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COMMUNICATION

Visible light photoredox organocatalysis: a fully transition metal-free direct asymmetric α-alkylation of aldehydes†

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Rose Bengal, a dye sensitizer, was found to be active as a visible light photoredox catalyst for the direct enantioselective α-alkylation of aldehydes in environmentally benign and simple conditions. Starting from a SOMO converse mechanism, the catalytic activity of the imidazolidinone organocatalyst was improved using an electrophilic cocatalyst. The resulting methodology and optimal conditions led to efficient and transition-metal-free direct photoredox organocatalysis.

The development of new and green activation modes in selective synthesis is a fundamental objective for organic chemists. Asymmetric organocatalysis is an important area that has been intensively studied over the past few years,[1] one that is complementary to transition-metal-based catalysis.[2] This kind of process has become very attractive since environmentally friendly and metal-free transformations are very much in demand.

In 2007, MacMillan introduced the concept of organo- singly occupied molecular orbital (SOMO) catalysis.[3] This one electron mode of activation has enabled the development of several useful transformations, such as C–C[4] and C–Heteroatom[5] bond formation. In the organo-SOMO catalysis, the central need of an oxidant in a stoichiometric amount (CAN) prompted MacMillan to develop a photoredox catalytic system *via* a SOMO converse mechanism.[6]

Light can be considered as an ideal reaction condition for environmentally friendly, green chemical synthesis as it is abundant, non toxic and generates no waste.

Recently, the application of visible light photoredox catalysis has emerged as a growing field in organic synthesis[7] in particular for applications using combinations of metal and organocatalysts.[2] The applications in SOMO catalysis were performed using the well-known organometallic polypyridyl complexes such as $[Ru(bpy)_3]^{2+}$ or *fac*-Ir(ppy)$_3$ as photoredox catalysts.[7d,8] In this SOMO converse mechanism termed photoredox organocatalysis, the cooperative combination of a photocatalytic process with an organocatalytic cycle offers an efficient catalytic method for the enantioselective α-alkylation, α-arylation and α-trifluoroalkylation of aldehydes *via* the formation of an enamine.

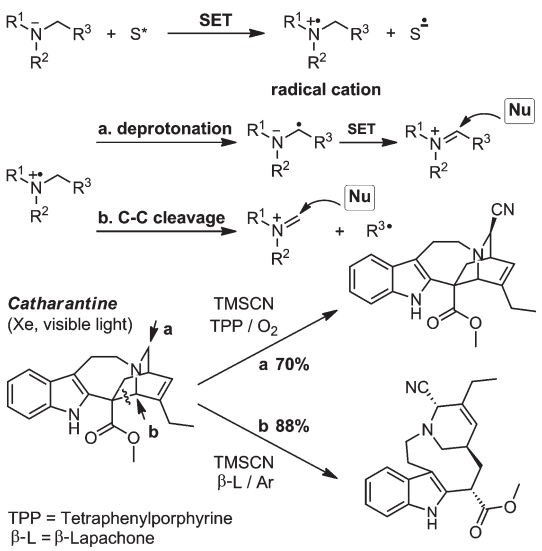
However the potential toxicity of the ruthenium or the iridium salts as well as their future limited availability is the major weakness of these transition metal-based methods for the manufacturing of fine chemicals and pharmaceuticals.

Herein we present a versatile transition-metal-free process, using a fully organic visible light photoredox catalyst.

Previously in our laboratory, the photo-oxidation of tertiary amines[9] mediated by an organosensitizer has been widely developed to make a C–C bond on the α position of the nitrogen atom *via* the formation of highly reactive iminium ions (Scheme 1).

Among the various organic sensitizers, xanthene dyes have given rise to active interest in the last few years due to their high absorption in the visible domain. For instance, several useful transformations induced by the photo-oxidation of activated tertiary amines such as tetrahydroisoquinoline derivatives were performed by C.-H. Tan *et al.*[10] and B. König & D. P. Hari[11] using organic dyes like Rose Bengal or Eosin Y.

In 2011, K. Zeitler's group first published an alternative[12] to the use of the ruthenium photocatalyst for the enantioselective



Scheme 1 Previous laboratory work showing the competitive pathways in the photo-oxidation of tertiary amines.

