DOI: 10.1002/cctc.201200435

Organic Dye-Photocatalyzed Acylnitroso Ene Reaction

Yew Chin Teo,[a] Yuanhang Pan,[a] and Choon Hong Tan*[b]

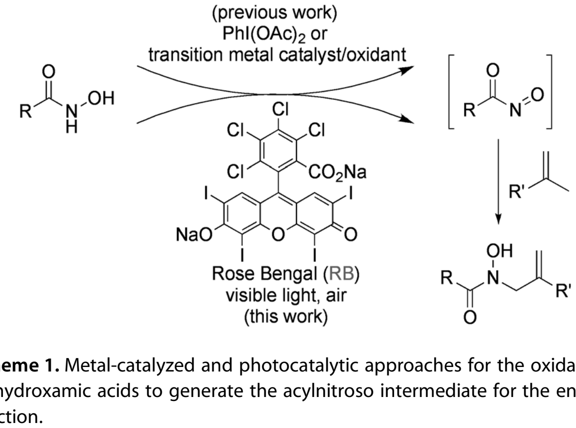
Rose bengal, an inexpensive and readily available organic dye, is demonstrated to be a photoredox catalyst for the formation of transient acylnitroso intermediates under visible light irradiation. This method is operationally simple and uses air as the terminal oxidant. Reactions of acylnitroso with a range of functionalized alkenes give intermolecular acylnitroso ene products in moderate to good yields. This is an environmentally friendly allylic amination methodology that avoids the use of metal catalysts and stoichiometric amount of oxidants. A plausible reaction mechanism is proposed on the basis of singlet oxygen and fluorescence quenching studies.

Introduction

Allylamines are versatile and fundamental building blocks for the construction of α- and β-amino acids, alkaloids, and carbohydrate derivatives.[1] The acylnitroso ene reaction constitutes a mild and valuable synthetic methodology to obtain allylamines through the direct allylic amination of olefins.[2] However, this methodology remains underdeveloped because of the in situ decomposition of the hydroxylamine adduct.[2a]

Owing to their high reactivity, acylnitroso compounds are difficult to isolate and usually generated in situ through the oxidation of hydroxamic acids.[3] Keck[4] and Kirby[5] developed independently a two-step protocol through which the acylnitroso species are formed from periodate oxidation and are first trapped by cycloaddition; they are then released through thermal retro-cleavage. Adam et al. demonstrated a simple one-pot procedure using the oxidant iodosobenzene diacetate.[6] More recently, oxidation methods that use transition-metal catalysts have been reported. Ru^{II}, Ir^{I}, Fe^{III}, or Cu^{I} catalyzed oxidation of hydroxamic acids with stoichiometric amounts of hydrogen peroxides has also been reported.[7] However, some of the aforementioned methods had certain limitations. The use of stoichiometric amounts of oxidant often leads to poor atom economy.[8] Some of the transition-metal catalysts used, such as Ru^{II} and Ir^{I} catalysts, are expensive and present potential environmental problems.

In 2011, Alaniz et al. demonstrated the use of the CuCl catalyst and air as the terminal oxidant for the oxidation of hydroxamic acids, which gives the acylnitroso ene products in good yields with a wide substrate scope.[9] Encouraged by their results, we became interested in developing an alternative metal-free approach to generate the acylnitroso species. In recent years, there has been greater interest in photochemical transformations under visible light irradiation owing to the mild conditions required for substrate activation.[10] The use of organic dyes has received increasing attention because they are inexpensive and are a viable alternative to the conventional inorganic transition-metal photocatalysts. Several examples have been reported on the use of organic dyes as photoredox catalysts under visible light irradiation.[11] König and co-workers demonstrated the Eosin Y-catalyzed direct C–H bond arylation of heteroarenes with aryl diazonium salts under visible light irradiation.[11f] Our group demonstrated previously that rose bengal (RB) was able to catalyze the α-oxyamination of 1,3-dicarbonyl compounds and 2,2,6,6-tetramethylpiperidine-1-oxyl with excellent yields under visible light irradiation.[12a] We reported recently the use of RB as a photoredox catalyst for dehydrogenative coupling reactions.[12b,c] Herein, we report a simple one-pot method for the acylnitroso ene reaction that uses organic dyes as photoredox catalysts and air as the terminal oxidant (Scheme 1).



Scheme 1. Metal-catalyzed and photocatalytic approaches for the oxidation of hydroxamic acids to generate the acylnitroso intermediate for the ene reaction.

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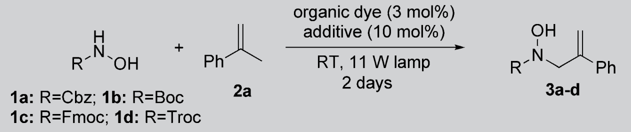
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201200435.

