Tetrahedron Letters 50 (2009) 6491–6493

Contents lists available at ScienceDirect

Tetrahedron Letters

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

Palladium-catalyzed carboxylative cyclization of α-allenyl amines in dense carbon dioxide

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ARTICLE INFO

Article history:
Received 12 August 2009
Revised 31 August 2009
Accepted 3 September 2009
Available online 6 September 2009

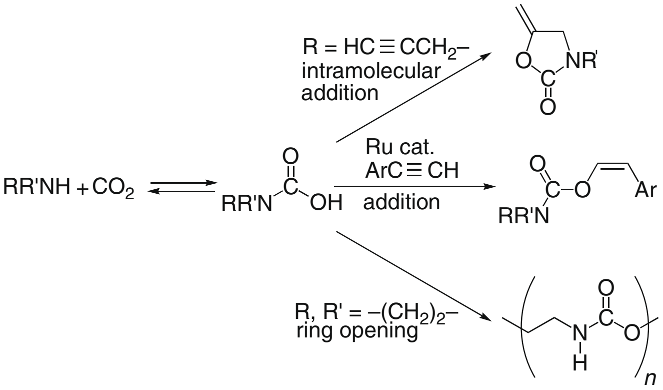
Keywords:
Allenes
Carbon dioxide fixation
Homogeneous catalysis
Palladium
Urethane

ABSTRACT

Carboxylative transformation of 2,3-allenic amines into 5-vinyl-1,3-oxazolidin-2-ones was promoted by palladium catalysts under a pressurized CO_2 condition. The presence of a stereogenic center adjacent to the allene group resulted in the formation of the corresponding cyclic urethane as a single trans-diastereomer.

Transformation of carbon dioxide (CO_2) into synthetically useful compounds is of great interest from the viewpoints of utilization of naturally abundant carbon resources.[1] The CO_2 molecule having a Lewis acidic character can react with primary and secondary amines to form carbamic acids or ammonium carbamates, however, the resulting carbamate moieties revert easily to the parent amines by releasing CO_2 under atmospheric or reduced pressure.[2] As principal methods for transformation of the thermodynamically less stable carbamic acid families into robust functionalized molecules, urethane synthesis from CO_2 and amines has been broadly reported.[3,4] On the basis of our spectroscopic studies on the facile formation of *N*,*N*-dialkylcarbamic acids from secondary amines in supercritical CO_2 ($scCO_2$), we have recently demonstrated the inter- and intra-molecular additions of the carbamic acids generated in $scCO_2$ to carbon–carbon triple bonds as well as ring-opening copolymerization of aziridines with $scCO_2$ affording stimuli-responsive poly(urethane-amine)s (Scheme 1).[5,6] On the other hand, the addition of carbamic acid derivatives to carbon–carbon double bonds has scarcely been investigated, except for the stoichiometric transformation of ammonium carbamates and cyclic diolefins bound to a Pd center,[7] the three-component reaction of CO_2, secondary amines, and vinyl ethers,[8] and the iodine-mediated cyclization of allylic and homoallylic amines with CO_2.[9] With regard to various metal-catalyzed nucleophilic cyclization of allenic compounds,[10] aminoallenes are potential candidates for substrates in catalytic CO_2 fixation reactions. Here, we disclose the intramolecular addition of amines having two cumulated double bonds with Pd catalysts in dense CO_2, affording cyclic urethanes.

The carboxylative cyclization of aminoallenes with CO_2 was conducted in a batch autoclave (50 mL) containing palladium catalysts with a substrate/catalyst ratio of 150. Table 1 summarizes the results of a test reaction of *N*-methyl-2,3-butadienylamine (**1a**) and CO_2 under supercritical conditions of 8.0 MPa and 50 °C for 15 h (Eq. 1). Although **1a** was quantitatively recovered after the reaction in the absence of metal catalysts (entry 1), palladium acetate catalyzed the CO_2 incorporation to give 3-methyl-5-



Scheme 1. Urethane synthesis via formation of carbamic acids.

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doi:10.1016/j.tetlet.2009.09.015

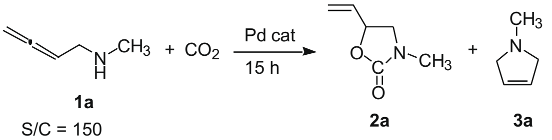
Table 1
Carboxylative cyclization of **1a**[a]

Entry	Catalyst	Solvent	Yield of **2a**[b] (%)
1	–	–	0
2	$Pd(OCOCH_3)_2$	–	41
3	$PdCl_2[P(OC_2H_5)_3]_2$	–	20
4	$Pd(OCOCH_3)_2$	Toluene	46
5	$PdCl_2[P(OC_2H_5)_3]_2$	Toluene	30
6	$PdCl_2(CH_3CN)_2$	Toluene	37
7	$Pd(dba)_2$	Toluene	37
8	$PdCl_2[P(OC_6H_5)_3]_2$	Toluene	27
9	$Pd[P(OC_6H_5)_3]_4$	Toluene	33
10	$PdCl_2[P(C_6H_5)_3]_2$	Toluene	0
11	$Pd[P(C_6H_5)_3]_4$	Toluene	0

[a] Reaction conditions: The reaction was carried out using **1a** (1.5 mmol) with a substrate/catalyst ratio of 150 at 50 °C for 15 h under CO_2 (8.0 MPa).

