

Reductive Coupling of Imines with Redox-Active Esters by Visible Light Photoredox Organocatalysis

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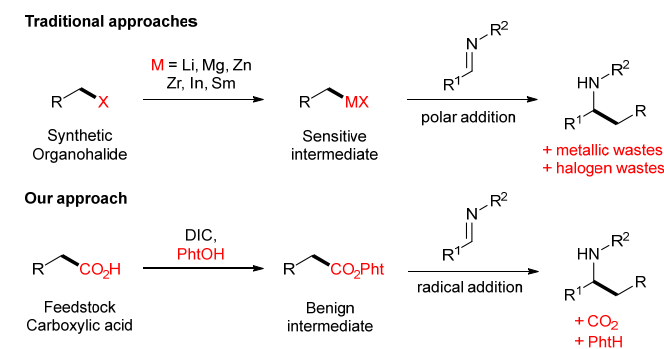
The addition of organometallic compounds to imines is a direct way for accessing α -branched secondary amines which are found in numerous bioactive molecules. Although convenient, such reactions typically involve the formation and isolation of the nucleophile in the case of Grignard reactions, or the *in situ* formation of the nucleophile for Barbier reactions, leading to stoichiometric amounts of metallic wastes. Herein, we report the direct alkylation of imines with redox-active esters by visible light photoorganocatalysis. With Rose bengal as inexpensive photocatalyst, and green light as sustainable energy source, the synthesis of a wide range of amines and θ -amino esters was achieved from inexpensive feedstock chemicals, in a highly modular fashion.

Introduction

Imines can easily be prepared via condensation of amines with aldehydes and ketones and are widely used for the synthesis of more complex amines. Beside reduction of imines by hydride addition which is a well established protocol, direct alkylation reactions to give α -branched secondary amines have attracted growing attention from the scientific community. Early reports using organolithium reagents showed the feasibility of such 1,2 additions, although cryogenic temperatures and anhydrous conditions were required, and substrates bearing acidic functional groups could not be used due to competitive deprotonation events.¹ To improve the chemoselectivity of the reaction, Grignard reagents were used, sometimes in combination with catalytic amounts of zinc salts.² Barbier conditions involving *in situ* activation of an organohalide by zinc or indium salts were also developed and

resulted in more practical conditions, as the intermediate organometallic species was not isolated.³ However, in all cases, stoichiometric amounts of metallic wastes are generated (Scheme 1, top), which is concerning from a sustainable chemistry perspective. To partially tackle these issues, another mechanism of activation involving coordination of catalytic amounts of metals such as titanium, zirconium or nickel to the imine, followed by alkylation was reported.⁴ An alternative to polar addition onto C=N bonds would be the addition of a radical, followed by single-electron reduction to give the same product. However, iminyl radicals are prone to β -scission, which renders the addition reversible and unfavorable in most cases. Therefore, derivatives such as oxime ethers and hydrazones are the most commonly used radical acceptors due to their stabilization of the iminyl radical and their faster radical addition rates.⁵ Very recently, several groups including ours took advantage of the persistent character of the α -amino radical anion, the amine equivalent of the radical ketyl anion, to perform photoredox-catalyzed selective cross-coupling of imines with transient radicals.⁶ In all cases redox-neutral strategies were developed, thus limiting the scope of the coupling partner to oxidizable substrates.

As part of our research program in photoredox catalysis using transition metal complexes or organic molecules as photocatalysts⁷ and our interest in direct alkylation to install simple aliphatic chains,⁸ we decided to investigate the radical alkylation of imines (Scheme 1, bottom).⁹



Scheme 1 Strategies for the alkylation of imines.

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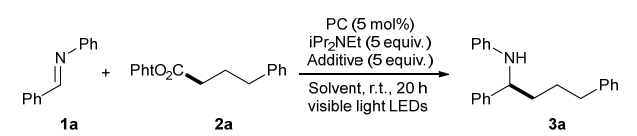
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Results and discussion

At the onset of our studies, we considered using simple and inexpensive carboxylic acids as starting materials for the generation of alkyl radicals. However, their oxidation potential is high, even in the presence of base ($E^{\text{ox}} > 1.0$ V vs SCE), thus complex photocatalysts should be used to promote their oxidative decarboxylation.¹⁰ To circumvent these shortcomings, we decided to investigate redox-active esters based on *N*-hydroxyphthalimide (NHPI esters). Indeed, these derivatives can easily be prepared in one step from carboxylic acids and exhibit relatively accessible reduction potentials ($E^{\text{red}} \sim -1.1$ V vs SCE for *N*-acetoxyphthalimide).¹¹ They have been successfully used in photoredox catalysis as well as in metal-catalyzed radical reactions for C-C and C-heteroatom bond formation.¹² In order to ensure the broadest scope possible, we directly focused on primary carboxylic derivatives, which give unbiased, non-stabilized primary radicals.

