Journal of Saudi Chemical Society (2015) 19, 112–115

King Saud University

Journal of Saudi Chemical Society

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ORIGINAL ARTICLE

N-heterocyclic carbene catalyzed synthesis of dimethyl carbonate via transesterification of ethylene carbonate with methanol

Guang-Fen Du [a,*], Hao Guo [a], Ying Wang [a], Wen-Juan Li [a,*], Wei-Jie Shi [b], Bin Dai [a]

[a] School of Chemistry and Chemical Engineering, Shihezi University, Xinjiang 832000, China
[b] College of Chemistry and Material Science, Shandong Agricultural University, Shandong 832000, China

Received 28 January 2014; revised 28 February 2014; accepted 3 March 2014
Available online 19 March 2014

KEYWORDS

N-heterocyclic carbene;
Dimethyl carbonate;
Transesterification;
Ethylene carbonate

Abstract An organocatalytic protocol for the synthesis of dimethyl carbonate has been developed. Under the catalysis of 5 mol% N-heterocyclic carbenes, ethylene carbonate undergoes transesterification reaction with methanol under very mild reaction conditions, producing dimethyl carbonate with high efficiency. Furthermore, this N-heterocyclic carbene promoted transesterification can be scaled-up easily without lose of the conversion of dimethyl carbonate.

1. Introduction

N-heterocyclic carbenes (NHCs) have gained considerable attention in the past decade, which have been applied broadly in transition-metal-catalysis [1] as well as organocatalysis [2–5]. As an important type of nucleophilic organocatalyst, NHCs can catalyze various reactions. In addition to the classical benzoin reaction [6,7] and Stetter reaction [8–10], a variety of organic transformations such as homoenolate reactions [11–13], redox reactions [14–16], formal cycloadditions [17–19], polymerization [20] and other reactions [21–23] can be catalyzed by NHCs. NHCs can also be utilized as highly efficient nucleophilic organocatalyst to catalyze transesterifications [24–26].

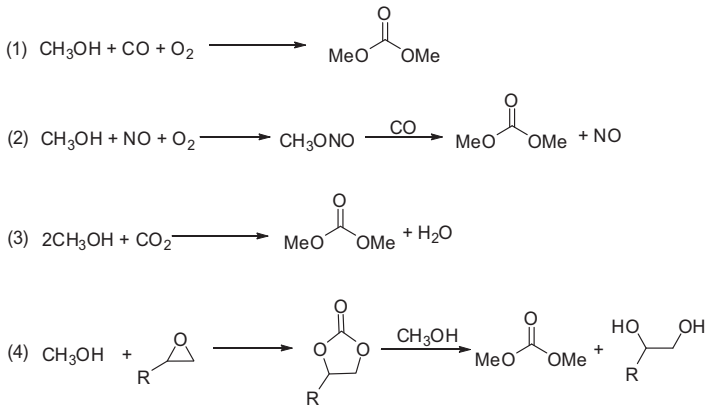
Dimethyl carbonate (DMC) is a non-toxic and environmentally benign building block that is used as a safe substitute for highly toxic phosgene, dimethyl sulfate and methyl iodine in carbonylation and methylation reactions [27]. DMC can also be used as a raw material in the production of polycarbonate resins [28] and owing to its high oxygen content, it can be used as a gasoline octane enhancer [29]. Therefore, the development of efficient and environmentally benign methods for the production of DMC has attracted broad attention in recent years [30]. Aside from the traditional phosgenation route, oxy-carbonylation of methanol and carbonylation of methyl nitrite have been established for the production of DMC. However, these routes suffer from the usage of toxic gases (CO or NO) and the production of corrosive hydrogen chloride (Scheme 1, Eqs. 1 and 2). The reaction of CO_2 with methanol provides another alternative method for the preparation of DMC, but unfortunately, the reaction is restricted by thermodynamics limitation and the

* Corresponding authors. Tel.: +86 993 2057213; fax: +86 993 2057270.
E-mail addresses: duguangfen@shzu.edu.cn (G.-F. Du), lwj01_tea@shzu.edu.cn (W.-J. Li).

