

1

온화한 조건에서 CO₂를 고리형 카보네이트에 화학적 고정하기 위한 효율적 금속 및 무용제 유기 분해 시스템



2

Lin Wang, Guangyou Zhang, Koichi Kodama and Takuji Hirose
Green Chem., 2016, 18, 1229

4

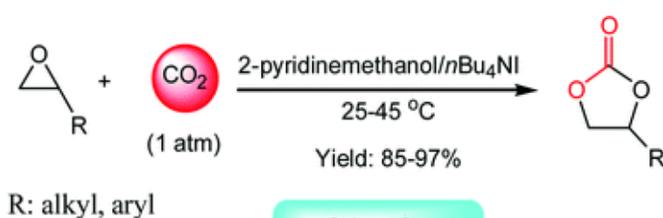
3

발표자 : 김다운
지도교수 : 남기평

An efficient, metal- and solvent-free catalytic system was developed for the conversion of CO₂ and epoxides to the corresponding cyclic carbonates under mild conditions (T = 25–45 °C, 1 atm CO₂) in high-to-excellent yields. The catalyst could be easily recycled, providing a more sustainable process for the chemical fixation of CO₂.

Introduction

The increasing emission of carbon dioxide (CO₂) into the Earth's atmosphere has raised several concerns about the environmental impact of this greenhouse gas, thus necessitating the need for mitigating CO₂ emission. However, the development of efficient catalysts for CO₂ activation and fixation is hindered by its inherent thermodynamic stability and kinetic inertness.



Solvent-free
Metal-free
Recyclable
Operationally simple

Herein, we report a new, metal- and solvent-free, binary catalyst system consisting of commercially available pyridinemethanol as the HBD (methanol) containing an organonitrogen component (pyridine) and nBu₄NI as the co-catalyst for the cycloaddition of epoxides to ambient CO₂, affording five-membered cyclic carbonates under ambient conditions.

Experiments

The reaction of epichlorohydrin with CO₂ was used as the model reaction to study the effect of various parameters on the reaction outcome.

Under the optimal reaction conditions, various epoxides were investigated in the presence of 2-pyridinemethanol/ nBu₄NI. After the extraction of cyclic carbonate with diethyl ether, the catalysts were dried in vacuo and used under the same reaction conditions for investigating the reusability and stability.

Results and Discussion

At atmospheric pressure of CO₂, when only pyridine was used as the catalyst, the corresponding cyclic carbonate was obtained. The result indicates that pyridine can activate CO₂ in this reaction and indicate that the OH group of 2-pyridinemethanol plays a crucial role in promoting the reaction: initiating the epoxide ring-opening reaction. The results of the binary catalytic system (entries 6–8, Table 1) show that the yield increased in the order: Cl– < Br– < I–

Table 1 Catalyst screening for the reaction conditions^a

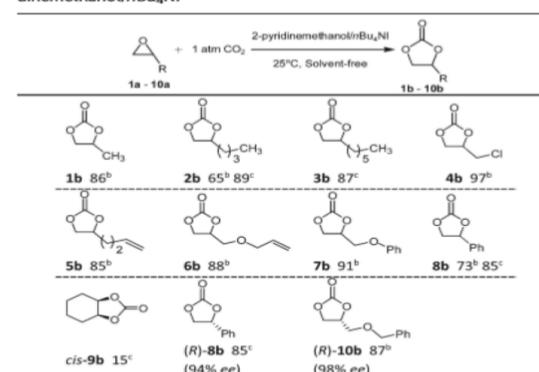
Entry	Catalyst	T (°C)	Yield ^b (%)
1	Pyridine	25	3
2	2-Pyridinemethanol	60	39
3	2-Pyridinemethanol	25	18
4	2-Pyridinemethanol	60	73
5	2-Pyridinemethanol	60	0

6	Epichlorohydrin + nBu ₄ NCl	25	52
7	Epichlorohydrin + nBu ₄ NBr	25	67
8	Epichlorohydrin + nBu ₄ NI	25	92
9	nBu ₄ NI	25	26
10	Epichlorohydrin + nBu ₄ NI	25	78
11	Epichlorohydrin + nBu ₄ NI	25	58
12	Epichlorohydrin + nBu ₄ NI	25	73
13	Epichlorohydrin + nBu ₄ NI	25	92

^a Reaction conditions: epichlorohydrin (6 mmol), catalyst (0.3 mmol, 5 mol%), CO₂ (99.999%, balloon), 24 h. ^b Isolated yield.

Epichlorohydrin gave the best result because of the electron-withdrawing effect of the substituent, favouring the nucleophilic attack at the epoxide ring carbon atom, and the functional group was stable in the reaction, indicating the excellent efficiency of the catalytic system. However, because of the higher steric hindrance of the epoxides than the other epoxides, a slightly higher reaction temperature (45 °C) was required for higher product yields.

Table 3 Cycloaddition of CO₂ to various epoxides catalyzed by 2-pyridinemethanol/nBu₄NI^a



^a Reaction conditions: epoxide (6 mmol), binary catalyst (8 mol%), CO₂ (99.999%, balloon), reaction time 20 h. ^b T = 25 °C, isolated yield. ^c T = 45 °C, isolated yield.

In the experiment for the reusability and stability, there's no significant loss of activity after six catalytic cycles, indicating that the organocatalytic system is very stable.

conclusions

A simple and efficient binary organocatalytic system was developed for the synthesis of cyclic carbonates from epoxides and CO₂ under metal- and solvent-free conditions.

2-Pyridinemethanol/nBu₄NI is one of the few metal-free systems for the synthesis of cyclic carbonates from epoxides.

Diverse epoxides were transformed into the corresponding cyclic carbonates in high-to-excellent yields under almost ambient conditions.

Optically pure epoxides were converted to the corresponding cyclic carbonates with minimal loss in the ee values. (2,6-pyridinedimethanol/nBu₄NI is recyclable at least six times without any significant loss of activity)

References

- T. Sakakura, J. C. Choi and H. Yasuda, Chem. Rev., 2007, 107, 2365.
- B. Schöffner, F. Schöffner, S. P. Verevkin and A. Börner, Chem. Rev., 2010, 110, 4554.
- J. Ma, J. Song, H. Liu, J. Liu, Z. Zhang, T. Jiang, H. Fan and B. X. Han, Green Chem., 2012, 14, 1743.

5