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Organic dye-catalyzed radical ring expansion reaction†

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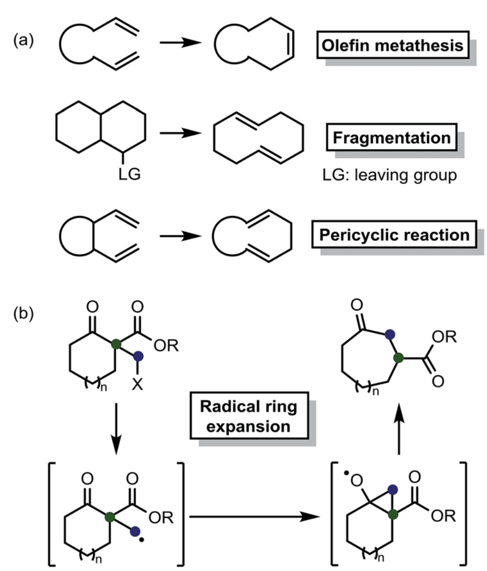
Herein, we reported an attractive method for synthesizing medium-sized rings that are catalyzed by erythrosine B under fluorescent light irradiation. This synthetic approach featured mild conditions, a facile procedure, a broad substrate scope, and moderate-to-good yields.

Medium-sized rings are present in numerous important natural products and pharmaceuticals.[1] Therefore, several researchers have strived to develop various methods, including olefin metathesis,[2] fragmentation,[3] and pericyclic reactions[4] (Scheme 1(a)), for synthesizing these materials. Nevertheless, unfavorable transannular interactions and entropic factors typical of rings of this size make this task quite challenging.[5] Thus, we believe that new methods need to be developed to solve these problems.



Scheme 1 (a) Examples of conventional approaches for the synthesis of medium-sized rings. (b) Beckwith–Dowd ring expansion reaction.

More than 30 years ago, the Beckwith–Dowd ring expansion reaction[6] was introduced as a novel method to form medium-sized rings (Scheme 1(b)). This approach can be an attractive alternative to conventional strategies for synthesizing the abovementioned structures. Actually, the fact that no new unsaturated C–C bonds are formed as part of this method renders hydrogenation processes unnecessary, thereby minimizing the impact of transformation on the substrate. Certainly, this approach could be applicable to the synthesis of natural products.[7] However, the original method requires reagents, *e.g.*, azobisisobutyronitrile (AIBN) or tributyltin hydride (Bu_3SnH), that are difficult to handle. Some related methods that employ other reagents, including Sm,[8] Zn or In,[9] B_{12}–TiO_2 hybrid catalyst,[10] silane,[11] and amines,[12] have been reported. Recently, a few synthetic approaches based on photo-induced reactions have been developed.[12b,12d,13] A previous study reported that even α-(ω-carboxyalkyl) β-keto esters could be employed as relevant substrates.[13]

In this context, we aimed to establish a more efficient and facile method than conventional ones to prepare a broad range of medium-sized rings *via* a ring expansion reaction. We continuously investigated various photo-initiated reactions by employing a photosensitizer and a fluorescent lamp as a light source.[14] For example, the CDC cross-coupling reaction[14a] and 1,3-dipolar cycloaddition/aromatization reaction[14d] under photooxidative reaction conditions have been reported. While investigating these reactions, we found that organic dyes induced electron transfer from amine substrates to molecular oxygen.[14a,14d] Thus, we envisioned that C–halogen bonds can be cleaved in the presence of a sacrificial amine using photosensitized substrates as a springboard. Herein, we reported a convenient and environmentally friendly method that employs a photo-induced reaction as part of the Beckwith–Dowd ring expansion route to synthesize medium-sized rings.