Results and Discussion

We started our investigation by screening a number of organic dyes for photocatalytic activities by using the reaction between benzyl hydroxycarbamate (**1a**) and α-methylstyrene (**2a**) (Table 1). An 11 W household fluorescent lamp was used as the visible light source. Of the dyes screened, RB showed the highest efficiency (Table 1, entry 1). Eosin Y gave a slightly lower yield, whereas other dyes gave poor yields (Table 1, entries 2–6). Solvent optimization showed that acetonitrile was the best solvent for this photocatalytic reaction (Table 1, entries 1, 7–9). As the reaction was sluggish, optimizations were further performed by using additives (Table 1, entries 10–12). An addition of 10 mol% pyridine resulted in higher reaction efficiency and improved yield (Table 1, entry 11). If the reaction was run at an elevated temperature, 35 °C, the product yield increased to 77% and the reaction was completed in 10 h (Table 1, entry 13). However, if the temperature was increased to 45 °C, the yield decreased slightly (Table 1, entry 14). The amount of **2a** was found to be lowered to 3 equiv compared with that of **1a** without any adverse effect on the yield (Table 1, entry 15). Although hydroxylamines protected with Boc, Fmoc, and Troc groups all participated in the reaction, only modest yields were achieved (Table 1, entries 16–18). In the absence of either the photocatalyst or the light source, no product was obtained (Table 1, entries 19 and 20).

Table 1. Acylnitroso ene reaction between benzyl hydroxycarbamate (**1**) and α-methylstyrene (**2a**).[a]

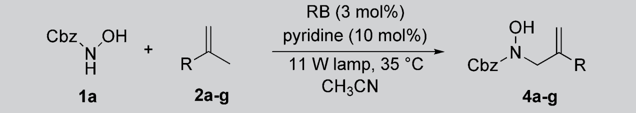


Entry	Organic dye	Solvent	Additive	1	Yield [%][b]
1	RB	CH$_3$CN	–	**1a**	35
2	eosin Y	CH$_3$CN	–	**1a**	31
3	fluorescein	CH$_3$OH	–	**1a**	22
4	rhodamine B	CH$_3$CN	–	**1a**	10
5	methylene blue	CH$_3$CN	–	**1a**	8
6	TPP	CH$_3$CN	–	**1a**	5
7	RB	CH$_3$OH	–	**1a**	24
8	RB	DMF	–	**1a**	25
9	RB	CH$_3$CN/H$_2$O (1:1)	–	**1a**	25
10	RB	CH$_3$CN	AcOH	**1a**	44
11	RB	CH$_3$CN	pyridine	**1a**	60
12	RB	CH$_3$CN	DMAP	**1a**	58
13[c]	RB	CH$_3$CN	pyridine	**1a**	77
14[d]	RB	CH$_3$CN	pyridine	**1a**	71
15[e]	RB	CH$_3$CN	pyridine	**1a**	78
16[f]	RB	CH$_3$CN	pyridine	**1b**	45
17[f]	RB	CH$_3$CN	pyridine	**1c**	53
18[f]	RB	CH$_3$CN	pyridine	**1d**	50
19	none	CH$_3$CN	–	**1a**	0
20[g]	RB	CH$_3$CN	–	**1a**	0

[a] Reaction was performed by using 0.10 mmol of **1** and 0.50 mmol of **2a** in 0.5 mL of the solvent. RB = rose bengal; TPP = tetraphenylporphyrin; [b] Isolated yield with respect to **1**; [c] Reaction was performed at 35 °C and completed after 10 h; [d] Reaction was performed at 45 °C and completed after 7 h; [e] Reaction was performed at 35 °C by using 0.30 mmol of **2a** and completed after 12 h; [f] Reaction was performed at 35 °C by using 0.30 mmol of **2a**; [g] Reaction was performed in the dark.

With the established conditions, the substrate scope of the intermolecular ene reaction with **1a** and styrene derivatives was investigated (Table 2). A range of styrene derivatives **2a–f**, with electron-withdrawing and electron-donating substituents, underwent the desired reaction with **1a** to provide the ene products **4a–f** in moderate to good yields (Table 2, entries 1–6). However, if 2-(prop-1-en-2-yl)naphthalene (**2g**) was used, a relatively low yield was obtained (Table 2, entry 7).

Table 2. Substrate scope studies for the acylnitroso ene reaction.[a]



Entry	R	t [h]	Compound	Yield [%][b]
1	Ph (**2a**)	12	**4a**	78
2	p-MeC$_6$H$_4$ (**2b**)	9	**4b**	81
3	p-MeOC$_6$H$_4$ (**2c**)	8	**4c**	50
4	p-FC$_6$H$_4$ (**2d**)	9	**4d**	76
5	p-ClC$_6$H$_4$ (**2e**)	8	**4e**	83
6	p-CNC$_6$H$_4$ (**2f**)	10	**4f**	82
7	2-naphthyl (**2g**)	30	**4g**	33

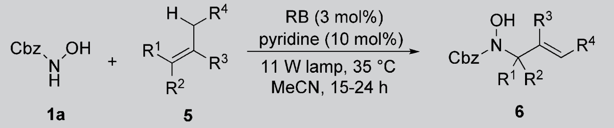
[a] Reaction was performed by using 0.10 mmol of **1a** and 0.30 mmol of **2** in 0.5 mL of CH$_3$CN; [b] Isolated yield with respect to **1a**.

