

Visible-Light-Driven Alkene Dicarboxylation with Formate and CO₂ Under Mild Conditions

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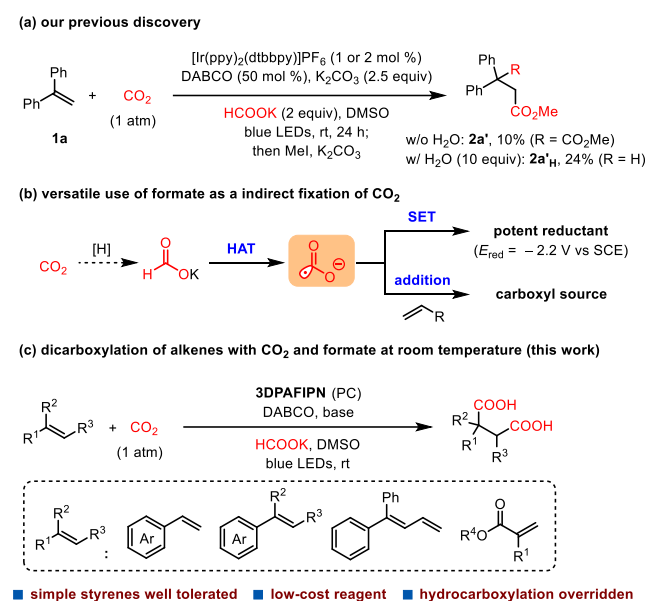
ABSTRACT: The low-cost formate salt was used as the reductant and part of the carboxyl source in a visible-light-driven dicarboxylation of diverse alkenes, including simple styrenes. The highly competing hydrocarboxylation side reaction was successfully overridden. Good yields of products were obtained under mild reactions at ambient temperature and pressure of CO₂. The dual role of formate salt may stimulate the discovery of a range of new transformations under mild and friendly conditions.

INTRODUCTION

Over the past decade, great progress has been made in the catalytic utilization of carbon dioxide (CO₂) using visible light.¹ However, many of these transformations require the use of stoichiometric reductant. Recently, we developed an arylcarboxylation of alkenes with CO₂ using formate salt as a low-cost terminal reductant and also as part of the CO₂ source.² In this study, it was first realized that the CO₂ radical anion (CO₂^{•−}) (E_{1/2}(CO₂/CO₂^{•−}) = −2.2 V vs SCE),³ readily available from the formate via hydrogen atom transfer (HAT), could be used as a potent reductive intermediate for direct reduction of substrates in visible-light-induced organic synthesis, avoiding the need to generate a highly reductive photocatalyst (PC). This discovery has been employed in a series of photocatalytic reactions involving challenging reduction of substrates recently.^{4–6} Moreover, in the control experiments of this work, we also discovered dicarboxylation and hydrocarboxylation of alkene **1a** in the absence of an aryl halide (Scheme 1a).² Afterwards, the groups of Jui,^{4a} Wickens,⁷ Li,⁸ and Mita⁹ also proved that CO₂^{•−} generated from formate could act as a source of carboxyl via Giese-type radical addition to alkenes and (hetero)aromatics to deliver hydrocarboxylation reactions.^{10,11} Since formate could potentially be produced from CO₂, e.g. via hydrogenation, photoreduction and electroreduction,¹² the use of formate for the dicarboxylation of alkenes to produce diacids can be considered as an attractive indirect method for CO₂ fixation (Scheme 1b).¹³

Diacids such as succinic acid derivatives are important core structures of many bioactive molecules and useful monomers for polymers.¹⁴ The production of diacids using CO₂ as the carboxyl source is a sustainable strategy, but only limited methods have been developed to date.¹⁵ Traditionally, electrochemical dicarboxylation of alkenes with CO₂ has been investigated, but these processes generally require a sacrificial anode.^{15,16} In addition, Martin and co-workers reported a Ni-catalyzed site-selective dicarboxylation of 1,3-dienes with CO₂, which used stoichiometric Mn as the reductant.¹⁷ In 2021, the group of Yu reported an elegant dicarboxylation of alkenes with CO₂ via a sequential single electron transfer (SSET) process, in which the reduction of the alkene substrate to a radical anion intermediate was the key step.¹⁸ Recently, the same group disclosed a remote

