Visible-Light-Mediated Ir(III)-Catalyzed Concomitant C3 Oxidation and C2 Amination of Indoles

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Supporting Information

Organic



ABSTRACT: A visible-light-mediated concomitant C3 oxidation and C2 amination of indoles has been achieved at room temperature using an Ir (III) photocatalyst. This reaction proceeds without an isatin intermediate via the attack of a singlet oxygen at the C3 position followed by C2 amination leading to difunctionalization of indoles.

Recently, photocatalytic functionalizations have emerged as powerful synthetic tools in modern organic chemistry/ synthesis.¹ Compared to traditional functionalizations, the photocatalytic strategy has emerged as an alternative method for the rapid construction of highly functionalized structures by amplifying their chemical diversity.² In particular, the photocatalytic functionalizations of indoles have attracted considerable attention since functionalized indole motifs have found significant applications in biological and medicinal chemistry and are present in various natural and artificial bioactive products (Figure 1).³



Figure 1. Representative bioactive products containing functionalized indoles.

Among significant photocatalytic reactions of indoles, in 2017, Yoon et al. reported a Diels–Alder cycloaddition with dienes leading to tetrahydro-1,4-ethanocarbazoles.⁴ A chemodivergent oxygenation of indole to isatins and formylformanilides under visible-light photocatalysis has been developed by Jiang et al.⁵ The Stephenson group reported an efficient addition of malonyl radicals to indoles under Ru-photocatalysis.⁶ To the best of our knowledge, there is no reported photocatalytic functionalization of indoles leading to selective C3 oxidation and C2 amination. Our group is actively involved in the design and development of operationally simple and efficient methodologies for the functionalization of various heterocycles.⁷ Herein, we report a visible-light-mediated protocol for the selective difunctionalization of *N*-substituted indoles using benzohydrazides in an oxygen atmosphere leading to concurrent C3 oxidation and C2 amination of indoles.

By judicious selection of photocatalysts and other reaction parameters, a concomitant bis-functionalization of indoles has been accomplished (Scheme 1b). While this manuscript was under preparation, Borhan et al. published an elegant C3oxidation and C2-amination of indoles involving a Cu(I) catalyst and an acyl nitroso reagent such as hydroxycarbamate (Scheme 1a).⁸ This method has advantages in terms of

Scheme 1. Approaches toward Difunctionalization of Indoles via Selective C3 Oxidation and C2 Amination





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"Reaction conditions: 1a-m,s,t (0.25 mmol), 2a-g (0.25 mmol), P1 (3 mol %), TBAI (30 mol %), CH₃CN (5 mL), white LED (2 × 10 W, λ_{max} 455 nm) at room temperature. "Reaction carried out on a 1 mmol scale.

peroxide-free oxidation and use of hydroxycarbamate as the source of both oxygen and the amide, making this protocol advantageous over previous methodologies involving difuctionalization of indoles.⁹ Nevertheless, this method has an inherent limitation as it is applicable only to C2-protected indoles and C2-free indoles failed to functionalize.

Our initial investigation began by using indole (1f) (0.25 mmol), benzohydrazide (2a) (0.25 mmol), [Ir(dtbbpy)-(ppy)₂]PF₆ (P1, 1 mol %), and TBAI (10 mol %) in 1,2dichloroethane (DCE) at room temperature in an oxygen atmosphere under an irradiation of visible light (2 \times 10 W white LEDs, λ_{max} 455 nm). Interestingly, the reaction resulted in the formation of a new product (3f, 30%). Spectroscopic (IR, ¹H, and ¹³C), HRMS, and crystallographic analysis of the isolated product confirmed its structure to be (E)-N'-(1isopropyl-3-oxoindolin-2-ylidene)benzohydrazide (3f) (Table S1, entry 1; see the Supporting Information). In contrast to other preparations of 3-oxindoles, here formation of this product (3f) is accompanied by regioselective C3-oxidation and C2-amination.¹⁰ Oxindoles are an important class of heterocycles and have attracted considerable attention in the field of antimicrobial and anticancer research.¹¹ The classical as well as photocatalytic approaches for the synthesis of 2oxindoles frameworks are well documented,^{12,13} whereas there are only limited reports on the synthesis of 3-oxindoles.^{10,14,15} The two well-established strategies are (i) a Pd-catalyzed, $MnO_2/TBHP$ -mediated oxidative dearomatization of indoles¹⁴ and (ii) a redox annulation of nitroalkynes with indoles in the