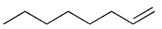
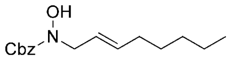
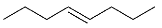
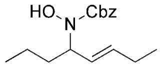
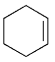
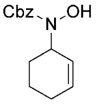
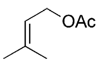
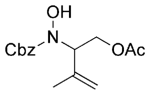
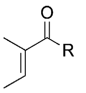
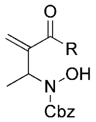
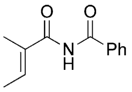
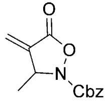
Next, the scope of the reaction was expanded to include a series of aliphatic alkenes (Table 3). The reaction proceeded smoothly to give allylic *N*-hydroxycarbamates in moderate to good yields (Table 3, entries 1–9). Disubstituted *trans*-4-octene gave better results than did monosubstituted 1-octene, possibly owing to higher reactivity of the more electron-rich disubstituted olefins (Table 3, entries 1 and 2).[2a] Notably, the acylnitroso enophile abstracts an allylic hydrogen from the geminal alkyl group on the more substituted side of the alkene (Table 3, entry 4).[13] Although singlet oxygen ene products were detected if cyclohexene (Table 3, entry 3) was used, they were formed in negligible amounts.

We next turned our focus to nitroso ene reactions with tiglic acid derivatives (Table 3, entries 5–9). The products obtained provide access to α,β-disubstituted amino acids, which have few direct synthetic methodologies.[14] Poor yields were reported previously by using tiglic acid derivatives as the ene substrates because of the electron-deficient double bonds.[6] Moderate-to-good yields were obtained with tiglic acid, tiglic esters, and tiglic amide as the alkene partners under our reaction conditions (Table 3, entries 5–8). The benzamide analogue also underwent the ene reaction but cyclized in situ to form α-methylene isoxazolidinone (Table 3, entry 9).

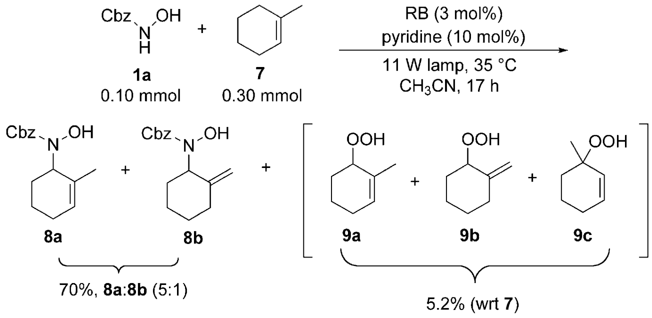
The reaction with 1-methyl-1-cyclohexene demonstrated a remarkable preference for allylic hydrogen abstraction from the

Table 3. Substrate scope studies for the acylnitroso ene reaction.[a]



Entry	Olefin	Product	Yield [%][b] (E/Z)
1			44[c] (4:1)
2			70[c] (4:1)
3			71
4			70
			
5	R=OH	R=OH	50
6	R=OMe	R=OMe	77
7	R=OBn	R=OBn	59
8	$R=NH_2$	$R=NH_2$	81
9			68

[a] Reaction was performed by using 0.10 mmol of **1 a** and 0.30 mmol of olefin in 0.5 mL of CH_3CN; [b] Isolated yield with respect to **1 a**; [c] Combined yield of both regioisomers.

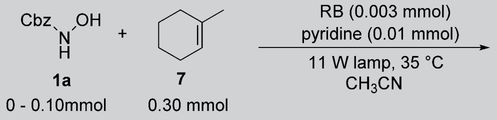


Scheme 2. Acylnitroso ene reaction of benzyl hydroxycarbamate (**1 a**) with 1-methyl-1-cyclohexene (**7**).

cis position (Scheme 2). This difference in regioselectivity has been rationalized in terms of steric hindrance during the attack. The nitroso enophile follows the skew trajectory in the favored twix arrangement, in which the Cbz group points to the free corner of the alkene to reduce steric interactions.[15] Notably, the formation of side products **9 a**–**c** arises from the ene reaction of the alkene with singlet oxygen.

