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Visible-Light Photoredox-Catalyzed Semipinacol-Type Rearrangement: Trifluoromethylation/Ring Expansion by a Radical–Polar Mechanism**

*Basudev Sahoo, Jun-Long Li, and Frank Glorius**

Dedicated to Professor F. Ekkehardt Hahn on the occasion of his 60th birthday

Abstract: *A visible-light-mediated photoredox-catalyzed semipinacol-type rearrangement proceeding via 1,2 alkyl migration was developed. In this transformation, trifluoromethylation of the C=C bond of α-(1-hydroxycycloalkyl)-substituted styrene derivatives is followed by ring expansion of the 1-hydroxycycloalkyl group to deliver novel cycloalkanones with all-carbon quaternary centers. The reaction proceeds via a radical–polar mechanism, with trifluoromethylation (radical) and ring expansion (ionic) occurring in the same transformation.*

Organic reactions conducted in the presence of visible light have drawn the attention of synthetic organic chemists because of their sustainability, cost effectiveness, and attractive environmental performance.[1,2m] However, this approach suffers from poor substrate scope since relatively few organic molecules are capable of absorbing photons in the visible range of the spectrum. To overcome this limitation, photosensitizer compounds capable of absorbing visible light and passing the energy on to organic substrates have become widely employed. Over the last few years in particular, visible-light photoredox catalysis has enabled the development of many novel organic transformations.[2] Visible-light-mediated photoredox catalysis has also been combined with other modes of catalysis in dual catalytic systems to achieve new reactivity and increase efficiency.[3]

A typical mechanistic cycle for photoredox catalysis involves the initial excitation of the photocatalyst (often transition-metal–polypyridyl complexes such as $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (bpy = 2,2′-bipyridine)or organic dyes) by visible light followed by single electron transfer (SET) either to or from the substrate of interest.[4] This generates radical anion or cation intermediates, which invariably release organic radicals capable of engaging in classical radical reactions such as in atom transfer radical additions (ATRAs)[5] or Meerwein-type reactions.[2h] As well as providing a mild and sustainable route into radical chemistry, a key feature of visible-light photoredox catalysis concerns its ability to facilitate radical–polar crossover[6] reactions. In these processes, a radical intermediate generated during the reaction undergoes SET with the reduced or oxidized photoredox catalyst to afford anions or cations. The combination of both radical and polar steps in a single mechanism is an attractive concept for the development of novel reactions, and impressive visible-light-mediated transformations have been disclosed over the last few years.[2j]

We[7] considered whether radical–polar crossover processes mediated by visible-light photoredox catalysis could provide new routes towards valuable trifluoromethylated compounds.[8,2n] The CF_3 group is widely incorporated into pharmaceuticals and agrochemicals owing to its advantageous influence on the lipophilicity, metabolic stability, and membrane permeability of many compounds.[9] Visible-light photoredox catalysis has enabled many impressive trifluoromethylations of alkenes, (hetero)arenes, and other compounds, most often through the use of electrophilic trifluoromethylating ($\mathbf{CF_3^+}$) reagents (e.g, Umemoto's reagents, Togni's reagents, CF_3I, and CF_3SO_2Cl) as CF_3 radical precursors.[5c,10]

In 2012, Koike, Akita et al. reported oxytrifluoromethylation of activated alkenes with the use of Umemoto's reagent as a CF_3 source (Scheme 1).[10d] In this process, the cation generated upon oxidation of the alkyl radical is trapped by an internal or external oxygen nucleophile.[10d,e,j,o] Similar transformations have since been reported with nitrogen, halogen, and carbon nucleophiles.[5c,10i,k,l] On the other hand, deprotonation[10m,11] or deboronation[10h] of a hydrogen or boron in the α-position to the cation can also occur to form the trifluoromethylated alkene derivatives. Alternative reaction pathways for the alkyl cation have not been widely explored, however, and much potential exists for further, complexity-building steps after addition of the photoredox-generated radical. A major reactivity pathway characteristic of cations that has not been developed for photoredox radical–polar crossover reactions involves 1,2 alkyl migration. Such processes would give concise access to sp^3-trifluoromethylated compounds featuring a quaternary all-carbon center. Herein, we report the successful development of a visible-light-mediated trifluoromethylation reaction to form CF_3-substituted cycloalkanone compounds directly from styrene derivatives. The reaction constitutes the first photoredox-catalyzed

