

Letter

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# Decarboxylative Olefination of Activated Aliphatic Acids Enabled by Dual Organophotoredox/Copper Catalysis

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**ABSTRACT:** Herein, we demonstrate a dual organophotoredox/copper catalytic strategy towards challenging decarboxylative olefination processes proceeding in high yields and selectivities. This operationally simple method uses photoactive organic molecules and Cu(II)-complexes as catalysts to provide rapid access to a wide variety of olefins from inexpensive synthetic and biomass-derived carboxylic acids under mild light-mediated conditions. Mechanistic investigations suggest that the reaction rate for this process is controlled solely by the incident photon flux.

KEYWORDS: photoredox catalysis, copper catalysis, decarboxylation, olefin synthesis, dual catalysis

Aliphatic carboxylic acids are important molecules in organic chemistry as they are stable, readily available, inexpensive and synthetically versatile. Therefore, methods that are able to transform these building blocks into other relevant functionalities have gained attention in recent years.<sup>1</sup> Among the processes developed, olefination methods occurring via catalytic decarbonylation and decarboxylation pose as promising strategies to convert aliphatic acids into synthetically valuable olefins (Scheme 1a).<sup>2</sup> However, to date, these processes generally require forcing conditions (>110 °C), the use of expensive precious metals as catalysts, and proceed with a narrow scope of primary aliphatic acids. Moreover, the challenge of attaining high selectivity towards the targeted terminal olefin is yet to be fully addressed since isomerization to the thermodynamically more stable internal alkene often occurs in the presence of metallic hydrides.<sup>2</sup> More recently, enzymatic catalysis has emerged for the oxidative decarboxylation of some fatty acids generally proceeding with high selectivity (Scheme 1b). Nonetheless, poor biocatalyst stability, and volumetric productivity are still major drawbacks.<sup>3</sup>

In light of the aforementioned limitations for the conversion of structurally diverse aliphatic acids into olefins, we questioned whether a series of consecutive single-electron transfer steps could be engineered to provide an overall lowenergy pathway for this long-standing synthetic problem. Furthermore, we reasoned that through the proper election of steps, a redox- and pH-neutral-method could be developed for a milder and more functional group tolerant protocol. Based on these considerations, we devised a synthetic strategy that merges visible-light-mediated radical decarboxylation with copper catalysis.<sup>4-5</sup> As shown in Scheme 1c, the first step takes advantage of the photoinduced formation of alkyl radicals from bench-stable activated aliphatic acids (also known as redox-active esters), which are attractive reagents due to their low synthetic cost and versatile reactivity as sources of C(sp<sup>3</sup>)- and C(sp<sup>2</sup>)-centered radicals.<sup>6,7</sup> Next, we envisioned that a Cu(II)-catalyst would promote the oxidation of the photogenerated alkyl radical to form an alkene 58 moiety with high selectivity, as demonstrated in the pioneer-59 ing work of Kochi and co-workers.<sup>8</sup> 60



#### Scheme 1. Strategies for the conversion of aliphatic acids into olefins.

Herein, we demonstrate the realization of our dual catalytic approach, which resulted in the development of an efficient, operationally simple, and scalable method to convert a wide range of synthetic and naturally abundant carboxylic acid feedstocks into olefins. Moreover, our developed method features excellent yields and selectivities while using inexpensive Copper(II) complexes and simple organic molecules as catalysts.

With the aim to provide an inexpensive photocatalytic system to generate alkyl radicals from redox-active esters ( $E_{1/2}$  = -1.28 V vs. SCE in MeCN),<sup>6a</sup> we started our investigation by identifying a suitable organophotocatalyst, which possesses a strongly reducing excited state. Recently, *N*,*N*-diaryl dihydrophenazines were introduced as photocatalysts featuring excited state oxidation potentials spanning from -1.71 to -2.50 V (vs. SCE) depending on the aryl moieties attached to the heterocyclic core.<sup>9</sup> Inspired by these findings, we began our optimization studies by performing the decarboxylative olefination of **1** in the presence of dihydrophenazine-based

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photocatalysts and copper(II) 2-ethylhexanoate, which is a commercially available catalyst that has good solubility in a wide range of organic solvents.