We initiated our study with the optimization of the reaction conditions (Table 1). Methyl 1-(iodomethyl)-2-oxocyclohexane-1-carboxylate (**1a**) was chosen as a substrate. A mixture of **1a** and different types of amines and photocatalysts was irradiated with four fluorescent lamps under a nitrogen atmosphere for

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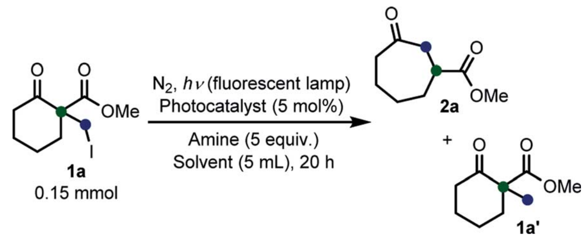
† Electronic supplementary information (ESI) available: Experimental procedures, product characterization, time course of **1a** and **2a**, emission spectrum of the fluorescent lamp, and detailed information of the DFT calculation. See DOI: 10.1039/c8ra02383b

Table 1 Optimization of the reaction conditions



Entry	Photocatalyst	Solvent	Amine	2a[a] (%)	1a'[a] (%)	1a[a] (%)
1	Erythrosine B (EB)	DMSO	$^{i}Pr_2NEt$	78(83)	5	10
2	Eosin Y	DMSO	$^{i}Pr_2NEt$	50	18	0
3	AQN-2-Cl	DMSO	$^{i}Pr_2NEt$	12	10	63
4	EB	DMSO	Et_3N	51	26	22
5	EB	DMSO	1-Methyl imidazole	11	15	74
6	EB	DMSO	$^{i}Pr_2NH$	36	21	40
7	EB	MeCN	$^{i}Pr_2NEt$	70	0	26
8	EB	DMF	$^{i}Pr_2NEt$	18	15	18
9	EB	$CHCl_3$	$^{i}Pr_2NEt$	0	79	14

[a] Yields are determined by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. The number in parentheses denotes isolated yield.

20 h in DMSO. After extensive investigations, we found that a combination of erythrosine B (EB) and $^{i}Pr_2NEt$ was the most efficient combination for this transformation, affording the desired product **2a** in 83% isolated yield (entry 1).[15] This result can be explained by two facts: (a) the maximum absorption of EB (∼520 nm)[16] coincides with the wavelength of the fluorescent lamp and (b) $^{i}Pr_2NEt$ is an effective reductive quencher ($E_{ox}(^{i}Pr_2NEt^{\bullet+}/^{i}Pr_2NEt) = +0.68$ V *vs.* SCE; *e.g.*, $E_{ox}(NEt_3^{\bullet+}/NEt_3) = +0.99$ V *vs.* SCE).[17a,17b] In fact, when we employed other combinations of photocatalysts, amines, and solvents, **2a** was obtained in a relatively lower yield. Furthermore, in our experiments, we recovered **1a** and/or its undesired hydrogenation product **1a′** from the reaction mixture in substantial amounts (entries 2–9).

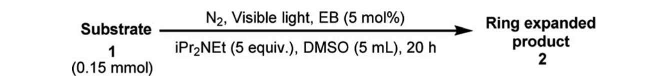
With the optimized reaction conditions in hand, we next explored the substrate scope of this transformation (Table 2). We found that compounds comprising 5–8-membered rings were suitable substrates for the reaction and gave the desired products in good yields (**2a–2e**). When we employed 1,2,3,4-tetrahydro naphthalene-type substrate **1f**, the desired reaction proceeded smoothly. On the other hand, indane-based substrate **1g** gave a mixture of the desired product and the aromatized product (**3g**). Due to the difficulty of achieving complete separation of the desired product and **3g**, we further investigated the reaction conditions in order to obtain a single product. Although the changes in the reaction time and in the composition of the overhead atmosphere did not substantially affect the course of the reaction, we found that the addition of 3 equiv. of LiOH led to the formation of the aromatized product **3g** exclusively in moderate yield. Furthermore, we tested whether compounds that contain the C–Br bond could also be used as substrates for this reaction. When we applied the standard reaction conditions to substrate **1h**, the yield of the desired product **2a′** was around 10%. However, adding a catalytic amount of Ag_2CO_3 and extending the reaction time increased the yield. Additionally, it is worth noting that this reaction could be carried out in an air atmosphere with almost no decrease in product yield. This result indicates that the presence of oxygen or water in the atmosphere above the reaction mixture has a negligible impact on *in situ* radical generation and subsequent steps to furnish the ring expanded product.

