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## COMMUNICATION

# Synthesis of oxazoles by silver catalysed oxidative decarboxylation-cyclization of $\alpha$ -oxocarboxylates and isocyanides

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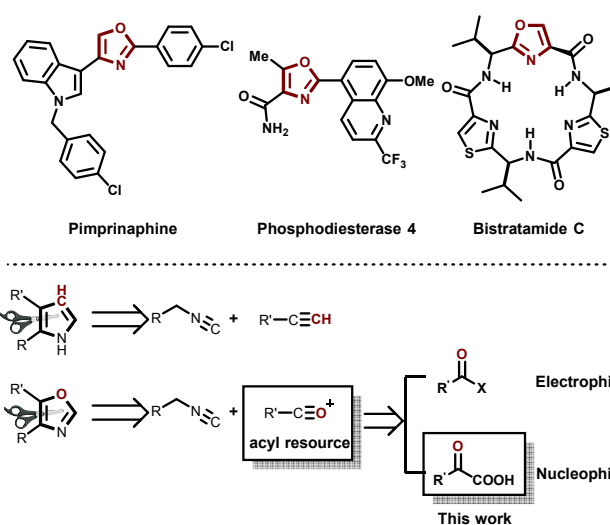
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A silver catalysed synthesis of oxazoles by oxidative decarboxylation-cyclization of  $\alpha$ -oxocarboxylates and isocyanides was developed. This method provided a novel strategy to construct oxazole rings comparing to traditional methods. The mechanistic investigations such as *operando* IR, EPR and radical inhibiting experiment were carefully done and confirmed the acyl cation and Ag(II) as the intermediate in this transformation and a radical decarboxylative process is related.

Five-membered heterocycle containing nitrogen atom is one of the most prevailing compounds<sup>1</sup>, which widely exists in numerous natural products, biologically active alkaloids, pharmaceuticals, and agrochemicals<sup>2</sup>. In addition, these key cores are also the basic constituents of organic dyes and material molecules<sup>3</sup>. Various efforts in recent years have focused on the development of improved methods for the synthesis of these heterocycles<sup>4</sup>. Recently, Bi's group and our group has developed a novel pyrrole synthesis from the [2+3] cycloaddition of terminal alkynes and isocyanides by silver catalysis<sup>5</sup>. This efficient and highly regioselective protocol intrigued us to apply this method for synthesis of other five-membered heterocycles synthesis. For example, when the carbon atom at 3-position of pyrrole was replaced by an oxygen atom, there comes out another widely applied aromatic heterocycle-oxazole. The unique structural nature of oxazole moiety endows its derivatives to exhibit various bioactivities and some special properties, and thus results in their wide potential application in medicinal and agrochemical field as well as materials sciences and so on (Scheme 1)<sup>6</sup>. Therefore, the synthetic methods of oxazole ring have been receiving increasing attention, and a large amount of effort has been directed towards its syntheses<sup>7</sup>. In fact, similar to pyrrole synthesis by terminal alkynes and isocyanides, from the retrosynthetic analysis, oxazoles can also be synthesized from acyl compounds and isocyanides. Though there are several examples using acyl halogens, esters and amides as electrophiles with isocyanides to oxazoles<sup>8</sup>, using nucleophilic acyl reagents is still rare. Thus, the development of a new oxidative cyclization for the synthesis of oxazoles from nucleophilic acyl reagents is still highly attractive (Scheme 1).



**Scheme 1.** (A) Representative oxazoles moiety in functional materials and bioactive molecule; (B) Strategy to synthesis of oxazoles from retrosynthetic analysis.

Transition metal catalysed decarboxylative coupling have received much attention for their applications to construct C-C and C-hetero bonds in recent years<sup>9</sup>. Among various resources of carboxylic acids,  $\alpha$ -oxocarboxylic acids have emerged as a novel class of acyl surrogate after releasing a CO<sub>2</sub> molecular<sup>10</sup>. Theoretically, there are three types of acyl reagents from decarboxylation of  $\alpha$ -oxocarboxylates: acyl anion, acyl radical and acyl cation<sup>11</sup>. In 2008, Gooßen first demonstrated a Pd-catalyzed direct decarboxylative acylation of aryl bromides with  $\alpha$ -oxocarboxylates as acyl anion to afford diaryl ketones<sup>12</sup>. Recently, You and co-workers reported a transition metal free decarboxylation of  $\alpha$ -oxocarboxylates with C(sp<sup>3</sup>)-X<sup>13</sup>. In addition, it has also been reported that oxidative decarboxylation of  $\alpha$ -oxocarboxylic acids via the acyl radical intermediates, which led to acylation of aromatic and heterocyclic ring in recent years<sup>10b, 14</sup>. In spite of the significant progress offered by these reactions from acyl anions and acyl

radicals, the oxidative decarboxylation of  $\alpha$ -oxocarboxylic acids or salts via acyl cations is still rare. Based on our continuing interests in oxidative decarboxylation of  $\alpha$ -oxocarboxylic acids<sup>15</sup>, we present our progressive development for the oxidative decarboxylation-cyclization of  $\alpha$ -oxocarboxylates and isocyanides.