To better understand about the occurrence of side products with singlet oxygen, a concentration study was conducted. The same reaction (Scheme 2) was performed with varying amounts of **1 a**, and their corresponding product compositions were tabulated (Table 4). The singlet oxygen ene products **9 a**–**c** were formed in smaller amounts with the increasing concentration of **1 a**. Hence, either **1 a** or the acylnitroso ene products **8** are good singlet oxygen quenchers that prohibit the reaction of singlet oxygen with the alkene. However, the alkenes mentioned in Table 3 are less electron-rich compared with 1-methyl-1-cyclohexene (**7**), which makes them less reactive toward singlet oxygen and thus no or only negligible amount of singlet oxygen ene products was observed.

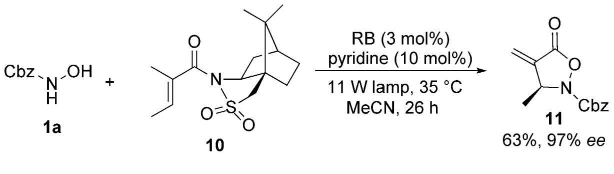
Table 4. Product composition of the reaction between benzyl hydroxycarbamate (**1 a**) and 1-methyl-1-cyclohexene (**7**).[a]



Entry	1 a [mmol]	Yield of 8 [%][b]	Yield of 9 [%][c]	Product ratio (8/9)[d]
1	0	–	52	–
2	0.01	57	17	0.1:1
3	0.03	64	13	0.5:1
4	0.05	67	10	1.1:1
5	0.10	70	5	4.4:1

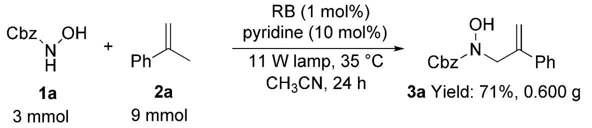
[a] Reaction was performed by using 0–0.10 mmol of **1 a** and 0.30 mmol of **7** in 0.5 mL of CH_3CN; [b] Combined isolated yield of both regioisomers with respect to **1 a**; [c] Combined yield of all regioisomers with respect to **7**; [d] **8** (mmol)/**9** (mmol).

α-Methylene isoxazolidinone compounds are found to have biological activity similar to that of α-methylidene-γ-lactones, and asymmetric strategies for the synthesis of such potential novel therapeutics would be useful for future studies of their activity.[16] On the basis of the work of Adam[17] and Alaniz,[8] tiglic acid with Oppolzer's sultam (**10**) was synthesized and subjected to the optimized reaction conditions in the presence of **1 a** (Scheme 3). This asymmetric strategy gave α-methylene isoxazolidinone (**11**) as predominantly a single enantiomer (97% enantiomeric excess). A low catalyst loading of 3% was required.



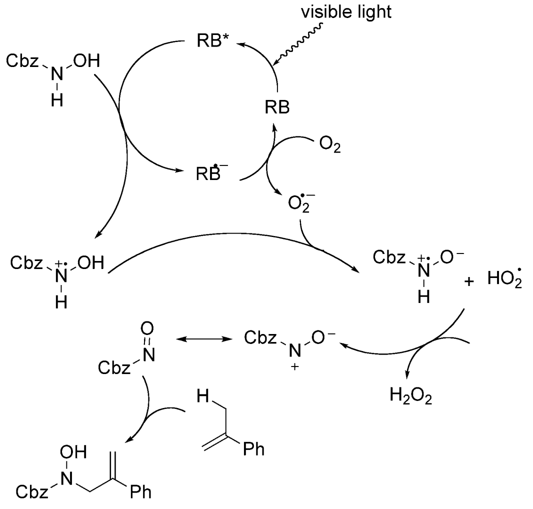
Scheme 3. Asymmetric synthesis of α-methylene isoxazolidinone (**11**).

To demonstrate the scalability of this visible light-driven photocatalytic reaction, the reaction was performed with 3 mmol of **1 a** and 0.600 g (71%) of **3 a** was obtained (Scheme 4). The catalyst loading was lowered to 1 mol%.



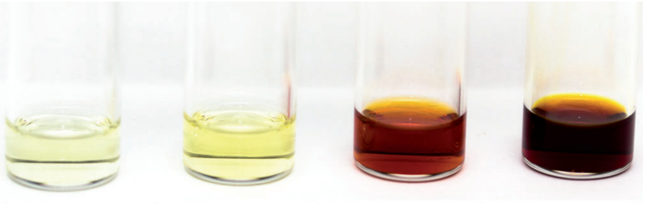
Scheme 4. Scaled-up acylnitroso ene reaction between benzyl hydroxycarbamate (**1a**) and α-methylstyrene (**2a**).

