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A facile synthesis of 1,2-azidoalcohols by $(TBA)_4PFeW_{11}O_{39} \cdot 3H_2O$-catalyzed azidolysis of epoxides with NaN_3

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The catalytic efficiency of transition metal substituted polyoxometalates in the azidolysis of 1,2-epoxides has been studied in acetonitrile/water, using NaN_3 as the source of the azido group. The reaction is regioselective and afforded the corresponding products in high to excellent yields under mild reaction conditions. Fe (III) substituted polyoxometalate was identified as the optimal catalyst.

KEY WORDS: 1,2-azidoalcohols; catalysis; epoxide; polyoxometalate; sodium azide.

1. Introduction

Epoxides are often used as starting materials and intermediates in organic synthesis partly because their opening leads to 1,2-difuctionalized systems and partly because such a cleavage usually occurs specifically with regioselectivity. Indeed, reactions of epoxides with nucleophiles, Lewis acids, radicals, reducing agents, oxidizing agents, acids, and bases have all been well documented and utilized in synthesis [1]. Among the various nucleophiles employed in epoxide opening reactions, the azidolysis of epoxides enjoys a prominent position. 1,2-Azidoalcohols are versatile intermediates in organic synthesis since they are very important precursors of β-amino alcohols and vicinal diamines, which are present in numerous natural products [2]. Further, their importance is significant in the chemistry of carbohydrates and nucleosides [3].

Therefore, there is significant current interest in the ring opening of epoxides using azide. They are usually prepared through ring opening of epoxides by using different azides in suitable solvents. The classical protocol uses [3a,b,4] mixtures of NaN_3 and NH_4Cl in alcohol–water at 65–80 °C. Under these conditions, the azidolysis reaction requires a long reaction time (12–48 h) and the azidohydrin is often accompanied by isomerization, epimerization, and rearrangement of products [3a,b]. The improved methodologies developed for azidolysis of epoxides include the use of NaN_3 or $TMSN_3$ and a Lewis acid or a transition metal complex [5] or reaction in the presence of tetrabutylammonium salts of Cl, Br, and I [6]. pH-controlled azidolysis of epoxides was also studied in water using various Lewis acids and NaN_3 [4a,7], and in a recently reported system Sabitha and coworkers described the use of $CeCl_3 \cdot 7H_2O/NaN_3$ in acetonitrile for synthesis of 1,2-azidoalcohols [8].

Although all of the above methods and procedures have their own advantages, many of these procedures suffer from one or more drawbacks such as longer reaction times, strongly acidic conditions, unsatisfactory yields, and lack of regioselectivity, cost, and stability of the reagents. In this context, there is a great need to develop a mild and efficient method, which can be a valuable alternative for the synthesis of 1,2-azidoalcohols.

In this paper we report the azidolysis of epoxides in the presence of transition metal substituted polyoxometalates ($(TBA)_4PW_{11}MO_{39} \cdot 3H_2O$, M = V(III), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II)) as catalyst. Polyoxometalates provide a good basis for the molecular design of mixed oxide catalysts and they have high capability in practical uses. The catalytic function of heteropoly compounds has attracted much attention and they are used in solution as well as in the solid state. They are applied in bulk or supported forms, and both homogeneous and heterogeneous catalysis are possible [9]. Heteropoly compounds have several advantages as catalysts, which make them economically and environmentally attractive. On the one hand, heteropoly compounds have a very strong Bronsted acidity approaching the superacid region; on the other, they are efficient oxidants, exhibiting fast reversible multielectron redox transformations under rather mild conditions. These properties render heteropoly compounds potentially promising acid, redox, and bifunctional catalysts in

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homogeneous as well as in heterogeneous systems. In the last two decades, the broad utility of heteropoly compound acid and oxidation catalysis has been demonstrated in a wide variety of synthetically useful selective transformations of organic substrates [10]. However, there has been very little exploitation of their catalytic reactivity in nucleophilic ring-opening of epoxides [11].

2. Experimental

2.1. Preparation of the catalyst

In the course of our studies on polyoxometalates catalysis [12], we herein disclose our results on regioselective azidolysis of epoxides with sodium azide using transition metal substituted Keggin-type polyoxometalates ($(\mathrm{TBA})_4\mathrm{PW}_{11}\mathrm{MO}_{39} \cdot 3\mathrm{H}_2\mathrm{O}$, M = V(III), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II)) in a mixture of acetonitrile and water as solvent. These catalysts are readily available and easily prepared from $\mathrm{Na}_2\mathrm{WO}_4 \cdot 2\mathrm{H}_2\mathrm{O}$, $\mathrm{Na}_2\mathrm{HPO}_4$, and $\mathrm{M(NO}_3)_n$ by a slight modification of the previously reported method [13]. The formation of keggin structure and composition of the compounds were confirmed by IR, NMR and elemental analysis. Thermal gravimetric analysis was performed on all of the catalysts (between 25 and 600 °C). The results indicated that the hydration numbers are about 3.