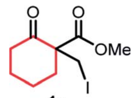
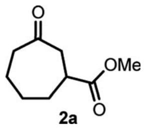
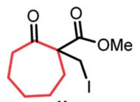
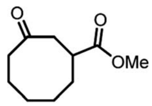
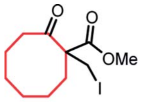
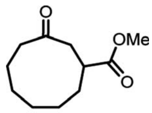
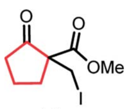
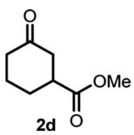
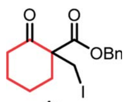
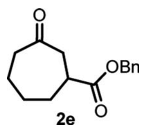
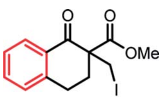
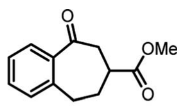
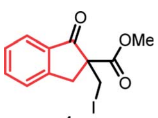
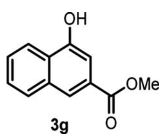
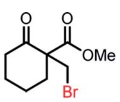
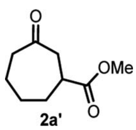
Scheme 2 summarizes the results of additional experiments conducted to investigate the substrate scope. We tested a substrate with an iodopropyl side chain, **1i**, and found that the addition of a silver salt and extension of the reaction time led to the formation of a tertiary alcohol with a fused ring, **3i**, instead of the corresponding cyclononanone (eqn (1)). Additionally, we found that this reaction is applicable to substrates with ketones in open-chain moieties, such as **1j** and **1k**. Particularly, although **2j** was volatile, and we needed to treat it carefully during isolation, these substrates gave the rearranged product in high yield (eqn (2) and (3)).

Next, we performed some experiments to elucidate the reaction mechanism (Scheme 3). We observed that no ring expansion product **2a** was obtained when we omitted EB or $^{i}Pr_2NEt$ or photo-irradiation from the fluorescent lamps. Additionally, if we added 1 equiv. of TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl free radical), the desired product was obtained in low yield and the presence of a TEMPO-adduct was detected.[18] This result confirms the idea that this reaction proceeds *via* a radical pathway.

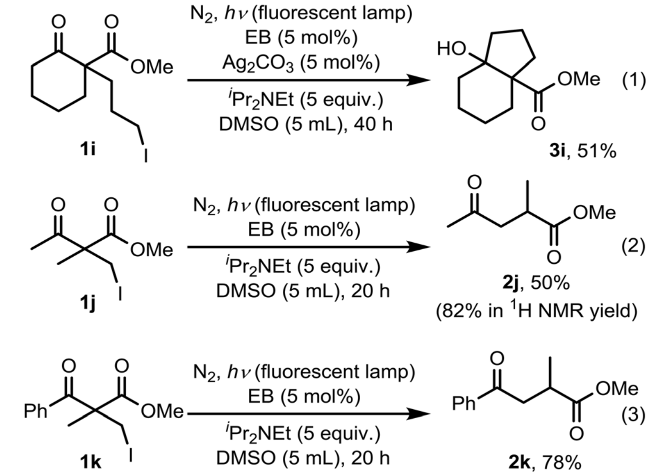
Based on these results, previous reports on the Beckwith–Dowd ring expansion reaction,[6] and recent reports of radical

Table 2 Substrate scope

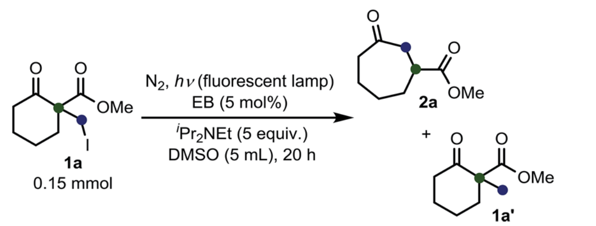


Substrate	Product	Yields[a] (%)
 1a	 2a	83% 83%
 1b	 2b	82% 81%
 1c	 2c	77% 74%
 1d	 2d	67% 76%
 1e	 2e	64% 62%
 1f	 2f	67%
 1g	 3g	71%[b]
 1h	 2a'	71%[c]

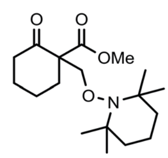
[a] Yields shown in the table are all pure, isolated yields. The underlined percentages are the yields when the reactions were performed under air atmosphere. [b] 3 equiv. of LiOH added. [c] 5 mol% of Ag_2CO_3 added, reaction time is 40 h.



