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Photocatalytic Oxidative Heterocyclization of Semicarbazones: An Efficient Approach for the Synthesis of 1,3,4-Oxadiazoles

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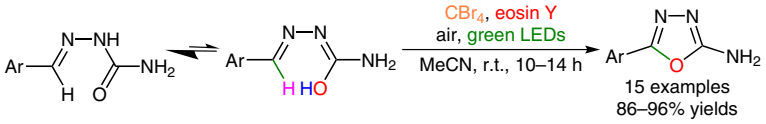

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Abstract A highly efficient eosin Y catalyzed oxidative heterocyclization of semicarbazones was established under visible-light photoredox catalysis using CBr_4 as a bromine source. The protocol renders a rapid, mild, and efficient access to valuable 5-substituted 2-amino-1,3,4-oxadiazoles in an operationally simple way utilizing visible light and atmospheric oxygen.

Key words visible light, eosin Y, photoredox catalysis, 1,3,4-oxadiazole, oxidative heterocyclization

The development of mild methods for the formation of C–C and C–N bonds is of great importance and remains a pre-eminent goal in current synthetic chemistry.[1] To this end, photocatalysis using visible light represents a unique strategy because of its inherently green features.[2] Photosensitizers or photocatalysts are generally used to induce visible-light-triggered reactions as most organic compounds do not absorb visible light.[3] Polypyridyl metallic complexes of ruthenium and iridium have been developed as visible-light photoredox catalysts,[4] although these transition-metal-based photocatalysts suffer the disadvantages of being toxic and highly expensive. In search of a cost-effective and metal-free catalyst, the organic dye eosin Y has been found to produce high photocatalytic performances.[5] As with the ruthenium and iridium complexes, eosin Y also sustains photoexcitation via oxidative or reductive quenching to furnish a radical cation and anion, respectively.[5e,6]

Use of atmospheric oxygen has opened a further chapter in the field of visible-light photoredox catalysis.[7] The oxygen generally acts to regenerate the photoredox catalyst after its reductive quenching to complete the catalytic cycle. The superoxide radical anion ($O_2^{\bullet-}$) thus formed also plays a pivotal role in the synthetic process.[2,8]

Among five-membered heterocyclic compounds, 2,5-disubstituted 1,3,4-oxadiazoles have become an important motif for the development of new drugs. Compounds containing 1,3,4-oxadiazole cores have a broad spectrum of biological activity including antibacterial,[9–11] antifungal,[12,13] anti-inflammatory,[14,15] anticancer,[16] anticonvulsant,[17] antiviral, analgesic, antihypertensive,[18–20] and antidiabetic properties.[21] These compounds have also attracted interest in medicinal chemistry as bioisostere surrogates for carboxylic acids, esters, and carboxamides.[22] Raltegravir®, an antiretroviral drug[23a] and Zibotentan®, an anticancer agent,[23b] are two examples of clinical medicines having a 1,3,4-oxadiazole unit in their chemical structure (Figure 1). Such types of heterocyclic scaffolds have also found applications as scintillators, fluorescent agents, and photographic materials.[24]

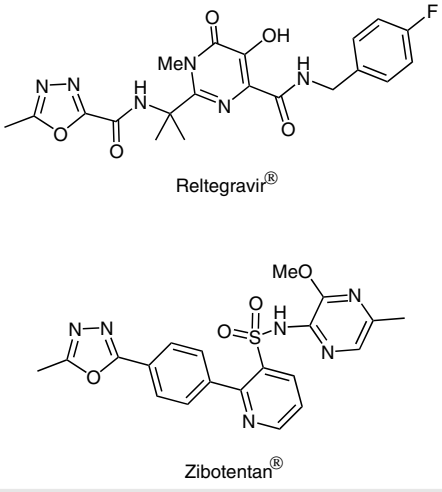
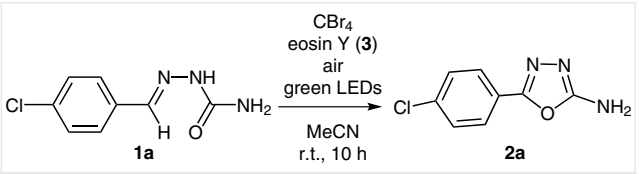


