19]</sup> are available for their preparation. Hence, these structures are ideal targets to test the scope of the [4+2] annulation reaction (Table 4). The requisite starting materials, *cis*-fused 5,4-membered (**6a–d**) and 6,4-membered (**6e** and **6f**) bicycles, were

readily accessible in four steps from commercially available cyclopentene and cyclohexene, respectively.<sup>[20,21]</sup> Under the optimized conditions, a pair of diastereomeric 5,4-membered bicycles (6a and 6b), which differ in the stereochemistry at C6, underwent the annulation with phenylacetylene 2a to provide 7a as the major product in similar yields and almost identical d.r.s (Table 4, entries 1 and 2). High diastereoselectivity was achieved (>10:1) with 7a being trans-fused. This data is consistent with regioselective ring opening of 6a or 6b at the C5-C6 bond, which leads to formation of the identical distonic radical iminium ion<sup>[22]</sup> and subsequent loss of the stereochemical integrality of the C6 stereocenter. The observed regioselective ring opening was probably driven by the formation of a more stable secondary carbon radical versus a primary radical. Incorporation of a strong electronwithdrawing group (e.g., CF<sub>3</sub>; entry 3) into the N-aryl ring showed little effect on both the yield and diastereoselectivity. Internal alkyne 2h successfully participated in the annulation reaction, affording the annulation products 7c and 7c' in excellent yield albeit lower diastereoselectivity when compared to terminal alkynes (entries 1-3). The annulation of 6,4membered bicycles (6e and 6f) with terminal alkynes (2a and 2c) furnished *cis*-fused decalin derivatives (7e, 7e' and 7f, 7 f') in excellent yields, although a decrease in diastereose-

Table 4: [4+2] Annulation of alkynes with bicyclic cyclobutylanilines.



[a] Reaction conditions: substrate (0.2 mmol, 0.1 м in degassed MeOH), **2a**, **2c**, **2h**, **2i** (0.6 mmol), and **4a** (2 mol%), irradiation with two 18 W LED light bulbs for 12 h. [b] Combined yields of the two isomers after column chromatography. [c] Determined by <sup>1</sup>H NMR analysis of the crude product. n.a. = not available.

lectivity was observed in comparison to 5,4-membered bicycles (entries 6 and 7). Two *cis*-fused decalin derivatives were obtained along with a third diastereomer whose relative configuration was unidentified in both examples (**6e** and **6f**).<sup>[23]</sup> The structure and stereochemistry of the annulation products were assigned by 2D NMR spectroscopy. X-ray crystallographic analysis of **7d** was also performed to further support our assignments.<sup>[24]</sup>

A catalytic cycle similar to the [3+2] annulation is proposed for the [4+2] annulation (see SI).<sup>[3b,c]</sup> The oxidation peak potential of **1a** was found to be 0.8 V versus SCE, which is more positive than the reduction potential of the photoexcited **4a** (Ir<sup>3+\*</sup>/Ir<sup>2+</sup>: 0.66 V vs. SCE). Although thermodynamically unfavorable, such SET processes have been reported.<sup>[25]</sup> Stern–Volmer quenching studies revealed that cyclobutylaniline **1a** quenches the photoexcited **4a** whereas alkynes **2a** and **2h** showed little quenching (see SI).

In conclusion, we have accomplished the first example of cleaving C–C bonds of cyclobutylanilines enabled by visiblelight photoredox catalysis. Monocyclic and bicyclic cyclobutylanilines undergo the [4+2] annulation with terminal and internal alkynes to produce amine-substituted six-membered carbocycles. Good to excellent diastereoselectivity is observed for the latter class of the compounds, yielding new



hydrindan and decalin derivatives. Finally, the approach we have developed to overcome cyclobutylanilines' lower propensity for ring cleavage can be potentially applied to open rings larger than three- and four-membered rings with suitable built-in ring strain.

**Keywords:** cyclohexenes · iridium catalyst · *N*-aryl cyclobutyl amines · photocatalysis · small ring systems

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