2.2. Typical procedure

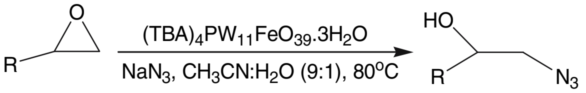
This procedure is performed by refluxing a mixture of the epoxide (1 mmol) and NaN_3 (1.1 mmol) in the presence of catalytic amounts of $(\mathrm{TBA})_4\mathrm{PW}_{11}\mathrm{FeO}_{39} \cdot 3\mathrm{H}_2\mathrm{O}$ (5 mol%) in an acetonitrile and water mixture (9:1) (3 mL) to give the corresponding 1,2-azidoalcohol (scheme 1). The progress of the reaction was monitored by GLC. The 1,2-azidoalcohols were purified by flash chromatography over silica gel and fully characterized by comparison of their spectral and physical data with those of known samples (table 1).

2.3. Catalytic reactions of phenyl glycidyl ether in the presence of different polyoxometalates

A mixture of phenyl glycidyl ether (1 mmol), NaN_3 (1.1 mmol) and catalytic amount of various substituted polyoxometalates (5 mol%) in $\mathrm{CH}_3\mathrm{CN}/\mathrm{H}_2\mathrm{O}$ (9:1) (3 mL) was stirred at reflux temperature to give the corresponding 1-azido-3-phenoxy-2-propanol for the selected reaction time. The progress of the reaction was monitored by GLC. The 1-azido-3-phenoxy-2-propanol was purified by flash chromatography over silica gel.

3. Results and discussion

We first examined the reaction of phenyl glycidyl ether with NaN_3 using catalytic amounts of various polyoxometalate complexes to give the corresponding 1-azido-3-phenoxy-2-propanol. Although the reaction without catalyst after 24 h gave a trace amount of product (below 5%), it was preceded catalytically upon addition of polyoxometalate complexes. Among the catalysts tested, $(\mathrm{TBA})_4\mathrm{PW}_{11}\mathrm{FeO}_{39} \cdot 3\mathrm{H}_2\mathrm{O}$ was found to be highly active for the reaction (94% yield), and the optimum ratio for this catalyst was found to be 0.05 equivalent. The catalytic activity for the other transition metal substituted polyoxometalates appears to be in the following order: $(\mathrm{TBA})_5\mathrm{PW}_{11}\mathrm{CuO}_{39}{\cdot}3\mathrm{H}_2\mathrm{O}(82\%) > (\mathrm{TBA})_5\mathrm{PW}_{11}\mathrm{ZnO}_{39} \cdot 3\mathrm{H}_2\mathrm{O}(80\%) > (\mathrm{TBA})_4\mathrm{PW}_{11}\mathrm{VO}_{40}{\cdot}3\mathrm{H}_2\mathrm{O}(70\%) > (\mathrm{TBA})_4\mathrm{PW}_{11}\mathrm{CrO}_{39}{\cdot}3\mathrm{H}_2\mathrm{O}(65\%) > (\mathrm{TBA})_5\mathrm{PW}_{11}\mathrm{MnO}_{39} \cdot 3\mathrm{H}_2\mathrm{O}(54\%) > (\mathrm{TBA})_5\mathrm{PW}_{11}\mathrm{CoO}_{39} \cdot 3\mathrm{H}_2\mathrm{O}(42\%) > (\mathrm{TBA})_5\mathrm{PW}_{11}\mathrm{NiO}_{39} \cdot 3\mathrm{H}_2\mathrm{O}(34\%) > (\mathrm{TBA})_5\mathrm{H}_2\mathrm{PW}_{11}\mathrm{O}_{39}{\cdot}\ 3\mathrm{H}_2\mathrm{O}(7\%)$. The reaction in 6:1 ratio of acetonitrile and water gave both of 1,2-azidoalcohol and 1,2-diol products but in 9:1 ratio of acetonitrile and water, we have only the azidolysis of epoxide. The optimum amount of NaN_3 in this system was found 1.1 mmol and when the higher amount of sodium azide was employed, a significant increase in the yield of reaction was not observed. The optimum temperature for all of the reactions was 80 °C.