Inspired by our previous findings in the field of alkylation of imines by photoredox catalysis,¹³ we initially mixed *N*-benzylideneaniline and a primary redox-active ester in DMF, in the presence of $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ as photocatalyst, $i\text{Pr}_2\text{NEt}$ as reductive quencher and aqueous HBF_4 as a proton source.¹⁴ Upon irradiation with blue LEDs for 20 h, we were pleased to observe the expected coupling product **3a** in 69% NMR yield (Table 1, entry 1).

Table 1 Optimization of the reaction conditions^a

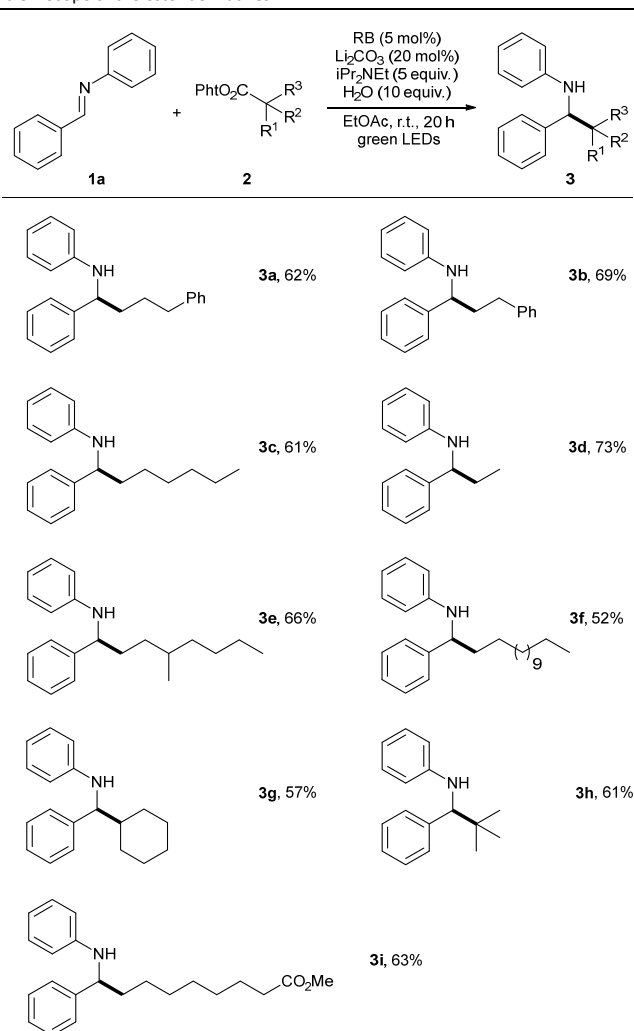


Entry	Photocatalyst	Additive	Solvent	LEDs	Yield (%) ^b
1	$[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$	HBF_4^c	DMF	Blue	69
2	Fluorescein	HBF_4^c	DMF	Blue	48
3	Eosin Y	HBF_4^c	DMF	Blue	50
4	Rose Bengal	HBF_4^c	DMF	Blue	53
5	Rose Bengal	HBF_4^c	DMF	Green	57
6	Rose Bengal	HBF_4^d	DMF	Green	Traces
7	Rose Bengal	H_2O^e	DMF	Green	40
8	Rose Bengal	H_2O^e Li_2CO_3^f	DMF	Green	58
9	Rose Bengal	H_2O^e Li_2CO_3^f	EtOAc	Green	72
10	-	H_2O^e Li_2CO_3^f	EtOAc	Green	0
11	Rose Bengal	H_2O^e Li_2CO_3^f	EtOAc	-	0
12	Rose Bengal	Li_2CO_3^f	EtOAc	Green	36

^a Reaction conditions: imine **1a** (0.2 mmol, 2 equiv.), ester **2a** (0.1 mmol, 1 equiv.), $i\text{Pr}_2\text{NEt}$ (0.5 mmol, 5 equiv.), additive (0.5 mmol, 5 equiv.) and photocatalyst (5 mol%) in degassed solvent (1 mL) under argon, blue or green LEDs, 20 hours. ^b Yield determined by ^1H NMR; ^c 48% in water; ^d Diethyl ether complex; ^e 10 equiv. ^f 0.2 equiv.