We proposed mechanistically that the highly reactive acylnitroso intermediate was formed through the oxidation of hydroxamic acids. The excited state of rose bengal, RB*, is populated after visible light irradiation. Two possible photoinduced sensitization mechanisms occur. The first pathway involved single electron transfer between substrate **1a** and photoexcited dye to give the radical cation of **1a** and the radical anion $RB^{\bullet-}$ (Scheme 5). The photoredox cycle is accomplished by reoxidizing the radical anion $RB^{\bullet-}$ to the ground state RB through the molecular oxygen. The alternative pathway is based on energy transfer, leading to singlet oxygen generation. RB is a well-known singlet oxygen sensitizer, which acts through energy transfer from RB* to ground state triplet oxygen in polar aprotic solvents.[18] The resulting singlet oxygen can oxidize **1a** to give the same radical cation $\mathbf{1a}^{\bullet+}$. The relatively acidic $\mathbf{1a}^{\bullet+}$ can be deprotonated by the strongly basic superoxide anion $O_2^{\bullet-}$. A hydrogen atom is then removed to form the nitroso intermediate, which generates H_2O_2 as the byproduct. The highly reactive acylnitroso intermediate then undergoes the ene reaction with alkene to give the final product.



Scheme 5. Proposed mechanism for the organic dye-photocatalyzed generation of acylnitroso species for ene reactions.

Hydrogen peroxide was detected after the reaction was completed by using the iodide test (KI in glacial acetic acid), in which a color change to brown was observed (Figure 1). In addition, the reaction conducted under nitrogen atmosphere led to a significant reduction in the yield (10% by using **1a** and **2a**). This confirmed that oxygen is crucial in this reaction as it ensures catalytic turnover.



(a)	(b)	(c)	(d)
KI in glacial acetic acid	Addition of reaction mixture[a] at *t*=0 to (a)	Addition of reaction mixture[a] at *t*=12 h to (a)	Addition of H_2O_2 to (a)
Colorless	Pale yellow	Brown	Dark brown

Figure 1. Test for the production of hydrogen peroxide. [a] Reaction mixture of 0.10 mmol of **1a** and 0.30 mmol of **2a** in 0.5 mL of MeCN under optimized conditions.

Further mechanistic studies were performed to confirm the expected reaction pathway. To probe singlet oxygen involvement in the reaction, solvent effects were studied. The lifetime of singlet oxygen highly depends on the solvent used, and its lifetime is significantly longer in deuterated solvents compared to their protonated counterparts.[19] An increase in the product yield with the change in the solvent from CH_3CN to CD_3CN would suggest the involvement of a singlet oxygen pathway.[19] Product formation was monitored at regular time intervals in both CH_3CN and CD_3CN, and the kinetic measurements of the product yields were comparable in both solvents (Figure 2). Therefore, singlet oxygen was likely not a key participant in the reaction, because there was no significant rate enhancement in CD_3CN. Previous mechanistic studies performed on the basis of a similar reaction by conducting controlled experiments with fluorescein also indicated that singlet oxygen is not crucial.[12c]

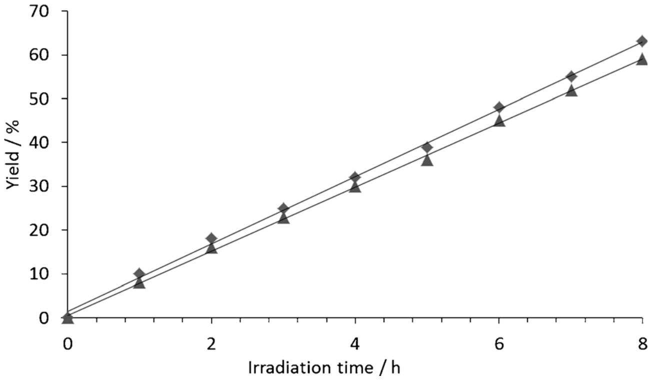


Figure 2. Photocatalytic acylnitroso ene reaction of benzyl hydroxycarbamate (**1a**) and α-methylstyrene (**2a**) to give compound **3a** in the presence of rose bengal; reaction kinetics was monitored by using ^1H NMR spectroscopy; CD_3CN (◆), CH_3CN (▲)

To give evidence of the proposed pathway in which **1a** would be initially oxidized by RB*, we performed fluorescence quenching experiments (Stern–Volmer studies) of RB.[20] Nota-

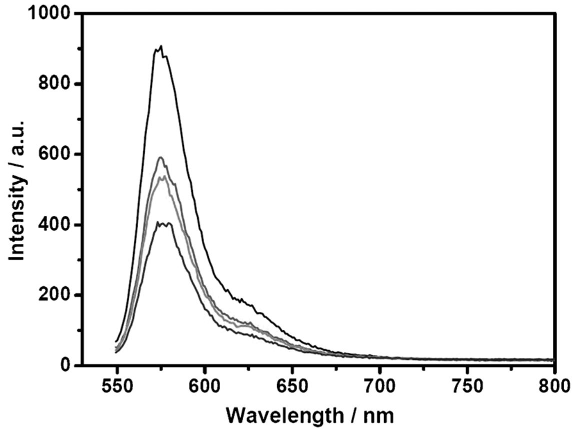


Figure 3. Fluorescence quenching of rose bengal by benzyl hydroxycarbamate (**1 a**).

bly, the fluorescence intensity decreased in the presence of increasing concentration of **1 a** (Figure 3). A plot of the ratio of the fluorescence intensity without a quencher (I_0) versus the fluorescence intensity with a quencher (I) was shown to be first-order dependent on the concentration of **1 a**, which is indicative of its role as a reductive quencher of RB* (Figure 4). Hence, the reaction likely occurs predominantly by electron-transfer process rather than by singlet oxygen (Figure 3).