The combination of  $\text{Ag}_2\text{CO}_3$ , 1,10-phen and  $\text{K}_2\text{S}_2\text{O}_8$  in DMF at 80 °C gave the corresponding oxazole (3a) with the best result for the oxidative decarboxylation-cyclization of potassium oxophenylacetate (1a) and ethyl 2-isocyanoacetate (2a) (Table 1, entry 1). The choice of catalyst was crucial for this reaction. When  $\text{Ag}_2\text{CO}_3$  was replaced by  $\text{AgOAc}$  or  $\text{AgNO}_3$ , the yield decreased respectively (entry 2 and 3). The usage of  $\text{Cu}(\text{OAc})_2$  as catalyst decreased the yield dramatically (entry 4). In the absence of catalyst, essentially trace amount of product was obtained (entry 5). Without 1,10-phen as additive, the yield dropped to 78% (entry 6). As to oxidants,  $\text{K}_2\text{S}_2\text{O}_8$  gave the highest yield for this oxidative reaction.  $\text{Na}_2\text{S}_2\text{O}_8$  and  $\text{O}_2$  showed less or no efficiency in terms of chemical yield (entry 7 and 8). Changing the solvent from DMF to MeCN or DMSO, relatively lower yield of the corresponding oxazole product was obtained (entry 9 and 10).

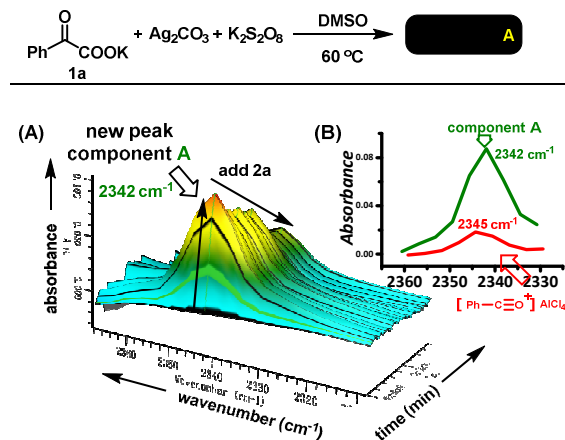
**Table 1.** Ag-catalyzed oxidative cyclization of potassium oxophenylacetate (1a) and Isocyanides (2a): effects of reaction parameters.<sup>a</sup>

$\text{Ph-COOK} + \text{CN-CH}_2\text{-COOEt} \xrightarrow[\text{DMF, 80 }^\circ\text{C, 12 h}]{\text{Ag}_2\text{CO}_3, \text{ 1,10-phen, K}_2\text{S}_2\text{O}_8} \text{Ph-C}_5\text{H}_4\text{N-OEt}$		
1a	2a	3a
Entry	Variation from standard conditions	Yield[%] <sup>[b]</sup>
1	none	93(88) <sup>[c]</sup>
2	$\text{AgOAc}$ (0.2 equiv.), instead of $\text{Ag}_2\text{CO}_3$	69
3	$\text{AgNO}_3$ (0.2 equiv.), instead of $\text{Ag}_2\text{CO}_3$	64
4	$\text{Cu}(\text{OAc})_2$ (0.2 equiv.), instead of $\text{Ag}_2\text{CO}_3$	<5
5	without $\text{Ag}_2\text{CO}_3$	trace
6	without 1,10-phen	78
7	$\text{Na}_2\text{S}_2\text{O}_8$ , instead of $\text{K}_2\text{S}_2\text{O}_8$	13
8	$\text{O}_2$ , instead of $\text{K}_2\text{S}_2\text{O}_8$	0
9	MeCN, instead of DMF	45
10	DMSO, instead of DMF	35

<sup>a</sup> Standard reaction conditions: 1a (0.25 mmol), 2a (0.50 mmol),  $\text{Ag}_2\text{CO}_3$  (0.025 mmol), 1,10-phen (0.125 mmol),  $\text{K}_2\text{S}_2\text{O}_8$  (0.75 mmol), DMF (1.0 mL), in  $\text{N}_2$ , 80 °C, 12 h. <sup>b</sup> The yield was determined by GC, calibrated using biphenyl as internal standard. <sup>c</sup> Yield in the parentheses is isolated yield.