Scheme 2 Applying the reaction conditions on substrates with three-carbon lateral chain and acyclic β-keto esters.

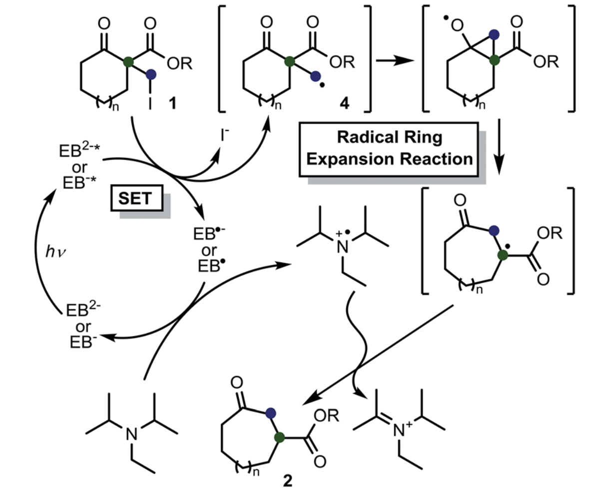


	2a	1a'	1a
Without EB:	0%	trace	65%
Without $^i Pr_2NEt$:	0%	trace	72%
Without $h\nu$:	0%	4%	91%
Addition of TEMPO (1 equiv.):	34%	10%	23%

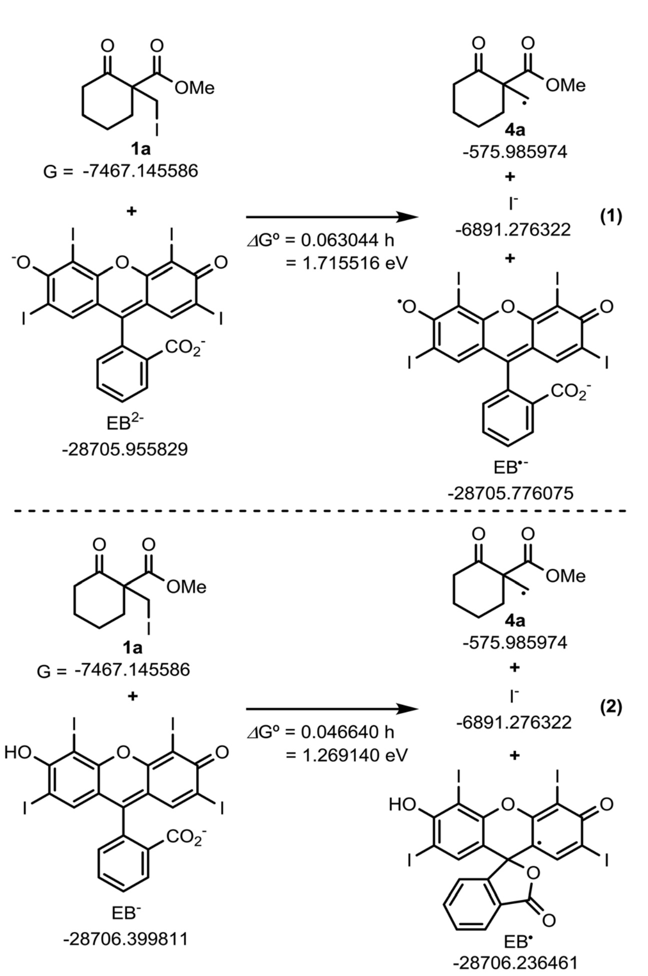
TEMPO addcut: 

