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Alkoxy carbonyl radicals from alkyloxalyl chlorides: photoinduced synthesis of isoquinolinediones under visible light irradiation†

Mingjuan Ji,‡^a Liang Xu,‡^a Xiangxiang Luo,^a Minghui Jiang,^a Siyu Wang,^a Jian-Qiang Chen*^a and Jie Wu *^{a,b,c}Received 13th September 2021.
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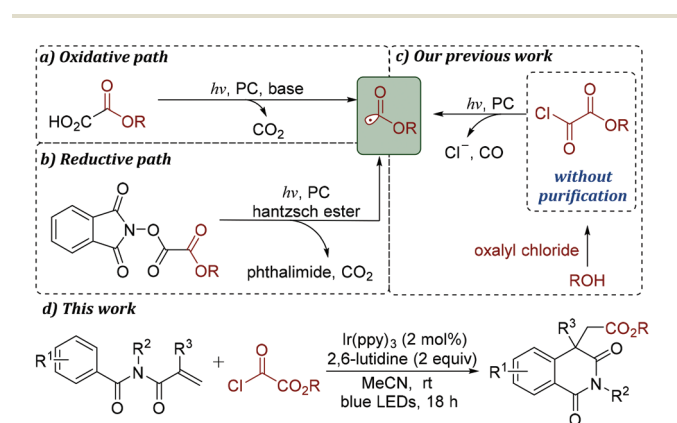
Alkyloxalyl chlorides, generated from alcohols and oxalyl chlorides, are used as alkoxy carbonyl radicals in the reaction of *N*-acryloyl benzamides under photocatalysis at room temperature. In this report, we demonstrate that this approach can be compatible with a variety of alcohol-containing pharmaceutically active compounds under visible light irradiation. A variety of isoquinoline-1,3(2*H*,4*H*)-diones are prepared in moderate to good yields.

Carbonylation reactions are of crucial importance in the field of modern organic synthesis since they provide access to carbonyl-containing derivatives, such as ketones, amides and carboxylic esters, which play an important role in fields ranging from organic chemistry to medical and pharmaceutical sciences.¹ In these fields, acyl/carbamoyl/alkoxy carbonyl radicals are useful reactive intermediates which can be combined with carbon fragments to obtain unique carbonyl-containing derivatives.² So far, many methods for the generation and application of acyl/carbamoyl radicals have been reported.^{3–12} For example, acyl radicals can be obtained either by single-electron reduction of acyl chlorides,⁴ anhydrides,⁵ and hypervalent iodine reagents,⁶ or upon oxidation of α -ketoacids⁷ and acyl silanes.⁸ Carbamoyl radicals can also be generated from the corresponding 4-carbamoyl dihydropyridines,⁹ *N*-hydroxyphthalimido oxamides,¹⁰ oxalate monoamides¹¹ and carbamoyl chlorides¹² in the presence of a photocatalyst under visible light irradiation.

However, compared with acyl/carbamoyl radicals, alkoxy carbonyl radicals have remained largely unexplored.¹³ Although alkoxy carbonyl radicals can attack unsaturated C–C bonds leading to carboxylic esters, the concurrent decarboxylation step to form stable tertiary carbon radicals often plays a domi-

nant role in synthesis. Thus, much effort has been devoted to alkoxy carbonyl radical decarboxylation through photocatalysis in recent years.¹⁴

Traditionally, alkoxy carbonyl radicals can be generated most commonly from the corresponding xanthates and selenides.¹⁵ Additionally, these radicals can also be formed from carbazates by treatment with metal catalysts and stoichiometric quantities of oxidants.¹⁶ Recently, it was reported that alkoxy carbonyl radicals could be produced by photoredox-catalyzed fragmentation of alkyl oxalates and methyl *N*-phthalimidoyl oxalates (Schemes 1a and b).^{13,14} The existing approaches for providing alkoxy carbonyl radical precursors often require multistep synthetic processes. Thus, the development of a robust strategy for the rapid generation of alkoxy carbonyl radicals under mild conditions, especially using readily available and inexpensive substrates, is highly desirable.