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α-alkylation of aldehydes. In this case, using a green LEDs irradiation system, the authors have shown the ability of Eosin Y to perform this reaction with attractive results, however low temperatures and somewhat longer reaction times were needed.

In this work, we intend to develop a Rose Bengal photoredox catalysis taking particular advantage of room temperature mild conditions with limited irradiation times.

As enamine compounds are known to be oxidized easier than the corresponding amines,[13] our preliminary studies began with the screening of various photosensitizers as photoredox catalysts in asymmetric organocatalytic C–C bond formation according to the methodology developed by MacMillan *et al.* Between a large choice set, we selected sensitizers in line with their prior use in the photo-oxidation of tertiary amines. Some organic dyes were particularly attractive as they exhibited a remarkable resemblance with the redox properties of the metal complexes previously used by MacMillan (Fig. 1).[6d,8d,14]

To test the ability of these dyes to act as photoredox catalysts, we selected the direct and enantioselective α-alkylation of aldehydes as a representative transformation.‡ Experimentally, the alkylation protocol was first performed in DMF with the combination of the imidazolidinone **1** and a photosensitizer **S** as the catalytic system for the α-alkylation of hydrocinnamaldehyde **2a** by diethyl bromomalonate **3a** used as a SOMO electrophilic precursor (Scheme 2).

As a central design consideration, the photoactivation reveals the ability of the photosensitizer to absorb in the visible domain and to act both as a strong oxidant in the excited state **S*** and as an efficient reductant in its semi-reduced form **S**$^{\bullet-}$ (Fig. 2).

As outlined in Fig. 3, the mechanistic picture of this whole organocatalytic cycle could involve two closely interwoven catalytic cycles. We speculated that a more stable triplet state in a polar solvent such as DMF will promote the mechanism, avoiding any thermodynamically favourable back electron transfer. In fact, in this "light part" of the mechanism, the high-energy intermediate **S*** would efficiently strip one electron from a sacrificial enamine so that the semi-reduced form **S**$^{\bullet-}$ with a high reduction potential could initiate the formation of the electron-deficient radical from the halide.

Besides, the "dark part" would resume the organocatalytic cycle. This part began with the condensation of the catalyst **1** with the aldehyde **2** providing the enamine **5**. In the presence of a radical, the somophilic enamine could play the role of a trapping radical species. The generation of an electron-rich α-amino radical **6** that is more readily oxidizable than the corresponding enamine should enforce the formation of the iminium ion **7** by reducing the halide **3** as a propagation step directly or *via* a second photocatalytic cycle as described. The enamine formation, the liberation of the catalyst from the iminium intermediate, and the interconnection of the two cycles with the radical trapping are the major steps of this mechanism.

According to the general procedure described in Scheme 2, a number of organosensitizers studied were effective for this

