Tetrahedron Letters 53 (2012) 4267–4272

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

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

Efficient solvent-free aminolysis of epoxides under $(C_4H_{12}N_2)_2[BiCl_6]Cl{\cdot}H_2O$ catalysis

Hong-Fei Lu *, Lei-Lei Sun, Wen-Jun Le, Fei-Fei Yang, Jun-Tao Zhou, Yu-Hua Gao

School of Biology and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, People's Republic of China

ARTICLE INFO

Article history:
Received 16 March 2012
Revised 16 May 2012
Accepted 18 May 2012
Available online 24 May 2012

Keywords:
Epoxides
Amines
Aminolysis
β-Amino alcohols

ABSTRACT

An efficient and rapid procedure for ring opening of various epoxides with aromatic, aliphatic and heterocyclic amines is developed at room temperature under solvent-free conditions in the presence of $(C_4H_{12}N_2)_2[BiCl_6]Cl{\cdot}H_2O$ (1 mol %). This catalyst can be reused several times without losing of its activity.

© 2012 Elsevier Ltd. All rights reserved.

β-Amino alcohols are versatile building blocks in the synthesis of a wide range of biologically active natural and synthetic products, unnatural amino acids, medicinal chemistry, and chiral auxiliaries for asymmetric synthesis.[1–5] The most practical and commonly used method for synthesizing these compounds is the direct aminolysis of an epoxide with an excess of amine by heating.[6] However, under these conditions, it reacts very slowly because of low reactive epoxides and sluggish amine. Sensitive functional groups also undergo undesirable side reactions, which mean a poor regioselectivity. To eliminate such problems in the ring opening of epoxides by amine nucleophiles, several activators or promoters, such as Lewis acids ($BiCl_3$,[7] $ZnCl_2$,[8] $CoCl_2$,[9] and $ZrCl_4$[10]) heteropoly acids,[11] ionic liquids,[12–14] metal amides,[15–19] and others are developed to perform reaction under mild conditions.[20–24]

But some of these methods often involve other problems like the use of large amounts of expensive agents, air and/or moisture sensitive catalysts, the long reaction times, low selectivity, and hazardous organic solvents. There has been reported a method of the ring-opening of epoxides with a variety of aliphatic amines in water at room temperature without using any catalyst.[25] The procedure of this reaction is very simple and the yields are generally high, but additions of aromatic amines to epoxides are sluggish and give very low yields. In previous work, we used[26] acidic ionic liquid and alkaline ionic liquid in a similar reaction, and made some achievements. While in this reaction, the rearrangement of epoxides to allyl alcohols under basic conditions as well as polymerization in strongly acidic conditions gets many by-products, which resulting in a low yield of the desired products. Moreover, the main disadvantage of above mentioned methods is that the catalysts cannot be recovered or reused because it will be destroyed in the procedure. Therefore, the introduction of new and efficient methods for this transformation is still in demand.

Here, we introduce an efficient and room-temperature procedure for regioselective ring opening of various epoxides with aromatic amines catalyzed by reusable catalyst $(C_4H_{12}N_2)_2[BiCl_6]Cl{\cdot}H_2O$[27] (Figs. 1 and 2) under solvent-free conditions. Compared $(C_4H_{12}N_2)_2[BiCl_6]Cl{\cdot}H_2O$ to $BiCl_3$, $Bi(OTf)_3$, and $Bi(TFA)_3$, it is particularly more attractive because it is a solvent-free reaction in a shorter reaction time and the most important is the catalyst can be recovered (see Scheme 1).

The reaction of aromatic amine with aliphatic epoxides was examined and only one product was observed in the reaction mixture. The predominant attack of amine on the less substituted carbon of epoxide, such as epichlorohydrin, propylene oxide, and glycidyl tertbutyl ether, provided an ideal yield of more than 84% within 5–10 min (Table 1, entries 1–15). Excellent regioselectivity toward the only product B was also achieved in each case. While the styrene oxide underwent cleavage by various aromatic amines

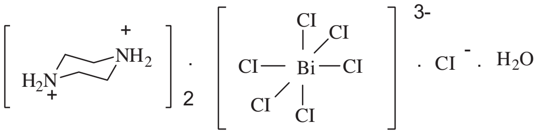


Figure 1. Crystal related structures.

---

* Corresponding author.
E-mail address: zjluhf1979@hotmail.com (H.-F. Lu).

0040-4039/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tetlet.2012.05.079

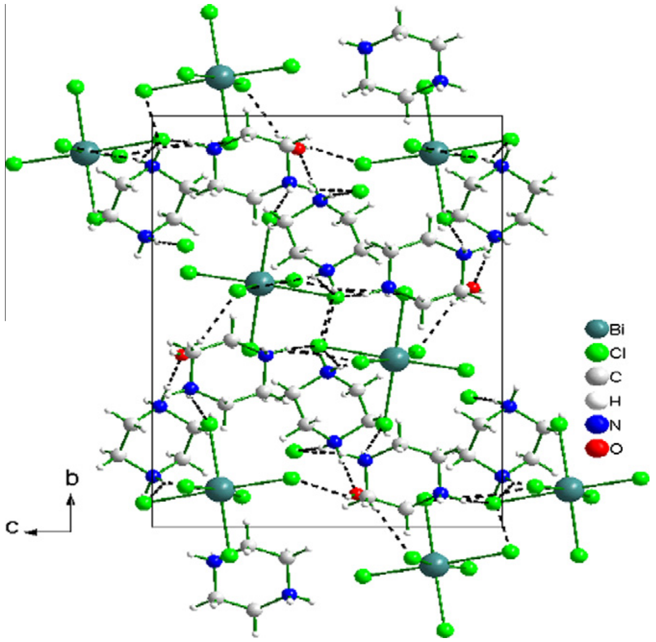


Figure 2. Crystal structures of polymers.