Scheme 1 Generation of alkoxy carbonyl radicals under photoredox catalysis.

^aSchool of Pharmaceutical and Materials Engineering & Institute for Advanced Studies, Taizhou University, Taizhou 318000, China. E-mail: chenjq@tzcu.edu.cn, jie_wu@fudan.edu.cn

^bState Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

^cSchool of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453007, China

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‡These authors contributed equally.

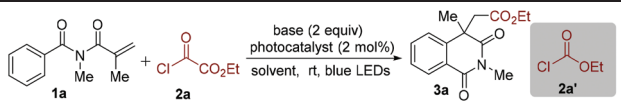
Xu and co-workers disclosed that single-electron reduction of aroyl chlorides with a photocatalyst would provide aroyl radicals.⁴ Inspired by this result, we expected that it might be possible to find a novel strategy for the generation of alkoxy-carbonyl radicals from the corresponding acyl chloride under photocatalysis. Recently, we have reported that alkyloxalyl chlorides, generated *in situ* from the corresponding oxalyl chloride and alcohols, can be used as alkoxy-carbonyl radical fragments under photoredox catalysis (Scheme 1c).¹⁷ To further demonstrate the advantage of this conversion, a variety of isoquinoline-1,3(2*H*,4*H*)-diones are prepared in moderate to good yields (Scheme 1d). An important feature of this alkoxy-carbonylation/cyclization reaction is the capacity of alkyloxalyl chlorides to produce alkoxy-carbonyl radicals through single-electron reduction/CO extrusion.

To verify the practicability of the above hypothesis, commercially available ethyl chlorooxoacetate (**2a**)¹⁸ as the alkoxy-carbonyl radical precursor and *N*-methacryloyl-*N*-methylbenzamide (**1a**) as the radical trapper were selected as substrates for reaction development (Table 1). The reactions were performed at room temperature under visible light irradiation with a blue LED strip in the presence of Ir(ppy)₃ as the photocatalyst. Since HCl would be released during the reaction process, 2,6-lutidine was added as the base. Gratifyingly, the desired alkoxy-carbonylation/cyclization product (**3a**) was obtained in good yield (70%) (Table 1, entry 1). This result demonstrated that our design was feasible and promising. The yield of compound **3a** was decreased to 37% when Ir(ppy)₂(dtbbpy)PF₆ was used as the photocatalyst (Table 1, entry 2). The donor-acceptor-type photocatalyst 3DPA2FBN, which is a strongly reducing organic photocatalyst,¹⁹ provided a lower yield (Table 1, entry

3). Next, the solvent effect was evaluated (Table 1, entries 4–7) and it was found that acetonitrile was the optimal reaction medium, giving rise to the corresponding product **3a** in 76% yield (Table 1, entry 6). Subsequently, other bases were screened, and the result showed that inorganic bases were less efficient, while 2,6-di-*tert*-butylpyridine was comparably effective. Additionally, blank experiments demonstrated that both a photocatalyst and visible light were necessary for this alkoxy-carbonylation/cyclization reaction (Table 1, entries 12 and 13). Meanwhile, the reaction could not occur when ethyl chloroformate (**2a'**) was used as the alkoxy-carbonyl radical source (Table 1, entry 14). This result might be rationalized by the more negative reduction potential of alkyl chloroformates than the excited-state photocatalyst. With the optimized conditions in hand, we then investigated the scope of *N*-acryloyl benzamides in this reaction. As shown in Table 2, it was found that a wide range of *N*-methacryloyl benzamide derivatives bearing electron-donating (methyl, methoxy, *tert*-butyl and dimethyl) and electron-withdrawing (F, Cl and Br) substituents in the aromatic ring were suitable substrates for this transformation. Notably, reactions of *para*-*t*-butyl- and 3,5-dimethyl-substituted substrates afforded the acyl migration products **3e'** and **3f'**, respectively. Substrates bearing different alkyl groups at the *N*-position of amides could readily convert into the isoquinoline-1,3(2*H*,4*H*)-diones (**3i–3t**). The excellent functional group tolerance of –Bn (**3o**), –CN (**3p**), and –CO₂Et (**3q**), and a terminal unsaturated bond (**3r**) supported the practicality of this reaction. Additionally, chiral *N*-methacryloyl benzamides served as radical trappers in this alkoxy-carbonylation/cyclization reaction, leading to the chiral isoquinoline-1,3(2*H*,4*H*)-diones (**3s** and **3t**) in moderate yields. Acrylamides with a benzyl and phenyl group at the α-position converted into the target products **3u** and **3v** as well. To demonstrate the practicability of this alkoxy-carbonylation/cyclization reaction, a gram-scale experiment was carried out, which provided the corresponding product **3a** in 62% yield.

