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Authors: Xiaokai Cheng; Bo Yang; Xingen Hu; Qing Xu; Zhan Lu

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Visible-Light-Promoted Metal-Free Aerobic Oxidation of Primary Amines to Acids and Lactones

Xiaokai Cheng,^[a,b] Bo Yang,^[a] Xingen Hu,^[b] Qing Xu,^[b] and Zhan Lu^{*[a]}

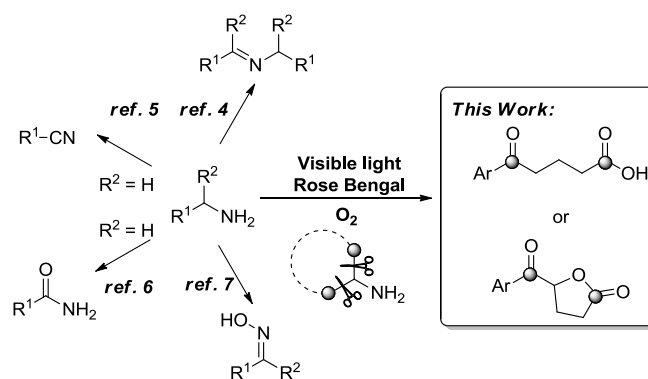
Dedication ((optional))

Abstract: A unique metal-free aerobic oxidation of primary amines via visible light photocatalytic double carbon-carbon bonds cleavage and multi carbon-hydrogen bonds oxidation was observed. Aerobic oxidation of primary amines could be controlled to afford acids by using dioxane with 18W CFL, and lactones by using DMF with 8W green LEDs, respectively. A plausible mechanism was proposed based on control experiments. This observation showed direct evidences for the fragmentation in the aerobic oxidation of aliphatic primary amines.

Selective oxidation is one of the most fundamental reactions in organic synthesis, as well as one of the most critical challenges facing the chemical industry.^[1] In most cases, oxidizing agents are required in stoichiometric amounts which are usually toxic or hazardous. Owing to increasing demand on environmental protection and decreasing pollution, dioxygen is regarded as an ideally clean and green terminal oxidant for catalytic oxidations.^[2]

Aerobic oxidations of primary amines^[3] under thermal and photosensitized conditions have been proven as powerful methods for synthesis of diverse products, such as imines,^[4] nitriles,^[5] amides,^[6] and oximes^[7] (**Scheme 1**). However, to the best of our knowledge, the unselective auto-oxidation of aliphatic primary amines with dioxygen to complicated fragmentation products has still not been well explored and is a remaining problem. We are particularly interested in visible-light-promoted nitrogen radical chemistry.^[8] Here, we developed a visible-light-promoted metal-free aerobic oxidation of amines to acids or lactones via double C-C bonds cleavage and multi carbon-hydrogen bonds oxidation.

The primary amine **1a** was chosen as a model substrate which was proposed to undergo intramolecular C-N bond formation via one electron oxidation of amine. The reaction of **1a** in the presence of Ru(bpy)₃(PF₆)₂^[9] in a solution of DMF with an oxygen balloon under the irradiation of 18W CFL did not afford any C-N bond formation product, however, an unexpected acid



Scheme 1. Diverse products from aerobic oxidation of aliphatic primary amines.

2a was observed in 18% yield. It should be noted that the reaction should undergo C-C bond oxidative cleavage to lose one carbon atom from an amine to an acid. Compared to aerobic oxidation of oxygen-containing cyclic compounds^[10] to provide the corresponding ring-opening products without losing any carbon atom, this aerobic oxidation of primary amines is unique.

Various photosensitizers such as [Ir(ppy)₂(dtbbpy)](PF₆), Ir(ppy)₃, Eosin Y, Mes-acridine and Rose Bengal (RB) were screened (entries 2-6) among which Rose Bengal^[11] could catalyze the reaction to afford **2a** in 49% yield. When 2.0 equiv of HCOOH and 2,6-lutidine was added in the reaction no significant increase in yields were observed (entries 7 and 8). Increasing the reaction to 24 h, the yield was up to 58% (entry 9). Among different solvents, such as MeOH, THF, DCM, CH₃CN, acetone and dioxane (entries 11-16), dioxane was the best solvent to give **2a** in 72% yield. Control experiments without O₂ or light did not afford any desired products (entries 17 and 18).

