Tetrahedron 74 (2018) 2914–2920

Contents lists available at ScienceDirect

Tetrahedron

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

Efficient synthesis of 2-oxazolidinones and quinazoline-2,4(1*H*,3*H*)-diones from CO_2 catalyzed by tetrabutylammonium fluoride

Akira Fujii, Hideaki Matsuo, Jun-Chul Choi, Tadahiro Fujitani, Ken-ichi Fujita*

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki, 305-8565, Japan

ARTICLE INFO

Article history:
Received 15 March 2018
Received in revised form
16 April 2018
Accepted 18 April 2018
Available online 21 April 2018

Keywords:
Carbon dioxide
Catalysis
Tetrabutylammonium fluoride

ABSTRACT

By employing tetrabutylammonium fluoride (TBAF) as a catalyst, the various carboxylative cyclizations of the propargylic amines having internal alkynes with CO_2 proceeded to afford the corresponding 2-oxazolidinones. In this case, it was also found that the generated 2-oxazolidinones were tautomerized into the corresponding 2-oxazolones due to the basicity of TBAF. In addition, we performed the synthesis of quinazoline-2,4(1*H*,3*H*)-dione from 2-aminobenzonitrile and CO_2 by using TBAF as a catalyst.

1. Introduction

The chemistry of carbon dioxide (CO_2) has drawn much attention in the last two decades because CO_2 is abundant, nontoxic, non-flammable, and easily available. Moreover, CO_2 is one of the most attractive C_1 building blocks to displace toxic reagents such as phosgene and carbon monoxide.[1] CO_2 also has great potential as a renewable resource for the production of value-added chemicals, and thus much effort has been expended to incorporate CO_2 in fine chemical synthesis.[2] However, because CO_2 is thermodynamically stable and kinetically inert due to its high oxidation state, organometallic complexes of noble metals must often be used as catalysts for the chemical fixations of CO_2.[3] Recently, transformations of CO_2 have also been achieved by metal-free organocatalysts through the activation of CO_2 or substrates.[4]

Previously, as an example of organocatalysts, tetrabutylammonium fluoride (TBAF) was reported to catalyze the cyclization reaction of β-alkynyl hydrazines to give the corresponding azaproline derivatives.[5] This transformation appeared to be caused by a quaternary ammonium cation−π interaction with the triple bond of alkynes.[6] In addition, several other TBAF-catalyzed cyclization reactions of alkynyl compounds have been reported.[7] Recently, we discovered that the carboxylative cyclization of a propargylic amine having a terminal alkyne with CO_2 is catalyzed by the quaternary ammonium salts to provide the corresponding 2-oxazolidinone.[8] Among the quaternary ammonium salts applied to the carboxylative cyclization, TBAF was found to be the most effective. We report herein the TBAF-catalyzed carboxylative cyclization of various propargylic amines with CO_2 to provide 2-oxazolidinones, and the quaternary ammonium salt-catalyzed tautomerization of a 2-oxazolidinone into the corresponding 2-oxazolone. Moreover, we found that TBAF was the most effective quaternary ammonium salt for the synthesis of quinazoline-2,4(1*H*,3*H*)-diones from 2-aminobenzonitriles and CO_2.[9]

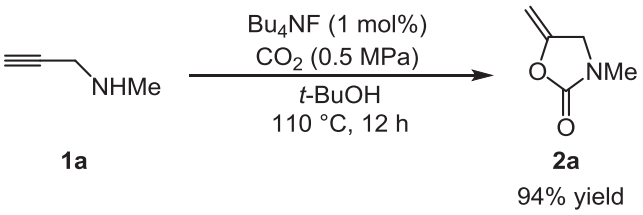
2. Results and discussion

2.1. Synthesis of 2-oxazolidinones from propargylic amines and CO_2

2-Oxazolidinones are important heterocyclic compounds in many applications in organic synthesis and pharmaceutical chemistry. For example, they can be used as cholesteryl ester transfer protein inhibitors and monoamine oxidase inhibitors.[10] Syntheses of 2-oxazolidinones by the carboxylative cyclization of propargylic amines with CO_2 have been reported to be catalyzed by organometallic complexes of noble metals[11] such as silver[12] and gold.[13] Recently, a number of metal-free catalysts, such as superbases,[14] N-heterocyclic carbenes,[15] triethanolamine,[16] and cyanuric acid,[17] which are less expensive and environmentally benign, have been used for the carboxylative cyclization of propargylic amines with CO_2 as alternatives to organometallic catalysts. Very recently, we found that 1 mol% of TBAF catalyzes the carboxylative

* Corresponding author.
E-mail address: k.fujita@aist.go.jp (K. Fujita).

https://doi.org/10.1016/j.tet.2018.04.059
0040-4020/



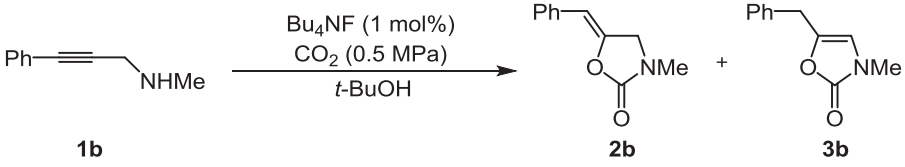
Scheme 1. Carboxylative cyclization of a propargylic amine **1a** with CO_2.

