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An efficient catalyst for ring opening of epoxides with phenol and thiophenol under solvent-free conditions

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ABSTRACT

An efficient and rapid procedure for ring opening reaction of various epoxides with phenol and thiophenol derivatives was developed. The procedure can be obtained at room temperature under solvent-free condition in presence of $(C_4H_{12}N_2)_2[BiCl_6]Cl\cdot H_2O$ (1 mol %). This catalyst can be reused several times without significant loss of activity.

1. Introduction

Epoxides are versatile and important intermediates in organic synthesis.[1,2] Nucleophile-involved epoxide ring opening reaction is of great importance in organic synthesis, since the reaction could offer a suitable route to get various kinds of β-substituted alcohols for different uses.[3] Therefore, how to develop a new catalyst and to improve the performance of the epoxide ring opening reaction have drawn an increasing attention. There have already been several references related to the ring opening of epoxides with alcohols, thiols, and amines, these reactions are mostly catalyzed by Lewis acids ($BiCl_3$, $FeCl_3$, $SnCl_4$, and $Al(OTf)_3$),[4–7] alumina,[8] metal complexes,[9–13] and silica gel.[14] Some examples of ring opening of epoxides under mild conditions are also reported.[15–19]

However, there are still many problems in these reported catalysis methods, such as the use of expensive reagents, catalyst activation difficulty, long reaction time, low selectivity, environmental hazards, and catalyst recycling problem. Therefore, the introduction of new methods for the nucleophilic-involved epoxides ring-opening, which could proceed under mild conditions, is still in demand and important for synthetic organic chemistry.

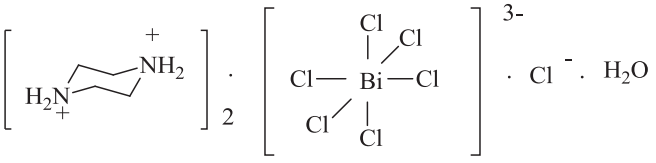

Fig. 1. Crystal related structures.

In our preliminary work, we used $(C_4H_{12}N_2)_2[BiCl_6]Cl\cdot H_2O$[20] (Figs. 1 and 2) to catalyze aminolysis of epoxides, and got a satisfied effect.[21] In order to indicate the extensive applicability of this catalyst, herein we investigated the ring opening reaction of epoxides with phenol and thiophenol derivatives under this reaction system (Schemes 1 and 2).

2. Results and discussion

Firstly, the reaction of phenolic derivatives with aliphatic monosubstituted epoxides was examined. The predominant product was observed through the attack of the hydroxy on the less hindered carbon of the compound, such as epoxypropane and phenyl

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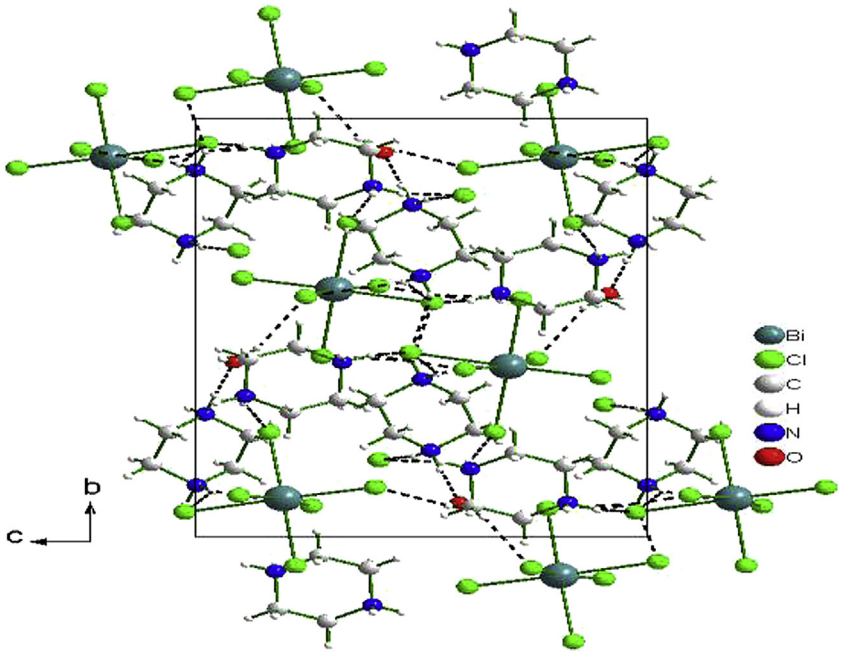
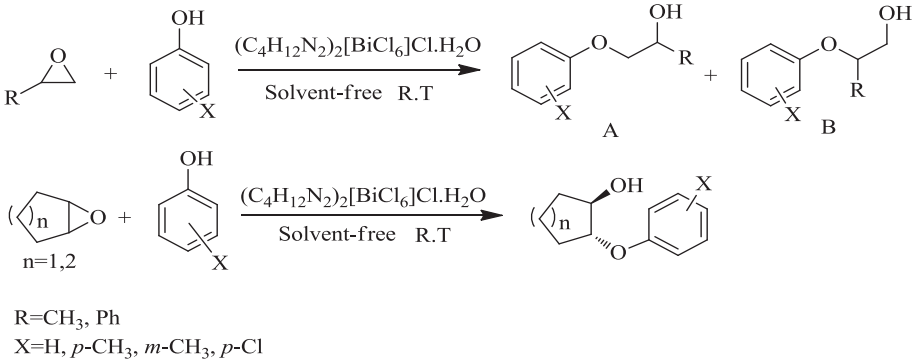
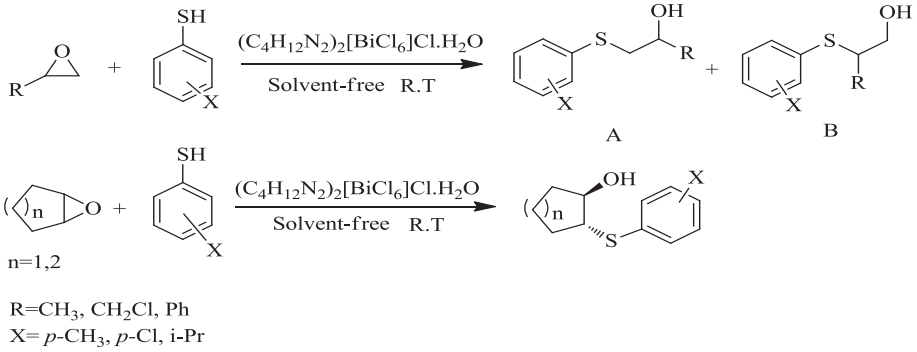


Fig. 2. Crystal structure of polymers.



Scheme 1. Alcoholysis of epoxides with phenols.



Scheme 2. Thiolysis of epoxides with thiophenol.

glycidyl ether, the reaction provided over 80% yield of the desired product within 10 min (Table 1, entries 1–5, 16–18). The possible reason was that steric effect predominated over electronic effect. However, in the reaction of phenolic derivatives with epoxyethylbenzene, the predominant attacking position of hydroxy was the benzylic position (Table 1, entries 6–8). We proposed that electronic effect predominated over steric effect in this reaction procedure. In the case of cyclohexene oxide and cyclopentene oxide, the reaction was generalized to phenolic derivatives, thus only the trans-isomer was formed (Table 1, entries 9–15). On the other