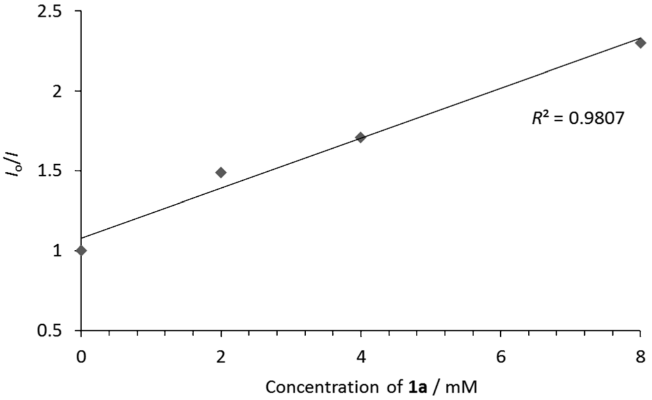


Figure 4. Plot of fluorescence intensity of rose bengal versus concentration of benzyl hydroxycarbamate (**1 a**).

Conclusions

We have demonstrated mild reaction conditions for the in situ formation of acylnitroso species catalyzed by an organic dye, rose bengal, under visible light irradiation. This method is operationally simple and uses air as the terminal oxidant. A range of alkenes can be used as ene substrates to afford the nitroso ene products in moderate to good yields. Mechanistic studies revealed that the reaction most likely involves direct electron transfer between the excited states of the dye and hydroxamic acids rather than singlet oxygen. An inexpensive and readily available organic dye was demonstrated to be a viable alternative to transition-metal catalysts. Hence, this process constitutes a simple and environmentally attractive route to the synthesis of allylamines.

Experimental Section

General

^{1}H and ^{13}C NMR spectra were recorded on a Bruker ACF 300 (300 MHz) or AMX 500 (500 MHz) spectrometer. Chemical shifts were reported in parts per million. The residual solvent peak was used as an internal reference. Low-resolution mass spectra were recorded on a FINNIGAN MAT LCQ spectrometer in the electrospray ionization mode. All high-resolution mass spectra were recorded on a FINNIGAN MAT 95XL-T spectrometer. Analytical TLC was performed with Merck precoated TLC plates (silica gel 60F-254, layer thickness 0.25 mm). Flash chromatography separations were performed on Merck 60 (0.040–0.063 mm) mesh silica gel. Reagents and solvents were of commercial grade and were used as supplied without further purification, unless otherwise stated. Visible light irradiation was performed by using a PowerPac 11 W household fluorescent lamp. Fluorescence spectra were recorded on a Shimadzu RF-5301 spectrophotometer.

Representative procedure for organic dye-photocatalyzed acylnitroso ene reaction

Benzyl hydroxycarbamate (**1 a**, 16.7 mg, 0.1 mmol, 1.0 equiv) and α-methylstyrene (**2 a**, 39 μL, 0.30 mmol, 3.0 equiv) were added to a solution of RB (3.0 mg, 0.003 mmol, 3 mol%) and pyridine (0.8 μL, 0.01 mmol, 10 mol%) in CH_3CN (0.5 mL). The reaction mixture was stirred at 35 °C under visible light irradiation from an 11 W household fluorescent lamp. After 12 h, the solvent was removed in vacuo and the crude product was loaded directly onto a short silica gel column. Flash chromatography was performed by using a hexane/ethyl acetate (4:1) mixture. After removing the solvent, product **4 a** (22.1 mg) was obtained as a colorless solid in 78% yield.

Procedure for asymmetric synthesis of benzyl 3-methyl-4-methylene-5-oxoisoxazolidine-2-carboxylate (11)

RB (3 mg, 0.003 mmol, 0.03 equiv) and pyridine (0.8 μL, 0.01 mmol, 0.10 equiv) were added to benzyl hydroxycarbamate (**1 a**) (16.7 mg, 0.10 mmol, 1.0 equiv) and (*E*)-1-{(6*S*,7a*S*)-8,8-dimethyl-2,2-dioxido-hexahydro-1*H*-3a,6-methanobenzo[*c*]isothiazol-1-yl}-2-methylbut-2-en-1-one (**10**; 36 mg, 0.12 mmol, 1.2 equiv) in CH_3CN (0.5 mL). The resulting solution was stirred at 35 °C under visible light irradiation from an 11 W household fluorescent lamp and monitored by using TLC. Upon reaction completion, the solvent was removed in vacuo and the crude product was loaded directly onto a short silica gel column. Flash chromatography was performed by using hexane/ethyl acetate (2:1) mixture to isolate the product. The solvent was removed under reduced pressure to obtain product as a colorless solid. The enantiomeric excess was determined by using chiral HPLC (Chiralpak IB column, 4.6 mm × 250 mm, 95:5 hexane/*i*PrOH, 1 mL min^{-1}, (*R* isomer: $R_t = 15.7$ min, *S* isomer: $R_t = 18.5$ min).