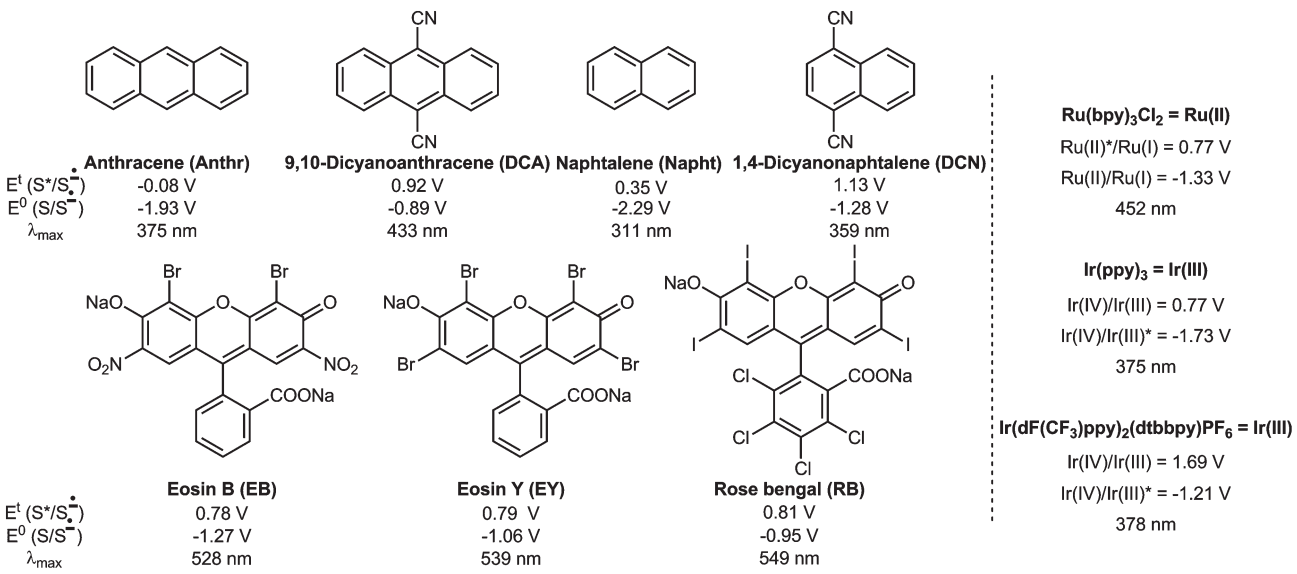
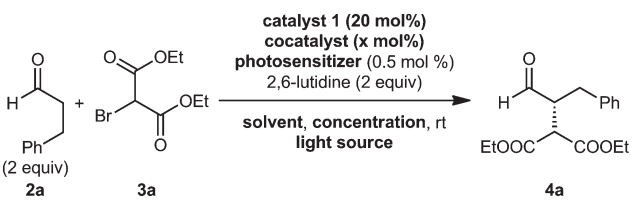


Fig. 1 Absorption and redox properties of the sensitizers used as photoredox catalysts (λ_{max}: in CH_3CN; Potential values: V/SCE).[6d,8d,14]



Scheme 2 General procedure for the α-alkylation of hydrocinnamaldehyde **2a** by diethyl bromomalonate **3a.**

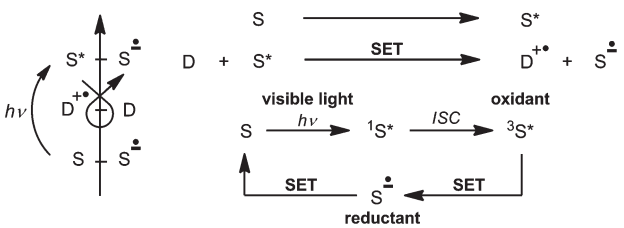


Fig. 2 Photoredox pathways.