Figure 1

Several methods have been reported in the literature for the preparation of 5-substituted 2-amino-1,3,4-oxadiazoles.[25–29] Most of these protocols are multistep in nature and generally involve the cyclization of acid hydrazides using a variety of reagents, such as phosphorus oxychloride,[30] sulfuric acid,[31] and thionyl chloride,[32] usually under harsh reaction conditions. Oxadiazoles have also been prepared by bromine oxidation of semicarbazide derivatives and the cyclodesulfurization of acylthiosemicarbazide derivatives in solution using iodine and sodium hydroxide or 1,3-dicyclohexylcarbodimide DCC[33–37] as well as mercury(II) acetate or mercury(II) oxide.[38–40] Hence, simple, efficient, and mild methods for the synthesis and modification of the oxadiazole motif still need to be developed.[41]

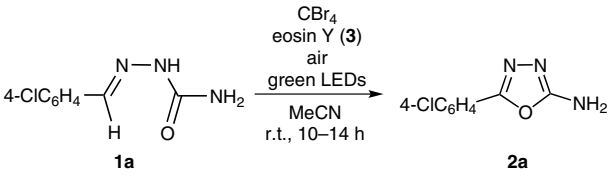
In view of the above discussion and our continued efforts towards developing straightforward, efficient, and cost-effective heterocyclization reactions,[42,43] we envisaged that eosin Y catalyzed visible-light-initiated cyclization of substituted semicarbazones to the corresponding 5-substituted 2-amino-1,3,4-oxadiazoles could be feasible (Scheme 1). For this purpose, we focused on CBr_4 in combination with eosin Y, which is easy to handle and absorbs visible light to generate active radical species[44] and hence was expected to be suitable for the cyclization.



Scheme 1 Synthesis of 2-amino-5-aryl-1,3,4-oxadiazole **2a** under photoredox catalysis

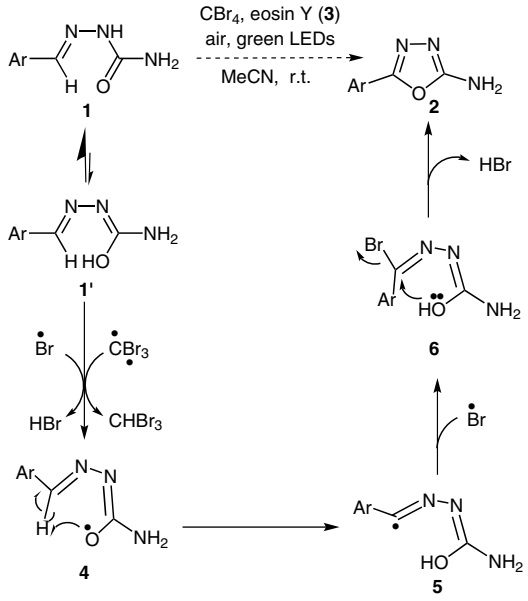
Our studies began with the model reaction of *p*-chlorobenzaldehyde semicarbazone (**1a**, 1 mmol) using a stoichiometric amount of CBr_4 in MeCN in the presence of 1 mol% of eosin Y in air (with no air bubbling). The reaction mixture was irradiated with visible light [green-light-emitting diodes (LED), λ_{max} = 535 nm] at room temperature. To our satisfaction, 2-amino-5-(*p*-chlorophenyl)-1,3,4-oxadiazole (**2a**) was produced in the excellent yield of 96% within ten

Table 1 Optimization of Reaction Conditions[a]



Entry	Reaction conditions	Solvent	Time (h)	Yield (%)[f]
1	CBr_4 (1 mmol), **3** (1 mol%), air, green LED	MeCN	10	96
2	CBr_4 (1 mmol), **3** (1 mol%), air, green LED	THF	14	35
3	CBr_4 (1 mmol), **3** (1 mol%), air, green LED	dioxane	14	45
4	CBr_4 (1 mmol), **3** (1 mol%), air, green LED	CH_2Cl_2	14	50
5	CBr_4 (1 mmol), **3** (1 mol%), O_2 balloon, green LED	MeCN	14	96
6[b]	CBr_4 (1 mmol), (1 mol%), N_2, green LED	MeCN	14	21
7[c]	CBr_4 (1 mmol), **3** (1 mol%), air, in dark	MeCN	14	0
8[d]	CBr_4 (1 mmol), no catalyst, air, green LED	MeCN	30	30
9	CBr_4 (1 mmol), no catalyst, N_2, green LED	MeCN	30	17
10	CBr_4 (1 mmol), **3** (1 mol%), air, day light	MeCN	14	35
11	CBr_4 (1 mmol), **3** (1 mol%), air, 18 W CFL	MeCN	14	39
12	CBr_4 (1 mmol), **3** (0.2 mol%), air, green LED	MeCN	10	46
13	CBr_4 (1 mmol), **3** (2 mol%), air, green LED	MeCN	10	96
14[e]	no bromine source, **3** (2 mol%), air, green LED	MeCN	14	0
15	TBAB, **3** (2 mol%), air, green LED	MeCN	14	0