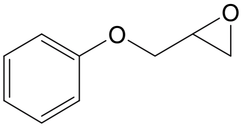
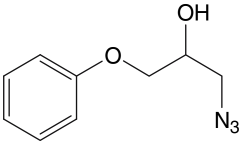
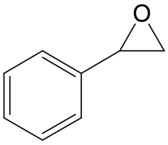
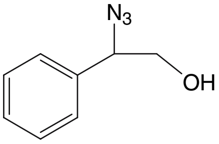
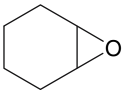
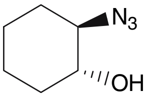
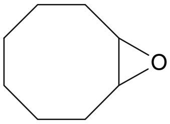
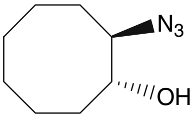
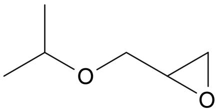
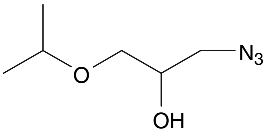
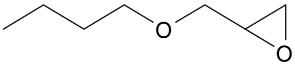
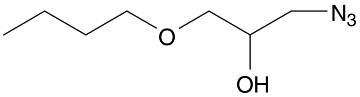
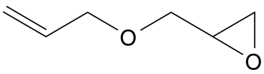
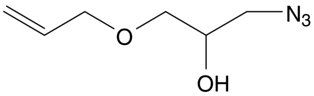
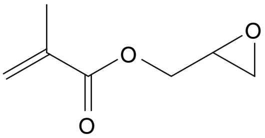
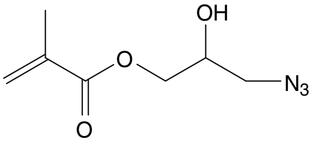
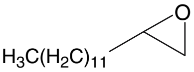
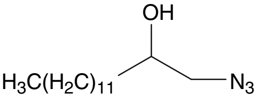
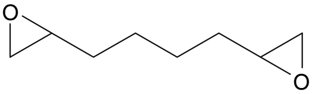
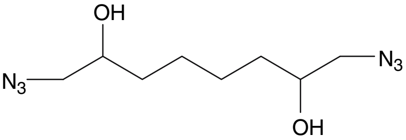
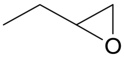
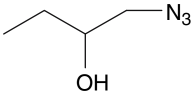
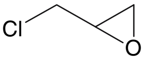
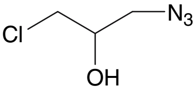


Scheme 1.

Phenyl glycidyl ether was treated with 1.1 equiv of sodium azide and 5 mol% of catalyst at reflux and after 4.5 h, there was formation of quantitative yield of 1-azido-3-phenoxy-2-propanol (table 1, entry 1). To show the scope of the reaction, we extended it to a variety of epoxides (scheme 1), and in all cases a very clean reaction was observed.

Because of the predominant attack of azide ion on the less hindered carbon of the epoxide, all the terminal epoxides gave highly regioselective azidohydrins in quantitative yields. Due to formation of the stabilized benzylic cation during the reaction, ring opening of styrene oxide with NaN_3 resulted in 2-azido-2-phenylethanol as the major product with selectivity 80:20 (table 1, entry 2). With cyclic epoxides, the ring opening completely took place via a trans-stereospecific pathway and giving only the trans isomers (table 1, entry 3). In order to see the effect of polar electron-withdrawing groups adjacent to the epoxide's ring, the reactions of 3-chloro-1,2-epoxypropane with azide was studied (table 1, entries 12), and in comparison of their physical and spectral data with those of authentic samples we only see the azidoalcohol product. This reaction was performed in short time with excellent yield. In case of acyclic terminal olefins (table 1, entry 9–11) the major product results from the attack of nucleophile at the less substituted carbon to give the 1,2-azidoalcohol in good

Table 1
Regioselective azidolysis of various epoxides with NaN_3 in the presence of $(TBA)_4PW_{11}FeO_{39} \cdot 3H_2O$ as catalyst under reflux.

Entry	Epoxide	Azidoalcohol	Time (h)	Yield (%)[a]
1			4.5	94
2			4.5	85[c]
3			2	93
4			17	4
5			2.5	97
6			3	83
7			3.5	93
8			3	86
9			17	90
10			5	58
11			5	95
12			3	95

[a] Yields refer to isolated yield.

[b] All products were identified by comparison of their physical and spectral data with those of authentic samples.

[c] The major product was 2-azido-2-phenylethanol with selectivity 80:20.

to excellent yields. In a comparison experiment, and in the same reaction conditions (scheme 1), we compare the reaction of phenyl glycidyl ether, styrene oxide and cyclohexene oxide in the presence of 5 mol% of our catalyst and $CeCl_3$. The results showed the superiority of our protocol in equivalent of catalyst, and thus in terms of regioselectivity, yields, and reaction times. The efficiency of the Fe (III) substituted polyoxometalate was tested in the reaction of phenyl glycidyl ether by a mixture of $(TBA)_5H_2PW_{11}O_{39} \cdot 3H_2O$ and $Fe(NO_3)_3$ as catalyst. In this reaction condition, we saw only 10% conversion.

4. Conclusion

In conclusion, we have demonstrated that $(TBA)_4[PFeW_{11}O_{39}] \cdot 3H_2O/NaN_3$ in an acetonitrile/water mixture (9:1) is a novel, stable, convenient and regioselective system for ring opening of epoxides to 1,2-azidoalcohols. It proceeds under mild and neutral reaction condition and many of advantages such as ease of preparation of catalyst, good reaction times, simplicity in operation, the low cost of reagents and catalyst, and high yields of the products make it a valuable alternative to the existing reagents reported in literature.

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