presence of Au(III)/chiralphosphoric acid dual catalysis.¹⁵ To the best of our knowledge, there is no report for the direct synthesis of 3-oxoindole involving indole with benzohydrazide and oxygen under photocatalysis. Encouraged by the synthesis of N'-(1-isopropyl-3-oxoindolin-2-ylidene)benzohydrazide (3f) via photocatalysis, further optimization of reaction parameters was tuned to enhance the efficacy of the reaction (Table S1). Use of different transition-metal-based photocatalysts such as $Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (P2) (20%) and $Ru(bpy)_3(PF_6)_2$ (P3) (10%) did not show any improvement in the reaction yields (Table S1, entries 2 and 3). On the other hand, organic dyes such as eosin B, eosin Y, and rose bengal were completely ineffective, leaving the starting material unreacted even after 24 h (Table S1, entries 4–6). Hence, it was found that the catalyst $[Ir(dtbbpy)(ppy)_2]PF_6$ (P1) is more suitable for the formation of 3f. Next, the catalyst loading was varied, and it was found that 3 mol % of [Ir(dtbbpy)- $(ppy)_2$]PF₆(P1) is ideal for the transformation, yielding product 3f in 55% yield (Table S1, entries 7-9). Further, an increase in the catalytic loading (3.5 mol %) did not show any significant enhancement in the yield (56%) (Table S1, entry 10). Subsequently, the effect of solvents on the reaction was examined. Solvent DCM (55%, Table S1, entry 11) was found to be equally effective to that of DCE. The use of polar aprotic solvents such as DMSO (40%) and DMF (45%) were found to be inferior to that of DCE (Table S1, entries 12 and 13). However, polar-protic solvents such as MeOH (60%) and EtOH (65%) were superior to DCE (Table S1, entries 14 and

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15). Incidentally, the polar-aprotic solvent CH₃CN was found to be the best in terms of yield (70%) with fewer side products (Table S1, entry 16). After the optimization of both catalyst and solvent, next we scrutinized the loading of various additives. When the loading of TBAI was increased from 10 to 15, 20, and 30 mol %, the yield of (3f) increased to 70%, 72%, and 75%, respectively (Table S1, entries 17-19). However, improvement in the yield (76%) was observed by further increasing the TBAI loading to 40 mol %. Other organic and inorganic halo additives such as tetrabutyl ammonium bromide, sodium iodide, and lithium bromide were less effective (Table S1, entries 20-23). Reaction without the photocatalyst $[Ir(dtbbpy)(ppy)_2]PF_6$ (P1) did not provide any trace of the product (3f) (Table S1, entry 24). The reaction in the dark, under otherwise identical reaction conditions, provided a trace (5%) of the desired product 3f (Table S1, entry 25). Reaction in open air yielded the desired product in 40% yield after 24 h; however, it was associated with the formation of some fluorescent impurities (Table S1, entry 26). When the reaction was performed under irradiation of 2 W, 5 W, and 10 W white LED light for 24 h, the yield of the product obtained was found to be 25%, 50%, and 60%, respectively (Table S1, entries 27-29). The temperature of the surrounding reaction mixture remained identical (28 °C) to that of room temperature during the progress of the reaction due to the use of a $(2 \times 10 \text{ W})$ LED as it was well ventilated, suggesting the photochemical nature of the reaction. To see the effect of wavelength of light, the reaction when performed with light of various wavelengths such as red (632 nm), green (513 nm), blue (430 nm), and white (449 nm, fwhm) LEDs of 5 W each. While red and green LEDs failed to give any product, and the blue LED (45%) was nearly as effective as that the white LED (50%) but was associated with the formation of other minor side products (Table S1, entries 28 and 30-32). Thus, the effective wavelength for this transformation lies in the region of 430-450 nm. Thus, the optimum conditions for the synthesis of 3f were the use of 1f (0.25 mmol), benzohydrazide (2a) (0.25 mmol), catalyst P1 (3 mol %), and TBAI (30 mol %) in 5 mL of CH₃CN under an atmosphere of oxygen by irradiation of 20 W white LEDs (λ_{max} 455 nm) at room temperature (see Table S1 for further details).