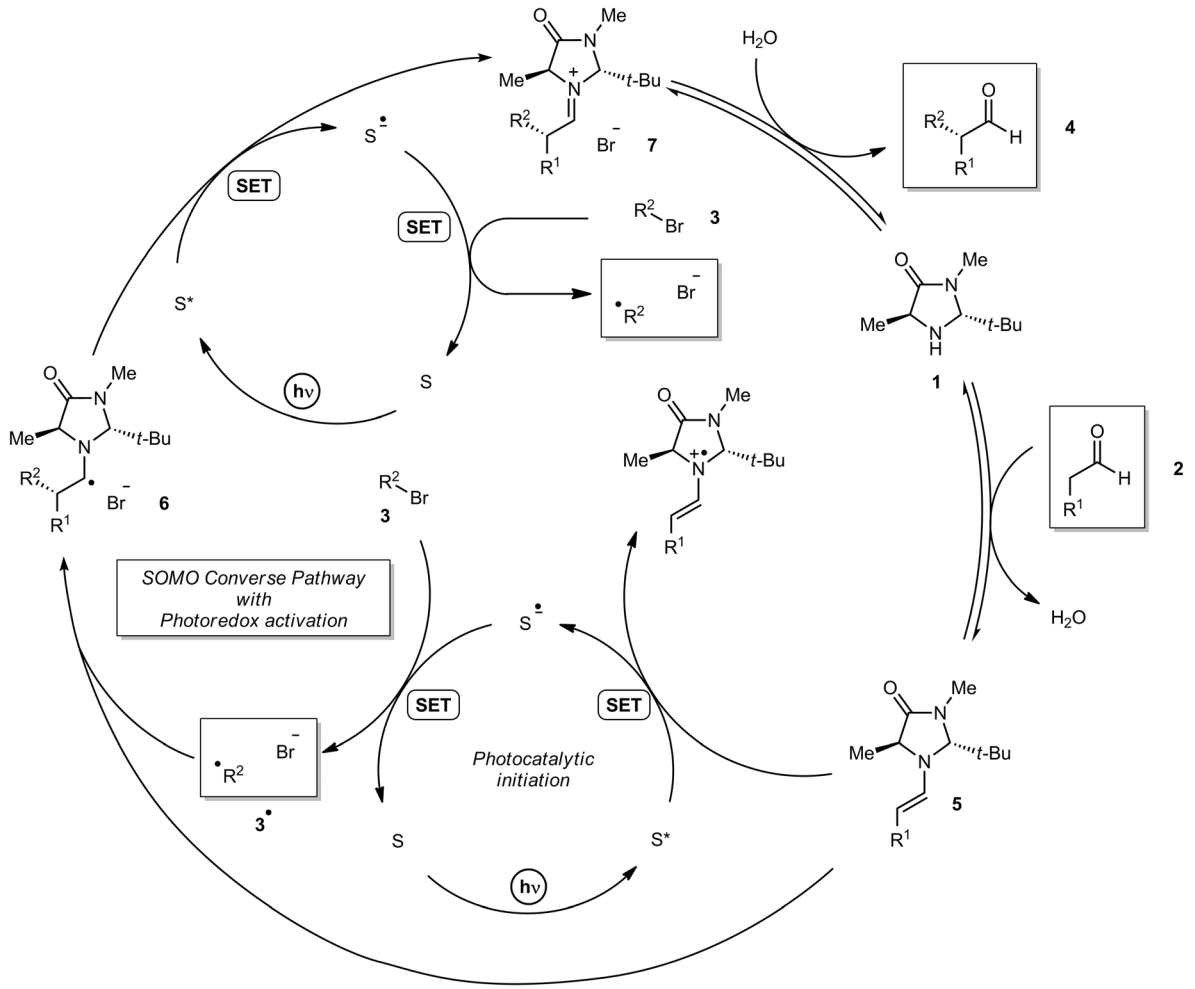


Fig. 3 Proposed mechanism for the α-alkylation of aldehydes.

transformation, albeit with different yields and enantioselectivities (Table 1, entries 1–7). The reaction can be conducted using different light sources.[15] Nevertheless, light as well as the photocatalyst were proved to be essential for this transformation (entries 14–15).

Table 1 Investigation on the light source and the photosensitizer[a]

Entry	Light source	S	Time (h)	Yield[b] (%)	ee[c] (%)
1	Hg 150 W	Anthr	3	72	88
2	Hg 150 W	Napht	3	6	81
3	Hg 150 W	DCA	6	0	nd
4	Hg 150 W	DCN	6	46	70
5	Hg 150 W	EB	4	87	82
6	Hg 150 W	EY	4	86	83
7	Hg 150 W	RB	2	quant	83
8	Fluo 24 W	EB	4	78	83
9	Fluo 24 W	EY	4	81	82
10	Fluo 24 W	RB	2	quant	82
11	LED 530 nm	EY	3	86	75
12	LED 530 nm	RB	3	66	76
13	LED 558 nm	RB	16	66	84
14	Dark	RB	8	trace	nd
15	Fluo 24 W	—	8	trace	nd

[a] All the experiments were conducted with 0.5 mmol of **3a** in a 0.5 M anhydrous DMF solution. [b] NMR yield was determined using a calibrated internal standard. [c] The ee was determined by chiral HPLC analysis.

Even if Eosin B seems to be the best sensitizer with regard to reduction potential (Fig. 1) for the halide reduction, Rose Bengal gives the best compromise between the yield and the ee (Table 1, entries 7 and 10). These results show that the reduction potential of sensitizers is not the only parameter to be considered. We speculated here that the triplet quantum yield plays a significant role in the photoactivation steps.[16] Under a 150 W high pressure Hg lamp light or even an economic eco-compatible 24 W 6500 K fluorescent bulb light, the reaction was achieved in only 2 h at room temperature and did not require any heating or cooling system.

