Visible-Light-Mediated Utilization of α-Aminoalkyl Radicals: Addition to Electron-Deficient Alkenes Using Photoredox Catalysts

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Ⓢ Supporting Information

ABSTRACT: Synthetic use of α-aminoalkyl radicals formed by single electron oxidation of amines is quite limited. Here we demonstrate addition of α-aminoalkyl radicals to electron-deficient alkenes by visible-light-mediated electron transfer using transition metal polypyridyl complexes as photocatalysts, via a sequential redox pathway.

Direct functionalization of an sp³ C−H bond adjacent to the N atom of amines is one of the most important methods for conventional and efficient synthesis of N-containing organic compounds.[1,2] The generation of iminium ions by two-electron oxidation of amines and transformations by the addition of various nucleophiles are extensively studied (Scheme 1a).[2,3] On the other hand, α-aminoalkyl radicals[4] formed by a single electron oxidation are expected to work as reactive intermediates, but successful examples for their use are limited (Scheme 1b)[5,6] because they are readily oxidized into iminium ions in the presence of a stoichiometric amount of oxidants.[7]

Scheme 1. Oxidation of Amines
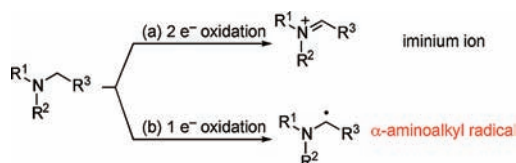
Oxidation of amines into iminium ions and α-aminoalkyl radicals via photoinduced electron transfer has been extensively studied.[8] Although some examples of photolytic use of α-aminoalkyl radicals as reactive intermediates have been reported, high-energy UV irradiation is necessary to promote these transformations, and applicable substrates are limited.[9−13] Recently, use of photoredox catalysts such as transition metal polypyridyl complexes has promoted useful organic transformations under visible light irradiation, where only the generation of α-aminoalkyl radicals in situ has been described.[3,14−18] We have envisaged that visible-light-mediated single electron transfer using photoredox catalysts is suitable for utilization of α-aminoalkyl radicals in organic synthesis. Here we report preliminary results on visible-light-mediated addition of α-aminoalkyl radicals to electron-deficient alkenes, where the oxidation of amines to α-aminoalkyl radicals (**A**) and the reduction of alkyl radicals (**B**) generated from the addition of **A** to alkenes are key steps (Scheme 2).

Scheme 2. Addition of α-Aminoalkyl Radicals to Electron-Deficient Alkenes Mediated by Visible Light
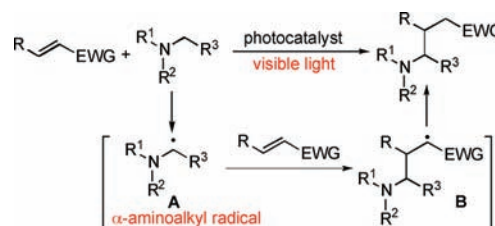
Table 1. Photocatalytic Reaction of Diethyl Ethylidenemalonate (1a) with Methyldiphenylamine (2a)[a]

entry	photocatalyst	solvent	yield (%)[b]
1	[4a][BF₄]	NMP	90
2	[4b][BF₄]	NMP	68
3	[4c][BF₄]	NMP	72
4	[Ru(bpy)₃][BF₄]₂	NMP	32
5	Eosin Y	NMP	9
6	[4a][BF₄]	DMF	45
7	[4a][BF₄]	MeCN	0
8	[4a][BF₄]	MeOH	0

4a: R = ᵗBu
4b: R = H

4c

Eosin Y

[a]All reactions of **1a** (0.25 mmol) with **2a** (0.30 mmol) were carried out in the presence of photocatalyst (0.0025 mmol) in solvent (2.5 mL) with 14-W white LED illumination at 25 °C for 18 h. [b]Isolated yield.