[b] Determined by ^1H NMR, using hexamethyldisilane as an internal standard.

vinyl-2-oxazolidinone (**2a**) in 41% yield as a 5-*exo* cyclization product (entry 2). A CO_2-soluble $P(OC_2H_5)_3$–Pd complex, which has been demonstrated as a suitable catalyst precursor for homogeneous reactions in $scCO_2$,[11] afforded a lower yield of **2a** (20%; entry 3). When toluene (1.5 mL) was added as a cosolvent to both the catalyst systems, the yields of **2a** were improved to 46% and 30%, respectively (entries 4 and 5), implying that the reaction may proceed in a liquid phase. In fact, visual inspection using a high-pressure view cell containing **1a** and toluene revealed that phase separation from the CO_2 phase occurred under the reaction conditions. Among the catalysts examined, both Pd(0) and Pd(II) precursors worked equally well. Pd complexes having $P(OC_6H_5)_3$ were also applicable to the urethane formation, whereas the use of the $P(C_6H_5)_3$ analogues resulted in a loss of catalytic activity (entries 8–11). Consequently, the following reactions were performed in the presence of toluene with $Pd(OCOCH_3)_2$ as the comparably effective catalyst.



(1)

By varying the CO_2 pressure at constant temperature of 50 °C, the maximum **2a** yield of 65% was obtained under the condition of 11.5 MPa (d_{CO_2} = 0.5 g mL^{-1}) for 15 h, as shown in Figure 1. The positive pressure effect can be explained by the enhancement of CO_2 uptake by amines. The reaction under higher pressure of CO_2 resulted in a drop in the yield, possibly due to a reduction of the liquid reaction phase in the high density region. Notably, a careful ^1H NMR analysis of each crude reaction mixture showed that a slight amount (<10%) of 1-methyl-3-pyrroline (**3a**) was formed simultaneously as a 5-*endo-trig* cyclization[12] product regardless of the CO_2 pressure.

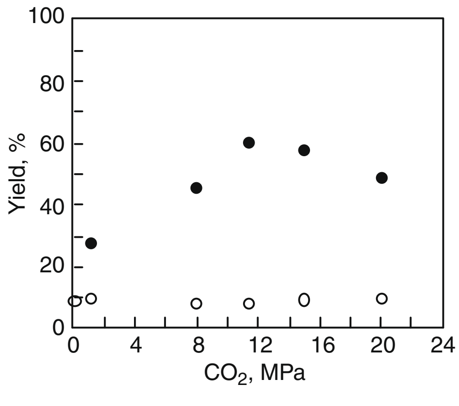
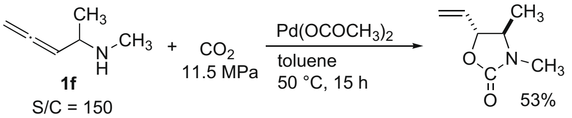


Figure 1. CO_2 pressure effect on yields of **2a** (●) and **3a** (○) for the carboxylative cyclization of **1a**. Reaction conditions: **1a** (1.5 mmol), $Pd(OCOCH_3)_2$ (0.01 mmol), toluene (1.5 mL) at 50 °C for 15 h.

Figure 2 shows the temperature dependence on the yields of **2a** at a constant density of CO_2 (0.5 g mL^{-1}). Although the catalytic activity was improved significantly by changing the temperature from 30 to 50 °C, a further increase in the temperature to 100 °C resulted in a lowering of the ratio of **2a**/**3a** to 30/22. It can be ascribed to the easy release of CO_2 from carbamic acid upon heating, as confirmed by our preceding NMR experiments.[5c] Under the optimized conditions of 11.5 MPa and 50 °C, the use of other cosolvents such as CH_2Cl_2 and THF had an insignificant effect on the yield of **2a**.

The scope of the carboxylative cyclization under the standard conditions is summarized in Table 2. While secondary 2,3-butadienylamines (**1a**–**d**) were converted into the desired products with a yield range of 44–65%, the primary amine (**1e**) provided a poor result in line with our previous studies (entries 1–5).[5b] It is noteworthy that the reaction of **1f** bearing a stereogenic center adjacent to the allene group proceeded smoothly to give the desired urethane as a single trans-diastereomer (Eq. 2). The relative stereochemistry was determined by a $^3J_{HH}$ coupling constant of 7.8 Hz between the hydrogens attached to the C-4 and C-5 carbons on the oxazolidinone ring in the ^1H NMR spectrum, in addition to an NOE experiment. Similar diastereoselective reactions have been reported for the related 5-*exo* cyclization of α-substituted allenic substrates promoted by Pd catalysts.[13]



