Advanced Synthesis & Catalysis

Accepted Article

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To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201800616

Link to VoR: http://dx.doi.org/10.1002/adsc.201800616

10.1002/adsc.201800616

UPDATE

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Copper-Catalysed (Diacetoxyiodo)benzene-Promoted Aerobic Esterification Reaction: Synthesis of Oxamates from Acetoacetamides

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Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.

Abstract. A copper-catalysed (diacetoxyiodo)benzene-promoted aerobic esterification reaction of acetoacetamides was developed for the synthesis of oxamates, which are useful precursors in synthetic organic chemistry. This practical and mild synthetic approach proceeded at 25 °C under open-air conditions and afforded methyl 2-oxo-2-(phenylamino)acetates in good to excellent yields combined with C–C σ-bond cleavage and formal oxidative C–H bond functionalization. A mechanism is proposed.

Keywords: (Diacetoxyiodo)benzene; Copper catalysis; Acetoacetamides; Esterification; C–C bond cleavage; Oxamates

Carbon–carbon (C–C) bond cleavage is a common and useful transformation in chemical synthesis.[1] In general, cleaving single C–C σ-bonds in chemical transformations is relatively difficult, as the C–C bond energy is higher than that of π-bonds in C–C double and triple bonds.[1a] However, highly strained ring C–C bond systems are cleaved relatively easily with the help of transition metal complexes.[1b-d, 2] For cleaving unstrained C–C bond systems, Jiao et al.[3] have proposed three main challenges facing this strategy: "1) The selectivity between C–C bond and C–H bond cleavage of unstrained substrates should be controlled; 2) There should be enough energy to activate C–C sigma-bond under mild conditions; 3) The reaction system should ensure that other starting materials do not undergo degradation under the necessary oxidative reaction conditions." Therefore, unstrained C–C bond activation and the functionalization of inert starting materials remains a highly desirable but challenging goal.

Oxamates are important units in many biologically active compounds[4] and useful precursors in synthetic organic chemistry.[5] Traditionally, oxamates can be generated through the ammonolysis of amines with excess chlorooxoacetates[5f, 6] or oxalates[5c, 7] (Figure 1, path a). Oxamates can also be accessed through -a dehydrogenative cross-coupling of amines and ethyl glyoxalate in the presence of an oxidant under acidic or alkaline conditions via a metal-free oxidative amidation reaction (Figure 1, path b).[8] Furthermore, the synthesis of oxamates through an oxidative double cross-carbonylation of amines and alcohols in the presence of palladium catalyst under low-pressure CO/O_2 has been well documented (Figure 1, path c).[9] More recently, Adib et al. reported that enamine oxidation[10] using 2.5 equiv. of *tert*-butyl hydroperoxide (TBHP) in chlorobenzene solvent under heated conditions also produced oxamates. Unfortunately, attempts to extend the substrate scope showed that enamines bearing an alkylamino group

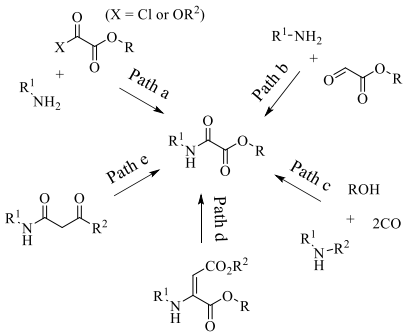

Figure 1. General routes to the oxamates motif.

were ineffective in this reaction (Figure 1, path d). All strategies mentioned above suffer from using

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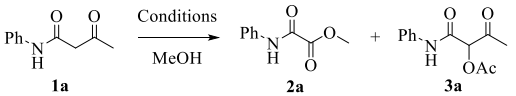
toxic or pungent reagents. Furthermore, harsh reaction conditions, such as low or high reaction temperatures, are usually selected reluctantly. In 1999, Nair *et al*.[11] reported subjecting ten types of acetoacetamides to cerium ammonium nitrate ($Ce(NH_4)_2(NO_3)_6$, CAN) oxidation under an O_2 atmosphere in MeOH at room temperature, which gave the corresponding oxamates in 70%–88% yields. Notably, 2 equiv. of CAN was required in the reaction, with less than 2 equiv. resulting in the consumption of a proportionate amount of the starting material (Figure 1, path e).