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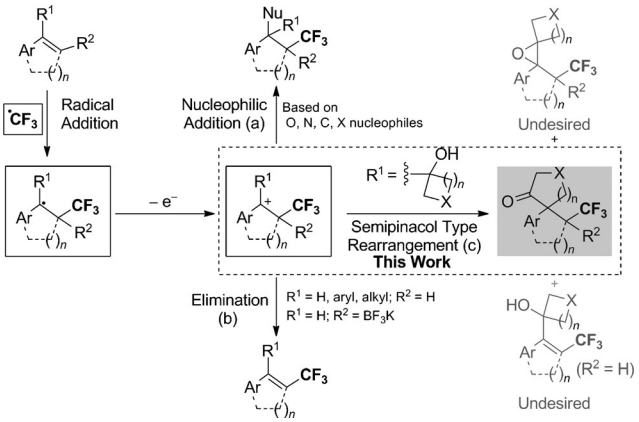
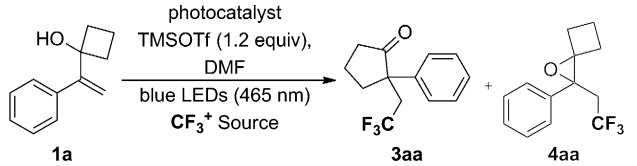


Scheme 1. Visible-light-mediated photoredox-catalyzed trifluoromethylation of alkenes via a radical–polar mechanism.

semipinacol-type rearrangement[12] and it benefits from mild and convenient conditions (room temperature, no solvent degassing) and uses light from readily available commercial sources.

Our reaction design starting from cycloalkanol-substituted styrene derivatives is shown in Scheme 1. After addition of the photoredox-generated CF_3 radical and subsequent single-electron oxidation, the cation would then undergo 1,2 alkyl migration of the cycloalkanol group. To validate the process, alternative reaction pathways involving undesired intramolecular trapping by the alcohol or deprotonation would have to be suppressed. In a preliminary test, 1-(1-phenylvinyl)cyclobutanol (**1a**) was reacted with 1.4 equivalents of the electrophilic trifluoromethylating reagent 5-(trifluoromethyl)dibenzothiophenium trifluoromethanesulfonate (**2a**) in *N*,*N*-dimethylformamide (DMF, 0.1 M) in the presence of $[Ru(bpy)_3](PF_6)_2$ (2 mol%) under visible-light irradiation from 5 W blue LEDs ($\lambda_{max} = 465$ nm). We were delighted to observe ring-expanded 2-phenyl-2-(2,2,2-trifluoroethyl)cyclopentanone (**3aa**) as the major product in 60% GC yield, along with the undesired byproduct 2-phenyl-2-(2,2,2-trifluoroethyl)-1-oxaspiro[2.3]hexane (**4aa**) in a **3aa**/**4aa** ratio of 2.3:1 (Table 1, entry 1). To suppress the formation of byproduct **4aa**, the reaction was performed in the presence of a stoichiometric amount of trimethylsilyl trifluoromethanesulfonate (TMSOTf, 1.2 equiv) to protect the hydroxy group in situ and reduce its nucleophilicity. Gratifyingly, the desired product **3aa** was formed exclusively (98% GC yield) under these conditions, with no **4aa** being detected (Table 1, entry 2). In a screening of different trifluoromethylating reagents, Umemoto's reagent with a tetrafluoroborate counteranion (**2b**, 1.4 equiv) gave the product **3aa** in a reduced yield of 81% (GC yield), while Togni's reagents **2c** (1.4 equiv) and **2d** (1.4 equiv) were not suitable (9% GC yield and no reaction, respectively; Table 1, entries 3–5). After a short solvent screen, DMF remained as the best solvent.[13] In a survey of different photoredox catalysts, $[Ir(ppy)_3]$ and $[Ir(ppy)_2(dtbbpy)](PF_6)$ (dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) delivered **3aa** in high GC yields respectively, while fluorescein dye unfortunately did not catalyze the formation of **3aa** (Table 1, entries 6–8). A 23 W compact

