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

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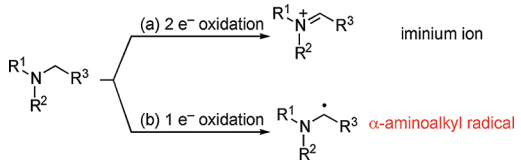
Supporting Information

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 sp^3 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

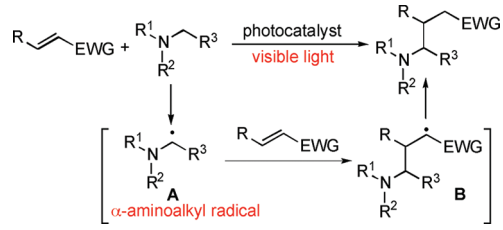
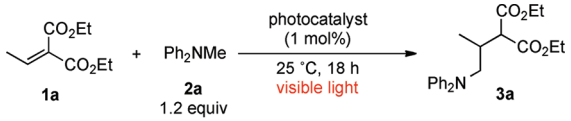
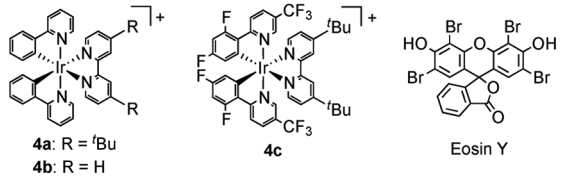


Table 1. Photocatalytic Reaction of Diethyl Ethylidenemalonate (1a) with Methyldiphenylamine (2a)[a]



entry	photocatalyst	solvent	yield (%)[b]
1	[**4a**][BF_4]	NMP	90
2	[**4b**][BF_4]	NMP	68
3	[**4c**][BF_4]	NMP	72
4	$[Ru(bpy)_3][BF_4]_2$	NMP	32
5	Eosin Y	NMP	9
6	[**4a**][BF_4]	DMF	45
7	[**4a**][BF_4]	MeCN	0
8	[**4a**][BF_4]	MeOH	0



[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**][BF_4] 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 $[Ru(bpy)_3][BF_4]_2$ (bpy = 2,2′-bipyridyl) and Eosin Y as photoredox catalysts dramatically decreased the yield

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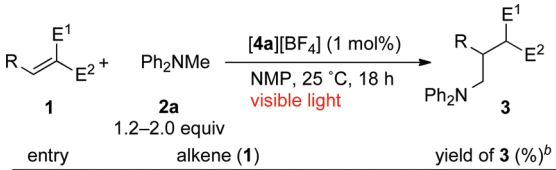
of **3a** (entries 4 and 5). The choice of solvents is an important factor to promote the addition. When *N*,*N*-dimethylformamide (DMF) was used in place of NMP, **3a** was obtained in 45% yield (entry 6), while no reaction occurred in other solvents such as acetonitrile and methanol (entries 7 and 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]



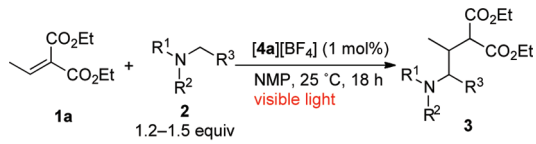
1 **2a** (1.2–2.0 equiv) **3**

entry	alkene (**1**)	yield of **3** (%)[b]
1[e]	R = ^{n}Pr, E^1 = E^2 = CO_2Et (**1b**)	91 (**3b**)
2[e]	R = ^{i}Bu, E^1 = E^2 = CO_2Et (**1c**)	91 (**3c**)
3[e]	R = Cy, E^1 = E^2 = CO_2Et (**1d**)	61 (**3d**)
4[c]	R = Ph, E^1 = E^2 = CO_2Et (**1e**)	89 (**3e**)
5[d]	R = *p*-MeC_6H_4, E^1 = E^2 = CO_2Et (**1f**)	68 (**3f**)
6[c]	R = *m*-MeC_6H_4, E^1 = E^2 = CO_2Et (**1g**)	86 (**3g**)
7[d]	R = *p*-ClC_6H_4, E^1 = E^2 = CO_2Et (**1h**)	83 (**3h**)
8[d]	R = *p*-PhC_6H_4, E^1 = E^2 = CO_2Et (**1i**)	81 (**3i**)
9[d]	R = 2-naphthyl, E^1 = E^2 = CO_2Et (**1j**)	84 (**3j**)
10[e]	R = EtO, E^1 = E^2 = CO_2Et (**1k**)	52 (**3k**)
11[d]	R = Ph, E^1 = CO_2Et, E^2 = COMe (*Z*-**1l**)	78 (**3l**)[f]
12[d]	R = Ph, E^1 = COMe, E^2 = CO_2Et (*E*-**1l**)	79 (**3l**)[f]
13[d]	R = Ph, E^1 = E^2 = COMe (**1m**)	36 (**3m**)
14[c]	R = CO_2Et, E^1 = CO_2Et, E^2 = H (**1n**)	81 (**3n**)
15[c]	R = Me, E^1 = H, E^2 = CO_2Et (**1o**)	9 (**3o**)

[a]All reactions of **1** (0.25 mmol) with **2a** were carried out in the presence of [**4a**][BF_4] (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.