In 2013, Jiao *et al*.[3] described a CuBr-catalysed esterification of diaroylmethanes for the practical and mild synthesis of α-ketoesters in the presence of pyridine (0.5 equiv.) in toluene under an O_2 atmosphere at 90 °C. However, in our initial esterification attempts in this work, 2-oxo-2-(phenylamino)acetate (**2a**) was afforded in only 15% yield, along with an unidentified complex mixture, when the optimized conditions were applied to β-ketoamide 3-oxo-*N*-phenylbutanamide (**1a**). Therefore, a slight change in the substrate structure can lead to different reaction conditions being necessary to access similar products. Although a variety of synthetic strategies based on amine derivatives have been employed in the reaction, the development of a diverse synthetic procedure to access oxamates from similar types of substrate, such as β-ketoamides, are highly desirable, even for reaction conditions that have proven to be efficient for particular substrates. Herein, we present our recent research on a Cu-catalysed (diacetoxyiodo)benzene (PIDA)-promoted practical esterification reaction of β-ketoamides at 25 °C under open-air conditions via C–C σ-bond cleavage and oxidative C–H bond functionalization. This method was performed with safe and odourless starting materials, oxidants, and catalysts under mild conditions, with methanol serving as both solvent and reactant.

β-Dicarbonyl compounds are versatile building blocks in organic synthesis.[12] Recently, we developed two facile, reliable, mild, and efficient β-ketoamide functionalization reactions for the synthesis of 2-hydroxy-3,3-dimethoxy-*N*-substituted butanamides and vicinal tricarbonyl amides in the presence of a hypervalent iodine reagent via an oxidative C–O bond forming reaction.[13] While further exploring the synthetic potential of β-ketoamides in the presence of an organoiodine reagent,[13b] a catalytic amount of CuCl catalyst (10 mol%) was added to the reaction of **1a** in MeOH solvent. The resulting product, **2a**, was isolated and further characterized by NMR analysis. These pleasing preliminary findings encouraged us to further explore optimizing the reaction conditions for using β-ketoamides to prepare oxamates **2**, which are highly useful substrates in synthetic organic chemistry.[5a-g] Initial attempts showed that desired product **2a** could be isolated in 76% yield when **1a** was treated with PIDA (1.5 equiv.) and CuCl (0.1 equiv.) under open-air conditions at 25 °C after 1.5 h (Table 1, entry 1). Pleasingly, a 90% yield of **2a** was achieved when the amount of CuCl was increased to 0.2 equiv. (Table 1, entry 2). However, increasing or decreasing the amount of PIDA did not improve the product yield (Table 1, entries 3–5). Using other trivalent and pentavalent organoiodine reagents, including [bis(trifluoroacetoxy)iodo]benzene (PIFA), PhIO, 2-iodoxybenzoic acid (IBX), and 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one (DMP), gave lower yields of **2a** (Table 1, entries 6–9). Furthermore, performing the reaction at lower or higher temperatures did not further promote the reaction (Table 1, entries 10 and 11). Other copper salts, such as CuBr, CuI, Cu_2O, Cu_2S, $CuSO_4•5H_2O$, $Cu(NO_3)_2•3H_2O$, and $Cu(OAc)_2$, were also tested, but gave lower conversions and lower yields of **2a** than CuCl (Table 1, entries 12–18). Notably, α-acetoxylated compound **3a** was isolated as the major product, without the formation of desired product **2a**, when the reaction was performed in the other non-nucleophilic solvents, such as benzene and THF (Table 1, entries 19 and 20).