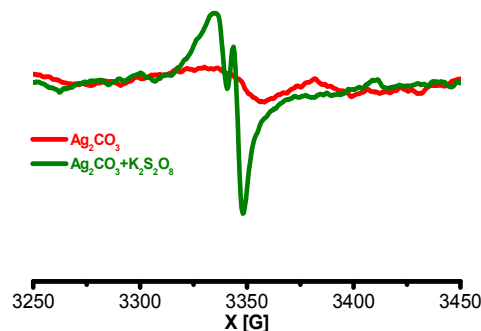
In order to investigate the mechanism of this silver catalysed decarboxylation of  $\alpha$ -oxocarboxylates, the reaction between potassium oxophenylacetate (1a) and ethyl 2-isocyanoacetate (2a) with  $\text{Ag}_2\text{CO}_3$  and  $\text{K}_2\text{S}_2\text{O}_8$  was monitored by *operando* IR. As can be seen from the kinetic profiles of relative absorbance in Figure 1(A), when mixing 1a with  $\text{Ag}_2\text{CO}_3$  and  $\text{K}_2\text{S}_2\text{O}_8$  in DMSO, we found a new peak component A (at 2342  $\text{cm}^{-1}$ ) increased very quickly. While 2a was added to the solution, the absorbance of 2a started to decrease. This result suggested that the component A might be the reactive intermediate in this transformation. We noticed that the band of 2300–2400  $\text{cm}^{-1}$  usually could be attributed to the absorbance of  $\text{C}\equiv\text{C}$  or  $\text{C}\equiv\text{O}$ . Therefore, component A which has an infrared absorption at the 2342  $\text{cm}^{-1}$  might be assigned as benzoyl-acylium ion. In order to confirm our assumption, the reaction between benzoyl chloride and one equivalent of  $\text{AlCl}_3$  were performed in DCE and monitored by *operando* IR. A weak band at 2345  $\text{cm}^{-1}$  was observed which was reported as the characteristic infrared absorption of benzoyl-acylium salt --  $[\text{Ph-C}\equiv\text{O}^+]\text{AlCl}_4^-$  (Figure 1B)<sup>16</sup>. Comparing the absorbance of component A at 2342

$\text{cm}^{-1}$  and benzoyl-acylium ion at 2345  $\text{cm}^{-1}$ , we could assign the component A to be the benzoyl cation --  $[\text{Ph-C}\equiv\text{O}^+]$  respectively.



**Figure 1.** (A) The absorbance of component A in 3D-Kinetic profile; (B) Spectra of the component A (green curve) and standard sample (benzoyl-acylium salt, red curve).

To confirm Ag(II) intermediate in this oxidative reaction<sup>17</sup>, the electron paramagnetic resonance (EPR) was applied to study it. As shown in Figure 2, no EPR signal was observed when  $\text{Ag}_2\text{CO}_3$  was tested alone in DMF, 80 °C,  $\text{N}_2$  for 2 hours (red color). However, when the  $\text{Ag}_2\text{CO}_3$  and  $\text{K}_2\text{S}_2\text{O}_8$  were mixed the same condition, a strong EPR signal could be detected (green color). According to relative literatures, we may ascribe this obvious signal to Ag(II) species<sup>18</sup>. Therefore, this oxidative decarboxylation referred a Ag(I)-Ag(II) catalytic circle.

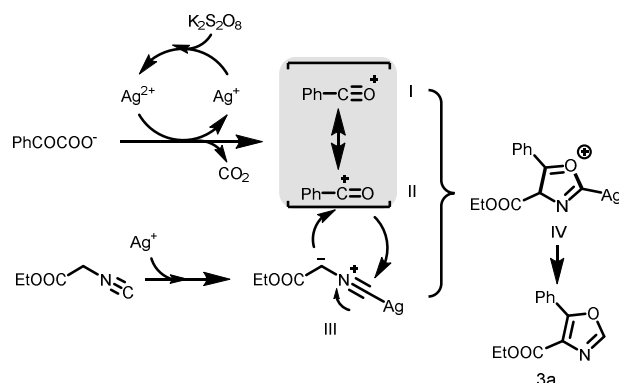


**Figure 2.** Evidence of Ag(II) species in EPR spectra.

Moreover, radical scavengers, such as TEMPO and BHT, were employed in the reaction to confirm whether this reaction related to radical process (see Supporting Information, Figure S4). As a result, the reactions was profoundly suppressed, which could indicate that this transformation involved radical intermediates. We proposed the decarboxylation of oxocarboxylates could be a radical process<sup>19</sup>: oxocarboxylates firstly experienced a single electron transfer (SET) to be oxidized to oxocarboxylic radical, then it decarboxylate and release  $\text{CO}_2$  to give the acyl radical and subsequently a second SET process happened to form the acyl cation<sup>10b, 11</sup> which was confirmed by *operando* IR.