At first, we carried out the reaction of diethyl ethylidenemalonate (**1a**) with 1.2 equiv of methyldiphenylamine (**2a**). When a solution of **1a** and **2a** in the presence of 1 mol % of [**4a**][BF₄] in N-methylpyrrolidone (NMP) was illuminated with a 14-W white LED at 25 °C for 18 h, diethyl 2-(1-diphenylaminopropyl)-malonate (**3a**) was obtained in 90% yield (Table 1, entry 1). Reactions using similar Ir complexes **4b** and **4c** as catalysts also proceeded smoothly to give **3a** in moderate yields (entries 2 and 3). Use of [Ru(bpy)₃][BF₄]₂ (bpy = 2,2′-bipyridyl) and Eosin Y as photoredox catalysts dramatically decreased the yield
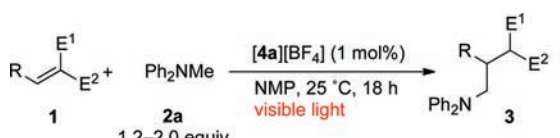
of **3a** (entries 4 and 5). The choice of solvents is an important factor to promote the addition. When N,N-dimethylformamide (DMF) was used in place of NMP, **3a** was obtained in 45% yield (entry 6), while no reaction occurred in other solvents such as acetonitrile and methanol (entries 7 and 8). Separately, we confirmed that no formation of **3a** was observed in the absence of visible light or photocatalyst.

Other reactions of a variety of alkenes **1** were investigated by using **4a** as a photocatalyst. Typical results are shown in Table 2. The reactions of **1b–1d** bearing an alkyl group at the β-position proceeded smoothly to give the corresponding alkylated amines (**3b–3d**) in good to high yields (entries 1–3). Diethyl arylmethylidenemalonates (**1e–1j**) and diethyl ethoxymethylidenemalonate (**1k**) were also applicable to this reaction system, giving the corresponding alkylated amines (**3e–3k**) in good yields (entries 4–10). On the other hand, use of β-ketoesters (E/Z-**1l**) in place of diester gave similar yields of **3l** as a mixture of two diastereoisomers (entries 11 and 12), but a lower yield of **3m** was observed when the alkene bearing a 1,3-diketone moiety (**1m**) was used (entry 13). The reaction of diethyl maleate (**1n**) also took place smoothly to give **3n** in 81% yield (entry 14). However, a small amount of **3o** was obtained when ethyl crotonate (**1o**) was used as a substrate (entry 15). Results for other alkenes are shown in Scheme S1. These results indicate that the introduction of two electron-withdrawing groups at the alkenes is essential to obtain **3** in high yields.

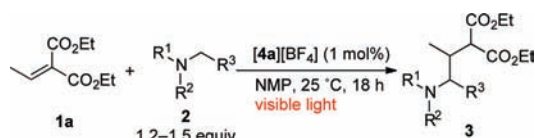**Table 2. Photocatalytic Reactions of Alkenes (1) with Methyldiphenylamine (2a)[a]**

entry	alkene (1)	yield of 3 (%)[b]
1[e]	R = nPr, E1 = E2 = CO2Et (**1b**)	91 (**3b**)
2[e]	R = iBu, E1 = E2 = CO2Et (**1c**)	91 (**3c**)
3[e]	R = Cy, E1 = E2 = CO2Et (**1d**)	61 (**3d**)
4[c]	R = Ph, E1 = E2 = CO2Et (**1e**)	89 (**3e**)
5[d]	R = p-MeC6H4, E1 = E2 = CO2Et (**1f**)	68 (**3f**)
6[c]	R = m-MeC6H4, E1 = E2 = CO2Et (**1g**)	86 (**3g**)
7[d]	R = p-ClC6H4, E1 = E2 = CO2Et (**1h**)	83 (**3h**)
8[d]	R = p-PhC6H4, E1 = E2 = CO2Et (**1i**)	81 (**3i**)
9[d]	R = 2-naphthyl, E1 = E2 = CO2Et (**1j**)	84 (**3j**)
10[e]	R = EtO, E1 = E2 = CO2Et (**1k**)	52 (**3k**)
11[d]	R = Ph, E1 = CO2Et, E2 = COMe (Z-**1l**)	78 (**3l**)[f]
12[d]	R = Ph, E1 = COMe, E2 = CO2Et (E-**1l**)	79 (**3l**)[f]
13[d]	R = Ph, E1 = E2 = COMe (**1m**)	36 (**3m**)
14[c]	R = CO2Et, E1 = CO2Et, E2 = H (**1n**)	81 (**3n**)
15[c]	R = Me, E1 = H, E2 = CO2Et (**1o**)	9 (**3o**)

