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Formation of Carbonyl Compounds from Amines through Oxidative C−N Bond Cleavage using Visible Light Photocatalysis and Applications to *N*-PMB-Amide Deprotection

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Dedicated to Prof. Stephen L. Buchwald on the occasion of his 60th birthday.

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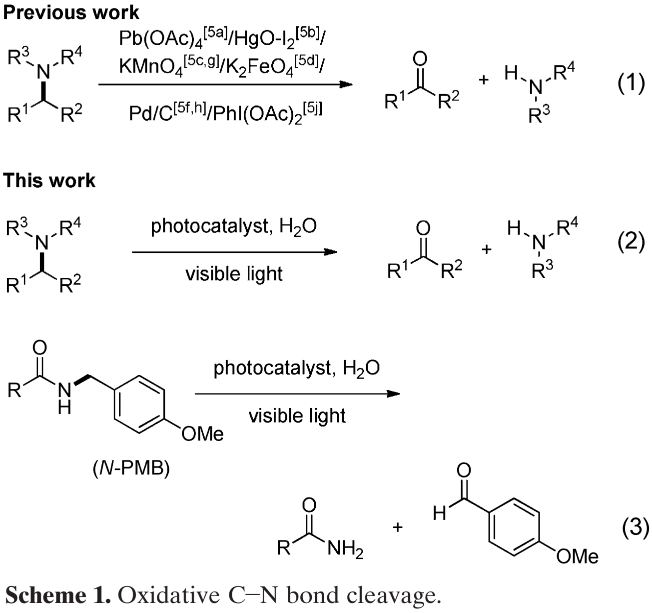
Abstract: A method has been developed for C−N bond cleavage that utilizes visible light photocatalysis. The process, which utilizes 1 mol% of the ruthenium complex $Ru(bpy)_3Cl_2$ as the photocatalyst, potassium persulfate ($K_2S_2O_8$) as the oxidant and water/acetonitrile (H_2O/CH_3CN) as the solvent, transforms a variety of primary, secondary and tertiary amines to the corresponding carbonyl compounds. In addition, this method was applied to the removal of a *p*-methoxylbenzyl (PMB) group from *N*-PMB protected amides.

Keywords: carbonyl compounds; C−N bond cleavage; photocatalysis; PMB deprotection; visible light

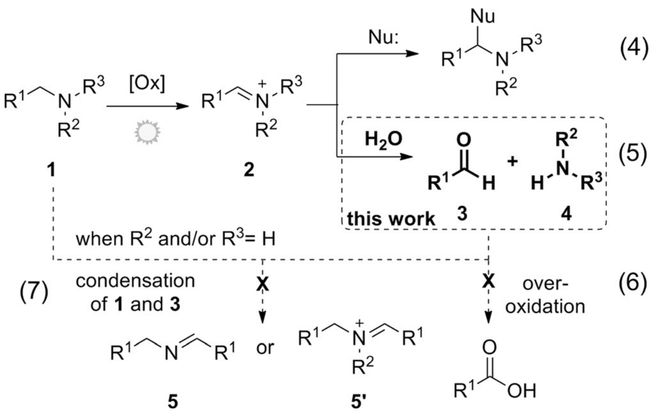
In living systems, enzyme-catalyzed reactions are involved in a large number of pathways leading to structurally diverse and complex natural products. The efficiencies and mild nature of these enzymatic processes have encouraged organic chemists to develop transformations which mimic those promoted by enzymes.[1] A well-known biological transformation involves the enzyme-promoted oxidative deamination of amines to form the corresponding carbonyl products.[2] An important example of this process is the monoamine oxidase-catalyzed reaction of neurogenic primary amines, which employs FAD cofactors as oxidants and proceeds through pathways involving oxidative formation and hydrolysis of iminium ion intermediates.[2d] These reactions generate ammonia and carbonyl compounds.

Carbonyl groups, especially those of aldehydes and ketones, are not only found in a wide range of natural products but they also participate in an array of organic transformations.[3] As a result, a demand exists for new, facile and mild methods to prepare substances that contain the carbonyl functional group. An alternative to the conventional method for producing aldehydes and ketones by oxidation of alcohols,[4] involves oxidations of readily abundant amines. Several protocols have been developed for this purpose [Scheme 1, Eq. (1)],[5] however, despite their efficiency these methods suffer from the required use of stoichiometric amounts of toxic metal-containing reagents and incompatibility with other readily oxidized functional groups.