With standard conditions in hands, the scope was shown in **Table 2**. Various substrates with electron-rich and electron-poor substituents on the phenyl ring were suitable to give the corresponding acids **2b-j** in 50–71% yields. The reaction of *anti*-**1d** could also occur to afford **2d** in a slightly low yield.^[12] The TBS-protected phenol and benzyl alcohol could undergo the oxidation reaction to afford **2k** and **2l** in 56% and 63% yield, respectively. The free benzyl alcohol was tolerated to afford **2m** in 46% yield. The diol-protected or unprotected ketones were also survived to deliver **2n** and **2o** in 55 and 54% yield. Other polycyclic rings and heterocycles such as 2-naphenyl (**2p**), 1,3-benzodioxole (**2q**) could be converted in 45–64% yields. The reaction of 2-(5'-indyl)cycloamine (**1r**) was slow under standard conditions, however, afforded **2r** in 36% yield under 8W green LEDs probably due to the power density of light sources. The

[a] X. Cheng, B. Yang, Prof. Z. Lu
Department of Chemistry, Zhejiang University
Hangzhou, Zhejiang 310058, China
E-mail: luzhan@zju.edu.cn

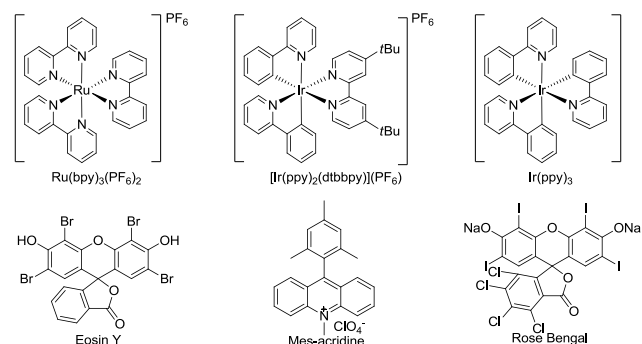
[b] X. Cheng, Prof. X. Hu, Prof. Q. Xu
College of Chemistry and Materials Engineering, Wenzhou University
Wenzhou 325035, P. R. China

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Table 1. Optimization of Aerobic Oxidation of Primary Amines to Acids^[a]

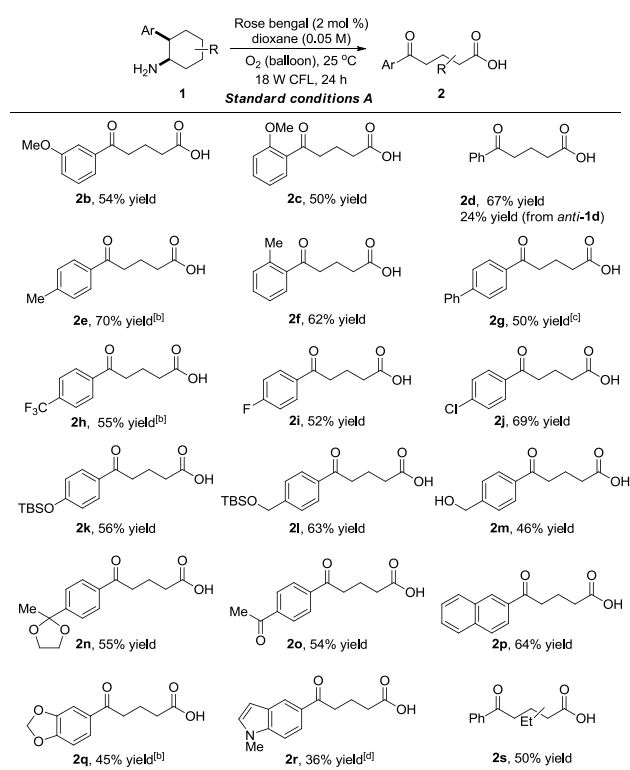
Entry	Photocatalyst	Solvent	t (h)	Yield ^[b] of 2a (%)
1	Ru(bpy) ₃ (PF ₆) ₂	DMF	12	18
2	[Ir(ppy) ₂ (dtbbpy)]PF ₆	DMF	12	0
3	Ir(ppy) ₃	DMF	12	9
4	Eosin Y	DMF	12	8
5	Mes-acridine	DMF	12	0
6	Rose Bengal	DMF	12	49 ^[c]
7 ^[d]	Rose Bengal	DMF	12	42
8 ^[e]	Rose Bengal	DMF	12	45
9	Rose Bengal	DMF	24	58 ^[c]
10	Rose Bengal	DMF	36	53 ^[c]
11	Rose Bengal	MeOH	24	0
12	Rose Bengal	THF	24	51 ^[c]
13	Rose Bengal	CH ₂ Cl ₂	24	18
14	Rose Bengal	CH ₃ CN	24	32
15	Rose Bengal	acetone	24	16
16	Rose Bengal	dioxane	24	72 ^[c]
17 ^[f]	Rose Bengal	dioxane	24	0
18 ^[g]	Rose Bengal	dioxane	24	0