The scope and generality of the visible-light-mediated reaction were extended to a variety of substituted indoles and benzohydrazides under the optimized reaction conditions (Table S1, entry 19). As shown in Scheme 2, a diverse array of N-substituted and mono- and disubstituted (1,5 and 1,7) indoles (1a-m,s,t) could be transformed to their corresponding 3-oxindoles (3a-t) in good yields. At first, the effect of various alkyl substituents (R^2) at the indole nitrogen were examined, and the results are summarized in Scheme 2. It was found that the isolated yields of product improve as the alkyl chain length increases. Alkyl substituents such as methyl (1a), ethyl (1b), n-propyl (1c), n-butyl (1d), and n-pentyl (1e) provided their corresponding bifunctionalized products 3a, 3b, 3c, 3d, and 3e in 65%, 68%, 72%, 74%, and 80% yields, respectively. These primary alkyl groups are expected to stabilize the nitrogen radicals to similar a extent and, hence, should provide equal yields. The better isolated yields for higher alkyl chains could be because of easy elution (isolation) due to the enhanced hydrophobic character during silica gel column chromatographic purification as highly nitrogenous compounds often stick to the column. Similarly, secondary N-

alkyl substituents such as isopropyl- (1f) and cyclopentylsubstituted (1g) indoles yielded their corresponding products 3f and 3g in 75 and 78% yields, respectively.

Next, the compatibility of various benzyl substituents (R²) was tested as they are often prone to oxidation.¹⁶ Substrates having N-benzyl substituents, bearing either electron-donating p-CH₃ (1h) or electron-withdrawing p-Cl (1i) or o-Br (1j) groups, reacted efficiently with benzohydrazide (2a) to give good yields of their products (3h, 72%; 3i, 70%; and 3j, 70%) in almost identical yields without undergoing oxidation at the benzylic position. An N-allyl-substituted indole (1k) underwent the present photocatalytic bifunctionalization to give the product 3k in 65% yield without affecting the oxidation sensitive allylic group. After demonstrating the compatibility of various N-protected indoles, we examined the nature of various substituents (EDG and EWG) present on either the homocyclic ring of indoles or the phenyl rings of benzohydrazides. Irrespective of the nature of the substituents [electron-donating 5-Me (11) and electron-withdrawing 5-Br (1m and 1s) or 7-F (1t) in the indolyl moiety and electrondonating p-Me (2b), p-OMe (2c), or m-OMe (2d) and electron-withdrawing p-CF₃ (2e) and p-Br (2f) in the benzohydrazide ring] or their positions of attachments all provided moderate to good yields of their products (31, 68%; 3m, 75%; 3n, 75%; 3o, 74%; 3p, 72%; 3q, 85%; 3r, 82%; 3s, 87%; and 3t, 85%), revealing no obvious electronic impact from the substituents. The structures of all of the synthesized (E)-N'-(1-alkyl/benzyl-3-oxoindolin-2-ylidene)benzohydrazides (3a-t) were fully characterized by IR, ¹H NMR, and ¹³C NMR spectroscopy and HRMS analysis. Further, the structure of one of the representatives (E)-N'-(1isopropyl-3-oxoindolin-2-ylidene)benzohydrazide (3f) was unambiguously established by single-crystal X-ray diffraction analysis (see Figure S1 for further details).

Reaction with an alkyl hydrazide gave a very poor yield of the product, which is also associated with an inseparable mixture of uncharacterized impurities, whereas sulfonyl hydrazide failed to give the anticipated oxidative amination product (see Scheme S2 for details). Unlike benzimidazoles, this photocatalytic process was not successful for the functionalization of analogous heterocycles, such as benzothiazoles, benzoxazoles, and many other N-bearing heterocycles (Scheme S3). Thus, as far as further functionalization is concerned, the bifunctionalized product could be hydrolyzed to an isatin analogue albeit in low yield (Scheme S4).