α-C−H activation of amines (**1**) *via* formation of iminium ion intermediates (**2**) has been employed in a wide variety of organic transformations.[6] Recently, visible light photocatalysis[7,8] has been used to pro-



Scheme 1. Oxidative C−N bond cleavage.

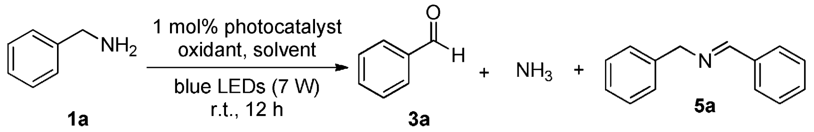


Scheme 2. α-C–H activation of amines.

mote the formation of iminium ions that are captured by nucleophiles in processes that lead to the generation of α-functionalized amines [Scheme 2, Eq. (4)].[9] We planned to use water as the nucleophile to capture iminium ions formed in this manner which would result in C–N bond cleavage[9i,10] and production of carbonyl products (**3**) and truncated amines (**4**) [Scheme 2, Eq. (5)]. Importantly, in order for a method which follows this mechanistic pathway to be synthetically applicable, over-oxidation of the carbonyl and amine products needs to be avoided [Scheme 2, Eqs. (6) and (7)].

In the investigation described below, we developed a green, mild, efficient and operationally simple method for oxidative C–N bond cleavage of amines, which utilizes visible light photoredox catalysis and that generates carbonyl compounds [Scheme 1, Eq. (2)]. In addition, we have shown that this procedure can be applied to the efficient removal of *p*-methoxybenzyl (PMB) groups from *N*-PMB protected amides

Table 1. Optimization of the reaction conditions for the C–N bond cleavage reaction of **1a**.[a]



Entry	Photocatalyst	Oxidant	Solvent (0.1 M)	Yield [%][b] 3a	Yield [%][b] 5a
1	$Ru(bpy)_3Cl_2$	O_2	H_2O	10	80
2	$Ru(bpy)_3Cl_2$	O_2	CH_3OH	3	94
3	$Ru(bpy)_3Cl_2$	O_2	CH_3CN/H_2O (1/1)	70	15
4	$Ru(bpy)_3Cl_2$	O_2	dioxane/H_2O (1/1)	57	23
5	$Ru(bpy)_3Cl_2$	O_2	DMF/H_2O (1/1)	60	29
6	$Ru(bpy)_3Cl_2$	O_2	THF/H_2O (1/1)	66	24
7	$Ru(phen)_3Cl_2$	O_2	CH_3CN/H_2O (1/1)	68	14
8	$Ir(ppy)_3$	O_2	CH_3CN/H_2O (1/1)	19	76
9	$Ir(dFppy)_3$	O_2	CH_3CN/H_2O (1/1)	25	68
10	$[Ir(ppy)_2(dtbbpy)]PF_6$	O_2	CH_3CN/H_2O (1/1)	55	31
11	$Ir(dFppy)_2phen]PF_6$	O_2	CH_3CN/H_2O (1/1)	39	51
12	$Ir(dFppy)_2(CH_3CN)]PF_6$	O_2	CH_3CN/H_2O (1/1)	18	75
13	Pt(ppy)acac	O_2	CH_3CN/H_2O (1/1)	21	64
14	$Ru(bpy)_3Cl_2$	open_air	CH_3CN/H_2O (1/1)	60	18
15	$Ru(bpy)_3Cl_2$	1 equiv. $K_2S_2O_8$	CH_3CN/H_2O (1/1)	80	-
16	$Ru(bpy)_3Cl_2$	1 equiv. $K_2S_2O_8$	CH_3CN/H_2O (2/1)	50	-
17c)	$Ru(bpy)_3Cl_2$	1 equiv. $K_2S_2O_8$	CH_3CN/H_2O (1/1)	4	10
18	-	1 equiv. $K_2S_2O_8$	CH_3CN/H_2O (1/1)	5	11
19	$Ru(bpy)_3Cl_2$	no oxidant	CH_3CN/H_2O (1/1)		-

[a] Reaction scale: **1a** (0.1 mmol).

[b] The yield was determined by using gas chromatography with dodecane as the internal standard.

[c] No visible light irradiation.