Subsequently, various alkyloxalyl chlorides were examined, giving rise to the results shown in Table 3. It was found that alkyloxalyl chlorides generated directly from the corresponding alcohols could smoothly provide the alkoxy-carbonyl radicals. The yield of the alkoxy-carbonylation/cyclization product decreased to 85% (**4a** vs. **3p**) when methyl oxalyl chloride was used as the radical precursor in the reaction with *N*-(2-cyanoethyl)-*N*-methacryloyl benzamide **1p**. Further underscoring the compatibility of this transformation, some alkyloxalyl chlorides were obtained by treatment of alcohols with a slight excess of oxalyl chloride in DCM, which were employed in this radical cascade reaction after the removal of the solvent and the excess oxalyl chloride.²⁰ The alkyloxalyl chloride derived from long-chain aliphatic alcohols was found to be successful in this transformation (**4b**). To further demonstrate the synthetic robustness of this conversion, we applied this approach for the construction of a series of diversely functionalized isoquinoline-1,3(2*H*,4*H*)-diones. Chlorooxoacetates derived from natural products including menthol (product **4c**, 80% yield), (–)-borneol (product **4d**, 58% yield), β-cholestanol (product **4e**,

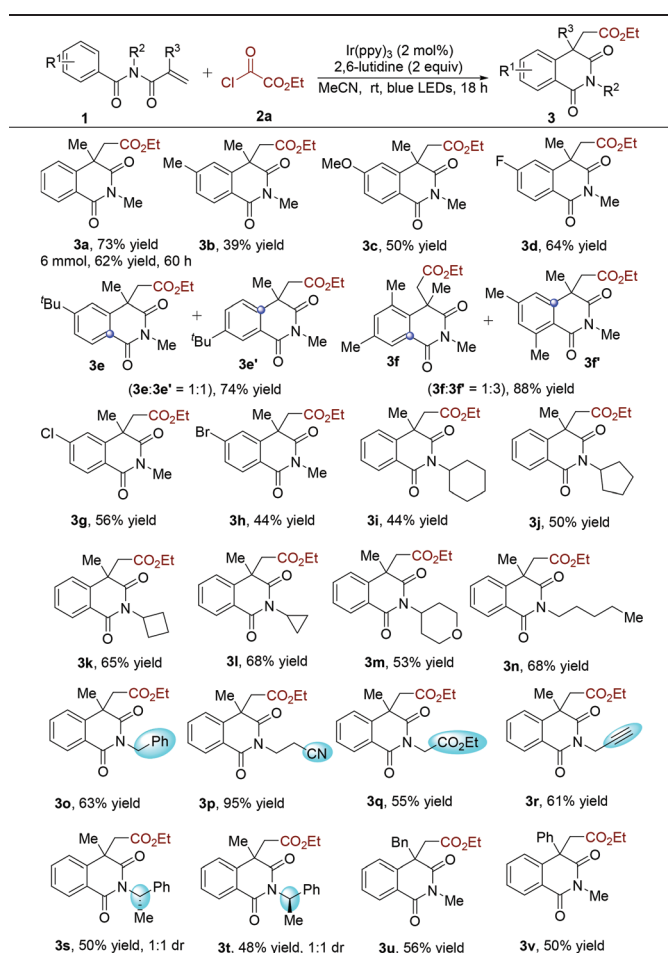
Table 1 Optimization of reaction parameters^{a,b}