Test for hydrogen peroxide production

The production of hydrogen peroxide was detected by using the iodine test (KI in glacial acetic acid). Addition of H_2O_2 to a solution of KI gave a brown solution because of the formation of iodine.

This color change could be used for the qualitative analysis of hydrogen peroxide. Several test tubes of KI in glacial acetic acid were prepared to test for color change upon addition of the reaction mixture before and after light irradiation.

Kinetic experiments to probe singlet oxygen involvement

To monitor the reaction progress, ^{1}H NMR measurements were used. RB (3 mg, 0.003 mmol, 0.03 equiv) and pyridine (0.8 μL, 0.01 mmol, 0.10 equiv) were added to **1a** (16.7 mg, 0.10 mmol, 1.0 equiv) and **2a** (39 μL, 0.30 mmol, 3.0 equiv) in CH_3CN (0.5 mL) and CD_3CN (0.5 mL), respectively. The resulting solutions were stirred at 35 °C under visible light irradiation from an 11 W household fluorescent lamp. Appropriate numbers of samples were prepared, and ^{1}H NMR spectra were recorded after suitable time of irradiation.

Fluorescence quenching of Rose Bengal by benzyl hydroxycarbamate (1a)

In a 10 mL volumetric flask, a solution of RB (10.2 mg, 0.01 mmol, 10 mM) in CH_3CN was prepared (solution A). Then, solution A (0.1 mL) was added to a 100 mL volumetric flask and diluted to give the stock solution of RB in CH_3CN (10 μM, solution B). To another 100 mL volumetric flask, stock solution A (0.1 mL) and **1a** (16.7 mg, 0.1 mmol) were added and diluted with CH_3CN to 100 mL (solution C, with 10 mM of **1a**). Next, solution C (2, 4, and 8 mL) was added to three 10 mL volumetric flasks and diluted with solution B to give a series of **1a** solutions with the concentration of 2, 4, and 8 mM, respectively. Fluorescence spectra of these solutions were recorded (excitation wavelength: 539 nm; emission wavelength: 575 nm).

Acknowledgements

This work was supported by a research grant from GSK-Singapore Partnership for Green and Sustainable Manufacturing.

Keywords: organic dyes · photocatalysis · photoredox · rose bengal

[1] For a review on allylic amination, see: M. Johannsen, K. A. Jørgensen, *Chem. Rev.* **1998**, *98*, 1689 – 1708.

[2] For recent reviews on nitroso ene reaction, see: a) W. Adam, O. Krebs, *Chem. Rev.* **2003**, *103*, 4131 – 4146; b) S. Iwasa, A. Fakhruddin, H. Nishiyama, *Mini-Rev. Org. Chem.* **2005**, *2*, 157 – 175.

[3] For alternative methods to generate acylnitroso for ene reactions, see: a) P. Quadrelli, M. Mella, P. Caramella, *Tetrahedron Lett.* **1998**, *39*, 3233 – 3236; b) P. Quadrelli, M. Mella, P. Caramella, *Tetrahedron Lett.* **1999**, *40*, 797 – 800.

[4] G. E. Keck, R. R. Webb, J. B. Yates, *Tetrahedron* **1981**, *37*, 4007 – 4016.

[5] G. W. Kirby, H. McGuigan, D. McLean, *J. Chem. Soc. Perkin Trans. 1* **1985**, 1961 – 1966.

[6] W. Adam, N. Bottke, O. Krebs, C. R. Saha-Möller, *Eur. J. Org. Chem.* **1999**, 1963 – 1965.

[7] a) A. Fakhruddin, S. Iwasa, H. Nishiyama, K. Tsutsumi, *Tetrahedron Lett.* **2004**, *45*, 9323 – 9326; b) D. Atkinson, M. A. Kabeshov, M. Edgar, A. V. Malkov, *Adv. Synth. Catal.* **2011**, *353*, 3347 – 3351.

[8] R. A. Sheldon, I. W. C. E. Arends, U. Hanefeld in *Green Chemistry and Catalysis*, Wiley-VCH, Weinheim, **2007**, pp. 1 – 47.

[9] C. P. Frazier, J. R. Engelking, J. Read de Alaniz, *J. Am. Chem. Soc.* **2011**, *133*, 10430 – 10433.