[a] All reactions of **1** (0.25 mmol) with **2a** were carried out in the presence of [**4a**][BF4] (0.0025 mmol) in NMP (2.5 mL) with 14-W white LED illumination at 25 °C for 18 h. [b] Isolated yield. [c] 1.2 equiv of **2a** was used. [d] 1.5 equiv of **2a** was used. [e] 2.0 equiv of **2a** was used. [f] The ratio of isomers is ca. 1/1.

Next, we examined photocatalytic reactions with a variety of tertiary amines **2**. Typical results are shown in Table 3. Reaction of **1a** with ethyldiphenylamine (**2b**) proceeded smoothly to give **3p** in 89% yield (entry 1). Introduction of a substituent such as methyl, methoxy, fluoro, or chloro at the para-position in the benzene ring of **2a** did not affect much the yield of **3** (entries 2–5). The amine bearing a highly electron-withdrawing ester group (**2g**) is slightly more difficult to be oxidized, and use of **4c** in place of **4a** is important to obtain **3u**

Table 3. Photocatalytic Reactions of Diethyl Ethylidenemalonate (1a) with Amines (2)[a]

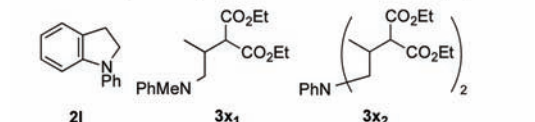| entry	amine (2)	yield of 3 (%)[b]
1[c]	R1 = R2 = Ph, R3 = Me (**2b**)	89 (**3p**)[g]
2[d]	R1 = p-MeC6H4, R2 = Ph, R3 = H (**2c**)	89 (**3q**)
3[d,e]	R1 = p-MeOC6H4, R2 = Ph, R3 = H (**2d**)	80 (**3r**)
4[d]	R1 = p-FC6H4, R2 = Ph, R3 = H (**2e**)	91 (**3s**)
5[d]	R1 = p-ClC6H4, R2 = Ph, R3 = H (**2f**)	79 (**3t**)
6[d,f]	R1 = p-MeO(CO)C6H4, R2 = Ph, R3 = H (**2g**)	80 (**3u**)
7[d]	R1 = tBu, R2 = Ph, R3 = H (**2h**)	90 (**3v**)
8[d]	R1 = iPr, R2 = Ph, R3 = H (**2i**)	73 (**3w**)
9[d]	R1 = Me, R2 = Ph, R3 = H (**2j**)	97 (**3x1/3x2**)[h]
10[d]	R1 = R2 = iPr, R3 = H (**2k**)	94 (**3y**)
11[d]	N-Phenylindoline (**2l**)	83 (**3z**)[g]

[a] All reactions of **1a** (0.25 mmol) with **2** were carried out in the presence of [**4a**][BF4] (0.0025 mmol) in NMP (2.5 mL) with 14-W white LED illumination at 25 °C for 18 h. [b] Isolated yield. [c] 1.2 equiv of **2** was used. [d] 1.5 equiv of **2** was used. [e] For 48 h. [f] [**4c**][BF4] was used as photocatalyst. [g] The ratio of isomers is ca. 1/1. [h] The ratio of **3x1** and **3x2** is 3.6/1.

