

## PAPER

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click for updatesCite this: *RSC Adv.*, 2017, 7, 7158Solvent-free one-pot oxidation of ethylarenes for the preparation of  $\alpha$ -ketoamides under mild conditions†Fuyan Liu,<sup>a</sup> Kuan Zhang,<sup>a</sup> Yanfeng Liu,<sup>a</sup> Shan Chen,<sup>\*b</sup> Yiping Chen,<sup>a</sup> Dela Zhang,<sup>a</sup> Chunfu Lin<sup>ab</sup> and Bo Wang<sup>\*ab</sup>

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Here we developed a highly efficient solvent-free, one-pot procedure for synthesizing  $\alpha$ -ketoamides from ethylarenes and amines, by oxidizing a C–H bond  $sp^3$  center. A copper catalyst was employed, and the reactions proceeded smoothly at ambient temperatures. Most of the tested ethylarenes and amines were successfully converted to their corresponding  $\alpha$ -ketoamides in moderate to excellent yields of up to 93% with three equivalents of the oxidant *tert*-butyl hydroperoxide.

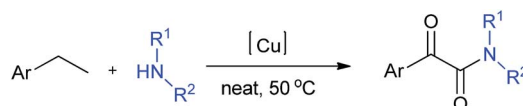
## Introduction

$\alpha$ -Ketoamides are key structural motifs in a variety of natural products, biologically important compounds, and pharmaceuticals, such as the immunosuppressant drug FK-506, rapamycin, serine, cysteine proteases and other enzymes, and epoxide hydrolase inhibitors.<sup>1</sup> All of these compounds, as well as the HIV replication inhibitors complestatin and chloropectin I,<sup>2</sup> include  $\alpha$ -ketoamide frameworks. Furthermore,  $\alpha$ -ketoamides are also used as valuable precursors and synthetic intermediates in synthetic organic chemistry, for instance in the synthesis of medicinally useful compounds tetrasubstituted 2-oxazolidin-4-one and 2-oxindoles.<sup>3</sup>

Because of the significance of the  $\alpha$ -ketoamide scaffold, it is of great interest and importance to develop efficient methods to synthesize the many types of  $\alpha$ -ketoamides that are in demand. Over the past decades, several approaches have been developed for synthesizing  $\alpha$ -ketoamides.<sup>4–15</sup> Most of these procedures involved the direct amidation of  $\alpha$ -keto acids and  $\alpha$ -keto acyl halides,<sup>4</sup> but in most conditions hazardous reagents were usually involved and harsh conditions were required. Direct oxidations of  $\alpha$ -hydroxyamides and  $\alpha$ -aminoamides have also been used to successfully produce the corresponding  $\alpha$ -ketoamides.<sup>5</sup> Recently, one-pot procedures for synthesizing  $\alpha$ -ketoamides have attracted the focus of researchers worldwide. Jiao and his co-workers introduced a one-pot procedure for synthesizing  $\alpha$ -ketoamides by using a copper catalyst to cleave  $Csp^3$ –H,  $Csp^2$ –H, and N–H bonds of

aryl acetaldehyde and aniline reactants.<sup>6</sup> Some recently developed one-pot approaches have included the direct oxidative amidation of aryl methyl ketones,<sup>7c</sup> <sup>n</sup>Bu<sub>4</sub>Ni-catalyzed multiple  $sp^3$  C–H bond oxidation of ethylarenes and sequential coupling with dialkylformamides,<sup>8</sup> I<sub>2</sub>/IBX-catalyzed oxidative amidation of terminal alkenes with amines in dimethyl sulfoxide (DMSO),<sup>9a</sup> oxidative amidation of terminal alkynes catalyzed by copper(II) triflate,<sup>10a</sup> iron-2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)-catalyzed oxidative amidation of  $\alpha$ -keto alcohols,<sup>11a</sup> copper-catalyzed oxidative amidation of 1-arylethanol with amines,<sup>12b</sup> amidation of halogen benzenes promoted by palladium nanoparticles,<sup>13a</sup> DMSO-promoted oxidative amidation of  $\alpha$ -ketoaldehydes,<sup>14c</sup> and *tert*-butyl hydroperoxide/I<sub>2</sub> (TBHP/I<sub>2</sub>)-promoted tandem reactions of  $\beta$ -diketones with amines.<sup>15</sup> Most of these methods, however, suffer from the need to carry out extra steps involving the starting materials before the reactions for making the  $\alpha$ -ketoamides. They also suffer from low yields, harsh conditions and toxic reagents, and the need to use large amounts of oxidants that are considered to not be environmentally benign.