Table 1. Visible-light-mediated decarboxylative olefination of  $1.^{a}$ 

Brth	1 Organophotoc Cu(ii) 2-ethylher solvent (50 3W LEDs ℓ <sub>max</sub> = rt, 18 h, an	atalyst canoate mM) Br 7 7 7 7 7 7 7 7 7 7 9 9 9 9 9 9 9 9 9 9 9 9 9	OPC (1-5)
Entry	Photocatalyst (mol%)	Solvent	Yield $(\%)^b$
1	<b>OPC-1</b> (X = F) (10)	Acetone	0
2	<b>OPC-2</b> (X = H) (10)	Acetone	0
3	<b>OPC-3</b> (X = CN) (10)	Acetone	< 5
4	<b>OPC-4</b> (X = $CF_3$ ) (10)	Acetone	17
6	<b>OPC-5</b> (X = Ph) (10)	Acetone	< 5
$7^{c}$	<b>OPC-6</b> (10)	Acetone	0
8 <sup>d</sup>	<b>OPC-4</b> $(X = CF_3)$ (2.5)	Toluene	87 (78)

<sup>*a*</sup>General conditions: **1** (0.10 mmol), photocatalyst, copper(II)-catalyst (10 mol%), and solvent (2.0 mL) under argon. <sup>*b*1</sup>H NMR yields using CH<sub>2</sub>Br<sub>2</sub> as internal standard. <sup>*c*</sup>2-Naphthyl derivative. <sup>*d*</sup>Copper(II)-catalyst (2.5 mol%). Isolated yield in parenthesis using 0.40 mmol scale of **1**.

Gratifyingly, after irradiation at room temperature with LEDs  $(\lambda_{max} = 400 \text{ nm})$  in acetone for 18 hours, 1a was observed in 17% yield when using 10 mol% of both **OPC-4** and copper(II) 2-ethylhexanoate (Table 1, entry 4). Remarkably, the observed photoinduced reduction of 1 with **OPC-4** represents the first example of the use of an organic dye to promote the direct radical decarboxylation of redox-active esters, which have previously required sacrificial reductants or hydrogenbond activation.<sup>6</sup> Encouraged by these results, further studies showed that optimal catalytic performance was obtained when using toluene as the solvent and 2.5 mol% of both **OPC-4** and the Cu(II)-catalyst.<sup>10</sup>

With the optimized reaction conditions in hand, we investi-38 gated the substrate scope of our olefination protocol. To our 39 delight, a wide range of primary activated aliphatic acids was 40 converted into terminal olefins in high yield and with perfect 41 selectivity. Notably, our method was amenable for the syn-42 thesis of allylic-type compounds such as methyl eugenol 5a 43 (found in essential oils) and 6a, which are challenging sub-44 strates as isomerization to form their aryl conjugated isomers 45 is facile under forcing reaction conditions. Interestingly, 46 expanding the scope towards secondary carboxylic acids 47 allowed for the preparation of cyclic olefins 7a-12a. Previously, these motifs could be prepared via stepwise diene synthe-48 sis followed by ring-closing metathesis, however, our method 49 allows for their direct synthesis from commercially available 50 carboxylic acids. Unfortunately, when moving towards an 51 asymmetric secondary activated acid, where two possible 52 regioisomers could be formed, a mixture of both terminal 53 and internal olefin was obtained (14a). Finally, activated drug molecules such as Chlorambucil (used in chemotherapy), Mycophenolic acid (an immunosuppressant drug), and Gemfibrozil (used to lower lipid levels) could be easily used in their activated form to access olefins 15a-17a in good yields.



**Scheme 2.** Scope of synthetic activated aliphatic acids. General conditions: 0.40 mmol of 2-17.<sup>*a*</sup>11:1 (*Z*:*E*) ratio. <sup>*b*</sup>1:1.7 ratio of terminal:internal olefin. <sup>*c*</sup>2:1 (*E*:*Z*) ratio. <sup>*d*</sup>3:1 ratio of terminal:internal olefin. <sup>*e*</sup>Performed with 7 mmol of 10.

The synthetic utility of our method was further demonstrated by employing inexpensive naturally abundant aliphatic acid feedstocks (Scheme 3). Fatty acids such as palmitic, stearic, oleic, and linoleic acid, which are arguably the most important biomass materials produced by the chemical industry today,<sup>11</sup> were efficiently converted into odd-numbered mono-, di- and tri-olefins (**18a–21a**). Interestingly, other suitably-protected naturally abundant acids such as  $\gamma$ aminobutyric acid (a neurotransmitter), aleuritic acid (major component of a resin secreted by the female lac bug) and bile acids could also be used to deliver their corresponding olefins (**22a–25a**). Next, the scalability of our decarboxylative olefination was demonstrated using activated acids **10**, **19** and **25** to access their corresponding olefins in good yield and gram scale (Schemes 2 and 3).<sup>12</sup>