with preferred attacking at the benzylic position by using $(C_4H_{12}N_2)_2[BiCl_6]Cl\cdot H_2O$ (1 mol %) as the catalyst at room temperature. The reaction of aromatic amine with styrene oxide provided a yield of more than 90% with a regioselectivity of product A. In the case of cyclohexene and cyclopentene oxides (Scheme 2 and Table 1, entries 21–30), the reaction was generalized to various aromatic amines. Only one trans-isomer was formed, complete conversion of raw materials to the desired product within 5–10 min is observed. The procedure of these reactions is very simple, and the yields are generally high. To the best of our knowledge, these results represent the highest regioselectivity reported to date for nucleophilic ring opening of epoxide with aromatic amines. Therefore, we suggest that the attack of nucleophile is governed by the nature of oxirane and the stability of carbonium ion.[28] In aryl oxirane, the positive charge on oxygen appears to be localized on the more highly substituted benzylic carbon and gets the major product. For aliphatic oxirane gave the opposite regiochemistry of the aromatic substrates, possibly steric factors predominate over electronic factors.

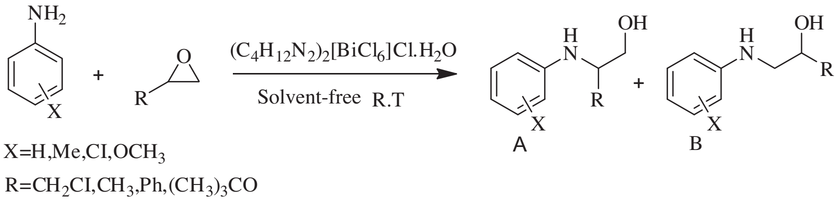
To claim $(C_4H_{12}N_2)_2[BiCl_6]Cl\cdot H_2O$ as a general catalyst for the activation of epoxides for nucleophilic attack by amines, we then investigated the ring opening of cyclohexene oxide with heterocyclic amines[29] in the presence of $(C_4H_{12}N_2)_2[BiCl_6]$ $Cl\cdot H_2O$ (1 mol %) and the results are summarized in Table 2.

Quantitative yields of the corresponding amino alcohols were obtained in the reaction of the ring opening of cyclohexene oxide with heterocyclic amines such as 4-aminopyridine, imidazole, pyrazole, piperidine, and pyrrolidine. Only one trans-isomer was formed. Thus, the catalyst $(C_4H_{12}N_2)_2[BiCl_6]Cl\cdot H_2O$ enabled efficient coupling of heteroaromatic amines with cyclohexene oxide providing excellent yields of desired products.

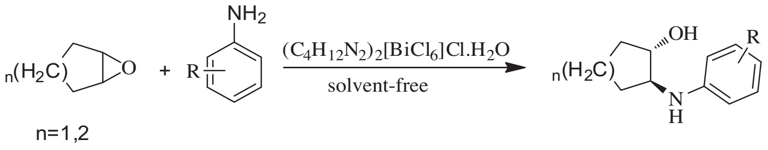
In a typical study, the reaction of cyclohexene oxide with aniline was carried out in the presence of various complexes at room temperature under solvent-free condition to evaluate which complex is more effective. The $(C_4H_{12}N_2)_2[BiCl_6]Cl\cdot H_2O$ provided excellent yield within a short reaction time (10 min), and afforded high regioselectivity . Only one tran-isomer (Table 3, entries1–5) was formed. Then using $(C_4H_{12}N_2)_2[BiCl_6]Cl\cdot H_2O$ (1 mol %) as the catalyst, the ring opening of cyclohexene oxide with aniline was investigated under various solvents. Solvents such as water, methanol, dichloromethane, toluene, and cyclohexane (Table 3, entries 6–10) provided low yields of the desired product (21–68%) within 180 min, while the same reaction under solvent-free condition afforded a yield of 97% within 10 min. Perhaps the most possible reason for the high reaction rate is due to the fact that under solvent-free condition, the concentration of catalyst is greater, so leading to reaction rate faster than the same reaction in the presence of various solvents.

The actual mechanism of these reactions is not clear at present. However, a plausible mechanistic pathway can be offered where $(C_4H_{12}N_2)_2[BiCl_6]Cl\cdot H_2O$ is recycled continuously throughout the course of the reaction (Fig. 3). This hypothesis is supported by recovery of the catalyst via a simple separation and its direct reuse for four times without significant loss of activity.

In conclusion, we have demonstrated a novel, mild, and efficient preparation method of β-amino alcohols by the ring opening of epoxides with amines using $(C_4H_{12}N_2)_2[BiCl_6]Cl\cdot H_2O$ at room temperature. The specific advantages of the reactions are that be carried out under solvent-free, in a shorter time, more simple operation, working for aromatic and aliphatic/ heterocyclic amines, less by-products, higher yields, the catalyst have the characters of reusable and excellent regioselectivity which are notable advantages of this protocol.



Scheme 1.



Scheme 2.

Download English Version:

https://daneshyari.com/en/article/5264885

Download Persian Version:

https://daneshyari.com/article/5264885

Daneshyari.com