



Synthesis of β -oxopropylcarbamates in a recyclable AgBr/ionic liquid catalytic system: An efficient assembly of CO₂ under ambient pressure

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ABSTRACT

A green and recyclable catalytic system based on AgBr and an ionic liquid (IL) was developed for the three-component coupling reaction of propargylic alcohols, secondary amines and carbon dioxide (CO₂). A series of target carbamates, especially those generated from challenging substrates, could be obtained smoothly at atmospheric CO₂ pressure in a straightforward one-pot process. Moreover, the catalyst loading reached the lowest level ever reported. Particularly, this catalytic system exhibited robust constancy and could be reused at least 5 times with retention of high catalytic activity. It is worth noting that this is the first catalytic system which could be recycled successfully for this reaction.

1. Introduction

Over the past few years, there has been a great deal of interest in the chemical fixation of carbon dioxide (CO₂) for its nontoxic, non-flammable, inexpensive, ubiquitous and renewable properties, which exhibits enormous possibilities for the constructions of carbon-carbon bonds and carbon-nitrogen bonds in organic synthesis [1]. However, the valorisation of CO₂ into valuable compounds remains a great challenge due to its high thermodynamic stability and kinetic inertness [2]. Gratifyingly, remarkable progress has been achieved in this area. Utilizing CO₂ to prepare various organic chemicals, such as carboxylic acids [2c,3], alcohols [3a,4], amides [1g,5], esters [6], carbonates [2c,3a,7], carbamates [2c,8] have been developed successfully through several effective catalytic processes. Among them, carbamates are a series of versatile compounds which have been widely employed in agriculture, pharmacology and organic synthesis [9]. However, carbamates are traditionally synthesized through the process involved with highly toxic phosgene or carbon monoxide, which may cause serious environmental pollutions and potential safety problems [9a]. Therefore, utilizing CO₂ to establish an environmentally friendly synthetic protocol which could efficiently afford carbamates is highly attractive [10].

As of late, the three-component reaction of propargylic alcohols,

secondary amines and CO₂ is regarded as a potential route to effectively prepare carbamates, namely β -oxopropylcarbamate due to its prominent synthetic characteristics such as high atom economy, easy operations, simple and inexpensive raw materials [8b]. Several strategies including the employments of Ag [11], Cu [12], Fe [13], La [14], Ru [15] compounds as the metallic catalysts or 7-methyl-triazabicyclodecene (MTBD), triazabicyclodecene (TBD) as the organocatalysts [16] have been reported to facilitate this three-component reaction. Particularly, He and co-workers [11b] developed the Ag₂WO₄/PPh₃ catalytic system which could smoothly convert diverse substrates into the target β -oxopropylcarbamates under 0.5 MPa. They attributed the excellent catalytic activity to the dual activation of Ag₂WO₄ towards both the propargylic alcohols and CO₂. Subsequently, they further [11e] reported a Ag₂CO₃/(*p*-MeOC₆H₄)₃P system for the three-component reaction with high turnover number (TON) and turnover frequency (TOF) value under 2.0 MPa in CHCl₃. Although remarkable progress has been achieved, there is still no catalytic system reported that allows for the efficient recycling and reuse of the catalyst in this coupling reaction, which has been one of the main barriers that limit its further applications. Therefore, developing a green and recyclable catalytic system which could efficiently catalyze the coupling reaction via eco-friendly process under mild conditions is desirable.

Ionic liquids (ILs) [17] are a series of green and promising solvents

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which have been widely applied in CO₂ capture and activation areas due to their superior affinity and capacity with CO₂. Particularly, the virtually unlimited tunability of ILs provides the possibilities to introduce several specific anions for the chemical activation of CO₂. Furthermore, the ILs are generally immiscible with low-polar solvents, which may facilitate the extraction of products and the separation of the catalysts. Moreover, ILs are extremely low volatile and highly thermally stable. The abovementioned properties suggest that introducing ILs for the green synthesis of β -oxopropylcarbamate is a feasible and promising methodology.

Herein, we reported an ionic liquid based AgBr/1-ethyl-3-methylimidazolium acetate ([C₂C₁im][OAc]) catalytic system for the one-pot synthesis of β -oxopropylcarbamates through the three-component reaction of propargylic alcohols, secondary amines and CO₂ at atmospheric pressure and mild temperature without any additives or traditional volatile solvents. Particularly, this catalytic system could be easily recycled at least 5 times with the lowermost catalyst loading ever reported. These excellent catalytic performances are attributed to the utilization of the green and recyclable ionic liquids which could act as the dual activators for both substrates and CO₂ [18].

2. Experimental

2.1. Materials

All the compounds involved including the substrates, silver salts and ionic liquids were purchased from Aladdin, Sigma-Aldrich, TCI, Macklin, Alfa in China and used without further manipulation. CO₂ used for purging and reacting was from Wuhan Zhongchunhua And Technology Ltd in the purity of 99.999%.

2.2. The three-component reaction of propargylic alcohols, secondary amines and CO₂

AgBr (0.05 mmol, 1 mol%), [C₂C₁im][OAc] (1.25 mmol, 25 mol%), propargylic alcohols (5 mmol) and secondary amines (5 mmol) were added to a Schlenk tube equipped with a stir bar. After the system was purged with CO₂ for three times, the mixture was stirred at 45 °C under 0.1 MPa of CO₂ for the desired time. When the reaction completed, the mixture was extracted with diethyl ether (3 × 15 mL). The upper layers were collected and dried under vacuum to give the crude products, which could be purified by further column chromatography on silica gel using petroleum ether/ethyl acetate (100:1-20:1) as an eluent (see part 2.3, Data in Brief).