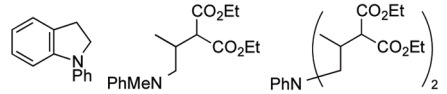
Next, we examined photocatalytic reactions with a variety of tertiary amines **2**. Typical results are shown in Table 3. Reaction of **1a** with ethyldiphenylamine (**2b**) proceeded smoothly to give **3p** in 89% yield (entry 1). Introduction of a substituent such as methyl, methoxy, fluoro, or chloro 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]



1a **2** (1.2–1.5 equiv) **3**

entry	amine (**2**)	yield of **3** (%)[b]
1[c]	R^1 = R^2 = Ph, R^3 = Me (**2b**)	89 (**3p**)[g]
2[d]	R^1 = *p*-MeC_6H_4, R^2 = Ph, R^3 = H (**2c**)	89 (**3q**)
3[d,e]	R^1 = *p*-$MeOC_6H_4$, R^2 = Ph, R^3 = H (**2d**)	80 (**3r**)
4[d]	R^1 = *p*-FC_6H_4, R^2 = Ph, R^3 = H (**2e**)	91 (**3s**)
5[d]	R^1 = *p*-ClC_6H_4, R^2 = Ph, R^3 = H (**2f**)	79 (**3t**)
6[d,f]	R^1 = *p*-$MeO(CO)C_6H_4$, R^2 = Ph, R^3 = H (**2g**)	80 (**3u**)
7[d]	R^1 = ^{t}Bu, R^2 = Ph, R^3 = H (**2h**)	90 (**3v**)
8[d]	R^1 = ^{i}Pr, R^2 = Ph, R^3 = H (**2i**)	73 (**3w**)
9[d]	R^1 = Me, R^2 = Ph, R^3 = H (**2j**)	97 (**3x$_1$**/**3x$_2$**)[h]
10[d]	R^1 = R^2 = ^{i}Pr, R^3 = H (**2k**)	94 (**3y**)
11[d]	*N*-Phenylindoline (**2l**)	83 (**3z**)[g]

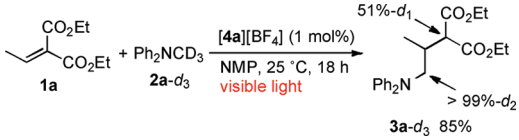


2l **3x$_1$** **3x$_2$**

[a]All reactions of **1a** (0.25 mmol) with **2** were carried out in the presence of [**4a**][BF_4] (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**][BF_4] was used as photocatalyst. [g]The ratio of isomers is ca. 1/1. [h]The ratio of **3x$_1$** and **3x$_2$** 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 monoalkylated product **3x$_1$** and dialkylated product **3x$_2$** was obtained with moderate selectivity (entry 9). Cyclic amine *N*-phenylindoline (**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-d_3



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.

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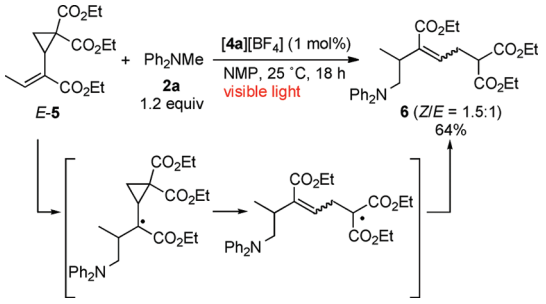
Scheme 4. Reaction of 5 as a Radical Clock



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 $(^tBuO)_2$ 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.

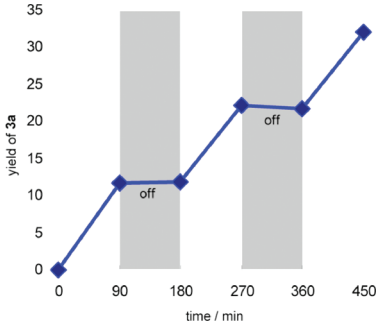
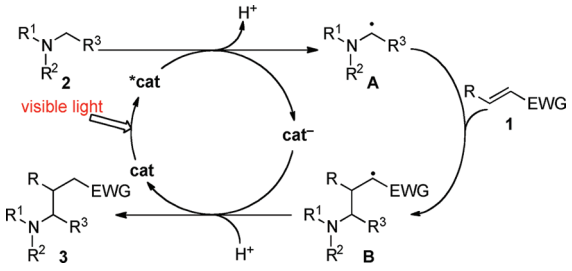


Figure 1. Time profile of reaction of **1a** with **2a**: light was swiched off during the "off" periods.

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

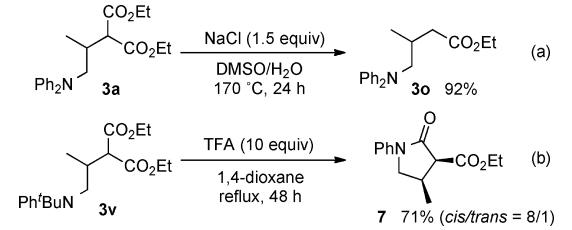
Scheme 5. Plausible Reaction Pathway



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

Ⓢ 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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