cyclization of propargylic amine **1a**, which has a terminal alkyne, to provide the corresponding 2-oxazolidinone **2a** under CO_2 pressure of 0.5 MPa at 110 °C, as shown in Scheme 1. This reaction was considered that the propargylic amine **1a** reacted with CO_2 to form the corresponding carbamic acid, then the carbamic acid was dually activated by a quaternary ammonium cation–π interaction with the triple bond and a fluoride ion–hydrogen interaction with O*H* of the carbamic acid.[8]

First, we performed the TBAF–catalyzed carboxylative cyclization of propargylic amine **1b**, which has an internal alkyne, with CO_2 as shown in Table 1. A *t*-butanol solution of propargylic amine **1b** and 1 mol% of TBAF as a catalyst were stirred for 12–24 h in a sealed autoclave under a CO_2 atmosphere of 0.5 MPa at 90–110 °C. By carrying out the carboxylative cyclization of **1b** at 110 °C for 12 h, the corresponding 2-oxazolidinone **2b** was obtained in an 83% chemical yield along with a small amount of a 2-oxazolone **3b** (3%; Table 1, entry 1). Similarly, in our previous report using an N-heterocyclic carbene as a catalyst, a small amount of 2-oxazolidinone was obtained in the carboxylative cyclization of a propargylic amine.[15a] Then, by carrying out the carboxylative cyclization of **1b** at 90 °C for 24 h, the corresponding 2-oxazolidinone **2b** was obtained in an 85% chemical yield and the formation of 2-oxazolone **3b** was suppressed, probably due to the low reaction temperature (1%; Table 1, entry 3).

We subsequently examined the time-course of the carboxylative cyclization of propargylic amine **1b** at 90 °C (Fig. 1). The results showed that the chemical yield of 2-oxazolidinone **2b** increased till

Table 1
Carboxylative cyclization of propargylic amine **1b** with CO_2.[a]



Entry	Temp (°C)	Time (h)	Yield of **2b** (%)[b]	Yield of **3b** (%)[b]	Recovery of **1b** (%)[b]
1	110	12	83	3	0
2	90	12	55	1	44
3	90	24	85	1	9

[a] Reaction conditions: **1b** (1 equiv.), TBAF (1 mol%), *t*-BuOH (1 M based on **1b**), carried out at 90–110 °C for 12–24 h in a sealed autoclave under a CO_2 atmosphere of 0.5 MPa.
[b] Determined by the integration of ^{1}H NMR with reference to an internal standard.

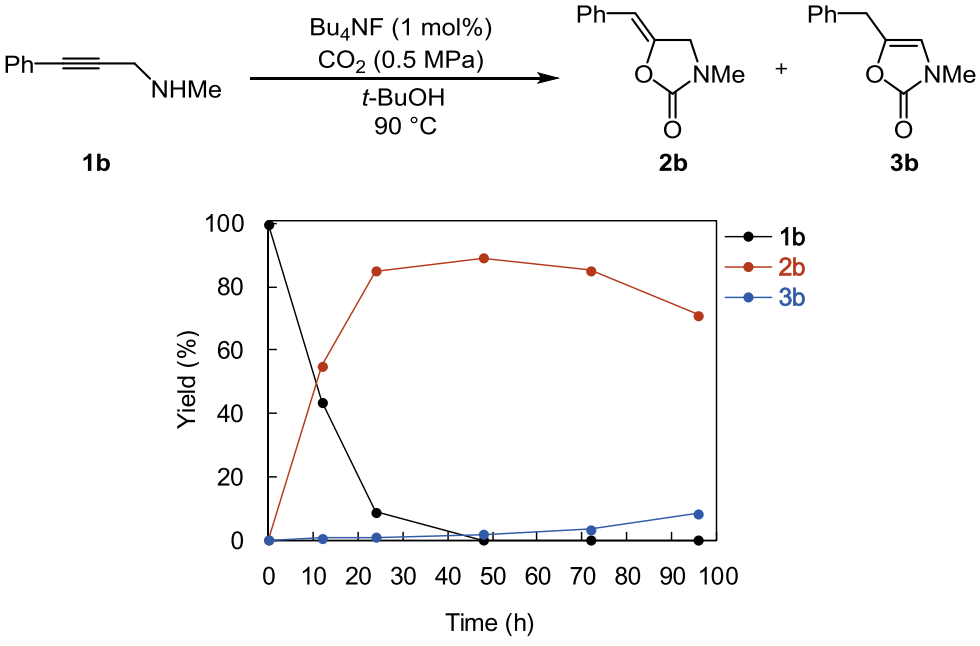


Fig. 1. Time-course curves of the carboxylative cyclization of propargylic amine **1b**.