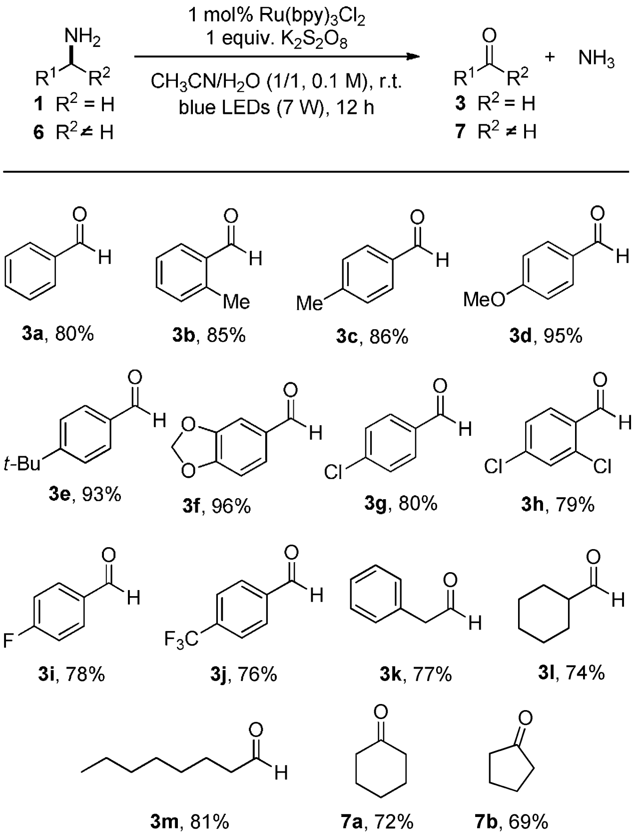
[Scheme 1, Eq. (3)].[11] The green nature of these processes is further heightened by the fact that water is a component of the solvent system used.[12]

Our initial exploratory studies, targeted at the development of a photocatalytic method for transforming amines to carbonyl compounds, employed benzylamine **1a** as a model amine, the widely used photocatalyst Ru(bpy)$_3$Cl$_2$, and visible light irradiation. We observed that irradiation of a solution of **1a** and Ru(bpy)$_3$Cl$_2$ in H_2O under an oxygen atmosphere leads to generation of *N*-benzylbenzaldimine (**5a**) as the major product along with a minor amount of benzaldehyde (**3a**) (Table 1, entry 1). Although imine **5a** was not the desired product, its formation by condensation of amine **1a** with aldehyde **3a** shows that the anticipated C–N bond cleavage process is proceeding efficiently under the photocatalytic, oxidative conditions employed.[13]

In order to enhance the formation of carbonyl product **3a** in this reaction, the effects of several parameters, including solvent, photocatalyst and oxidant were evaluated. Although the use of methanol as solvent does not alter the outcome of the reaction (Table 1, entry 2), a significantly increased yield of **3a** occurs when the aqueous medium contains organic co-solvents such as CH_3CN (Table 1, entries 3–6). While a change of the photocatalyst does not lead to an enhanced efficiency (Table 1, entries 7–13), a change in the oxidant from molecular oxygen to $K_2S_2O_8$ results in a highly selective C–N bond cleavage reaction that forms **3a** exclusively (Table 1, entry 15).[14] The results of control experiments demonstrated that the process requires visible light irradiation,[15] a photocatalyst, and an oxidant (Table 1, entries 17–19).

The amine scope of the process was explored next (Table 2). The results show that a variety of amines containing both aromatic and aliphatic substituents are converted in high yields to aldehyde and ketone products when the optimized reaction conditions are utilized. Various functional groups, such as an acetal (**3f**) and aromatic halides (**3g**, **3h**, and **3i**), are unaffected under the reaction conditions. In addition, substituents containing benzylic hydrogens, like in **3b**, **3c**, and **3k**, remain unaltered in this process. Benzylamines with *ortho*-substitution are also suitable substrates for the process (**3b** and **3h**). Reactions of substrates having electron-donating substituents (**3d**, **3e**, **3f**) on the aromatic ring give comparatively higher yields than those with electron-withdrawing groups (**3g**, **3h**, **3i**, **3j**). Application of this oxidation method to aliphatic amines (**3k**, **3l**, **3m**, **7a**, and **7b**) show the generality and practicality of the method.