Herein, we present a novel solvent-free and one-pot procedure for the synthesis of  $\alpha$ -ketoamides starting from commercially available ethylarenes and amines. In this approach, we used CuI as the catalyst and TBHP as the oxidant. No solvent was required, and the reactions proceeded under mild conditions (Scheme 1).



**Scheme 1** Oxidative synthesis of  $\alpha$ -ketoamides from ethylarenes and amines.

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## Results and discussion

Initial investigations for suitable reaction conditions were performed on a 5 mL scale by employing ethylbenzene (**1a**) and morpholine (**2a**) as the model substrates. Conditions such as the identities of the catalyst, oxidants, and solvents, as well as the amounts of loaded catalyst and oxidant, were evaluated, and the results are summarized in Table 1. Carrying out the reaction at 50 °C in acetonitrile in the presence of the oxidant *tert*-butyl hydroperoxide (TBHP) with copper iodide (CuI) as the catalyst afforded the desired product **3aa** in a 63% yield (entry 1, Table 1). CuI was shown to be the most suitable catalyst of all the catalysts tested since this 63% yield of **3aa** was better than the yields afforded by the other tested catalysts (CuCl<sub>2</sub>, Cu<sub>2</sub>O, CuBr and CuBr<sub>2</sub>) (see entries 1–5, Table 1). Therefore, in the subsequent investigations, all reactions were performed with CuI as the catalyst.

The effects of the identity and presence of the solvent on the yields were also evaluated for the purpose of finding suitable conditions. Organic solvents such as tetrahydrofuran (THF), MeCN, 1,4-dioxane, and MeOH were tested at 50 °C. Of all the

solvents evaluated, toluene was found to be the best one, having afforded the desired product **3aa** with a yield of 64% (entry 9, Table 1), and was thus considered suitable for further investigations. Nevertheless, for the purpose of adhering to at least some of the principles of green chemistry, reactions without organic solvent and with TBHP as the oxidant were also investigated. To our delight, when using three equivalents of TBHP in the absence of organic solvent, great enhancements in the yields of product **3aa** were achieved (entry 1, 15–21, Table 1), with yields of 88% for the reaction carried out at 70 °C (entry 16, Table 1), and 92% at 50 °C (entry 10, Table 1). Therefore, in the subsequent investigations, the reactions were performed without organic solvent.

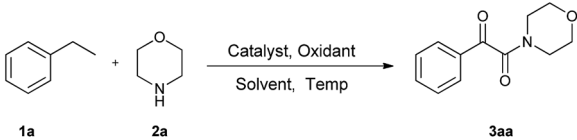
A variety of oxidants, such as TBHP, DTBP, H<sub>2</sub>O<sub>2</sub>, DDQ, and TEMPO, and their loadings were also tested to find optimum conditions for the designed reaction. As shown in Table 1, TBHP performed the best of all the oxidants tested. As indicated above, the desired product **3aa** was obtained with yields of up to 92% (entry 10, Table 1) when using three equivalents of this oxidant. Using more TBHP (four equivalents) or less of this oxidant (one and two equivalents) resulted in somewhat lower yields. Perhaps, more by-products were generated during the reaction with the larger loading of TBHP, and the oxidation actions were not great enough to convert substrate to product when less of the oxidant was loaded (entry 21, Table 1).

Reaction temperatures were also evaluated to find suitable conditions for the reaction. As shown in Table 1, a temperature of 50 °C was best of all the temperatures evaluated (entry 10, Table 1), with lower and higher temperatures (30 °C and 70 °C) not leading to higher yields of the product **3aa**. Therefore, 50 °C was chosen as the suitable reaction temperature for the subsequent reactions.

With all of the optimized conditions in hand, a wide range of ethylarenes and amines were then subjected to this reaction to explore the scope of substrates. The results of this investigation are summarized in Table 2. All reactions proceeded well in the absence of solvent at ambient temperature. Yields of product appeared to benefit from the presence of electron-withdrawn substituent(s) on the substrate. For example, the reaction of an ethylarene substrate bearing a nitro group on the ring resulted in the desired product with an excellent yield of 89% (**3ba**, Table 2). In contrast, the presence instead of an electron-donating ethyl group at the same position resulted in a poorer yield of 70% (**3fa**, Table 2). Substituent groups on the substrate could therefore either positively or negatively affect product yield, and possibly the reaction rate as well. Note that the reaction of substrates with more than one ethyl group, for example, *p*-diethylbenzene, with amines resulted in mono-oxidated amination products in relatively poor yields, possibly due to more by-products having formed.

