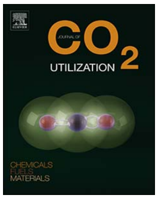
Journal of CO_2 Utilization 24 (2018) 120–127

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

journal homepage: www.elsevier.com/locate/jcou



Silver-catalyzed regioselective coupling of carbon dioxide, amines and aryloxyallenes leading to *O*-allyl carbamates

Chaorong Qi[a,b,*], Donghao Yan[a], Wenfang Xiong[a], Huanfeng Jiang[a,**]

[a] *Key Lab of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China*

[b] *State Key Lab of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China*

ARTICLE INFO

Keywords:
Allenes
Carbamates
Carbon dioxide fixation
Multicomponent reactions
Silver

ABSTRACT

A silver-catalyzed regioselective three-component coupling reaction of carbon dioxide, amines and aryloxyallenes using triazabicyclo[4.4.0]dec-5-ene (TBD) as a base and ligand has been developed for the first time. The reaction provides a facile and efficient methodology for the synthesis of a wide range of new acetal-type *O*-allyl carbamates in moderate to excellent yields. NMR studies revealed that the cooperation of silver salt and TBD might be the key for the success of the transformation. The attractive features of this method include the mild reaction conditions, excellent regioselectivity, broad functional group tolerance, and simple procedure.

1. Introduction

The chemical fixation of carbon dioxide (CO_2) into value-added compounds has attracted much attention in recent years, because CO_2 is regarded as an abundant, nontoxic and renewable C1 resource [1]. However, due to its thermodynamical and kinetic stability, the activation of CO_2 often requires harsh reaction conditions (such as high temperature and high CO_2 pressure) or air– and moisture–sensitive catalysts or reagents, which will limit their application. Thus, the development of new and efficient methodologies for the conversion of carbon dioxide, especially under mild reaction conditions, is still highly desirable.

During the past decades, many carbon-heteroatom (C—N and C—O) bond formation reactions involving CO_2 have been developed for the synthesis of a range of functional molecules, such as ureas [2], carbamates [3], quinolinones [4], tetramic acids [5] and quinazolidinones [6]. Among these transformations, the atom-economical synthesis of organic carbamates via nucleophilic addition of the in situ generated carbamic acids to C—C unsaturated bonds, has become one of the most promising methods for the chemical utilization of CO_2, because organic carbamates constitute an important class of compounds, which have found a vast array of applications in organic synthesis [7], pharmaceutical [8] and agrochemical industries [9]. Conventionally, the preparation of organic carbamates is mainly based on the use of highly toxic phosgene and its derivatives such as isocynates as the raw materials, which might cause environmental and safety issues [10].

In the past decades, great progress has been achieved in the intramolecular addition of carbamic acids to C—C unsaturated bonds. Many substrates, such as propargylamines [11], o-alkynylanilines [12], amides [13], allenyl amines [14] and allyl amines [15], have been examined for the synthesis of various cyclic carbamates (Scheme 1a). However, in sharp contrast, the related intermolecular addition to access acyclic carbamates is rather limited (Scheme 1b). Only vinyl ethers [16] and terminal alkynes [17] have been reported previously as the coupling partner to react with CO_2 and amines under high CO_2 pressure conditions while vinyl ethers showed very low reactivity. Therefore, the activation of both CO_2 and other unsaturated hydrocarbons for the coupling reaction to assemble structurally interesting and useful carbamate products still remains a challenge.

As part of our ongoing program directed toward the development of novel multi-component reactions for the conversion of CO_2 into organic carbamates [18], herein, we wish to report a silver-catalyzed regioselective coupling reaction of CO_2, amines and aryloxyallenes using triazabicyclo[4.4.0]dec-5-ene (TBD) as a base and ligand, which provides an efficient and straightforward method for the synthesis of a wide range of new acetal-type *O*-allyl carbamates under mild very reaction conditions (Scheme 1c).

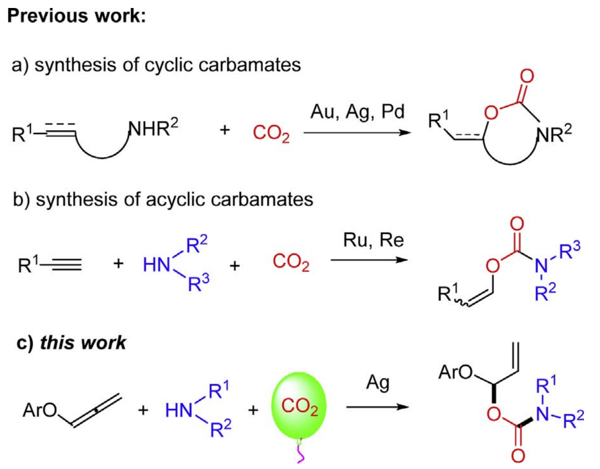
---

[*] Corresponding author at: Key Lab of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China.