Next we carried out a solvent screening, with Rose Bengal as photoredox catalyst, to ascertain the solvent scope in this reaction. The mild polarity governs the two equilibriums of the proposed mechanism. It is also a major concern for the solvent separated ion pairs. So as we expected, it was found (Table 2) that the more polar DMSO and DMF were the most suitable solvents both in yield and enantioselectivity. Switching the solvent to less polar MeCN, THF, or DME dropped the yield and increased the reaction time.

As generally expected in organocatalysis,[17] the concentration also displayed a significant effect on both yield and

Table 2 Solvent screening for the α-alkylation of aldehydes[a]

Entry	Solvent	Time (h)	Yield[b] (%)	ee[c] (%)
1	anh. DME	6	34	70
2	anh. THF	6	45	63
3	anh. MeCN	6	48	74
4	anh. DMF	2	quant	82
5	anh. DMSO	2	quant	87

[a] All the experiments were conducted as in entry 10 Table 1 with Rose Bengal and a 24 W fluorescent bulb. [b] NMR yield was determined using a calibrated internal standard. [c] The ee was determined by chiral HPLC analysis.

enantioselectivity. Between 0.1 and 1.0 M, the best results were obtained for 0.5 M (Table 3, entry 3).

We also examined the influence of cheaper Lewis acid salts as cocatalysts in order to reduce the amount of catalyst **1** in this reaction.

As reported in Table 4, lowering of the catalyst led to a remarkably slow conversion with very poor yields (Table 4, entries 2–3). An additional 10 mol% of anhydrous LiCl allowed the use of only 15 mol% of catalyst **1** thus recovering both yield and enantioselectivity (Table 4, entries 4–13). Furthermore, switching the DMF by DMSO provided the best result for this study (Table 4, entry 14). It could be noticed that leaving the reaction over 16 h decreased the selectivity (Table 4, entry 15). Moreover, we proved that this reaction can be efficiently scaled-up (Table 4, entries 16–17). Interestingly, irradiation under diffuse sunlight[18] provided the same results as a fluorescent light bulb (Table 4, entry 18), notably without any loss in enantioselectivity.

After establishing the optimal reaction conditions, several aldehydes were subjected to the direct enantioselective α-alkylation by diethyl bromomalonate **3a** (Scheme 3). Various aliphatic aldehydes were found to be suitable substrates for this reaction.

In conclusion, Rose Bengal was successfully applied as an organic photocatalyst to the asymmetric photoredox α-alkylation of aldehydes. The reaction proceeded smoothly under visible light irradiation at room temperature and with short reaction times providing good to excellent yields and enantioselectivities. The conditions described in this report are environmentally benign and operationally simple. Rose Bengal associated with a cocatalytic system (catalyst **1** and LiCl) gave superior or

Table 3 Concentration effect[a]

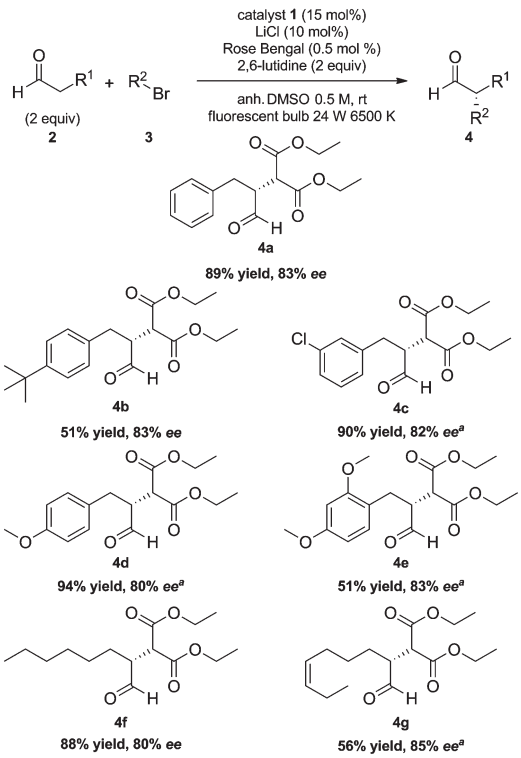
Entry	Concentration (M)	Time (h)	Yield[b] (%)	ee[c] (%)
1	0.10	3	66	77
2	0.25	3	75	80
3	0.50	2	quant	82
4	0.75	0.75	97	78
5	1.0	0.5	85	79

[a] All the experiments were conducted as in entry 10 Table 1 with Rose Bengal and a 24 W fluorescent bulb in DMF. [b] NMR yield was determined using a calibrated internal standard. [c] The ee was determined by chiral HPLC analysis.