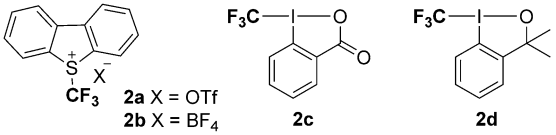
Table 1: Optimization studies.[a]



1a 3aa 4aa

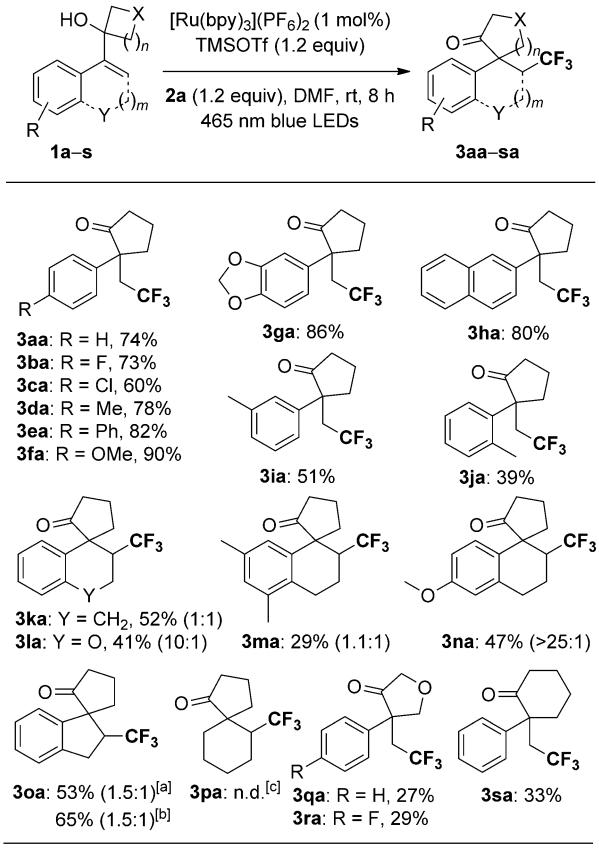
Entry	Photocatalyst (mol%)	CF_3^+ Source (equiv)	Yield [%][b]
1[c]	$[Ru(bpy)_3](PF_6)_2$ (2)	**2a** (1.4)	60
2	$[Ru(bpy)_3](PF_6)_2$ (2)	**2a** (1.4)	98
3	$[Ru(bpy)_3](PF_6)_2$ (2)	**2b** (1.4)	81
4	$[Ru(bpy)_3](PF_6)_2$ (2)	**2c** (1.4)	9
5	$[Ru(bpy)_3](PF_6)_2$ (2)	**2d** (1.4)	–
6	*fac*-$[Ir(ppy)_3]$ (2)	**2a** (1.4)	96
7	$[Ir(ppy)_2(dtbbpy)](PF_6)$ (2)	**2a** (1.4)	97
8	Fluorescein (2)	**2a** (1.4)	–
9	$[Ru(bpy)_3](PF_6)_2$ (2)	**2a** (1.2)	95
10	$[Ru(bpy)_3](PF_6)_2$ (1)	**2a** (1.2)	94 (74)
11	–	**2a** (1.2)	–
12[d]	$[Ru(bpy)_3](PF_6)_2$ (1)	**2a** (1.2)	–

[a] **1a** (0.1 mmol), trimethylsilyl trifluoromethanesulfonate (TMSOTf, 0.12 mmol), the CF_3^+ reagent (**2**), and the photoredox catalyst were mixed in *N*,*N*-dimethylformamide (DMF) and stirred at RT for 6 h under visible-light irradiation. [b] GC yield of **3aa** with mesitylene as an internal reference. Yields of isolated **3aa** are given in parentheses. [c] In the absence of TMSOTf, **3aa** was obtained along with **4aa** in a **3aa**/**4aa** ratio of 2.3:1, which was determined by ^{19}F NMR analysis. [d] The reaction was performed in the dark. bpy = 2,2′-bipyridine, ppy = 2-phenylpyridine, dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, LEDs = light-emitting diodes.