Peer review under responsibility of King Saud University.

ELSEVIER Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.jscs.2014.03.003



Scheme 1 Typical synthesis routes of DMC.

conversion of methanol is very low [29,31] (Scheme 1, Eq. 3). Based on the conversion of CO_2, the transesterification of cyclic carbonates with methanol provides a more promising approach for the production of DMC [32] (Scheme 1, Eq. 4).

In the past decade, great efforts have been devoted to this attractive process and numerous homogeneous as well as heterogeneous catalytic protocols have been developed [33–36]. However, some of these catalytic methods suffer from harsh reaction conditions, long reaction time and relatively low conversion or selectivity. Therefore, the development of efficient and environmentally benign catalytic approach for the reaction is still of desirable. In line with our continuing interest of NHCs catalysis, we proposed that NHCs can be used to promote the transesterification of cyclocarbonate with methanol to produce DMC. In this paper, we would like to disclose our preliminary results about this work.

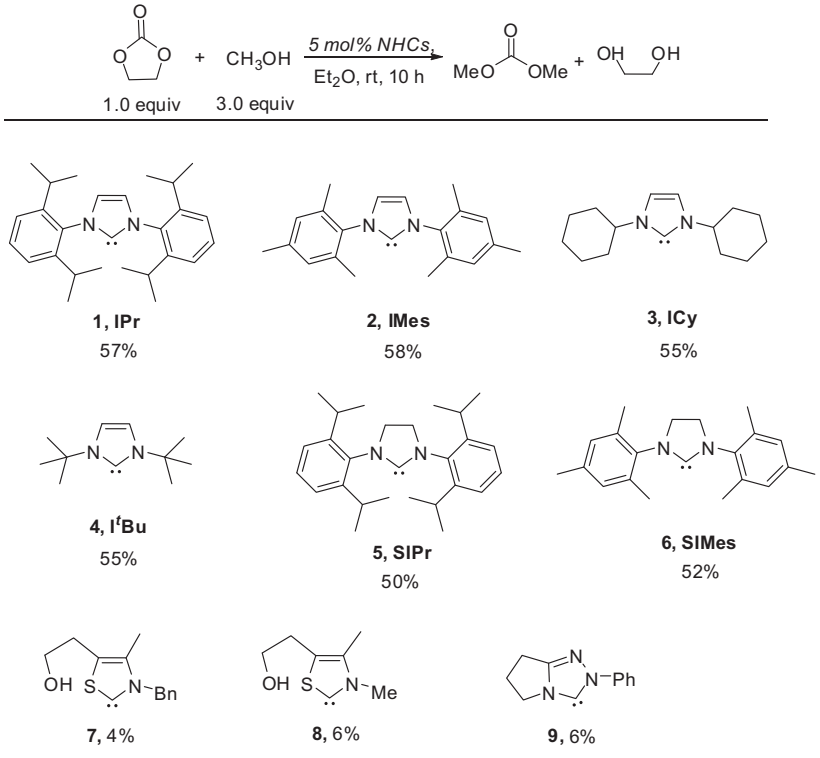
2. Experimental part

2.1. Materials and physical measurements

Unless otherwise indicated, all reactions were conducted under nitrogen atmosphere in oven-dried glassware with magnetic stirring bar. GC–MS spectra were measured on an Agilent 7890A/5975C GC–MS spectrometer. All starting materials were obtained from commercial supplies and used as received. Solvents were purified by standard methods.

2.2. General Procedure for NHC-Catalyzed Transesterification Reaction of Ethylene Carbonate with alcohol

To a suspension of IMes·HCl (18 mg, 0.05 mmol) in 1.0 mL anhy. toluene was added ^{t}BuOK (6.0 mg, 0.05 mmol) under N_2. After



Scheme 2 Evaluation of NHCs.