Table 4 Effect of a catalytic amount of cocatalyst[a]

Entry	Catalyst **1** (mol%)	Cocatalyst (mol%)		Time (h)	Yield[b] (%)	ee[c] (%)
1	20	—		2	quant	82
2	15	—		4	68	80
3	10	—		6	47	81
4	10	LiCl	5	6	46	73
5	10	LiCl	10	4	55	77
6	10	LiCl	20	8	42	78
7	15	LiCl	10	2	82	82
8	15	LiBr	10	2	53	84
9	15	$LiPF_6$	10	2	70	80
10	15	$LiBF_4$	10	2	80	74
11	15	LiOTf	10	2	90	76
12	15	$LiClO_4$	10	3	83	82
13	15	$MgCl_2$	10	3	54	nd
14[d]	15	LiCl	10	2	91	83
15[d]	15	LiCl	10	16	93	73
16[e]	15	LiCl	10	2	93	85
17[f]	15	LiCl	10	2	95	81
18[g]	15	LiCl	10	2	92	82

[a] All the experiments are conducted as in entry 10 Table 1 with Rose Bengal and a 24 W fluorescent bulb in DMF. [b] NMR yield was determined using a calibrated internal standard. [c] The ee was determined by chiral HPLC analysis. [d] Reaction performed in DMSO. [e] Scale-up in DMSO: 1 mmol of started **3a** instead of 0.5 mmol. [f] Scale-up in DMSO: 5 mmol of started **3a**. [g] Reaction performed in DMSO using sunlight as the light source.



Scheme 3 Scope of the α-alkylation by fully organic photoredox organocatalysis. [a]Reaction performed in DMF with 20 mol% catalyst without LiCl.

equivalent results in termsafter of enantioselectivity, yield, catalyst loading and particularly reaction times, when compared to other photoredox systems previously described in the literature.

The preliminary chemistry described herein underlines the susceptibility of the α-alkylation reaction to subtle changes in the reaction conditions. Mechanistic studies, the design of improved photocatalysts and their application to other types of reactions are currently investigated in our laboratory and will be reported in due course.

Acknowledgements

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Notes and references

‡ Typical procedure for enantioselective α-alkylation of aldehydes (synthesis of **4a**): an overnight oven dried Pyrex glass vial was equipped with a septum and a dried magnetic stir bar. Rose Bengal (0.0025 mmol, 0.005 equiv, 2.5 mg), the imidazolidinone **1** (0.075 mmol, 0.15 equiv, 24.0 mg), anhydrous LiCl (prior oven dried, 0.050 mmol, 0.10 equiv, 2.1 mg) and diethyl bromomalonate **3a** (0.50 mmol, 1.0 equiv, 84 μL) were added successively. After purging the container with argon for 1 min, anhydrous DMSO (0.5 M, 1 mL) was added followed by hydrocinnamaldehyde **2a** (1.0 mmol, 2.0 equiv, 132 μL) and 2,6-lutidine (1.0 mmol, 2.0 equiv, 115 μL). Then the stirred solution was degassed for 10 min under argon bubbling and the mixture was placed 2 cm from the 24 W 6500 K 1425 lm fluorescent light source for irradiation until the complete conversion of the bromide after 2 h (monitored by TLC and/or GC/MS analysis). Then 10 mL of water was added and the resulting solution was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by silica gel chromatography using cyclohexane–EtOAc (95 : 5) to afford the desired alkylation product **4a** (89% yield, 83% ee) as a colorless oil.

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16 See the ESI† for further information on the triplet quantum yield.

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