[a] Reaction conditions: *p*-chlorobenzaldehyde semicarbazone (**1a**, 1 mmol), CBr_4 (1 mmol), eosin Y (**3**, 1 mol%), solvent (3 mL), irradiation under an air atmosphere at r.t. using Luxeon Rebel high power green LED [2.50 W, λ_{max} = 535 nm (for the detailed procedure, see Supporting Information).
[b] Under a nitrogen atmosphere.
[c] In the dark.
[d] In absence of catalyst.
[e] In the absence of a bromine source.
[f] Isolated yield of **2a** after flash chromatography.



Scheme 2 A 5-*endo*-trig cyclization in the absence of sensitizer (Table 1, entry 8)

hours of irradiation. When the reaction was followed over a longer period (10–24 h), no increase in yield was observed. When we performed the model reaction employing CBr_4 in the absence of eosin Y, the desired product was obtained in substantially lower yield (Table 1, entry 8; Scheme 2).

Hence, we reached the conclusion that CBr_4 along with eosin Y and visible-light irradiation is the best system for the conversion of semicarbazones to oxadiazoles in terms of yield and reaction time. This is presumably because the presence of the catalyst facilitates the reaction by an energetically favorable formation of the radical **4** via **4'** (Scheme 3). Similarly, when the reaction was carried out in the dark, there was no conversion of **1a** (Table 1, entry 7).

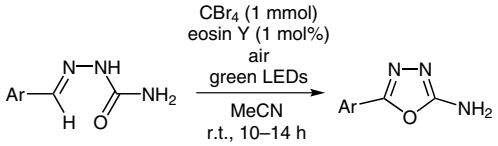
When the cyclization was performed under a nitrogen atmosphere, a decrease in yield was observed (Table 1, entry 6). The system also worked with equal efficiency using an oxygen balloon instead of under air (Table 1, entry 5). However, when the reaction was carried out in daylight, the yield decreased to 35%. Similarly, the reaction also did not give a satisfactory yield on irradiation with 18 W CFL (Table 1, entries 10, 11). On decreasing photosensitizer loading from 1 mol% to 0.2 mol%, the yield was considerably reduced (Table 1, entry 12). However, use of 2 mol% of the catalyst did not improve the yield of the product (Table 1, entry 13).

Next, optimization of the solvent was carried out, which demonstrated MeCN to be the solvent of choice (Table 1, entry 1). Other solvents such as THF, dioxane, and CH_2Cl_2 did not give satisfactory results (Table 1, entries 2–4).

To evaluate the effectiveness of the CBr_4 as an efficient bromine source, we considered another bromine-radical-producing reagent, tetrabutylammonium bromide (TBAB), but it was found that CBr_4 was the best in terms of the yield and reaction time (Table 1, entry 1). TBAB did not promote cyclization of *p*-chlorobenzaldehyde semicarbazone, possibly due to its inability to produce bromine radicals under the given reaction conditions (Table 1, entry 15).

We then turned to investigate the substrate scope of the reaction. As depicted in Table 2[44,45] semicarbazones bearing an electron-donating or electron-withdrawing substituent generally afforded 5-substituted 2-amino-1,3,4-oxadiazoles **2** in excellent yields (86–96%).