Table 1. Survey of reaction conditions.[a)]



Ent.	[O]/equiv	Cat.	T/°C	Rec. **1a**/%	**2a**/%	**3a**/%
1[b)]	PIDA (1.5)	CuCl	25	0	76	0
2	PIDA (1.5)	CuCl	25	0	90	0
3	PIDA (0.8)	CuCl	25	40	47	0
4	PIDA (1.2)	CuCl	25	0	84	0
5	PIDA (2.0)	CuCl	25	0	81	0
6	PIFA (1.5)	CuCl	25	0	15	--
7[c)]	PhIO (1.5)	CuCl	25	0	25	0
8	IBX (1.5)	CuCl	25	5	32	35
9	DMP (1.5)	CuCl	25	90	trace	0
10	PIDA (1.5)	CuCl	0	0	45	50

11	PIDA (1.5)	CuCl	50	20	62	0
12	PIDA (1.5)	CuBr	25	0	75	0
13	PIDA (1.5)	CuI	25	35	trace	50
14	PIDA (1.5)	Cu_2O	25	30	25	30
15	PIDA (1.5)	Cu_2S	25	20	23	35
16	PIDA (1.5)	$CuSO_4•5H_2O$	25	20	20	40
17	PIDA (1.5)	$Cu(NO_3)_2•3H_2O$	25	20	40	30
18	PIDA (1.5)	$Cu(OAc)_2$	25	30	30	35
19[d]	PIDA (1.5)	CuCl	25	15	0	60
20[e]	PIDA (1.5)	CuCl	25	30	0	40

[a] Reaction conditions: **1a** (0.2 mmol), organoiodine reagent, and copper salt (0.2 equiv.) in MeOH (2 mL) at 25 °C for 1.5 h. Ent. = Entry, Rec. = Recovered.

[b] 0.1 equiv. of CuCl was used.

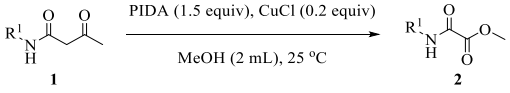
[c] A complex mixture was observed.

[d] In benzene.

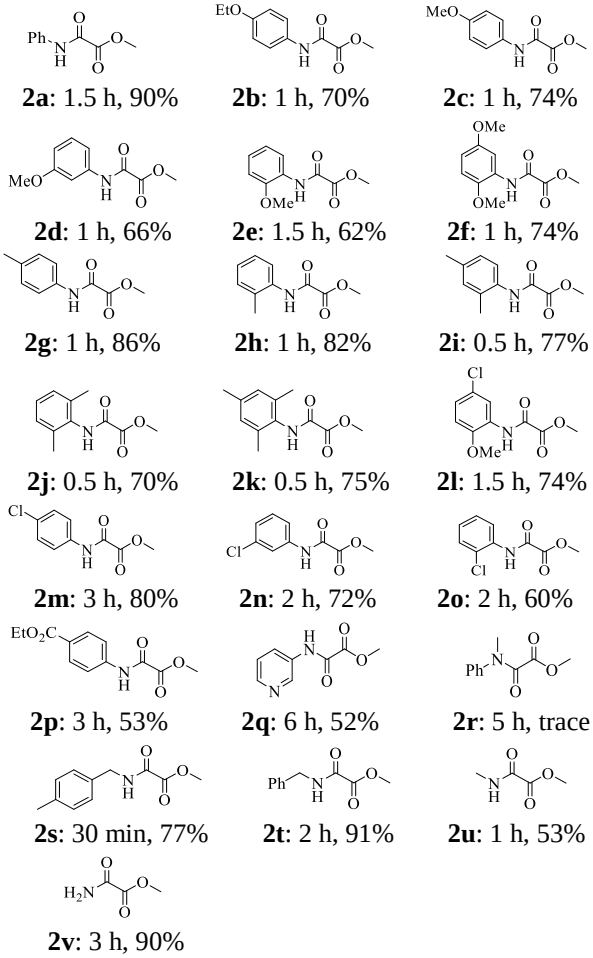
[e] In THF for 2 h.