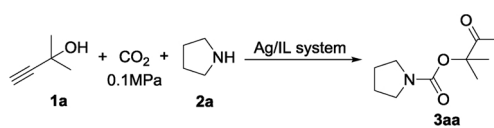
2.3. Characterizations

¹H NMR was recorded on a Bruker Avance III HD 500 MHz spectrometer with CDCl₃ used as the solvent referenced to TMS (0 ppm). ¹³C NMR was recorded at 126 MHz in CDCl₃ and CDCl₃ (77.0 ppm) was used as internal reference. Chemical shifts (δ) and coupling constants (*J*) are given in ppm and hertz (Hz), respectively. HRMS was recorded on a Bruker Daltonics microTOF-QII mass spectrometry instrument.

3. Results and discussion

The three-component coupling reaction of 2-methylbut-3-yn-2-ol (**1a**), pyrrolidine (**2a**) and CO₂ was selected as the model reaction for exploring the optimal catalytic system. As shown in Table 1, the blank reaction indicated that this reaction could not proceed without catalysts under present conditions (entry 1). Meanwhile, no products were detected in the presence of AgBr or [C₂C₁im][OAc] separately (entries 2–3). Gratifyingly, the usage of 1 mol% of AgBr in combination with [C₂C₁im][OAc] could efficiently catalyze this reaction (entry 4). On the basis, various Ag salts such as AgCl, AgI, AgOAc, Ag₂WO₄, AgPF₆, Ag₂O, AgNO₃ and Ag₂CO₃ were employed together with [C₂C₁im]

Table 1
Screening of the reaction conditions^a.



Entry	Catalytic system	Yield-(%) ^b
1	/	/
2	AgBr	/
3	/	[C ₂ C ₁ im][OAc]
4	AgBr	[C ₂ C ₁ im][OAc]
5	AgCl	[C ₂ C ₁ im][OAc]
6	AgI	[C ₂ C ₁ im][OAc]
7	AgOAc	[C ₂ C ₁ im][OAc]
8	Ag ₂ WO ₄	[C ₂ C ₁ im][OAc]
9	AgPF ₆	[C ₂ C ₁ im][OAc]
10	Ag ₂ O	[C ₂ C ₁ im][OAc]
11	AgNO ₃	[C ₂ C ₁ im][OAc]
12	Ag ₂ CO ₃	[C ₂ C ₁ im][OAc]
13	AgBr	[C ₄ C ₁ im][OAc]
14	AgBr	[C ₂ C ₁ im][BF ₄]
15	AgBr	[C ₂ C ₁ im][NTf ₂]
16	AgBr	[C ₂ C ₁ im]I
17	AgBr	[C ₂ C ₁ im]Br
18	AgBr	[C ₂ C ₁ im][OTf]
19	AgBr	[C ₂ C ₁ im][PF ₆]
20	AgBr	[C ₂ C ₁ im][ClO ₄]
21	AgBr	[C ₂ C ₁ im][HSO ₄]
22	AgBr	[C ₂ C ₁ im][(CH ₃) ₂ PO ₄]
23	AgBr	[C ₂ C ₁ im][NO ₃]

^a Reaction conditions: [Ag] (0.05 mmol), ILs (1.25 mmol), 2-methylbut-3-yn-2-ol (**1a**) (5 mmol), pyrrolidine (**2a**) (5 mmol), CO₂ (0.1 MPa), 45 °C, 8 h.

^b Yields were determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

[OAc] for the coupling reaction and moderate to excellent yields were successively obtained (entries 5–12). Compared with them, AgBr exhibited better catalytic performance. Afterwards, different cations and anions in the ILs were examined to evaluate the effects of the ions on catalytic activities (the structures of ionic liquids see part 1, Data in Brief). Firstly, the ethyl imidazole cation was replaced by the *n*-butyl one, which led to a slight reduce of the catalytic activity (entry 13). Subsequently, when using BF₄⁻, (CF₃SO₂)₂N⁻, Br⁻, CF₃SO₃⁻, PF₆⁻, ClO₄⁻, HSO₄⁻, (CH₃)₂PO₄⁻ or NO₃⁻ to replace OAc⁻, the yields of the desired carbamates decreased significantly (entries 14–15, 17–23). Furthermore, the coupling reaction could not proceed in [C₂C₁im]I with iodide ions as the anions (entry 16). These screening results indicated that [C₂C₁im][OAc] was the optimal choice for this reaction. Additionally, other reaction condition parameters such as temperature and reaction time were further investigated (see part 2.4–2.5, Data in Brief) and the results implied that the optimal AgBr/[C₂C₁im][OAc] system could efficiently catalyze the reaction at 45 °C and atmospheric CO₂ pressure.

With the establishment of the optimal catalytic system and reaction conditions, the substrate scope was further explored. The results were applied in Table 2 (product characterization details see part 3, Data in Brief). Firstly, a range of propargylic alcohols was employed to undergo the three-component reaction with **2a** and CO₂. It was satisfactory to see that various propargylic alcohols with different substituent groups, such as methyl, ethyl, isobutyl, cyclopentyl, cyclohexyl and phenyl groups could be converted into the desired β -oxopropylcarbamates in moderate to excellent yields (entries 1–7). Notably, the reaction outcome depends largely on the structure of the propargylic alcohol. For instance, this system performed well with high yields obtained in the cases of **1a-1c** bearing the less sterically hindered methyl or ethyl groups (entries 1–3). However, the introduction of a six-membered ring at the propargylic position led to a dramatic decrease on yields (entries

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