Finally, an additive-based robustness screen was performed for our developed decarboxylative olefination method in the presence of 14 different additives (See SI for details). The experimental results are depicted in histograms (Scheme 3). Interestingly, we observed that the presence of common functionalities such as alkene, alkyne, cyano, carbonyl, arene, and heterocyclic units has a minimum negative impact on the olefin yield while these molecules were well preserved after the reaction time.<sup>13</sup>

To gain insight into the mechanism of the visible-lightmediated decarboxylative olefination several experiments were performed. In the absence of light irradiation or **OPC-4**, olefin **1a** was not observed and **1** was completely recovered. Interestingly, whereas **1a** was not formed in the absence of Cu(II) 2-ethylhexanoate either, 1-bromodecane could be detected in this experiment suggesting that **OPC-4** is responsible for the photoinduced reduction of **1** (see SI, section 3.2). Moreover, by using **26** as a radical clock, 1,3-butadiene was

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produced in 59% yield under the standard reaction conditions (Scheme 4a).



Scheme 3. Scope of activated acids derived from biomass feedstocks and robustness screen. General conditions: 0.40 mmol of 18–25. <sup>a</sup>Performed with 7 mmol of 19. <sup>b</sup>Performed with 5 mmol of 25. See the SI for further details.

These results demonstrate the visible-light-mediated nature of our protocol as well as the intermediacy of radical species. Next, we sought to assess whether the olefination event at the photogenerated alkyl radical occurs *via* a formal oneelectron oxidation of this species by the Cu(II)-catalyst and subsequent deprotonation of the resulting carbocation. Interestingly, by using ethanol as a trapping agent we did not detect the presence of ether-adducts and considerable amounts of the corresponding olefins were still formed. This suggests that radical oxidation occurs *via* a different process, which does not involve the formation of carbocation intermediates.<sup>8</sup>

Kinetic experiments were then performed to determine the experimental rate law for the decarboxylative olefination using **19** as substrate (Scheme 4b). By using the initial rates method, the observed rate law was zero-order with respect to **OPC-4** and the Cu(II)-catalyst. Furthermore, by monitoring the concentration of the activated aliphatic acid over time a linear behavior was observed, implicating a zero-order on this species as well. Finally, a linear dependence on the reaction rate with respect to the incident photon flux was observed (Scheme 4c). Altogether, these kinetic experiments suggest that formation of the active **OPC-4** photoexcited state is turnover-limiting.<sup>14</sup> Further inspection of the kinetic data for our developed decarboxylative olefination method revealed a low quantum yield value for this photocatalytic process ( $\Phi = 0.01$ , see SI for details).



Scheme 4. Mechanistic experiments.

With these results in hand, the mechanistic proposal for the decarboxylative olefination is depicted in Scheme 5. Upon photoexcitation of **OPC-4** ( $*E_{ox} = -1.80$  V vs. SCE),<sup>9a</sup> single-electron transfer with the activated aliphatic acid leads to an alkyl radical after CO<sub>2</sub>-extrusion. This intermediate is then rapidly trapped by the Cu(II)-catalyst leading to an alkyl-copper(III) species **A**, which further reacts to the corresponding olefin and a Cu(I)-intermediate **B** *via* an oxidative elimination process.<sup>8</sup> The dual catalytic cycle is finally closed by single-electron transfer between [**OPC-4**]<sup>+</sup> and the Cu(I)-species **B**.<sup>15</sup>



Scheme 5. Proposed catalytic cycle.

In conclusion, we have developed an efficient, mild, and scalable protocol that enables rapid conversion of readily available synthetic and naturally abundant aliphatic acids into olefins in high yield and with high selectivity. Moreover, while operating under overall-redox neutral conditions, our method can be applied to an unprecedented broad scope of aliphatic acids and uses inexpensive photoactive organic molecules and Cu(II)-complexes as catalysts. Mechanistic insights into this decarboxylative olefination protocol suggest that formation of the active excite state of **OPC-4** is rate determining. Overall, our work demonstrates that singleelectron transfer chemistry can be engineered to provide a straightforward protocol for the light-mediated synthesis of

valuable organic molecules *via* challenging decarboxylative processes.

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#### Notes

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The authors declare no competing financial interest.

### ASSOCIATED CONTENT

#### SUPPORTING INFOMATION

Experimental procedures, mechanistic experiments and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org website at DOI:

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