With the optimized reaction conditions in hand (Table 1, entry 2), we next sought to define the β-ketoamide substrate scope. As shown in Table 2, variation of the amide moiety (R^1) was investigated first (R^2 = Me). Various substituents with different electronic features on the phenyl ring showed good to excellent reactivity. A phenyl group (**1a**) and substituted phenyl rings bearing electron-donating substituents (-OEt, -OMe, and Me) afforded desired products **2a**–**k** in 62%–90% yields, while other aryl groups bearing electron-withdrawing substituents (-Cl and -CO_2Et) were also tolerated, producing the corresponding oxamate derivatives **2l**–**p** in 53%–80% yields. Notably, a nitrogen-containing heterocyclic substituent (**2q**) was also tolerated, affording the desired oxamate in 52% yield, although a slightly longer reaction time was required. However, only a trace amount of **2r** was afforded when *N*-methyl-substituted tertiary amide **1r** was applied to the reaction, which indicated the importance of the amide moiety for this conversion. Further investigation showed that *N*-alkyl-substituted aliphatic secondary amides **1s** (4-methylbenzyl), **1t** (benzyl), and **1u** (methyl) were well tolerated, affording products **2s**–**u** in 53%–91% yields. To our delight, acetoacetamide (**1v**) also showed high reactivity, affording useful product **2v** in 90% yield, which indicates the potential for application to the further functionalization of similar types of small organic molecules.

Table 2. Substrate scope of acetoacetamides.[a]



1 2



[a] Unless otherwise indicated, all reactions were performed using **1** (0.2 mmol), PIDA (1.5 equiv.), and CuCl (0.2 equiv.) under open-air conditions in MeOH (2 mL) at 25 °C.

Next, the reactions of various other β-dicarbonyl compounds were investigated (Table 3). The reaction of 3-oxo-*N*-phenylpentanamide (**1w**) afforded esterified product **2a** in a moderate yield (69%) that was higher than that of 3-oxo-*N*,3-diphenylpropanamide (**1x**) (40%) (Table 3, entries 1 and 2). Four types of acetoacetate, including ethyl 3-oxobutanoate (**1y**), *tert*-butyl 3-oxobutanoate (**1z**), and benzyl 3-oxobutanoate (**1a'**), were also applied to this esterification reaction, but all afforded α-acetoxylated compounds (**3y**–**a'**) (Table 3, entries 3–5). Substrates 1,3-diphenylpropane-1,3-dione, (**1b'**) 1-phenylbutane-1,3-dione (**1c'**), and 1-(*p*-tolyl)butane-1,3-dione (**1d'**) gave the corresponding products **2b'**, and **2c'** in lower yields (35%, 35%, and 36%, respectively) (Table 3, entries 6–8). Using alternative alcohols, including ethanol, *n*-propanol, and isopropanol, had a dramatic effect on the reaction. Desired product **2d'** was isolated in 52% yield in ethanol, which served as both the solvent and reagent.

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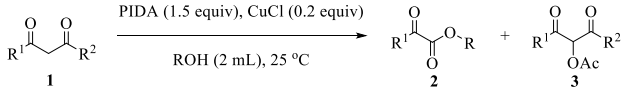
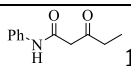
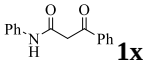
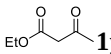
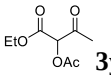
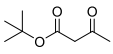
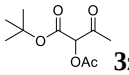
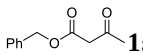
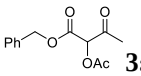
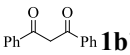
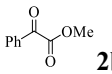
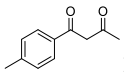
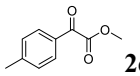
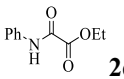
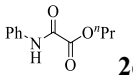
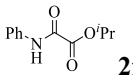
However, *n*-propanol and isopropanol performed poorly in the reaction, affording none of the corresponding oxamate derivatives **2e'** and **2f'** (Table 3, entries 9–11).

