



Photocatalytic anion oxidation achieves direct aerobic difunctionalization of alkenes leading to β -thiocyanato alcohols

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ABSTRACT

A novel visible light-driven oxidative cascade reaction for the synthesis of β -thiocyanato alcohols via difunctionalization of alkenes is described for the first time. In this protocol inorganic ion thiocyanate was successfully converted into radical through photocatalysis by employing Rose Bengal as a photocatalyst to mediate the single-electron transfer. This hydroxylation process did not need extra reducing agent and the new C–S and C–O bonds could be constructed in one pot. Molecular oxygen not only was used as an excellent terminal oxidant, but also served as a green oxygen source, which is one of the most ideal processes to realize C–H bond oxidation functionalization. Moreover, the reaction also proceeded very well under irradiation of sunlight.

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1. Introduction

Visible light-induced photoredox catalysis has been vastly explored recently due to their inherent green and sustainable features, and the photocatalytic platform has been widely applied in synthetic chemistry.¹ The success of the major transformations can be attributed to photocatalysts which can convert visible light into chemical energy with great efficiency.² Electronic duality is one trait of photocatalysts which refers that in their excited states they possess the oxidation and reduction potential simultaneously.³ These molecules operate with reaction substrates by single-electron transfer (SET), providing a direct and facile access to reactive intermediates. Rose Bengal (RB) as a typical organic dye photocatalyst plays an important role in photocatalysis owing to its high efficiency, low cost and long excited-state lifetimes. It has been used in sulfoxidation,^{4a} thioesterification,^{4b} decarboxylative amination,^{4c} amidation^{4d} and cyclization reactions.^{4e}

An efficient photoredox catalysis process (substrates directly quench the excited state of the photocatalyst) not only needs a suitable photocatalyst but also requires a compatible sacrificial

redox reagent. In these catalytic systems, photocatalysts are able to absorb light and then activate substrates, sacrificial species can return the photocatalysts to their resting state.⁵ Molecular oxygen is a perfect terminal oxidant as well as the most ideal oxygen source for construction of oxygen-containing compounds as the results of its abundance, cleanliness, environmental sustainability and high oxygen atom economy. So far, numerous elegant works have been achieved with the assistance of molecular oxygen.⁶

Generally, inorganic anions are cheap, readily available and easy to operate. Moreover, ions and radicals of the same kind differ by one electron only.⁷ So the conversion of ions into highly reactive radicals by photocatalysis is a practical synthetic strategy. However, up to now, the reported examples of photocatalytic single-electron oxidation delivering the corresponding inorganic radical used for organic synthesis are still rare.⁷ Several reported typical examples of this transformation include using nitrate,⁸ thiocyanate,⁹ sulfinate¹⁰ and triflate.¹¹ Employing inorganic ions as radical precursors is a promising and fascinating field.⁷ Therefore, it is highly desirable to find new transformations to broaden this area.

Thiocyanate salts have been proven to be one of the most efficient sulfur sources for the synthesis of various important organosulfur compounds which serve as building skeleton to generate bioactive and pharmaceutical molecules.¹² Few radical addition reactions involving thiocyanate have been reported, including

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thiocyanation of indole,^{9a} imidazo heterocycle,^{9b} arenes¹³ and oximes.¹⁴ However, the difunctionalization of alkenes related to thiocyanation still remains relatively unexplored. The thiocyanate functionality is a versatile sulfuration precursor for constructing diversified S-, N-heterocycles which are of great value for medicinal chemistry.¹⁵ β -Thiocyanato alcohols can be elaborated into a range of derivative functionalities. Herein, we report a direct aerobic difunctionalization of alkenes for the synthesis of β -thiocyanato alcohols through visible light photocatalytic one-electron oxidation of thiocyanate anion. In this reaction, molecular oxygen served as a terminal oxidant as well as an oxygen source, and RB was used as an environmentally friendly photocatalyst. It is noteworthy that this mild and green synthetic strategy can be employed to directly get substituted benzyl alcohols and allylic alcohol, without the need of extra reducing agent that is critical to other transformations for reducing peroxide to alcohol.¹⁶

2. Results and discussions

At the outset, the difunctionalization of α -methylstyrene (**1a**) utilizing ammonium thiocyanate under air atmosphere was selected as the initial conditions (Table 1). The reaction was first investigated with RB as a photocatalyst in MeCN under irradiation of a 32 W compact fluorescent lamp (CFL) at room temperature for 24 h. The reaction proceeded smoothly to afford the desired product 2-phenyl-1-thiocyanatopropan-2-ol (**2a**) in 50% isolated yield (Table 1, entry 1) as well as the major by-product (1,2-dithiocyanatopropan-2-yl)benzene in 15% isolated yield. It is noteworthy that no cyclization product (oxathiolane derivative) was observed in this reaction which was reported as the major product in the reaction of styrenes and ammonium thiocyanate catalyzed by Eosin Y with green LED.^{9c} Inspired by this result, several other photocatalysts were tested but they were inferior to RB except Ir (ppy)₃ which gave a slightly higher yield of 53% (Table 1, entries 2–4). Considering the low cost and the transition-

metal-free inherent advantages of RB, we chose it as the photocatalyst to optimize the reaction conditions. In order to evaluate the effect of solvent, we screened some common organic solvents, such as THF, DCE and MTBE (Table 1, entries 5–7), and MeCN was proved to be the optimal reaction medium. Furthermore, increasing the amount of NH₄SCN and photocatalyst loading, product **2a** was obtained in higher yields (52% and 54% respectively, Table 1, entries 8 and 9). Scanning on several acid additives revealed that benzoic acid could improve the reaction efficiency (Table 1, entries 10–12). We attempted to use KSCN instead of NH₄SCN but product **2a** was obtained with much lower efficiency (20% isolated yield, Table 1, entry 13). Finally, two control experiments indicated the critical roles of photocatalyst and light in this transformation (Table 1, entries 14 and 15).