Table 2. Oxidative C–N bond cleavage of primary amines to form carbonyl compounds.[a,b]



3a, 80%
3b, 85%
3c, 86%
3d, 95%
3e, 93%
3f, 96%
3g, 80%
3h, 79%
3i, 78%
3j, 76%
3k, 77%
3l, 74%
3m, 81%
7a, 72%
7b, 69%

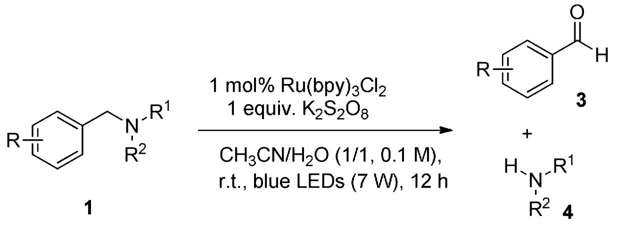
[a] Reaction scale: **1** (0.5 mmol).

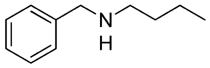
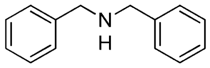
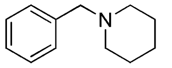
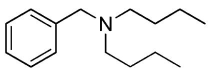
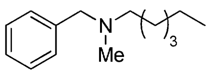
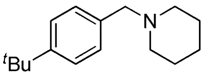
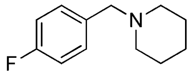
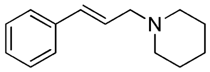
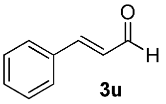
[b] The yields were isolated or GC yield (due to the volatility of the product).

The facile nature and efficiency of the photocatalytic reaction prompted a study aimed at probing its use for C–N bond cleavage of *N*-benzyl secondary and tertiary amines (Table 3). The results of the effort showed that a wide range of these types of amines undergo oxidative C–N bond cleavage exclusively at their benzylic positions to produce benzaldehyde derivatives. This regioselectivity of these reactions is a consequence of the comparatively higher acidity of the benzylic protons in amine cation radical intermediates formed by single electron transfer (SET) in this process. C–N bond cleavage reactions of cyclic and acyclic tertiary amines also take place smoothly. Moreover, the reactivity of the amines is not affected significantly by the electronic properties of aryl ring substituents as demonstrated by the fact that benzylamines with both electron-donating (**1s**) and electron-withdrawing (**1t**) substituents undergo the photocatalytic reaction in high yields (Table 3, entries 6 and 7). Interestingly, the styrene-containing tertiary amine (**1u**) reacts to form cinnamylaldehyde (**3u**) in moderately high yield (Table 3, entry 8).

Observations made in this effort suggested that the photocatalytic protocol might be applicable to the design of a new *N*-deprotection strategy. However, we envisaged that utilization of this method to deblock *N*-benzyl-protected amines might be complicated by

Table 3. Oxidative C–N bond cleavage reactions of secondary and tertiary amines.[a]

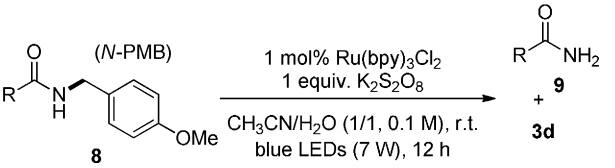


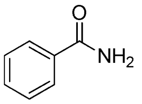
Entry		Substrate	Product (**3**)	Yield of **3**[b]
1	**1n**		**3a**	87%
2	**1o**		**3a**	83%
3	**1p**		**3a**	91%
4	**1q**		**3a**	88%
5	**1r**		**3a**	83%
6	**1s**		**3e**	97%
7	**1t**		**3i**	90%
8	**1u**		 **3u**	77%

[a] Reaction scale: **1** (0.5 mmol).

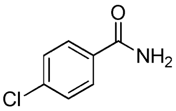
[b] The yields were isolated or GC yield (due to the volatility of the product).

Table 4. PMB deprotection of amides oxidative C–N bond cleavage.[a,b]

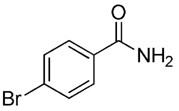




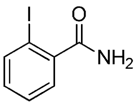
9a, 87%



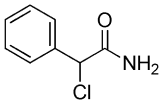
9b, 83%



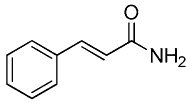
9c, 84%



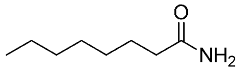
9d, 90%



9e, 78%



9f, 74%

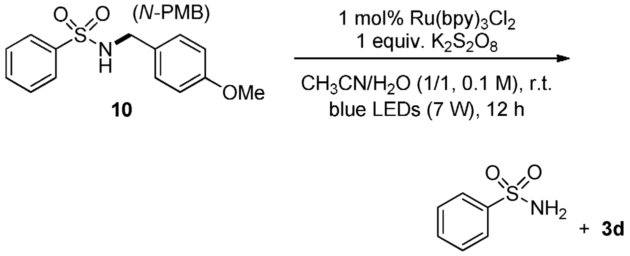


9g, 86%

[a] Reaction scale: **6** (1.0 mmol).