Scheme 1. The Development of Dicarboxylation of Alkenes with Formate and CO₂



dicarboxylation of alkene and benzylic C(sp³)–H bond via an intramolecular HAT.¹⁹ However, amine terminal reductants were necessary for these two transformations. Given the challenge of direct CO₂ reduction^{3,15,20} and the low cost of the formate salt that possessed dual role in our preliminary results of dicarboxylation (Scheme 1a,b),² we envisioned using the formate for alkene dicarboxylation to obtain diacids in a redox-economical and practical manner.²¹

Herein, we report a visible-light-induced dicarboxylation of diverse alkenes with CO₂ using formate as a low-cost reductant and part of the carboxyl source. Notably, simple styrenes were well tolerated, and the reaction could be performed under mild conditions at ambient temperature and pressure of CO₂. Importantly, the highly competing hydrocarboxylation side reaction was successfully overridden.

RESULTS AND DISCUSSION

Table 1. Optimization of Reaction Conditions^a

entry	deviations from standard conditions	2a yield [%]	2aH yield [%]
1	none	91% ^b	--
2	in the dark	--	--
3	w/o 3DPAFIPN	--	--
4	w/o HCOOK	--	--
5	w/o DABCO	32%	28%
6	w/o CO ₂ (N ₂ atmosphere)	--	76%
7	w/o K ₃ PO ₄	40%	12%
8	w/o Cs ₂ CO ₃ ; K ₃ PO ₄ (3 equiv)	44%	50%
9	w/o Cs ₂ CO ₃ and K ₃ PO ₄	11%	66%
10	HCOONa instead of HCOOK	70%	--
11	quinuclidine instead of DABCO	40%	--
12	4DPAIPN instead of 3DPAFIPN	65%	--
13	4CzIPN instead of 3DPAFIPN	39%	--
14	3DPAFIPN (2.0 mol %)	70%	--
15	3DPAFIPN (4.0 mol %)	86%	--
16	THF instead of DMSO	16%	--
17	DMA instead of DMSO	17%	--

^aReaction conditions: **1a** (0.2 mmol), 3DPAFIPN (6.2 mol %), DABCO (0.06 mmol), Cs₂CO₃ (0.6 mmol), K₃PO₄ (0.4 mmol), HCOOK (0.6 mmol) in DMSO (2 mL), 1 atm CO₂, 30 W blue LEDs, rt (25–33 °C), 24 h; then treated with 2 mL of HCl (2 N). Yield was determined by ¹H NMR with CH₂Br₂ as internal standard. ^bIsolated yield was 88%. 3DPAFIPN = 2,4,6-tris(diphenylamino)-5-fluoroisophthalonitrile; DABCO = triethylenediamine.

Our investigation began with using 1,1-diphenylethylene (**1a**) as the model substrate, which was treated with 30 W blue LEDs irradiation in the presence of a PC and an atmospheric pressure