[a] Unless otherwise noted, all reactions were conducted using **1** (0.4 mmol) and photocatalyst (2 mol%) in dry solvent (8 mL) with an O₂ balloon under the irradiation of a 18 W fluorescent lamp. [b] Yields determined by ¹H NMR using TMS-Ph as an internal standard. [c] Isolated yields. [d] HCOOH (2.0 equiv) was added. [e] 2,6-lutidine (2.0 equiv) was added. [f] Under an atmosphere of N₂. [g] Without light.

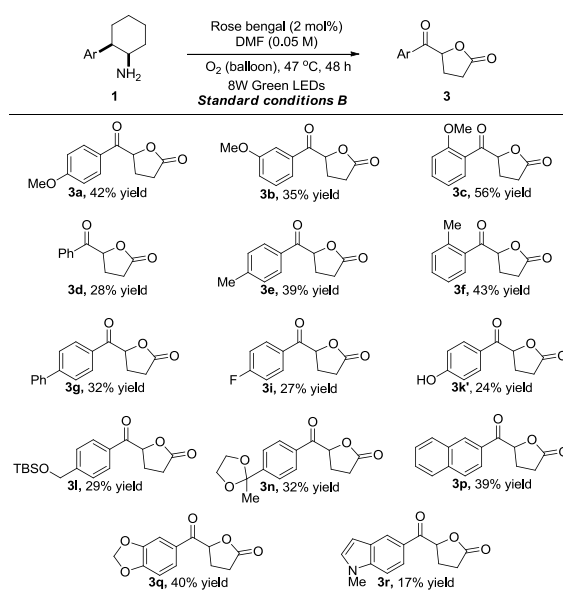


2-phenyl cyclohexylamine **1s** with ethyl substitution on the linker could participate to give **2s** in 50% yield.

To our surprise, the reaction of **1a** using DMF as a solvent under the irradiation of 8W green LEDs afforded the lactone **3a** in 42% yield. Although the yield of this transformation was a lightly low, this both solvent and light source-controlled^[13] phenomenon

Table 2. Aerobic oxidation of amines to acids^[a]

[a] Standard conditions A: using **1** (0.4 mmol) and Rose Bengal (2 mol%) in dry dioxane (8 mL) with O₂ balloon under the irradiation of 18W CFL for 24 h at 25 °C, average yields run twice. [b] For 60 h. [c] For 48 h. [d] With 8W green LEDs for 24 h.

Table 3. Aerobic oxidation of amines to acids^[a]

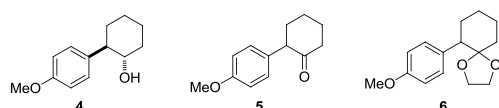
[a] Standard conditions B: using **1** (0.4 mmol) and Rose Bengal (2 mol%) in dry DMF (8 mL) with O₂ balloon under the irradiation of 8W green LEDs at 47 °C for 48 h.

(see **Table S1** in SI) is unexpected and interesting to lead to a significant increase in diversity.