Entry	PC	Solvent	Base	Time	3a (%)
1	Ir(ppy) ₃	DMF	2,6-Lutidine	12 h	70
2	Ir(ppy) ₂ (dtbbpy)PF ₆	DMF	2,6-Lutidine	12 h	37
3	3DPA2FBN	DMF	2,6-Lutidine	12 h	47
4	Ir(ppy) ₃	MeCN	2,6-Lutidine	18 h	76
5	Ir(ppy) ₃	THF	2,6-Lutidine	36 h	14
6	Ir(ppy) ₃	DCM	2,6-Lutidine	48 h	30
7	Ir(ppy) ₃	EA	2,6-Lutidine	48 h	17
8	Ir(ppy) ₃	MeCN	2,6-di ^t Bu-Py	18 h	70
9	Ir(ppy) ₃	MeCN	K ₂ HPO ₄	18 h	51
10	Ir(ppy) ₃	MeCN	Na ₂ HPO ₄	18 h	19
11	Ir(ppy) ₃	MeCN	KHCO ₃	18 h	16
12	—	MeCN	2,6-Lutidine	18 h	0
13 ^c	Ir(ppy) ₃	MeCN	2,6-Lutidine	18 h	0
14 ^d	Ir(ppy) ₃	MeCN	2,6-Lutidine	18 h	0

^a Unless otherwise noted, reaction conditions are as follows: **1a** (0.2 mmol), **2a** (0.6 mmol), photocatalyst (0.004 mmol), base (0.4 mmol), solvent (4 mL), and 36 W blue LEDs under a N₂ atmosphere. ^b Yield determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. ^c In the dark. ^d Compound **2a'** was used instead of ethyl chlorooxoacetate **2a**.

Table 2 Photoinduced synthesis of isoquinolinediones under visible light irradiation from *N*-acryloyl benzamides and ethyl chlorooxoacetates^a

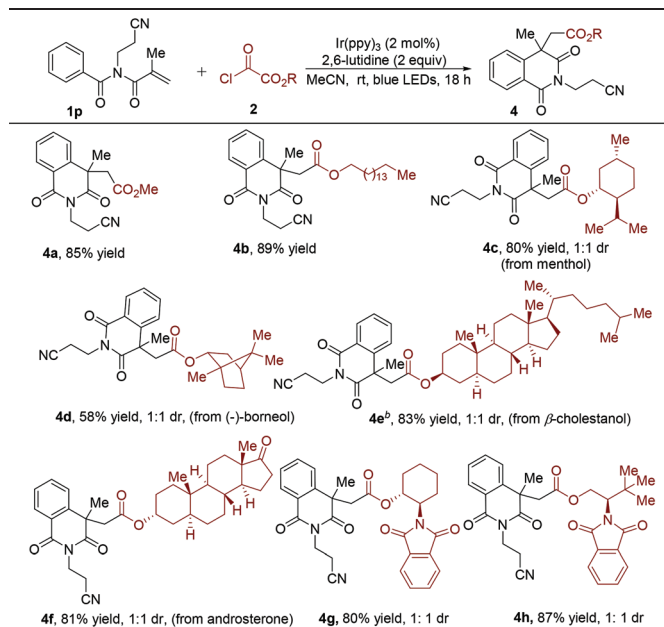


^a Unless otherwise noted, reaction conditions are as follows: **1** (0.2 mmol), **2a** (0.6 mmol), Ir(ppy)₃ (0.004 mmol), 2,6-lutidine (0.4 mmol), MeCN (4 mL), and 36 W blue LEDs under a N₂ atmosphere.

