



Regioselective oxidative ring-opening of cyclopropenyl carboxylates by visible light photoredox catalysis



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ABSTRACT

Catalyzed by Ir(dFCF₃ppy)₂(dtbbpy)PF₆, several aroyl methylidenemalonates were synthesized in good to excellent yields via visible light photoredox-catalyzed the oxidative ring-opening of cyclopropenyl carboxylate derivatives. The possible mechanism of oxidative quenching cycle was proposed.

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Introduction

Visible light catalysis has attracted tremendous attention from chemists owing to its wide applications in organic synthesis and its significance in sustainable chemistry.¹ Without stoichiometric activated reagents, this catalytic strategy make it easier to get access to various radical ions and/or radicals by photo-excited single electron-transfer under very mild conditions.^{2,3} These highly active *in situ* formed intermediates could participate in the innovative valuable reactions and transform into numerous interesting molecules in a controllable manner.⁴ Among the various reactions mediated by visible light catalysis, the oxidation of carbon-carbon double bonds and its subsequent transformation have drawn much attention. For example, Yoon group reported several [2+2] cross-cycloadditions through the photocatalytic oxidation of olefins to give a range of cyclobutane derivatives.⁵ Most noteworthy was that the oxidative dehydrogenative coupling of alkenes induced by photo-oxidation was also explored, such as the selective oxidative [4+2] annulation of imine and alkene for the synthesis of substituted dihydroisoquinolines,^{6a} the C–H/C–H cross-coupling between electron-rich arenes and styrene derivatives affording various substituted aryl alkenes,^{6b} and the cross-coupling of alkenes with alcohols or azoles generating multi-substituted enol ether.^{6c}

Cyclopropenes, the smallest unsaturated carbocycles, are readily prepared molecules. Because of the highly strained double bond, they have unique and higher reactivity than olefins, allenes and alkynes.⁷ With regard to the many types of cyclopropenes, substituted cyclopropene carboxylates have frequently been the focus of study. They easily undergo intramolecular cyclizations⁸ as well as C–C bond cleavage⁹ to arouse ring expansion and afford ring-opening products. Substantive studies showed that the 1,3 or 2,3 carbon-carbon bond cleavage of cyclopropene carboxylates is feasible, which gave totally different products. Under the nucleophilic attack of Grignard reagents,^{9c} halide ions,¹⁰ organolithium,^{8b,9b} organocuprate,^{9c} the 2,3 cleavage of cyclopropene carboxylates was attained extensively. In contrast, reports regarding the 1,3 bond cleavage of cyclopropylene carboxylates were very rare. For instance, the tri- and tetrasubstituted alkenes were synthesized by Fe(acac)₃-catalyzed ring-opening reactions of cyclopropene carboxylates with trialkylaluminum reagents.^{9a} Ma reported the ring-opening cycloisomerization of cyclopropenyldicarboxylates for the synthesis of 2,3,5-trisubstituted furans via tri(2-furanyl) phosphine catalysis.^{8a} On the other hand, aroyl methylidenemalonates have found a wide range of applications due to their bioactive¹¹ and pharmaceutical significance.¹² They can be used as Michael acceptors or starting materials for the synthesis of different compounds such as pyrroles,^{13a} furans,^{13b} pyridazines,¹⁴ indoles,¹⁵ enonediester,¹⁶ oxazoles,¹⁷ and etc. Generally, the preparation of aroyl methylidenemalonates was achieved by (1) BF₃·OEt₂-mediated ring-opening of D-A nitrocyclopropanes;^{18a} (2) one-pot reaction of 2-diazomalonate with

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epoxypropane catalyzed by $\text{Rh}_2(\text{OAc})_4$ and subsequently Wittig olefination¹⁶; and (3) oxidative radical reaction of aryl-substituted allenes with dimethylmalonate catalyzed by $\text{Mn}(\text{OAc})_3$.^{18b} Although these procedures are all good, they have also some obvious shortcomings such as multistep reactions, inaccessible starting materials and etc.

Result and discussion

Herein we wish to report a facile access to aroyl methylidene-malonate derivatives via visible light photocatalytic regioselective ring-opening reaction of cyclopropenyl carboxylates.

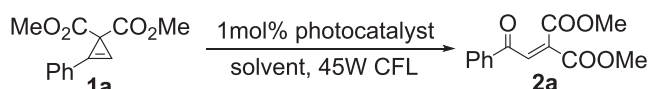
In order to obtain optimal conditions for the synthesis of aroyl methylidenemalonate derivatives, a variety of conditions were attempted (Table 1). Firstly dimethyl 2-phenylcycloprop-2-ene-1,1-dicarboxylate **1a** with 1 eq of PhN_2BF_4 in the presence of 1 mol% $\text{Ir}(\text{ppy})_3$ was illuminated under air by a 45 W white CFL at room temperature (entry 1). To our delight, the reaction afforded the desired **2a** in 36% yield. Without PhN_2BF_4 , the reaction turned to be complicated and several unidentified by-products could be observed (entry 2). Then several oxidants were examined. CBr_4 , CCl_4 and $\text{Na}_2\text{S}_2\text{O}_8$ all worked (entries 3–5). And 67% yield of **2a** could be obtained when $\text{Na}_2\text{S}_2\text{O}_8$ was used as an oxidant (entry 5). However, the reaction did not proceed well with $\text{K}_2\text{S}_2\text{O}_8$ or $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (entries 6–7). Catalyzed by $\text{Ru}(\text{bpy})_3(\text{BF}_4)_2$ or $\text{Ru}(\text{bpy})_3\text{Cl}_2$, moderate yield of **2a** was obtained with $\text{Na}_2\text{S}_2\text{O}_8$ as the oxidant (entries 8–9). It occurred to us that if the oxidizing ability of the photocatalyst was strong enough, the desired transformation may proceed as well even in the absence of extra oxidant. Based on the redox potential values of the photocatalysts,¹⁹ $\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ ($E_{1/2\text{III}^*/\text{II}} = +1.21\text{ V}$ vs SCE in CH_3CN) and $\text{Ru}(\text{bpz})_3(\text{PF}_6)_2$ ($E_{1/2\text{III}/\text{II}} = +1.86\text{ V}$ vs SCE in CH_3CN) were attempted under O_2 atmosphere (entries 10–11). To our delight, the desired target product could be obtained in 52% yield with $\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ as the catalyst (entry 11). Almost no **2a**