fluorescent lamp (CFL) bulb was also identified as a reliable source of visible light in this reaction (92% GC yield of **3aa**).[13] Upon lowering the equivalents of **2a** (1.2 equiv), the efficiency of the reaction was largely unaffected (95% GC yield of **3aa**, Table 1, entry 9), while reducing the catalyst loading of $[Ru(bpy)_3](PF_6)_2$ to 1 mol% also did not hamper the reaction significantly, with the product **3aa** being delivered in 94% GC yield and 74% isolated yield (Table 1, entry 10). Control experiments showed that both the photocatalyst $[Ru(bpy)_3](PF_6)_2$ and visible light were crucial for this transformation (Table 1, entries 11,12).

Under the optimal reaction conditions, the scope and limitations of this transformation were explored (Scheme 2). Several electron-withdrawing and electron-donating substituents on the benzene ring of 1-(1-arylvinyl)cyclobutanol (**1a–j**) were well tolerated. Substrates **1k–o**, derived from 1-tetralones, 4-chromanone, and 1-indanone, were also well tolerated. Interestingly, the reaction of highly electron-rich substrates **1l** and **1n** afforded products **3la** and **3na** in moderate yields but with good to excellent diastereoselectivity (d.r. 10:1 and > 25:1, respectively). Incomplete conversion of substrate **1o** under the optimized reaction conditions gave **3oa** as a mixture of diastereomers (d.r. 1.5:1) in 53% yield with 22% recovery of the starting material **1o**. Increasing the amount of **2a** (2.0 equiv), however, led to full conversion,

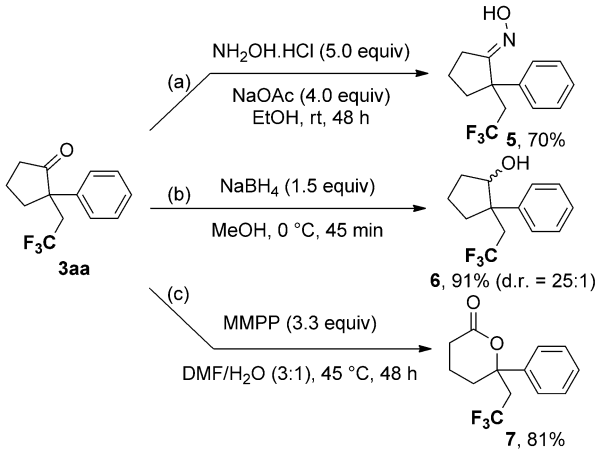


Scheme 2. Substrate scope of the trifluoromethylation/ring expansion. **1a–s** (0.20 mmol), TMSOTf (0.24 mmol), and DMF (2 mL) were stirred at RT for 2 h. The CF_3^+ reagent (**2a**, 0.24 mmol) and $[Ru(bpy)_3](PF_6)_2$ (0.002 mmol) were then added to the reaction mixture and stirred at RT for 6 h under visible-light irradiation from blue LEDs. d.r. values (given in parentheses) were determined by ^{19}F NMR analysis. [a] Incomplete conversion with 22% recovery of **1o**. [b] The reaction was performed with 2.0 equiv of **2a**. [c] Detected by GC–MS analysis.

with the formation of **3oa** in 65% yield with d.r 1.5:1. Substrate **1p**, which does not have an aryl ring in conjugation with the C=C bond, did not afford the product **3pa** in an isolable amount. Substituted oxacyclobutanol substrates (**1q–r**) also delivered the corresponding products **3qa** and **3ra** in lower yields. Despite low ring strain, 1-(1-phenylvinyl)cyclopentanol (**1s**) gave the desired product **3sa** in a reasonable yield.