In order to improve the sustainability of the process, we screened organic dyes and found that Rose bengal (RB) was the most effective, providing the product in 53% and 57% yield under irradiation with blue and green light, respectively (entries 4 and 5). Using the HBF_4 -diethyl ether complex did not give any product, hence we suspected that water plays a key role in this transformation. Indeed, using distilled water as additive afforded the product in 40% yield (entry 7). Addition of a catalytic amount of Li_2CO_3 increased the yield to 58%. A solvent screening established that EtOAc was the best solvent for this transformation, with a 72% NMR yield (entry 9). Control experiments showed that the reaction does not proceed in the absence of photocatalyst or light (entries 10 and 11). We believe that the combination of water and Li_2CO_3 forms and solubilizes the dianionic form of Rose bengal, which can then act as an efficient photocatalyst. Additionally, very recent work by Glorius suggests that water might be involved in hydrogen-bonding of the redox-active ester to promote its reduction by photoredox catalysis.^{12o}

Table 2 Scope of the ester derivatives^a



^a Reaction conditions: imine **1a** (0.4 mmol, 2 equiv.), ester **2** (0.2 mmol, 1 equiv.), $i\text{Pr}_2\text{NEt}$ (1.0 mmol, 5 equiv.), H_2O (2.0 mmol, 10 equiv.), Li_2CO_3 (20 mol%) and Rose bengal (5 mol%) in degassed EtOAc (1 mL) under argon, irradiated by green LEDs for 20 hours. Yields after purification.

As we explored the scope of the transformation, purification of the products from the reaction mixtures proved to be challenging and moderate to good yields of the expected products could be obtained after work-up and silica-gel column chromatography (Table 2). As previously stated, we focused on saturated fatty acid derivatives, as they are inexpensive feedstock chemicals and their use as precursors for primary radicals is quite limited.¹⁵ Various lengths of alkyl chains were accommodated, and secondary (**2g**) as well as tertiary (**2h**) derivatives underwent also the reaction. Most interestingly, the monomethyl ester of azelaic acid (**2i**), a compound found in crops and widely used in industry as precursor for polymers and skin conditioners, could be coupled

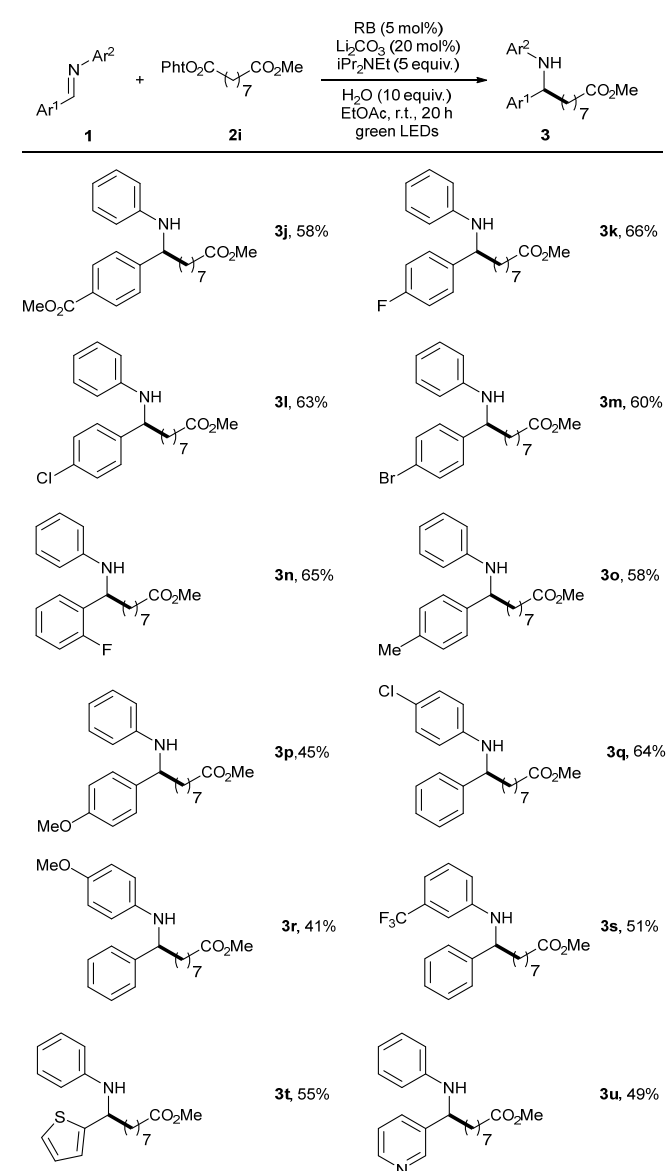
with *N*-benzylideneaniline to give the corresponding θ -amino ester **3i**, which might be of interest for unnatural peptide synthesis. We therefore explored the scope of the aniline part using this redox-active ester and the results are summarized in Table 3.