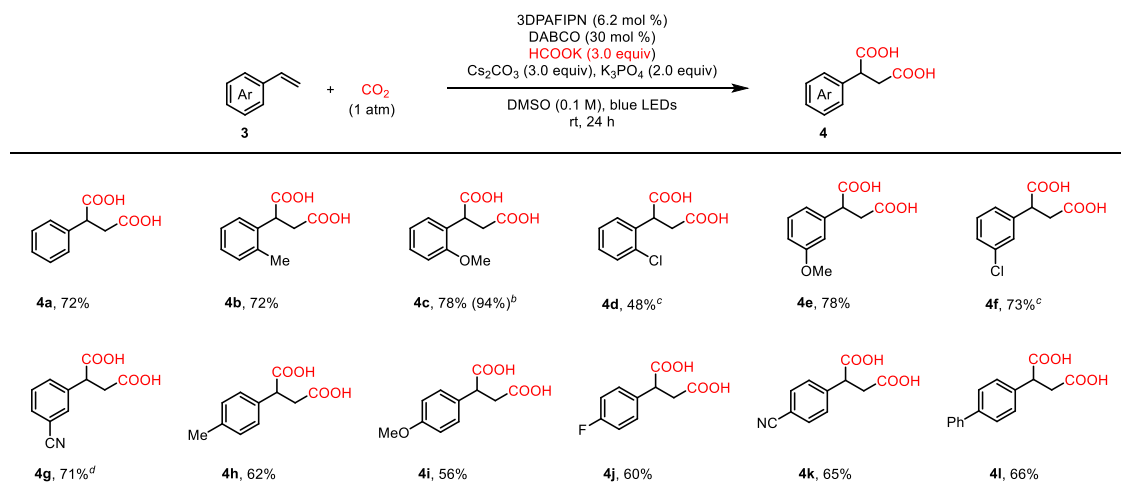
of CO₂ at ambient temperature (Table 1). After extensive investigation of the reaction conditions, the desired dicarboxylation product **2a** was generated in an 88% isolated yield using 3DPAFIPN as the PC in the presence of the HAT catalyst DABCO with HCOOK as the terminal reductant and Cs₂CO₃ and K₃PO₄ as the cooperative bases in DMSO (entry 1).²² No product was found in the absence of either visible light or the PC, indicating the reaction was a photocatalytic reaction (entries 2 and 3). Importantly, HCOOK was essential for the reaction (entry 4). Surprisingly, in the absence of DABCO, a modest yield of the desired product **2a** was obtained along with some hydrocarboxylation side-product **2aH**, suggesting that more than one HAT processes might be involved in this reaction (entry 5). Interestingly, only hydrocarboxylation product was received under nitrogen atmosphere without adding CO₂ (entry 6), suggesting HCOOK was also one of the carboxyl sources. Moreover, the addition of suitable bases was important to achieve a high yield of the desired product (entries 7–9, also see Supporting Information (SI) for screening of other bases). Other formates such as HCOONa were also used, but they were less effective than HCOOK (entry 10). Other HAT catalysts such as quinuclidine were also evaluated, but they were inferior to DABCO (entry 11).²³ Other PCs such as 4DPAIPN and 4CzIPN were also tested, but worse results were obtained (entries 12 and 13). In addition, lower yields were delivered while reducing the loading of 3DPAFIPN (entries 14 and 15). Finally, DMSO was the best solvent of all those used such as THF and DMA (entries 16 and 17).

With the optimized reaction conditions in hand, we first examined this protocol with a variety of 1,1-disubstituted ethylenes (Table 2). Good to excellent yields of desired dicarboxylation products were received with model substrate **1a** and mono- or di-substituted 1,1-diarylethylenes bearing a list of functional groups at *ortho*-, *meta*- or *para*-positions of the phenyl groups (**2a–2k**). Both electron-donating methyl (**2b**, **2d**, **2f**, and **2g**), methoxy (**2h**, **2i**, and **2k**) substituents and electron-

Table 2. Scope of 1,1-disubstituted ethylenes and acrylates^a

^aReaction conditions: **1** (0.2 mmol), 3DPAFIPN (6.2 mol %), DABCO (0.06 mmol), Cs₂CO₃ (0.6 mmol), K₃PO₄ (0.4 mmol), HCOOK (0.6 mmol) in DMSO (2 mL), 1 atm CO₂, 30 W blue LEDs, rt (25–33 °C), 24 h; then treated with 2 mL of HCl (2 N). Isolated yields. ^bYield of 1 mmol scale reaction (52 h). ^cMajor product 3,4-dicarboxylation product (**2q_a**, 37%) displayed; minor product: 1,4-dicarboxylation product (**2q_b**, 17%).

Table 3. Scope of Styrenes^a



^aReaction conditions: **3** (0.2 mmol), 3DPAFIPN (6.2 mol %), DABCO (0.06 mmol), Cs₂CO₃ (0.6 mmol), K₃PO₄ (0.4 mmol), HCOOK (0.6 mmol) in DMSO (2 mL), 1 atm CO₂, 30 W blue LEDs, rt (25–33 °C), 24 h; then treated with 2 mL of HCl (2 N). Isolated yields. ^bReaction temperature: 40–45 °C. ^cDesired product displayed; de-chlorination product (18% for **4d**, 16% for **4f**) not shown. ^dAbout 6% hydrocarboxylation side product.