Table 3. Substrate scope of other β-dicarbonyl compounds and alcohols.[a)]

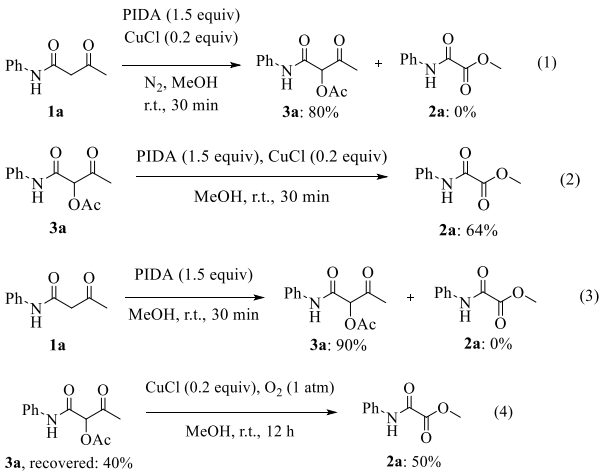


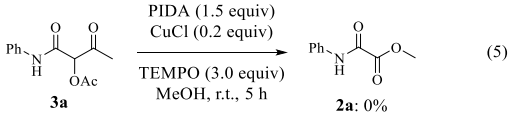
Entry	Substrate	Product	Time/h	Yield/%
1	 **1w**	**2a**	1.5	69
2	 **1x**	**2a**	1	40
3	 **1y**	 **3y**	2	80
4	 **1z**	 **3z**	2	80
5	 **1a'**	 **3a'**	2.5	75
6	 **1b'**	 **2b'**	2	35
7	 **1c'**	**2b'**	1	35
8	 **1d'**	 **2c'**	1	36[b)]
9	**1a**	 **2d'**	2	52
10	**1a**	 **2e'**	2	0
11	**1a**	 **2f'**	5	0

[a)] Unless otherwise indicated, all reactions were performed using **1** (0.2 mmol), PIDA (1.5 equiv.), and CuCl (0.2 equiv.) under open-air conditions in alcohol (2 mL) at 25 °C.

[b)] 1,3-Dioxo-1-(*p*-tolyl)butan-2-yl acetate **3d'** (55% yield) was obtained simultaneously.

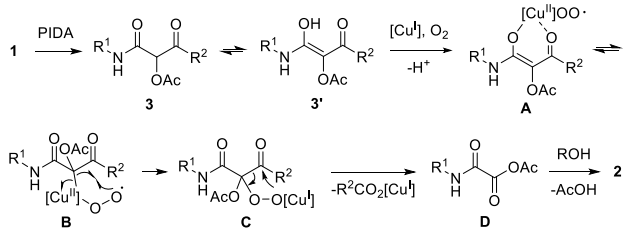
To clarify the mechanism, we performed the reaction of **1a** with methanol under a nitrogen atmosphere. The reaction gave α-acetoxylated β-dicarbonyl derivative **3a** in 80% yield without the formation of **2a** after 30 min under the optimized conditions (Eq. 1). The hypervalent iodine(III)-promoted methylene acetoxylation of acetoacetamides to form compounds **3** has been well documented.[14] Furthermore, isolated compound **3a** was readily converted into **2a** in 64% yield (Eq. 2). These observations indicated that compound **3a** was a possible intermediate in the reaction. Next, the role of CuCl was investigated. When the reaction was performed in the absence of CuCl, compound **3a** was obtained in 90% yield, while corresponding compound **2a** was not observed (Eq. 3). This result indicated that the CuCl catalyst played an important role in converting **3a** to **2a**, but may not promote the conversion of **1a** to **3a**. PIDA served as an acetoxy group donor in the conversion of **1a** to **3a**. Consequently, to further understand the role of PIDA and oxygen in the transformation of **3a** to **2a**, a control experiment was performed using **3a** under an oxygen atmosphere without added PIDA. This reaction afforded **2a** in 50% isolated yield after a longer reaction time of 12 h (Eq. 4). Obviously, this reaction was less efficient than that performed under open-air conditions in the presence of PIDA (Eqs. 2 *vs*. 4). Compared with the control reaction in Eq. 1, these control experiments indicated that PIDA promoted the transformation of **3a** to **2a**, and that the esterification reaction was a Cu-catalysed PIDA-promoted aerobic process.[3] Furthermore, a radical inhibition experiment showed that a radical process might be involved in the transformation of compounds **3** to **2**, with no **2a** being obtained in the reaction containing radical inhibitor 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (Eq. 5).