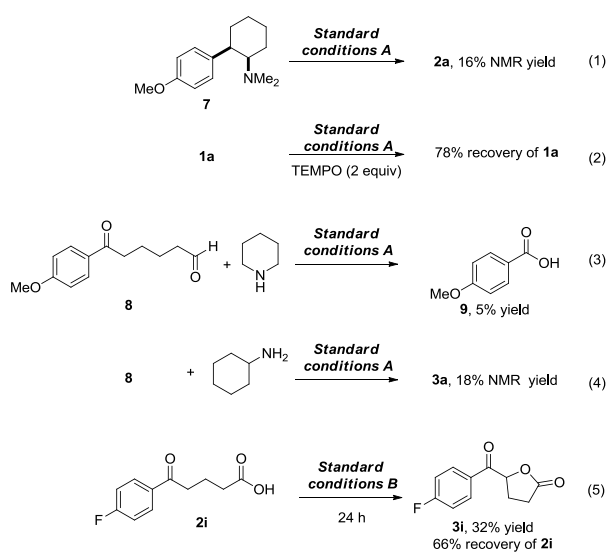
The scope of the oxidation to lactones under conditions B was shown in **Table 3**. The reaction of cyclohexyl amines with both electron-rich and electron-poor substitutions on the phenyl ring gave the corresponding lactones **3a-i** in 27–56% yields. The TBS-protected phenol gave the deprotected lactones **3k** in 24% yield. The TBS-protected benzyl alcohol and diol-protected ketone could be tolerated to the corresponding lactones **3l** and **3n** in 29% and 32% yield, respectively. Amines with heterocycles such as 2-naphthalene (**1p**), 1,3-benzodioxole (**1q**) and indole (**1r**) could be delivered to lactones in 17–40% yields.

Using hydroxyl, carbonyl or diol-protected carbonyl groups instead of amino group, no reaction occurred which indicated that these oxygen-containing substrates could not be oxidized under this mild conditions (**Scheme 2**).

Scheme 2. The unreacted oxygen-containing substrates



To demonstrate the mechanism of both novel transformations, several control experiments were carried out. The reaction of tertiary *N,N*-dimethylamine **7** could undergo smoothly to give **2a** in 16% yield (**eq.1**). This suggested that the initial step of the reaction might be single electron transfer (SET) oxidation of amine to nitrogen radical cation.^[14] The reaction in the presence of a radical trapper TEMPO did not occur with 78% recovery of **1a** (**eq.2**). This was also a good evidence for single electron oxidation of amine. The reaction of aldehyde **8** with piperidine afforded benzylic acid (**eq.3**). The similar transformation has been reported through a visible-light promoted C-C cleavage by forming imine/enamine intermediates.^[15] In the presence of cyclohexyl amine, lactone could be obtained from **8** in which the primary amine might accelerate the formation of the imine/enamine intermediates that could be easily oxidized (**eq.4**).



Under the conditions B, the acid **2i** could be converted to the lactone **3i** in 32% yield (**eq.5**, also see **Table S2**).^[16]

Based on above results, the plausible mechanism was proposed in **Figure 1**. Under irradiation of visible light, RB could absorb the visible light to form photoexcited state RB* which could undergo single electron transfer (SET) reaction to oxidize the amine, generating nitrogen radical cation **A** and radical ion RB⁻.^[17] The radical ion RB⁻ could be oxidized by dioxygen to regenerate RB and produce dioxygen radical anion. The nitrogen radical cation **A** underwent a radical ring-open fragmentation process^[18] to generate a distonic ϵ -radical iminium cation intermediate **B** which was quenched with dioxygen radical anion, forming a pair of tautomers **C** and **D**.^[19] A [2+2] cycloaddition of **D** with singlet dioxygen which was generated through energy transfer (ET) from photoexcited state RB*^[20] could lead to dioxetane **E**. Another plausible pathway was that **D** could be oxidized by photoexcited state RB* and then trapped by dioxygen radical anion to form the dioxetane **E**. The fragmentation reaction of **E** gave the aldehyde **F** which could be oxidized to the acid.^[21] The acid was isomerized to enol configuration which could be photo-peroxidized by singlet dioxygen to the peroxide **A'**. In this plausible pathway, the amine might accelerate the isomerization and oxidation reactions via formation of imine/enamine intermediates. An intramolecular nucleophilic substitution of the peroxide **A'** led to the lactone and released the side product hydroperoxide. The difference between 18 W CFL and green LEDs might be the light intensity which might affect the efficiency of activating the photosensitizer to undergo single electron transfer and energy transfer processes.