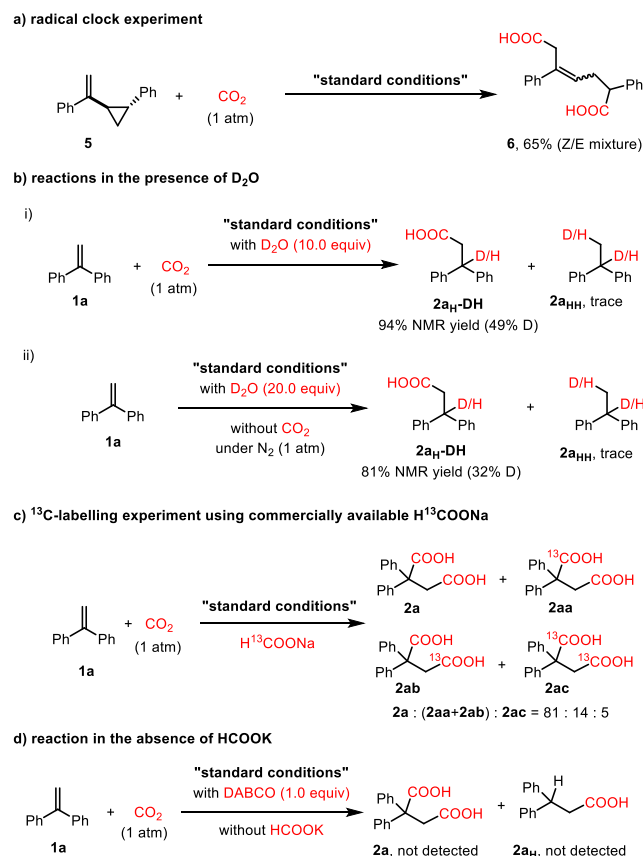
withdrawing fluoro (**2c** and **2j**), trifluoromethyl (**2e**) ones were tolerated. Moreover, thiofuran group was also compatible with this method. Other di-substituted ethylenes (**2m**, **2n**, and **2o**) and even a tri-substituted one (**2p**) were also viable to deliver acceptable yields of products. Note that the reaction with a diene substrate (**1q**) would give both 3,4-dicarboxylation and 1,4-dicarboxylation products. Finally, good results were obtained with methacrylates (**2r** and **2s**), although only a modest yield was obtained with a 2-benzylacrylate (**2t**).

We then moved on to investigate the scope of the more challenging simple styrenes, leading to generally good yields with a variety of substituted styrenes regardless of the electronic property and the position of the substituent on the aromatic ring. It should be noted that in Zhu's work, only very narrow scope of simple styrenes were tolerated with low yields.²² As shown in Table 3, the un-substituted styrene **3a** and the *ortho*-substituted styrenes with electron-donating methyl (**3b**) and methoxyl (**3c**) groups proceeded smoothly and gave good yields of the desired products. Notably, the yield of **4c** could be increased to 94% by slightly elevating the reaction temperature to 40–45 °C. Moderate yield was obtained with substrate **3d** bearing an *ortho*-chloro group, since some de-chlorination occurred. In addition, both electron donating (**4e**) and withdrawing (**4f** and **4g**) groups were well tolerated at the *meta*-position. Finally, good results were also obtained with substrates containing several representative substituents at the *para*-position of the phenyl ring (**4h–4l**). It is noteworthy that the hydrocarboxylation side product was not detected or only in trace amounts, and only substrate **3g** led to 6% of the hydrocarboxylation side product.

To obtain insights into the reaction mechanism, several control experiments were then carried out (Scheme 2). Ring-opening product **6** was afforded in the radical clock experiment, indicating a benzyl radical might be generated after CO₂^{•−} addition to the alkene (Scheme 2a). When the reaction was run in the presence of D₂O, hydrocarboxylation product **2a_H-DH** was produced instead of dicarboxylation with traces of reduction product **2a_{HH}**, indicating the formation of a benzylic anion intermediate and that the formation of anion at the alkene terminal position was trivial (Scheme 2bi). Similar results were received while the reaction was carried out without the addition of CO₂

gas (Scheme 2bi). The low deuteration ratio at the benzylic position in these two reactions (49% and 32%, respectively) might suggest a HAT process between benzylic radical and formate was also involved except the protonation of the benzylic anion under current reaction conditions. In addition, four possible dicarboxylation products were obtained when using ¹³C-labelled formate (i.e. commercially available H¹³COONa),²⁴ suggesting