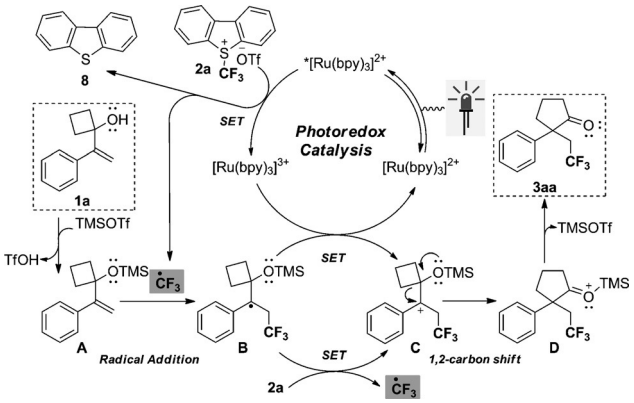
Since the products possess a carbonyl functionality, we further conducted some follow-up transformations to explore the versatility of the method (Scheme 3). The product **3aa** was converted to the corresponding oxime derivative **5** (70%), which serves as a potential precursor for Beckmann rearrangement (Scheme 3a). Reduction of **3aa** with $NaBH_4$ in MeOH delivered alcohol **6** in 91% yield with excellent diastereoselectivity (d.r. 25:1), while Baeyer–Villiger oxidation of the product **3aa** with magnesium monoperoxyphthalate (MMPP) afforded δ-lactone **7** in very good yield (Scheme 3b,c).

In order to gain mechanistic insight into the reaction, some preliminary mechanistic experiments were performed. The absence of either the photoredox catalyst $[Ru(bpy)_3](PF_6)_2$ or visible light shut down the reactivity completely, thus suggesting a crucial role for both of these elements for the transformation (Table 1, entries 11,12). The reaction was inhibited in the presence of the radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO), with a TEMPO-trapped CF_3 adduct being detected by GC–MS analysis.[13] During the screening of solvents for optimization, the formation of **3aa** was accompanied by the formation of a methanol-trapped intermediate (detected by GC-MS analysis) when methanol was employed as solvent.[13] These results support the involvement of both radical and ionic intermediates in this reaction.



Scheme 3. Derivatizations of **3aa**: a) Oxime formation from **3aa**. b) Reduction of **3aa**. c) Baeyer–Villiger oxidation of **3aa**. MMPP = magnesium monoperoxyphthalate.

Based on the above mechanistic information and literature reports,[10f,i] we propose a plausible mechanism for the reaction in Scheme 4. Under visible-light irradiation, the photoredox catalyst $[Ru(bpy)_3]^{2+}$ is excited to the strongly reducing excited state $*[Ru(bpy)_3]^{2+}$. SET from this species to Umemoto's reagent **2a** would then generate $[Ru(bpy)_3]^{3+}$ and an electrophilic CF_3 radical. Addition onto the double bond of the silyl-protected intermediate **A**, formed in situ from **1a** and TMSOTf, would lead to the stabilized radical intermediate **B**. At this point, the key radical–polar crossover step can



Scheme 4. Plausible mechanism for the visible-light photoredox-catalyzed trifluoromethylation/ring expansion.

occur with SET from **B** to $[Ru(bpy)_3]^{3+}$, thereby regenerating the photocatalyst and delivering the tertiary cation **C**. Alternatively, this step could proceed as part of a radical chain, with SET occurring directly from **B** to another molecule of **2a**. The involvement of this pathway is supported by the reaction quantum yield value (Φ) of 3.8.[13] A 1,2 alkyl shift with formation of a C=O π bond would then afford the product **3aa** upon loss of the silyl group.

In conclusion, we have successfully developed the first visible-light-induced photoredox-catalyzed semipinacol-type rearrangement, which proceeds via 1,2 alkyl migration. This transformation proceeds via a radical–polar mechanism , in which sequential SET processes involving the photoredox catalyst enable both radical and polar steps in the same mechanism. The reaction provides a novel route to densely-functionalized CF_3-containing compounds under mild conditions and uses visible light from readily available sources.

Keywords: fluorine · photocatalysis · radical reactions · ring expansion

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[13] See the supporting information.

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