in a high yield because the oxidizing ability of the excited state of **4c** is higher than that of **4a** (entry 6).[19] Dialkylarylamines (**2h**, **2i**) and diisopropylmethylamine (**2k**) were also applicable, giving the corresponding amines alkylated at the methyl group (**3v**, **3w**, **3y**) in high yields (entries 7, 8, and 10). When N,N-dimethylaniline (**2j**) was used as an amine, a mixture of mono-alkylated product **3x1** and dialkylated product **3x2** was obtained with moderate selectivity (entry 9). Cyclic amine N-phenyl-indoline (**2l**) was transformed into **3z** in 83% yield (entry 11). Separately, we confirmed that no conversion of a secondary amine such as N-methylaniline into the corresponding product was observed.

Scheme 3. Reaction of 1a with 2a-d3
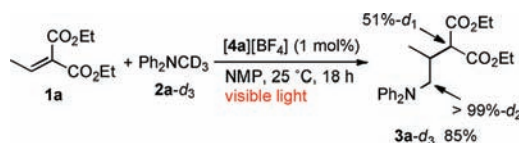
To obtain information on the reaction pathway, we investigated the reaction of **1a** with **2a**-d_3 (>99% D-enriched at the methyl protons) under similar conditions (Scheme 3). After purification by chromatography, the corresponding amine **3a**-d_3 (51% D-enriched at the activated methine proton and >99% D-enriched at the α-protons of the amino group) was obtained in 85% yield. No deuterium incorporation of **3a** was observed in the reaction of **1a** with **2a** in DMF-d_7. These results indicate that the activated methine proton of **3** is mainly derived from the α-proton of **2**, though hydrogen abstraction from other species is not excluded completely. Furthermore, we carried out the reaction of the alkene bearing a cyclopropyl moiety (**5**) as a radical clock (Scheme 4).[20] The cyclopropyl ring-opening product **6** was obtained in 64% yield. This result strongly supports the intermediacy of alkyl radicals in this transformation.

Scheme 4. Reaction of 5 as a Radical Clock
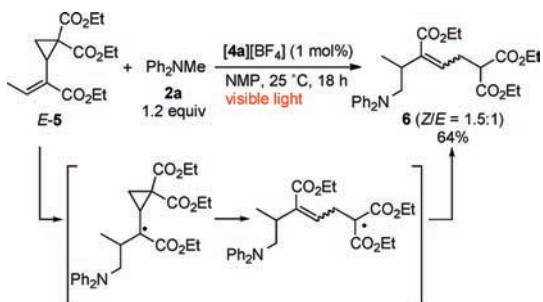
As a plausible reaction pathway, a radical chain process is possible, where abstraction of the α-H of 2 by alkyl radical B generated from the addition of α-aminoalkyl radical A to 1 affords 3 together with regeneration of A, and this reaction process is independent of photoirradiation. Previously, Hoffmann's group reported the addition of α-aminoalkyl radical to alkenes *under UV irradiation*, and their reaction system included a radical chain process as a main reaction pathway, where the quantum yield is larger than 1.[9] To verify the effect of photoirradiation, we investigated on−off switching of the light source in the reaction of 1a with 2a in DMF-d_7 (Figure 1). When the LED lamp was switched off at appropriate intervals, the reaction did not proceed during the "off" periods. In sharp contrast to Hoffmann's system,[9] the quantum yield in the reaction of 1a with 2a was estimated to be 0.32, which is in the range common for molecular transformations via photoinduced electron transfer mediated by transition metal polypyridyl complexes.[8a,b,21] Separately, we confirmed that use of radical initiators such as AIBN, BEt$_3$/air, and (^{t}BuO)$_2$ did not promote the reaction of 1a with 2a in NMP at 80 °C at all.[22] These results indicate that the dependence of a radical chain process is negligible in our reaction system.
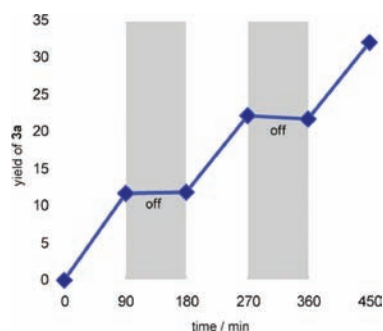

Figure 1. Time profile of reaction of 1a with 2a: light was swiched off during the "off" periods.