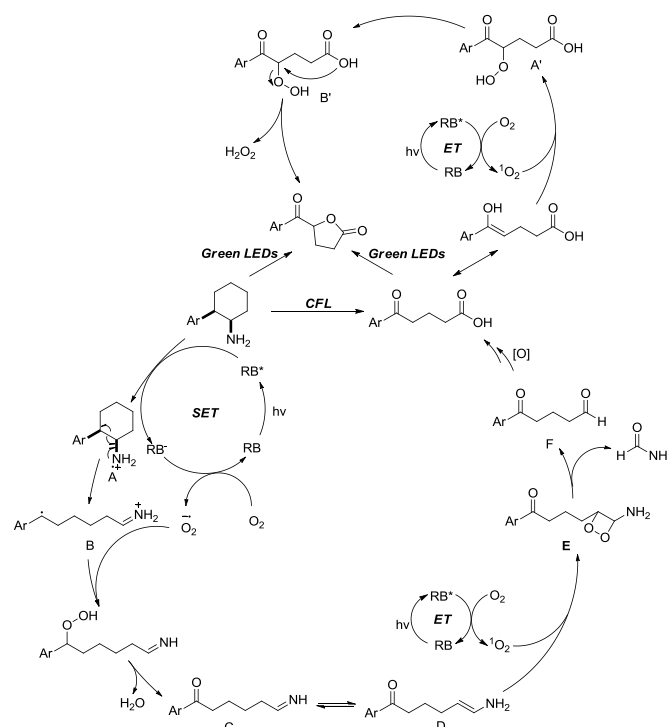


Figure 1. Proposed mechanism for aerobic photooxidation of primary amines to acids and lactones

In summary, we developed a visible-light-promoted metal-free aerobic oxidation of primary amines to acids and lactones via double carbon-carbon bonds cleavage and multi

carbon-hydrogen bonds oxidation. Aerobic oxidation of primary amines could be controlled to afford acids by using dioxane with 18W CFL, and lactones by using DMF with 8W green LEDs, respectively. A primary mechanism was proposed based on control experiments. This observation would give some fundamental evidences for systematical studies of amine oxidation, particularly for fragmentation processes.

Experimental Section

Standard conditions A: To an overdried reaction tube equipped with a magnetic stir bar under O₂ atmosphere was added Rose Bengal (0.0082 g, 0.008 mmol, 2 mol%), **1** (0.400 mmol, 1.0 equiv) and dioxane (8 mL, 0.05 M). The reaction was stirred under irradiation of 18 W CFL in a distance of 10 cm at room temperature for 24 h. Upon completion, the reaction was diluted with CH₃OH and concentrated in vacuo. The residue was purified by flash column chromatography (PE/EA/HCOOH = 100/50/1) to afford the corresponding acids.

Standard conditions B: To an overdried reaction tube equipped with a magnetic stir bar under O₂ atmosphere was added Rose Bengal (0.0082 g, 0.008 mmol, 2 mol%), **1** (0.400 mmol, 1.0 equiv) and DMF (8 mL, 0.05 M). The reaction was stirred under irradiation of 8 W Green LEDs in a distance of 5 cm at 47 °C for 48 h. Upon completion, the reaction was diluted with CH₃OH and concentrated in vacuo. The residue was purified by flash column chromatography (PE/EA = 2/1) to afford the corresponding lactones.

Acknowledgements

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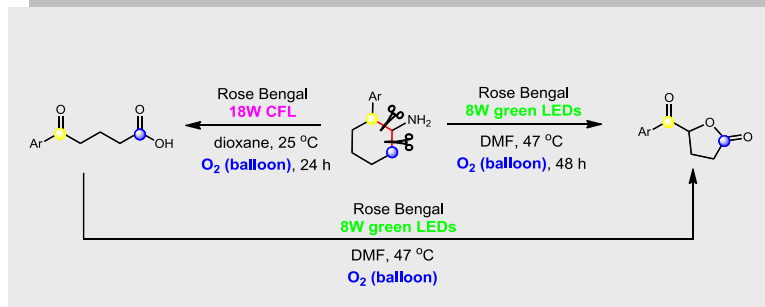
Keywords: aerobic oxidation • amines • carbon-carbon bond cleavage • visible light • acids

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COMMUNICATION



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