Scheme 3 Results of the control experiments.

reactions set off by C–halogen bond cleavage,[17b,19] we inferred a plausible mechanistic pathway for the reaction, which is depicted in Scheme 4. The first step in the C–I bond cleavage reaction of **1a** is photo-induced single electron transfer (SET) from the excited state of EB. In the experimental conditions employed, EB is considered to be a monoanionic (EB^-) or dianionic (EB^{2-}) species because its commercially available disodium salt ($EBNa_2$) is added to the reaction mixture containing DIPEA without acidic treatment. To gain further insight into this SET step, we calculated the Gibbs energies involved in the reaction between **1a** and EB in a solution environment (solvent: DMSO; $\varepsilon = 46.826$) simulated by the IEF-PCM model using the M06-2X functional.[20] The standard Gibbs energy change (ΔG°) calculated for the cleavage reaction of **1a** with EB^{2-} (**1a** + EB^{2-} → **4a** + I^- + $EB^{\bullet-}$) and with EB^- (**1a** + EB^- → **4a** + I^- + $EB^\bullet$) in the absence of light irradiation from the fluorescent lamp is 1.72 and 1.27 eV, respectively, as shown in Scheme 5. This indicates that these reactions are thermodynamically uphill electron-transfer processes. On the other hand, it is well known that the ΔG° values for excited $EB^{2-}(EB^{2-*}/EB^{\bullet-}$ and excited $EB^-(EB^{-*}/EB^\bullet)$ redox pairs are given by the amended Rehm–Weller equation with the excited-state energies ($E_{h\nu}$) as $\Delta G^\circ(EB^{2-*}/EB^{\bullet-}) = \Delta G^\circ(EB^{2-}/EB^{\bullet-}) - E_{h\nu}$ and $\Delta G^\circ(EB^{-*}/EB^\bullet) = \Delta G^\circ(EB^-/EB^\bullet) - E_{h\nu}$, respectively.[21,22] The reported excited-state energy of EB is 2.34 eV;[16a] thus, the ΔG° values for the two



Scheme 4 Plausible reaction mechanism.



Scheme 5 Standard Gibbs energies calculated for the species involved in the C–I bond cleavage reaction with EB^{2-} (1) and EB^{-} (2) using the M06-2X/PCM method with 6-31G (d) basis sets for hydrogen, carbon, and oxygen and the MIDI! basis set for iodine. Free energy corrections are made at standard conditions of 1 atm and 298.15 K.

mentioned C–I bond cleavage reactions (**1a** + EB^{2-}* → **4a** + I^- + $EB^{\bullet -}$ and **1a** + EB^{-}* → **4a** + I^- + $EB^{\bullet}$) involving photo-induced SET are −0.62 and −1.07 eV, respectively, which indicate that the $E_{h\nu}$ value is sufficiently high for both bond cleavage reactions to be thermodynamically feasible. These results indicate that the cleavage reaction of **1** is governed by an exergonic C–I bond cleavage mechanism involving SET from EB^{2-}* or EB^{-}*. The primary radical **4** thus generated attacks the ketone, and then a rapid cyclopropane ring opening occurs. Meanwhile, the oxidized EB is reduced by the sacrificial amine, and the catalytic cycle of EB is completed. No particular H donor was necessary for this reaction to proceed; therefore, we assumed that an "extra" hydrogen atom of the product is derived from $^iPr_2NEt$. It believed that abstraction of a hydrogen atom from the trialkylammounium radical cation could occur,[23] which strongly supports the above mechanism.

Conclusions

In conclusion, we have developed an environmentally friendly ring expansion reaction to synthesize medium-sized rings. This facile method involves the use of a fluorescent lamp as a source of irradiated light and an easy-to-handle photocatalyst. Attractively, this reaction proceeds under very mild conditions and is applicable to a broad spectrum of substrates. We believe that our method using a photo-triggered reaction course affords access to various pharmaceuticals and natural products. Studies to determine the mechanistic details of the reaction and expand its applicability to other useful substrates are currently underway in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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