Considering the experimental results, a plausible reaction pathway is proposed in Scheme 5. The initial step is the formation of the α-aminoalkyl radical A from a single electron oxidation of 2 by the excited photocatalyst (*cat) and subsequent deprotonation.[8] Addition of A to 1 results in formation of the alkyl radical species B. Finally, reduction of B by the one-electron-reduced form of photocatalyst (cat$^-$)[19,23] and subsequent protonation occur to give 3 accompanied by regeneration of photocatalyst (cat).

As mentioned above, Hoffmann's group reported the high-energy UV-light-mediated generation of α-aminoalkyl radical and addition to alkenes.[9] In the radical chain process they proposed, use of a large excess amount of amines (using as a solvent) is necessary to accelerate the addition reaction because

Scheme 5. Plausible Reaction Pathway
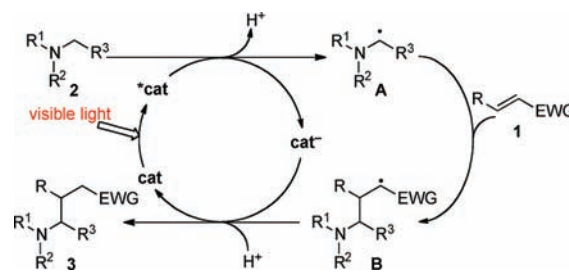
abstraction of the α-hydrogen of amines is a kinetically unfavorable step.[4,9c] In sharp contrast, our visible-light-mediated reaction proceeds via a sequential redox pathway as shown in Scheme 5, and a stoichiometric amount (1.2−2.0 equiv) of amines is sufficient to promote the reaction. The result described in this paper provides a new entry into the visible-light-mediated utilization of α-aminoalkyl radicals and a synthetically useful methodology for the direct functionalization of an sp^3 C−H bond adjacent to the N atom of amines.

Finally, we investigated synthetic applications of the produced alkylated amines (Scheme 6). Decarboxylation of 3a proceeded smoothly to give 3o in 92% yield (Scheme 6a). Intramolecular cyclization of dealkylated secondary amine proceeded in the reaction of 3v with an excess amount of trifluoroacetic acid (TFA) to afford the corresponding γ-lactam (7)[24] in 71% yield with a high diastereoselectivity (Scheme 6b).

Scheme 6. Transformations of 3
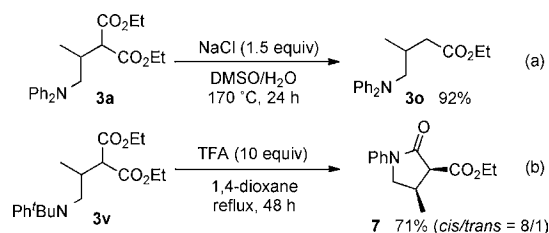
In summary, we have developed an efficient methodology for visible-light-mediated utilization of α-aminoalkyl radicals, which are difficult to be generated directly from amines under thermal reaction conditions. Our reaction system is applicable for addition of a variety of amines to electron-deficient alkenes. We also found that this photocatalytic reaction proceeds via a sequential redox pathway. We believe that the result described here provides a novel synthetic approach to direct functionalization of an sp^3 C−H bond adjacent to the N atom of amines. Further work is in progress to broaden the synthetic applicability of the α-aminoalkyl radicals under visible light irradiation.

■ ASSOCIATED CONTENT

S Supporting Information

Experimental procedures, spectroscopic data, and X-ray data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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