Based on some related publications,<sup>16</sup> a possible mechanism was proposed, as shown in Scheme 2. According to this mechanism, CuI catalyzed the breaking up of the oxidant TBHP into a *t*-butoxyl radical and a hydroxyl anion (eqn (1) and (2)),<sup>17</sup> with the *t*-butoxyl radical in the following step releasing one hydrogen from the C–H bond of ethylarene on the benzylic ring **1** to form the peroxide **5**, which further decomposed to

Table 1 Optimization of the model reaction conditions<sup>a</sup>

					
Entry	Catal.	Oxidant	Solvent	Temp. (°C)	Yield <sup>d</sup> (%)
1	CuI	TBHP <sup>b</sup>	MeCN	50	63
2	CuCl <sub>2</sub>	TBHP	MeCN	50	n.d.
3	Cu <sub>2</sub> O	TBHP	MeCN	50	n.d.
4	CuBr	TBHP	MeCN	50	36
5	CuBr <sub>2</sub>	TBHP	MeCN	50	<5
6	CuI	TBHP	THF	50	6
7	CuI	TBHP	Dioxane	50	<5
8	CuI	TBHP	MeOH	50	12
9	CuI	TBHP	Toluene	50	64
10	CuI	TBHP	Neat	50	92
11	CuI	DTBP	Neat	50	n.d.
12	CuI	H <sub>2</sub> O <sub>2</sub> <sup>c</sup>	Neat	50	n.d.
13	CuI	DDQ	Neat	50	n.d.
14	CuI	TEMPO	Neat	50	n.d.
15	CuI	TBHP	Neat	30	80
16	CuI	TBHP	Neat	70	88
17	CuI	TBHP	Neat	50	79 <sup>e</sup>
18	CuI	TBHP	Neat	50	90 <sup>f</sup>
19	CuI	TBHP	Neat	50	56 <sup>g</sup>
20	CuI	TBHP	Neat	50	78 <sup>h</sup>
21	CuI	TBHP	Neat	50	90 <sup>i</sup>

<sup>a</sup> Conditions: **1a** (1.0 mmol), **2a** (6.0 mmol), catalyst (20 mol%), and oxidant (3 equiv.) under an air atmosphere for 24 h, n.d., not detected; unless otherwise stated, all reaction were performed with 3 equiv. of oxidant. <sup>b</sup> TBHP: *tert*-butyl hydroperoxide (TBHP), 70% in water. <sup>c</sup> Hydrogen peroxide, 30% in water. <sup>d</sup> Unless otherwise stated, all yields were determined by HPLC analysis. <sup>e</sup> CuI (10 mol%). <sup>f</sup> CuI (30 mol%). <sup>g</sup> Yields obtained from the reaction using 1 equivalent of TBHP. <sup>h</sup> Yields obtained from the reaction using 2 equivalents of TBHP. <sup>i</sup> Yields obtained from the reaction using 4 equivalents of TBHP.



Table 2 Copper-catalyzed oxidative synthesis of  $\alpha$ -ketoamides<sup>a</sup>

$$\text{Ar-CH}_2\text{-CH}_3 + \text{HN}^{\text{R}^1}\text{R}^2 \xrightarrow[\text{neat, 50 } ^\circ\text{C}]{\text{CuI, TBHP}} \text{Ar-C(=O)-CH}_2\text{-C(=O)-N}^{\text{R}^1}\text{R}^2$$