(5)

Based on the results above, a plausible mechanism is proposed in Scheme 1. Initially, compound **3**, which also exists in its enol form **3'** in solution,[15] is formed through a PIDA-promoted methylene acetoxylation of acetoacetamide **1**.[14, 16] The reaction of **3'** with Cu(II) peroxo species [Cu^{II}]OO•,[17] generated *in situ* by CuCl and dioxygen,[17e, 18] forms copper enolates **A** and **B**.[17b] Subsequently, Cu(I) peroxo species **C**, derived from intermediate **B**,[17a-d, 19] affords anhydride **D** by releasing a $R_2CO_2^-$ anion and Cu(I) cation.[3, 11, 20] Further alcoholysis of anhydride **D** affords final product **2**.[21] Notably, β-ketoamides reacted better than other β-dicarbonyl starting materials in the present work (**1a**–**x** *vs.* **1y**–**d'**). Accordingly, we deduced that the nitrogen of the amide moiety contributed its lone pair of electrons to the conjugated system, which enhanced the coordination capacity of oxygen with the metal species to form more reactive intermediate **A**.[22]



Scheme 1. Proposed mechanism.

In conclusion, we have developed a Cu(I)-catalysed (diacetoxyiodo)benzene-promoted aerobic esterification reaction of acetoacetamides for the synthesis of oxamates, which are useful precursors in synthetic organic chemistry. This practical and mild synthetic approach proceeded at 25 °C under open-air conditions and provided a series of methyl 2-oxo-2-(phenylamino)acetates in good to excellent yields, combined with C–C σ-bond cleavage and formal oxidative C–H bond functionalization. Notably, this reaction has the advantages of using readily available, odourless, and safe starting materials, dense and flexible substitution patterns, simple operations, and moderate to good yields. Investigations into further applications of this chemistry are ongoing in our laboratory.

Experimental Section

Typical synthetic procedure for 2 (using 2a as an example): To a 25-mL round-bottom flask was added 3-oxo-*N*-phenylbutanamide **1a** (35.4 mg, 0.2 mmol), (diacetoxyiodo)benzene (96.6 mg, 0.3 mmol), CuCl (4 mg, 0.04 mmol). The mixture was stirred well for 1.5 h in MeOH (2 mL) under air at 25 °C and the reaction monitored by thin layer chromatography (TLC). After reaction completion, the residue was purified by short-column silica gel flash chromatography (eluent, EA/PE = 1:20) to give methyl 2-oxo-2-(phenylamino)acetate (**2a**) as a white solid (32 mg, 90%).

Typical synthetic procedure for 3a: To a 25-mL round-bottom flask was added 3-oxo-*N*-phenylbutanamide **1a** (35.4 mg, 0.2 mmol), (diacetoxyiodo)benzene (96.6 mg, 0.3 mmol), and CuCl (4 mg, 0.04 mmol). The mixture was stirred well for 0.5 h in MeOH (2 mL) under a nitrogen atmosphere at 25 °C and the reaction was monitored by TLC. After reaction completion, the residue was purified by short-column silica gel flash chromatography (eluent, EA/PE = 1:17) to give 1,3-dioxo-1-(phenylamino)butan-2-yl acetate (**3a**) as a white solid (38 mg, 80%).

Acknowledgements

We thank the NSFC (21772032, 21702051, and U1604285), PCSIRT (IRT1061), the 111 Project (D17007), Henan Provincial Natural Science Foundation (162300410180), Key Project of Henan Educational Committee (15A150015 and 18A150009), Science & Technology Innovation Talents in Universities of Henan Province (17HASTIT002), and Outstanding Young Talent Cultivation Project Funding of Henan Normal University (14YR002) for financial support. We thank Simon Partridge, PhD, from Liwen Bianji, Edanz Editing China (www.liwenbianji.cn/ac), for editing the English text of a draft of this manuscript.

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10.1002/adsc.201800616

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