To gain insight into the mechanism of this regioselective bisfunctionalization, a series of control experiments were conducted. To ascertain the origin of the carbonyl oxygen in the product, whether it is originating from O₂ or from other sources (moisture from the solvent) in the reaction mixture, a standard reaction of 1a and 2a was performed under a nitrogen atmosphere. The reaction failed to proceed efficiently, giving just 5% yield of the product 3a after 24 h. Further, to rule out the possibility of water as the source of carbonyl oxygen of the indole ring, a standard reaction was carried out in the presence of 5 equiv of H₂¹⁸O. The HRMS analysis of the isolated product revealed no traces of ¹⁸O incorporation, suggesting that water is not the source of the carbonyl oxygen in the product. These observations suggest that molecular oxygen is the only possible oxygen source of the carbonyl oxygen as in its absence the reaction is unsuccessful. To prove the photocatalytic radical pathway, a standard experiment between 1a and 2a was carried out in the presence of TEMPO (1 equiv)

Scheme 3. Plausible Mechanism for the Formation of 3f Supported by DFT-Calculated Energy Profile^a



"Relative energies (kcal/mol) and bond distances (Å) are calculated at the M06/6-31+G(d) level of theory.

under otherwise identical conditions, which provided 3a in only a trace amount. Most oxidations of indoles proceed via an isatin (indoline-2,3-dione) intermediate.¹⁷ Thus, a question arises whether this oxidative bifunctionalization is proceeding via a similar isatin intermediate? An isatin analogue, 1methylindoline-2,3-dione in lieu of 1a, was reacted with 2a under identical reaction conditions and gave no trace of 3a, confirming isatin not to be the intermediate in this reaction (see Scheme S1 for further details). On the basis of the control experiments carried and from the DFT calculations, a plausible mechanistic path is depicted in Scheme 3. In order to clearly understand the mechanism of the reaction we performed DFT calculations and modeled the reaction profile at the M06/6-31+G(d) level of theory. In the first step, indole (1f) is oxidized to an indole radical cation (A) through a reductive quenching process by the photocatalyst Ir(III)* (P1). Simultaneously, the molecular oxygen is reduced to a superoxide ion $O_2^{\bullet-}$ by Ir(II), and the catalyst is regenerated.^{18a} Next, we compared the possibility of attack of $O_2^{\bullet-}$ on two possible sites $(C_3 \text{ and } C_2)$ of the radical cation A through TS-1A and TS-1B. Clearly, TS-1A, i.e., attack at the C3-site, has a lower barrier and lower stabilization compared to TS-1B involving a C-2 attack as depicted in Scheme 3. Further, the forward reaction is preferred for TS-1A, and reverse reaction is preferred for TS-1B. Thus, the formation of transition state TS-1B via the C-2 attack of $O_2^{\bullet-}$ is ruled out. The highly reactive $O_2^{\bullet-}$ then attacks at the C-3 site of the intermediate A to form a peroxy iminium species B. The benzohydrazide 2a attacks at the C-2 site of intermediate B to form intermediate C through TS-2. This is perhaps the rate-determining step for this reaction, having an activation barrier of 22.14 kcal/mol.

The intermediate C is around 1.56 kcal/mol more stable compared to intermediate B. As expected, the barrier for removal of a molecule of water is very low (1.90 kcal/mol) from the intermediate C to form intermediate D, which is associated with higher stabilization. Finally, there is removal of two hydrogens, one each from indole and benzohydrazide (2a). The final step seems to be a facile one with an activation barrier of 4.89 kcal/mol. Moreover, the final product 3f is 14.91 kcal/mol more stable compared to the intermediate D. Thus, all of the proposed steps are highly favorable, which leads to a stable bifunctionalized product. Some of the selected interatomic distances found in the geometries of various transition states are depicted in Scheme 3 (see Figure S2 for further details). The reaction mixture was colorless at the beginning and turned violet as the reaction progressed. This is because of the oxidation of the iodide from tetrabutylammonium iodide to molecular iodine due to the generation of hydrogen peroxide in the medium. Formation of H₂O₂ has been detected by two other methods (see Supporting Information). All of these experiments support the formation of H_2O_2 in the medium.

In summary, a mild and efficient photocatalytic regioselective method has been developed for the selective difunctionalization of indoles by visible-light-induced photoredox Ir(III) catalysis. A wide range of indoles, as well as benzohydrazides, participate competently in the free-radical reaction to afford structurally diverse oxindoles in good yields. On the basis of control experiments, a plausible mechanism has been proposed which is well supported by DFT calculations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.9b00887.

Optimization table; spectra and spectral data for all compounds; X-ray crysatallographic data for 3f (PDF)

Accession Codes

CCDC 1901162 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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DEDICATION

Dedicated to Professor Vinod K. Singh on the occasion of his 60th birthday.

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