Although only aromatic imines could be used, both electron-withdrawing and electron donating groups were tolerated. Notably, no reduction of halogen was observed in the case of halogenated substrates. A PMP-protected product could also be obtained, showcasing the utility of this reaction for a straightforward access to θ -amino acids. Thiophene- and pyridine containing imines could also be alkylated in good yields.

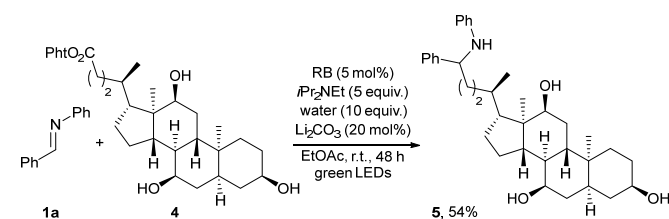
The exact mechanism of this net reductive alkylation of imines by visible light photoorganocatalysis is not clear at the moment. It is well established that dyes such as Eosin Y and Rose bengal are excited by green light and undergo rapid intersystem crossing to give a long-lived triplet state. Reductive quenching with a tertiary amine then provides the reduced form of the dye, which is moderately reducing ($E_{1/2}^{\text{red}}(\text{RB}/\text{RB}^-) = -0.99 \text{ V}$ or -0.78 vs SCE).¹⁶ When comparing the reduction potentials of both substrates, the redox-active ester is more likely to be reduced by the photocatalyst rather than the imine. After expulsion of the phthalimide anion and carbon dioxide, the corresponding radical adds to the C=N double bond of the imine. Such a productive transformation is rarely found in literature due to the reversibility of radical additions onto simple carbonyl compounds. We therefore believe that in our case the excess of ⁱPr₂NEt is crucial to promote a rapid hydrogen atom transfer and deliver the product.

To further demonstrate the applicability of our method, we attempted the direct coupling of the active ester of cholic acid with *N*-benzylideneaniline (Scheme 2). Pleasingly, the expected product was obtained in 54% yield after two days of irradiation, without the need for protection of the hydroxyl groups. We therefore expect our mild reaction conditions to be advantageous for decarboxylative late-stage functionalization of complex molecules. This functional group interconversion replaces a hydrophilic acidic site by a hydrophobic basic site, which might be of interest for logP tuning in prospective drugs.

Table 3 Scope of the imine^a



^a Reaction conditions: imine **1** (0.4 mmol, 2 equiv.), ester **2i** (0.2 mmol, 1 equiv.), ⁱPr₂NEt (1.0 mmol, 5 equiv.), H₂O (2.0 mmol, 10 equiv.), Li₂CO₃ (20 mol%) and Rose bengal (5 mol%) in degassed EtOAc (1 mL) under argon, irradiated by green LEDs for 20 hours. Yields after purification.



Scheme 2 Application to natural product derivatization. Reaction conditions: imine **1a** (0.4 mmol, 2 equiv.), ester **4** (0.2 mmol, 1 equiv.), ⁱPr₂NEt (1.0 mmol, 5 equiv.), H₂O (2.0 mmol, 10 equiv.), Li₂CO₃ (20 mol%) and Rose bengal (5 mol%) in degassed EtOAc (1 mL) under argon, irradiated by green LEDs for 2 days.

Conclusions

In conclusion, we developed a straightforward method to couple simple carboxylic acid derivatives with imines by visible light photoorganocatalysis. Extended amino esters could be synthesized in a modular, completely metal-free fashion. The mild reaction conditions contrast with typical Grignard and Barbier conditions and could be used to productively form and couple non-stabilized primary alkyl radicals, a performance rarely achieved in photoredox catalysis. Due to the ease of synthesis of the starting materials and the low cost of the catalytic system, we believe that our method could be widely used by the community. Efforts to extend the scope of this reaction to ketimines, ketones and aldehydes are currently underway and will be reported in due course.

Experimental

General procedure for the synthesis of compounds 3

A Schlenk-tube was charged with **1** (0.4 mmol, 2 equiv.), **2** (0.2 mmol 1 equiv.), rose bengal (5 mol%), and Li₂CO₃ (20 mol%). It was capped with a rubber septum, evacuated and backfilled with argon. Then, degassed EtOAc (2 mL) was added via syringe, at the same time the *i*Pr₂NEt (5 equiv.) and H₂O (10 equiv.) were also added. The vial was placed in a 100 mL beaker wrapped with green LEDs inside and the reaction mixture was stirred at rt for 20 h. After checking the course of the reaction by TLC, the solvent was evaporated under reduced pressure and the product was purified by column chromatography using Pentane/EA as eluent.

Conflicts of interest

There are no conflicts to declare.

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