**1**
**2**
**3**

**3aa**, 92%(87%)<sup>b</sup>

**3ba**, 89%(84%)

**3ca**, 84%(75%)

**3da**, 72%(69%)

**3ea**, 56%(51%)

**3fa**, 70%(62%)

**3ga**, 62%(50%)

**3ab**, 74%(68%)

**3bb**, 64%(60%)

**3cb**, 69%(65%)

**3ib**, 85%(75%)

**3ac**, 61%(56%)

**3bc**, 86%(82%)

**3cc**, 93%(90%)

**3dc**, 83%(76%)

**3gc**, 78%(70%)

**3hc**, 71%(66%)

**3ic**, 70%(60%)

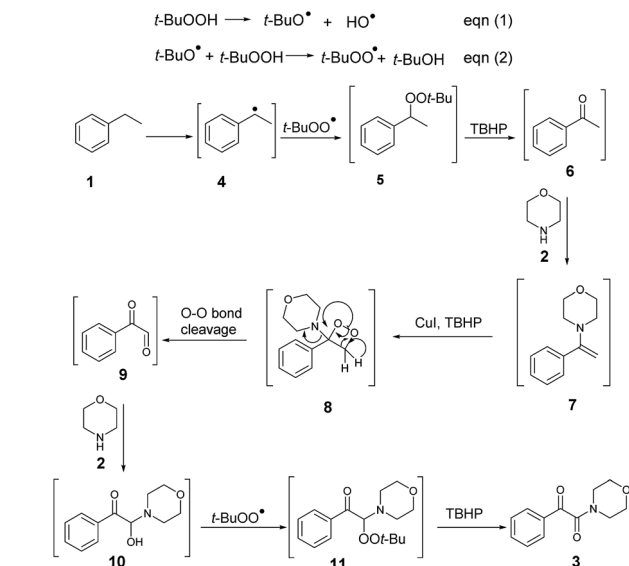
**3ad**, 86%(82%)

**3ae**, 58%(50%)

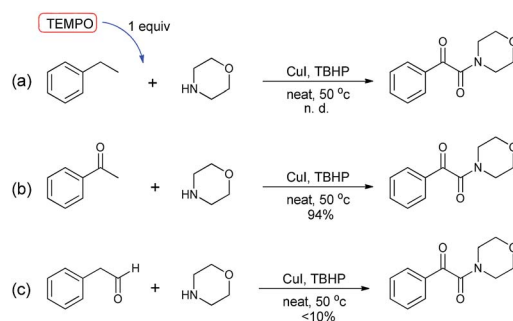
**3af**, 88%(83%)

acetophenone **6** with the assistance of TBHP.<sup>18</sup> Then, according to the proposed mechanism, acetophenone **6** reacted with amine **2** to form the enamine **7**,<sup>19</sup> which then further reacted with Cu(II) and *t*-butoxyl radicals from CuI and TBHP<sup>17</sup> to form aminodioxetane **8**. Then, according to the mechanism, cleavage of the O–O bond of **8** produced the aryl glyoxal **9**,<sup>20</sup> which reacted with the introduced amine **2** to give the intermediate **10**, and then the reaction of **10** with the *t*-butoxyl radical from TBHP yielded compound **11** and finally the  $\alpha$ -ketoamide **3** product.

To verify the mechanism proposed above, several control experiments were carried out, as are shown in Scheme 3. When the reaction was carried out in the presence of a radical scavenger, for instance TEMPO, the oxidative coupling reaction did not work (a),<sup>21</sup> indicating that this conversion likely involved



Scheme 2 Possible reaction pathway.



Scheme 3 Control experiments to test the proposed mechanism.

radical intermediates. When acetophenone was used instead of ethylbenzene to react with morpholine, an excellent yield of the product **3** was achieved (b). The reaction of experiment (c) was carried out by employing phenylacetaldehyde instead of ethylbenzene, and this reaction produced the desired compound in very low yield. These examples showed that the oxidation started from the benzylic C–H bond of ethylarene, and not from the methyl group.

## Conclusions

In summary, we have developed an efficient one-pot, solvent-free procedure for the synthesis of  $\alpha$ -ketoamides through a CuI-catalyzed sp<sup>3</sup> C–H bond coupling process aided by aerobic oxidation using ethylarenes and amines. No harsh conditions were needed for this reaction. When using only three equivalents of TBHP, the desired  $\alpha$ -ketoamide products were afforded with moderate to excellent yields of up to 93%. These results showed the promise of using this alternative and novel pathway to synthesize  $\alpha$ -ketoamides and to enrich the synthetic library for  $\alpha$ -ketoamide preparations. This procedure can also be



considered to adhere to some of the principles of green chemistry, as the reactions occurred without solvent. Overall, we believe this procedure to have potential in large-scale preparations of  $\alpha$ -ketoamides, especially for industrial purposes.

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