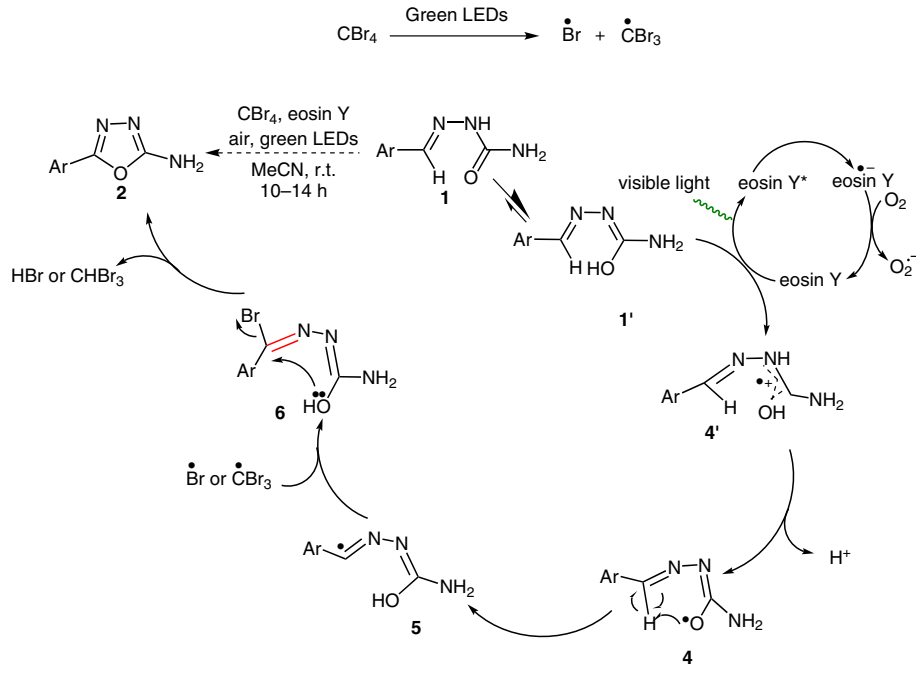
Table 2 Substrate Scope for the Photooxidative Cyclization of Semicarbazones[a]



Product	Ar	Yield[b] (%)
2a	4-ClC_6H_4	96
2b	Ph	93
2c	2-ClC_6H_4	94
2d	4-$O_2NC_6H_4$	90
2e	3-$O_2NC_6H_4$	86
2f	2-$H_2NC_6H_4$	86
2g	4-$H_2NC_6H_4$	88
2h	4-pyridyl	92
2i	4-HOC_6H_4	87
2j	4-*t*-BuC_6H_4	86
2k	4-$MeOC_6H_4$	92
2l	4-MeC_6H_4	89
2m	2-Cl-6-$O_2NC_6H_3$	90
2n	4-*n*-$BuOC_6H_4$	86
2o	2-MeO-5-BrC_6H_3	96

[a] All compounds are known and were characterized by comparison of their spectroscopic data with those reporte in the literature.[45]
[b] Yields are reported for the isolated pure products.

On the basis of our experimental results and literature precedents,[42,46] a plausible mechanism for the cyclization of substituted semicarbazones into 5-substituted 2-amino-1,3,4-oxadiazoles **2** is depicted in Scheme 3. That the reaction was quenched either with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), or 2,2-diphenyl-1-picrylhydrazyl (DPPH), traditional radical scavengers, shows that it follows a radical pathway.



Scheme 3 Photooxidative heterocyclization of semicarbazones

On irradiation with visible light (λ_{max} = 535 nm), eosin Y is excited to its singlet state which is converted into most stable triplet state through intersystem crossing.[5e,47] The triplet state of eosin Y may participate in the photoredox cycle via reductive quenching[5e,48] by semicarbazone **1** to generate the radical cation **4′**, which is deprotonated to give the resonance stabilized radical **4** (Scheme 3). Radical **4** then generates radical **5** by abstraction of a hydrogen atom through a six-membered transition state. Subsequent bromination of **5** forms derivative **6**, which undergoes an anti-Baldwin's rule[49] 5-*endo*-trig cyclization to afford the desired product **2**. There appears to be precedent for such a cyclization in the work of Poddubnyi et al.[46b] The formation of $CHBr_3$ could be detected during the reaction, which indicates that the mechanism proposed in Scheme 2 might also be operating to some extent even in the absence of eosin Y.

In summary, we have developed an efficient, metal-free pathway for a one-pot synthesis of 2-amino-5-aryl-1,3,4-oxadiazoles under mild conditions. The protocol involves the visible-light-mediated, photosensitized intramolecular, aerobic oxidative heterocyclization of substituted semicarbazones to 1,3,4-oxadiazoles using CBr_4 as an oxidant and eosin Y as the photoredox catalyst.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1380493.

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(44) **General Procedure for the Synthesis of 5-Aryl-1,3,4-Oxadiazoles 2**

A solution of semicarbazone **1** (1 mmol), CBr_4 (1 mmol), and eosin Y (**3**, 1 mol%) in MeCN (3 mL) was irradiated with green LED at r.t. in an air atmosphere for 10–14 h. After completion of the reaction (indicated by TLC), it was quenched with sat. aq $NaHCO_3$ (5 mL) and extracted with EtOAc (3 × 5 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel [200–300 mesh; eluent: hexane–EtOAc (10:1 to 5:1)] to afford an analytically pure sample of 2-amino-5-aryl-1,3,4-oxadiazole **2**. All the compounds are known and were characterized by comparison of their spectroscopic data with those reported in the literature (see ref. 45).

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