[**] Corresponding author.

E-mail addresses: crqi@scut.edu.cn (C. Qi), jianghf@scut.edu.cn (H. Jiang).

https://doi.org/10.1016/j.jcou.2017.12.013
Received 21 September 2017; Received in revised form 23 November 2017; Accepted 21 December 2017



Scheme 1. Synthesis of carbamates from CO_2.

2. Results and discussion

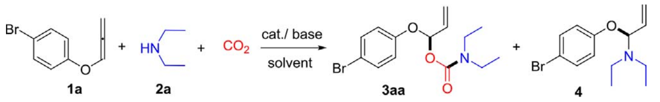
2.1. Optimization of the reaction conditions

Initially, 4-bromophenyl allenyl ether (**1a**) and diethylamine (**2a**) was chosen as the model substrates for the optimization of the reaction conditions, and the results are summarized in Table 1. Pleasingly, when the reaction was carried out under 1 atm of CO_2 in the presence of 10 mol% of AgOAc and 3 equiv of triazabicyclo[4.4.0]dec-5-ene (TBD) at 40 °C for 12 h, the desired product, 1-(4-Bromophenoxy)allyl diethylcarbamate (**3aa**), was obtained in 90% yield (entry 1). The reaction was very clean in this case and trace amount of direct hydroamination product **4** was observed by GC–MS analysis.[19] Two control experiments showed that both silver salt and base are necessary for the reaction to proceed smoothly (entries 2 and 3). With the exception of AgCl, other silver salts examined including Ag_2CO_3, $AgBF_4$, $AgNO_3$, and AgF could also catalyze the reaction efficiently under these conditions but the amount of the side product **4** was increased in those cases (entries 4–8). Copper salts such as CuOAc gave a complex mixture and no trace of desired product was detected (entry 9). The reaction also became complicated when $Pd(OAc)_2$ was used as the catalyst and **3aa** was formed in a low yield (entry 10). Screening of different bases showed that 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and triethylamine were also able to promote the transformation to give the desired product in 84% and 76% yields, respectively, while DABCO and pyridine were ineffective (entries 11–14). The solvent has great influence on the transformation. Beside toluene, THF as solvent could also furnish **3aa** in high yield, but the use of other solvents, such as DMF, MeCN, 1,4-dioxane and DMSO resulted in low yields (entries 15–19). Further optimization showed that decreasing the loading of AgOAc or TBD would diminish the yield (entries 20 and 21). Moreover, complete consumption of **1a** was observed after 12 h. Shortening the reaction time led to lower yield while prolonging the reaction time had no positive effect on the yield of the desired product (entries 22 and 23).

2.2. Substrate scope of the reaction

With the optimal reaction conditions in hand, we then explored the scope and limitations of the silver-catalyzed three-component coupling

Table 1
Optimization of the reaction conditions[a].



Entry	Catalyst	Base	Solvent	Conversion of **1a** (%)	Yield (%)[b]	
					3a	**4**
1	AgOAc	TBD	toluene	100	90 (85)	trace
2	AgOAc	–	toluene	52	27	trace
3	–	TBD	toluene	8	n.d.[c]	trace
4	Ag_2CO_3	TBD	toluene	100	85	4
5	$AgBF_4$	TBD	toluene	100	80	5
6	$AgNO_3$	TBD	toluene	99	81	9
7	AgF	TBD	toluene	100	89	3
8	AgCl	TBD	toluene	44	10	trace
9	CuOAc	TBD	toluene	46	n.d.	n.d.
10	$Pd(OAc)_2$	TBD	toluene	100	30	3
11	AgOAc	DBU	toluene	100	84	trace
12	AgOAc	NEt_3	toluene	99	76	12
13	AgOAc	DABCO	toluene	100	trace	trace
14	AgOAc	pyridine	toluene	12	trace	9
15	AgOAc	TBD	THF	99	80	4
16	AgOAc	TBD	DMF	68	38	15
17	AgOAc	TBD	MeCN	47	29	trace
18	AgOAc	TBD	1,4-dioxane	68	33	trace
19	AgOAc	TBD	DMSO	80	22	n.d.
20[d]	AgOAc	TBD	toluene	51	24	3
21[e]	AgOAc	TBD	toluene	62	40	5
22[f]	AgOAc	TBD	toluene	90	81	trace
23[g]	AgOAc	TBD	toluene	100	90	trace

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.5 mmol), CO_2 (1 atm, balloon), catalyst (0.025 mmol), base (0.75 mmol), solvent (2 mL), 40 °C, 12 h.

[b] GC yield with dodecane as internal standard. Number in parentheses is the yield of isolated product.

[c] n.d. = not detected.

[d] The reaction was carried out with 5 mol% of AgOAc.

[e] The reaction was carried out with 1.0 equiv of TBD.

[f] The reaction was carried out for 10 h.

[g] The reaction was performed for 14 h.