[10] a) K. Zeitler, *Angew. Chem.* **2009**, *121*, 9969 – 9974; *Angew. Chem. Int. Ed.* **2009**, *48*, 9785 – 9789; b) J. M. R. Narayanam, C. R. J. Stephenson, *Chem. Soc. Rev.* **2011**, *40*, 102 – 113; c) T. P. Yoon, M. A. Ischay, J. Du, *Nat. Chem.* **2010**, *2*, 527 – 532; d) D. A. Nicewicz, D. W. C. MacMillan, *Science* **2008**, *322*, 77 – 80; e) J. Du, L. R. Espelt, I. A. Guzei, T. P. Yoon, *Chem. Sci.* **2011**, *2*, 2115 – 2119; f) M.-H. Larraufie, R. Pellet, L. Fensterbank, J.-P. Goddard, E. Lacôte, M. Malacria, C. Ollivier, *Angew. Chem.* **2011**, *123*, 4555 – 4558; *Angew. Chem. Int. Ed.* **2011**, *50*, 4463 – 4466; g) P. V. Pham, D. A. Nagib, D. W. C. MacMillan, *Angew. Chem.* **2011**, *123*, 6243 – 6246; *Angew. Chem. Int. Ed.* **2011**, *50*, 6119 – 6122; h) Y.-Q. Zou, L.-Q. Lu, L. Fu, N.-J. Chang, J. Rong, J.-R. Chen, W.-J. Xiao, *Angew. Chem.* **2011**, *123*, 7309 – 7313; *Angew. Chem. Int. Ed.* **2011**, *50*, 7171 – 7175; i) S. Füldner, R. Mild, H. I. Siegmund, J. A. Schroeder, M. Gruber, B. Konig, *Green Chem.* **2010**, *12*, 400 – 406; j) R. Lechner, B. König, *Synthesis* **2010**, *2010*, 1712 – 1718.

[11] For selected examples, see: a) D. Ravelli, M. Fagnoni, *ChemCatChem* **2012**, *4*, 169 – 171; b) A. G. Griesbeck, M. Cho, *Org. Lett.* **2007**, *9*, 611 – 613; c) D. P. Hari, B. König, *Org. Lett.* **2011**, *13*, 3852 – 3855; d) M. Neumann, S. Füldner, B. König, K. Zeitler, *Angew. Chem.* **2011**, *123*, 981 – 985; *Angew. Chem. Int. Ed.* **2011**, *50*, 951 – 954; e) K. Fidaly, C. Ceballos, A. Falguieres, M. S.-I. Veitia, A. Guy, C. Ferroud, *Green Chem.* **2012**, *14*, 1293 – 1297; f) D. P. Hari, P. Schroll, B. König, *J. Am. Chem. Soc.* **2012**, *134*, 2958 – 2961.

[12] a) H. Liu, W. Feng, C. W. Kee, Y. Zhao, D. Leow, Y. Pan, C.-H. Tan, *Green Chem.* **2010**, *12*, 953 – 956; b) Y. Pan, C. W. Kee, L. Chen, C.-H. Tan, *Green Chem.* **2011**, *13*, 2682 – 2685; c) Y. Pan, S. Wang, C. W. Kee, E. Dubuisson, Y. Yang, K. P. Loh, C.-H. Tan, *Green Chem.* **2011**, *13*, 3341 – 3344.

[13] M. Liu, M. P. Sibi, *Tetrahedron* **2002**, *58*, 7991 – 8035.

[14] W. Adam, N. Bottke, O. Krebs, *J. Am. Chem. Soc.* **2000**, *122*, 6791 – 6792.

[15] W. Adam, O. Krebs, M. Orfanopoulos, M. Stratakis, *J. Org. Chem.* **2002**, *67*, 8395 – 8399.

[16] T. Janecki, T. Wąsek, M. Różalski, U. Krajewska, K. Studzian, A. Janecka, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 1430 – 1433.

[17] W. Adam, H.-G. Degen, O. Krebs, C. R. Saha-Möller, *J. Am. Chem. Soc.* **2002**, *124*, 12938 – 12939.

[18] C. Schweitzer, R. Schmidt, *Chem. Rev.* **2003**, *103*, 1685 – 1758.

[19] a) J. R. Hurst, J. D. McDonald, G. B. Schuster, *J. Am. Chem. Soc.* **1982**, *104*, 2065 – 2067; b) P. R. Ogilby, C. S. Foote, *J. Am. Chem. Soc.* **1983**, *105*, 3423 – 3430.

[20] A. Berlicka, B. Konig, *Photochem. Photobiol. Sci.* **2010**, *9*, 1359 – 1366.

[21] R. S. Davidson, K. R. Trethewey, *J. Am. Chem. Soc.* **1976**, *98*, 4008 – 4009.

Received: July 3, 2012