On the basis of the results described above, a proposed reaction pathway is depicted in Scheme 3. In the presence of  $\text{Ag}_2\text{CO}_3$  and  $\text{K}_2\text{S}_2\text{O}_8$ , the  $\alpha$ -oxocarboxylates experienced a fast oxidative decarboxylative process to generate the benzoyl-acylium ion I and II, which are two kind resonance structures. Meanwhile, silver salts could also coordinate to the isocyano group and activate isocyanides

to form **III** according to previous literatures<sup>20</sup>. Therefore, we believe that the silver catalyst played the dual roles in this reaction, which participated in the decarboxylation of  $\alpha$ -oxocarboxylates as well as activated the isocyanide. Subsequently, the cycloaddition between benzoyl cation and **III** would afford the intermediate **IV**. And finally, protonation and tautomerization gives the oxazole product **3a**.



**Scheme 3.** Proposed mechanism.

**Table 2.** Substrates scope of the cyclization of  $\alpha$ -oxocarboxylates **1** and isocyanides **2**<sup>a</sup>

		$\text{R}^1\text{COOK} + \text{CNCH}_2\text{C(=O)OR}^2 \xrightarrow[\text{DMF, 80 } ^\circ\text{C, 12 h}]{\text{Ag}_2\text{CO}_3, \text{1,10-phen, K}_2\text{S}_2\text{O}_8}$			
	<b>1</b>	<b>2</b>			<b>3</b>
Entry	<b>3</b>	R <sup>1</sup>	R <sup>2</sup>	Yield [%]	
1	<b>3a</b>	C <sub>6</sub> H <sub>5</sub>	Et	88	
2	<b>3b</b>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Et	76	
3	<b>3c</b>	<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Et	66	
4 <sup>b</sup>	<b>3d</b>	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	Et	80	
5 <sup>b</sup>	<b>3e</b>	<i>o</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	Et	68	
6 <sup>b</sup>	<b>3f</b>	<i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Et	63	
7	<b>3g</b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	Et	68	
8	<b>3h</b>	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub>	Et	65	
9	<b>3i</b>	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	Et	71	
10	<b>3j</b>	<i>m</i> -BrC <sub>6</sub> H <sub>4</sub>	Et	70	
11	<b>3k</b>	<i>p</i> -IC <sub>6</sub> H <sub>4</sub>	Et	60	
12	<b>3l</b>	C <sub>6</sub> H <sub>5</sub>	Me	84	
13 <sup>b</sup>	<b>3m</b>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	Et	33	
14 <sup>b</sup>	<b>3n</b>	CH <sub>3</sub>	Et	26	
15 <sup>b</sup>	<b>3o</b>		Et	54	
16	<b>3p</b>		Et	64	

<sup>a</sup>Unless otherwise specified, all reactions were carried out using **1** (0.25 mmol), **2** (0.50 mmol), Ag<sub>2</sub>CO<sub>3</sub> (0.025 mmol), 1,10-phen (0.125 mmol) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.75 mmol) in DMF (1.0 mL) at 80 °C for 12 h. Isolated yield. <sup>b</sup> without 1,10-phen.

We then applied this optimal reaction condition to various substituted oxocarboxylates. Our catalytic system was successfully amenable to a wide range of  $\alpha$ -oxocarboxylates, and good to excellent yields were achieved with substrates bearing both electron-deficient and electron-rich substituents (**3a-3f**). This transformation also showed satisfactory tolerance with halogen groups (Cl, Br and I) which provided useful handles for further functionalization through traditional cross coupling reactions (**3g-3k**). Methyl 2-

isocynoacetate also gave the products in good yields (**3l**). It is noteworthy that aliphatic  $\alpha$ -oxocarboxylates were compatible in this reaction as well albeit gave lower yields (**3m** and **3n**). Heterocyclic  $\alpha$ -oxocarboxylates were found to be favored under this catalytic system to afford the corresponding products (**3o**). In addition,  $\alpha$ -oxocarboxylates with naphthyl group (**3p**) also participated in this decarboxylative process with a high reactivity.

## Conclusions

In summary, we have developed a novel silver catalysed oxidative decarboxylation-cyclization of  $\alpha$ -oxocarboxylates and isocyanides to construct oxazoles. In this reaction, a variety of substituted  $\alpha$ -oxocarboxylates were well-tolerated. The mechanistic investigations including *operando* IR, EPR and radical inhibit experiments supported our proposed mechanism well. From these mechanistic experiments, acyl cation was observed utilizing *in-situ* IR and Ag(II) was also monitored through EPR. Finally, this reaction provided an efficient pathway to synthesize oxazoles and showed a potential application prospect.

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## Notes and references

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