was observed in the absence of light or photocatalyst (entry 12). Under the illumination of 7 W blue LED for 6hrs the target product was isolated in 63% yield (entry 13). The reaction could not proceed under N_2 atmosphere (entry 14). When the reaction was carried out in DMSO, DMF and THF, only complicated mixtures were obtained. Other solvents such as DCM, diethyl ether, toluene, MeCN, or acetone, could give **2a** in 42%, 10%, 50%, 52% and 53% yield respectively. Moreover, when 1–3 equiv. of water was added to the absolute DCE, the yield is almost same as the results of entries 3–5 which the AR grade DCE was used as the solvent (entry 15).

To explore the scope of the reaction, a series of cyclopropenyl carboxylates were tested under the optimized conditions (Scheme 1). The *para*-halogen on the aryl of **1** generated the corresponding products **2b**, **2c** or **2d** in moderate to reasonable yields. Substrates **1** with an aryl substituted by electron-donating group at the *para* position, such as Me, $n\text{-C}_5\text{H}_{11}$, *t*-Bu or MeO, afforded good yields (**2e–2h**). The target product **2j** was isolated in 90% yield when the substrate bearing 2-MeO on the phenyl ring was used, which showed no obvious steric effect on the reaction. Especially heterocyclic substituted dimethyl 2-(3-thienyl)cycloprop-2-ene-1,1-dicarboxylate **1i** also underwent the reaction smoothly to afford **2i** in 77% yield. When the ethyl, *i*-propyl and *t*-butyl esters were used as the substrates, moderate yields were also obtained (**2l–2n**). Unfortunately alkyl substituted substrate dimethyl 2-*n*-hexylcycloprop-2-ene-1,1-dicarboxylate is inert in this reaction, which was in accordance with the results reported.²⁰

It is worth mentioning that methyl 1,2-diphenylcycloprop-2-ene-1-carboxylate **3** could not give the corresponding oxidative ring-opening product (Scheme 2). Instead, the 2-oxo-2-phenylacetic acid methyl ester **4** and methyl benzoate **5** were obtained in 63% and 12% yields, respectively, which may be formed by the oxidative cleavage of ring opening product and subsequent intermolecular transesterification. Without additional oxidant CBr_4 , the reaction could not proceed.

Table 1
Optimization of the reaction conditions.^a



Entry	Photocatalyst	oxiDant	Time/h	Yield (%) ^b
1	$\text{Ir}(\text{ppy})_3$	PhN_2BF_4	14	36
2	$\text{Ir}(\text{ppy})_3$	–	4	16
3	$\text{Ir}(\text{ppy})_3$	CBr_4	10	65
4	$\text{Ir}(\text{ppy})_3$	CCl_4	14	65
5	$\text{Ir}(\text{ppy})_3$	$\text{Na}_2\text{S}_2\text{O}_8$	24	67
6	$\text{Ir}(\text{ppy})_3$	$\text{K}_2\text{S}_2\text{O}_8$	24	26
7	$\text{Ir}(\text{ppy})_3$	$(\text{NH}_4)_2\text{S}_2\text{O}_8$	24	trace
8	$\text{Ru}(\text{bpy})_3(\text{BF}_4)_2$	$\text{Na}_2\text{S}_2\text{O}_8$	2	48
9	$\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$	$\text{Na}_2\text{S}_2\text{O}_8$	2	46
10	$\text{Ru}(\text{bpz})_3(\text{PF}_6)_2$	O_2	24	20
11	$\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$	O_2	5	52
12 ^c	$\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$	O_2	36	trace
13 ^d	$\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$	O_2	6	63
14 ^e	$\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$	–	36	trace
15 ^f	$\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$	O_2	10	see footnote

^a **1a** (0.3 mmol), oxidant (0.3 mmol), photocatalyst (0.003 mmol, 1 mol%), 4 mL DCE (AR), 45 W compact fluorescent light (CFL) irradiation under O_2 at room temperature unless otherwise noted.

^b Yield of isolated product based on **1a**.

^c No photocatalyst or no light.

^d 7W blue LED instead of 45 W CFL.

^e Under N_2 atmosphere.

^f Distilled water (1 eq, 2 eq, 3 eq) was added to absolute DCE to give the product in 70%, 73%, 74% yield respectively.

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