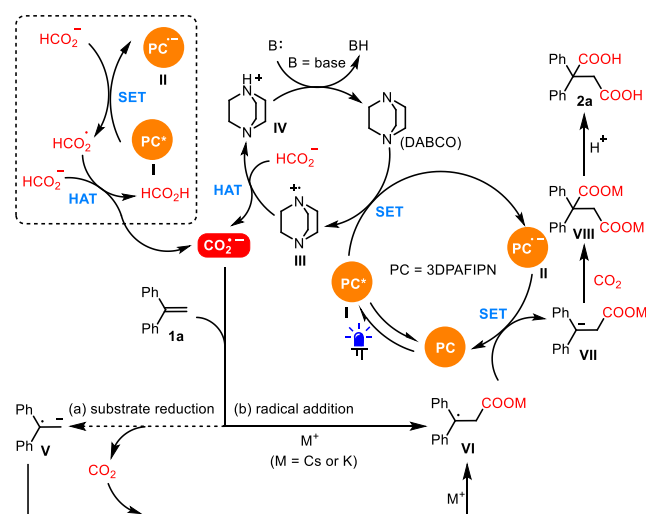
Scheme 2. Mechanistic Study Experiments



formate was also part of the carboxyl source (Scheme 2c). Moreover, no carboxylation products were detected when the reaction was performed using a stoichiometric amount of DABCO without formate, indicating the reduced 3DPAFIPN could not reduce the substrate **1a** or CO₂ to initiate the reaction (Scheme 2d). Finally, the Stern-Volmer quenching experiments showed the activated catalyst (PC*) was mainly quenched by DABCO, but it could also be slightly quenched by HCOOK (see SI).

Based on the above mechanistic studies, a possible catalytic cycle was proposed (Scheme 3). Upon blue light irradiation, the excited PC* (**I**) is generated and then quenched by DABCO to form PC^{•-} (**II**) ($E_{1/2}(\text{PC}^*/\text{PC}^{\bullet-}) = +1.09 \text{ V vs SCE in MeCN}$)²⁵ and radical cation of DABCO (**III**). A HAT between radical **III** and HCO₂⁻ produces CO₂^{•-} and cation **IV**. Alternatively, CO₂^{•-} can be partially generated by a HAT process between HCO₂⁻ and HCO₂[•] that is produced by reducing PC* with HCO₂⁻ ($E_{\text{ox}}(\text{HCO}_2^{\bullet}/\text{HCO}_2^-) = +1.25 \text{ V vs SCE}$)^{4b}, considering the results of Stern-Volmer quenching experiments with formate (see Figure S5 of SI) and the fact that some product could be received without DABCO (see entry 5 in table 1). Subsequently, CO₂^{•-} may reduce the substrate ($E^{\circ} = -2.25 \text{ V vs SCE for 1a}$)²⁶ to give radical anion **V**, considering product **2a** was the major product in the ¹³C-labelling experiment of Scheme 2c. However, the direct addition of CO₂^{•-} to the double bond of **1a** to afford intermediate **VI** is more likely based on the results in Scheme 2b. In this scenario, a potential facile electron transfer between ¹³CO₂^{•-} and the excess CO₂ may account for the observation of **2a** as the main product in Scheme 2c. Moreover, since the reduction of simple styrenes ($E_{1/2} = -2.58 \text{ V vs SCE in DMF for 3a}$)²⁷ is more demanding than **1a**, direct CO₂^{•-} addition is possibly the predominant pathway for substrates in Table 3. The radical intermediate **VI** was then reduced by PC^{•-} (**II**) to give the anion **VII**, which undergoes nucleophilic attack of CO₂ to afford the final product **2a** after acidification of the salt intermediate **VIII**.

Scheme 3. Proposed Catalytic Cycle



CONCLUSIONS

In conclusion, we have developed a visible-light-driven alkene dicarboxylation using formate and CO₂, overriding the highly competing hydrocarboxylation side reaction successfully. Good yields of products were obtained with diverse alkenes including simple styrenes under mild reactions at ambient

temperature. The dual role of the low-cost formate as a reductant and the C1 source may open up the discovery of a range of new transformations including indirect utilization of CO₂ under mild and friendly conditions.

ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interest.

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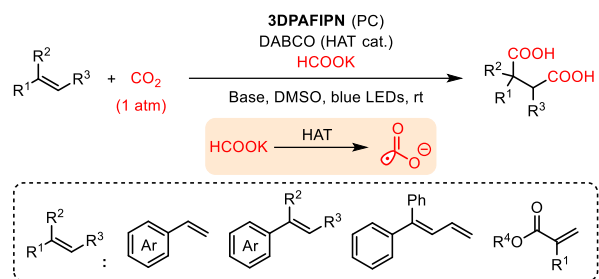
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