[b] Yields of isolated products are given.

secondary C–N bond cleavage reactions of the secondary and primary amines produced in these processes. In contrast, we reasoned that the photocatalytic method would be ideally suited to the deprotection of amides because the formed free amides would be less susceptible to over-oxidation. Moreover, an *N-p*-methoxybenzyl (PMB) group was selected for the proposed blocking/deblocking method owing to its expected higher susceptibility towards C–N bond cleavage.[16] Indeed, in studies aimed at evaluating the new protocol, we observed that PMB groups are efficiently removed from *N*-PMB protected aromatic and aliphatic amides by utilizing the photocatalytic conditions [1 mol% Ru(bpy)$_3$Cl$_2$, 1 equivalent K$_2$S$_2$O$_8$ in H$_2$O/CH$_3$CN] (Table 4). In these processes, minor amounts of *N*-acyl-4-methoxybenzaldimines are formed as a side product. Interestingly, the strategy also appears to be applicable to the removal of the PMB group from protected sulfonamides as exemplified by the conversion of **10** to benzenesulfonamide (**11**) under the conditions (Scheme 3).

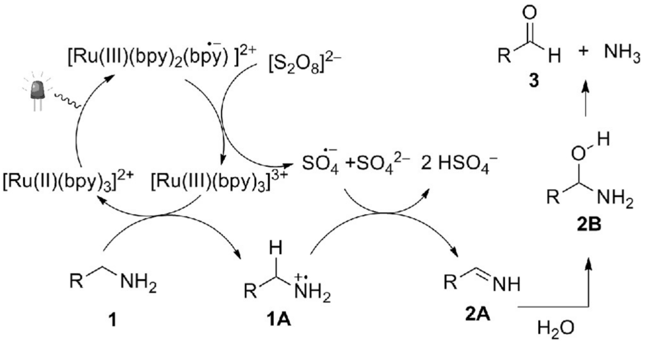


11, 77%

Scheme 3. Deprotection of *N*-PMB benzenesulfonamide.

A plausible mechanism for the oxidative C–N bond cleavage reaction begins with SET to [S$_2$O$_8$]$^{2-}$ from the metal-to-ligand charge transfer excited state of [Ru(II)(bpy)$_3$]$^{2+}$, generated by visible light irradiation (Scheme 4). This process leads to formation of SO$_4^{\bullet-}$ and SO$_4^{2-}$, through O–O bond cleavage of intermediate [S$_2$O$_8$]$^{3-}$. Reduction of [Ru(III)(bpy)$_3$]$^{3+}$ by SET from the amine or amide regenerates [Ru(II)(bpy)$_3$]$^{2+}$ along with the radical cation intemediate **1A**. Loss of an α-proton from **1A** followed by oxidation of the resulting α-amino radical generates the imine **2A**, which through hydrolysis produces the carbonyl compound **3**.

The study described above led to the development of a mild, eco-friendly and practical method for carry-



Scheme 4. Proposed mechanism for the C–N bond cleavage reaction.

ing out oxidative C–N bond cleavage of primary, secondary, and tertiary amines. These processes, which are promoted by visible light irradiation, efficiently generate carbonyl compounds. Finally, this process can be employed in a methodology for deblocking *N*-PMB protected amides.

Experimental Section

General Procedure

An oven-dried re-sealable tube, equipped with a magnetic stir bar, was charged with an amine or amide (0.5/1.0 mmol), $Ru(bpy)_3Cl_2$ (1 mol%), $K_2S_2O_8$ (1.0 equivalent) and MeCN/H_2O (1:1, 0.1 M). The tube was stoppered with a silicone septum screw-cap and placed under blue LEDs at room temperature. After 12 h irradiation, the tube was opened and the contents were diluted with ethylacetate/hexane. After aqueous work-up, the organic layers were combined, dried over $MgSO_4$ and concentrated under vacuum to give a residue that was subjected to flash column chromatography to give the desired product.

Acknowledgements

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