(2)

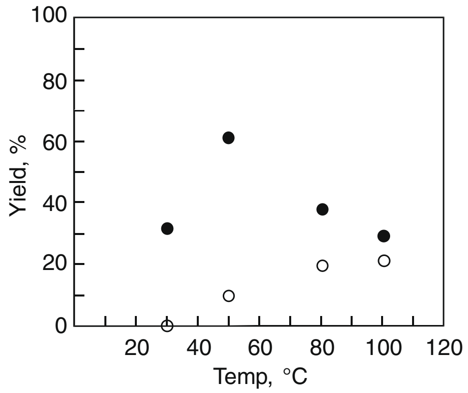


Figure 2. Reaction temperature dependence in the formation of **2a** (●) and **3a** (○). Reaction conditions: **1a** (1.5 mmol), $Pd(OCOCH_3)_2$ (0.01 mmol), CO_2 (d = 0.5 g mL^{-1}), toluene (1.5 mL) for 15 h.

Table 2
Carboxylative cyclization of **1**[a]

Entry	$CH_2{=}C{=}CHCH_2NHR$	Yield[b,c] (%)
1	R = CH_3, **1a**	65
2	R = C_2H_5, **1b**	44(39)
3	R = C_3H_7, **1c**	54(49)
4	R = $CH_2C_6H_5$, **1d**	53
5	R = H, **1e**	2

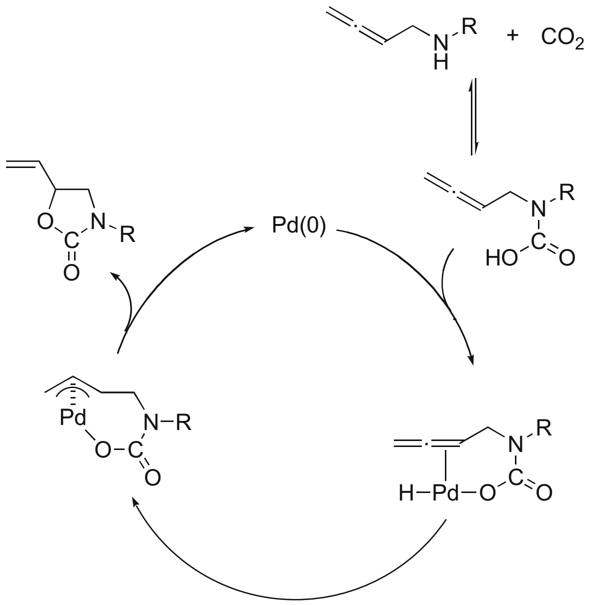
[a] Reaction conditions: The reaction was carried out using **1** (1.5 mmol) with a substrate/catalyst ratio of 150 in toluene (1.5 mL) at 50 °C for 15 h under CO_2 (11.5 MPa).

[b] Determined by ^1H NMR.

[c] Isolated yields were in parentheses.

A possible catalytic mechanism of the urethane formation is shown in Scheme 2. The catalytic reaction is likely initiated by the oxidative addition of carbamic acid generated from the allenic amine and CO_2, which is responsible for the formation of hydridopalladium species. The allene moiety inserts into the Pd–H bond to give an η^3-allylpalladium intermediate, and the following reductive elimination would furnish the cyclization product.[14] A similar mechanistic sequence has been expected for the Pd-catalyzed intramolecular hydroamination of allenes in which the presence of acetic acid enhances the rates and yields.[15] In the light of the reaction conducted in dense CO_2 favoring the carbamic acid formation from secondary amines, the hydropalladation mechanism seems to be feasible, while an alternative mechanism involving nucleophilic attack on the allene bound to a Pd(II) center[16] may be operative in the case of the 5-*endo* cyclization producing **3a**.[17] Although 1,3-dienes may also be accessible to the η^3-allylpalladium analogues by insertion into palladium hydrides, an attempt to extend the reaction to *N*-methyl-2,4-pentadienylamine was unsuccessful.

In summary, we have first accomplished the Pd-catalyzed cyclic urethane synthesis via intramolecular addition of carbamic acids across the carbon–carbon double bond in allenic substrates. The dense CO_2 conditions proved to be crucial for smooth CO_2 fixation. Although further improvement of the catalyst performance is needed for the reaction, the present direct addition system provides a straightforward method without forming salt waste, which is thus of great promise for achieving environmentally benign processes.



Scheme 2. A plausible mechanism for the palladium-catalyzed carboxylative cyclization of allenic amines.

Acknowledgments

This work is supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 18065007; 'Chemistry of *Concerto* Catalysis') and partially supported by GCOE program from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

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17. The cyclic urethane product **2a** containing an allylic carbon–oxygen bond proved to be stable even in the presence of Pd catalysts such as $Pd(OCOCH_3)_2$, $Pd(dba)_2$, and $Pd[P(OC_6H_5)_3]_4$ under the reaction conditions that will preclude the possibility of catalytic access from **2a** to **3a**.