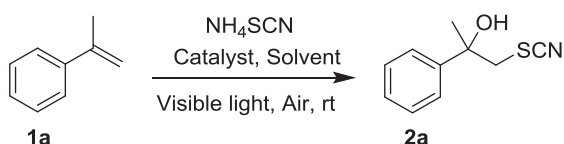
Additionally, the influence of wattage of lamp, the amount of benzoic acid, solvent volume and reaction time was investigated. Based on the experiment results, 32 W CFL, 1 equiv of benzoic acid, and 1.0 mL MeCN were chosen as the optimum conditions for the reaction system (for more details, please see the Supporting information Tables S1–S5).

Adopting the above optimized conditions, we turned our attention to explore the substrate scope, and the results were summarized in Table 2. In general, a series of α -methylstyrene derivatives containing a variety of substituents on benzene ring could react with NH₄SCN smoothly to afford the desired oxidative difunctionalization products in moderate to good yields (Table 2, **2a–2k**). The *para*-substituted α -methylstyrenes with different electronic natures, such as electron-donating groups 4-Me, 4-OMe and 4-Ph and electron-withdrawing groups like halogen and even nitro group were tolerated to give the corresponding products in yields of 45%–76% (**2b–2i**). The efficiency of this conversion was almost unaffected by the substituents in the *ortho* or *meta* position (**2j** and **2k** were obtained in 54% and 63% yields, respectively). Isopropenylnaphthalenes also served as suitable reaction partners giving corresponding products in moderate yields (**2l** and **2m**). When the methyl of α -methylstyrene was replaced with ethyl, the desired product still could be obtained in a reasonable yield of 63% (**2n**), however, when a larger phenyl replaced the methyl of α -methylstyrene, only a low yield of 38% was received (**2o**), which may be attributed to the larger steric hindrance. 1-Methylene-1,2,3,4-tetrahydronaphthalene was also proved to be a compatible substrate (**2p**). Non-terminal and cyclic styrene derivatives could be converted into the desirable products **2q** and **2r** albeit in somewhat diminished yields. We found styrene also proceeded smoothly in this reaction giving the desired product in 47% yield (**2s**) and no observable cyclization products were formed. Furthermore, 2-(prop-1-en-2-yl)thiophene was also amenable to this protocol (**2t**). These satisfactory results of aromatic olefins motivated us to explore aliphatic alkenes. Pleasingly, we found 2,3-dimethylbuta-1,3-diene also could be employed in this conversion (**2u**). In most reactions, besides the desired products, 1,2-dithiocyanato adducts and acetophenone or its analogues were observed as by-products (for the analysis of by-products, please see the Supporting information Scheme S1). Nineteen new β -thiocyanato alcohols were obtained, and their structures were confirmed by ¹H NMR, ¹³C NMR and HRMS.

Additionally, the strong electron-donating group substituted α -methylstyrene such as 2-(prop-1-en-2-yl)aniline couldn't complete this difunctionalization, and instead the benzene ring substituted thiocyanation compound was generated with low efficiency (for details, please see the Supporting information Scheme S2). The reason may be that the addition of thiocyanate radical preferred to occur at the electron-rich benzene ring rather than the double bond outside of benzene ring.

Natural sunlight is an ideal light source due to its features of

Table 1
Optimization of reaction conditions.^a



Entry	Catalyst	Solvent	NH ₄ SCN (mmol)	Note	Yield (%) ^b
1	RB	MeCN	1.0	—	50
2	Eosin Y	MeCN	1.0	—	42
3	Methylene Blue	MeCN	1.0	—	23
4	Ir (ppy) ₃	MeCN	1.0	—	53
5	RB	THF	1.0	—	43
6	RB	DCE	1.0	—	Trace
7	RB	MTBE	1.0	—	Trace
8	RB	MeCN	2.5	—	52
9 ^c	RB	MeCN	2.5	—	54
10 ^c	RB	MeCN	2.5	TFA	56
11 ^c	RB	MeCN	2.5	PhCOOH	61
12 ^c	RB	MeCN	2.5	Cu(OTf) ₂	12
13 ^{c,d}	RB	MeCN	2.5	PhCOOH	20
14	—	MeCN	1.0	—	18
15	RB	MeCN	1.0	Dark	Trace

^a Unless otherwise noted, reaction conditions: **1a** (0.5 mmol), NH₄SCN, catalyst (2 mol%), solvent (1.0 mL), under irradiation of a 32 W CFL in air atmosphere at rt for 24 h.

^b Isolated yield.

^c RB (3 mol%).

^d KSCN instead of NH₄SCN.

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