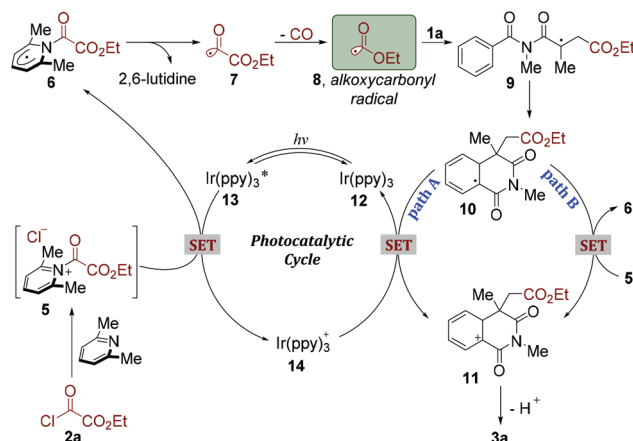
83% yield) and androsterone (product **4f**, 81% yield) were workable as well. Chiral amino alcohol derivatives were satisfactory starting materials and could uniformly produce the synthetically valuable isoquinoline-1,3(2*H*,4*H*)-diones with good yields (**4g** and **4h**).

As mentioned above, the control experiments demonstrated that both visible light and photocatalyst were crucial for this alkoxyacylation/cyclization reaction. On the basis of these results and previous reports,^{17,21} we proposed a plausible mechanism as depicted in Scheme 2. Ethyl chlorooxoacetate (**2a**) could react with 2,6-lutidine to afford the corresponding acyl pyridinium salt (**5**).²² On the other hand, this photocatalytic cycle was initiated by the excitation of the photocatalyst Ir(ppy)₃ (**12**) to the excited-state photocatalyst Ir(ppy)₃^{*} (**13**),²² which subsequently transferred a single electron to acyl pyridinium salt (**5**) to generate radical **6**. Homolysis of the C–N bond would liberate 2,6-lutidine and produce acyl radical **7**.²²

Table 3 Photoinduced synthesis of isoquinolinediones under visible light irradiation from *N*-acryloyl benzamide **1p** and alkoxyalyl chlorides^a



^a Unless otherwise noted, reaction conditions are as follows: **1p** (0.2 mmol), **2** (0.6 mmol), Ir(ppy)₃ (0.004 mmol), 2,6-lutidine (0.4 mmol), MeCN (4 mL), and 36 W blue LEDs under a N₂ atmosphere. ^b DMF was used instead of MeCN.



Scheme 2 Proposed mechanism.

The highly activated acyl radical **7** could rapidly go through CO extrusion and provide a stabilized alkoxyacyl radical **8**. Radical **8** would then react with *N*-methacryloyl-*N*-methylbenzamide (**1a**), giving rise to a tertiary carbon radical intermediate **9**. Subsequently, a radical-arene cyclization would occur leading to radical intermediate **10**, which was readily oxidized by Ir(ppy)₃⁺ to generate a cation intermediate **11** (path A). Alternatively, the species **10** could also be oxidized by acyl pyridinium salt (**5**) to provide cation **11**, along with the generated radical **6**. After deprotonation, the desired product **3a** would be produced.

In conclusion, we have developed an alkoxyacylation/cyclization reaction of *N*-acryloyl benzamides and alkyloxalyl chlorides under photocatalysis at room temperature. The application of alkoxyacyl radicals in the intermolecular conjugate addition to electron-deficient alkenes has also been demonstrated. The key finding is the use of alkyloxalyl chlorides as alkoxyacyl radical precursors, which are generated from the corresponding alcohols and oxalyl chloride. With this approach, a variety of isoquinoline-1,3(2*H*,4*H*)-diones are prepared in moderate to good yields. Additionally, this strategy is compatible with a variety of alcohol-containing pharmaceutically active compounds.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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