Inorganic Chemistry Communications 28 (2013) 37–40

Contents lists available at SciVerse ScienceDirect

Inorganic Chemistry Communications

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

Fe(III) substituted Wells–Dawson type polyoxometalate: An efficient catalyst for ring opening of epoxides with aromatic amines

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ARTICLE INFO

Article history:
Received 2 September 2012
Accepted 15 November 2012
Available online 23 November 2012

Keywords:
Catalysis
Ring opening
Epoxides
Aromatic amines
Aminolysis

ABSTRACT

Various β-aminoalcohols were prepared by the ring opening reaction of epoxides with aromatic amines in the presence of Fe(III) substituted Wells–Dawson type polyoxometalate, α_2-$[(n\text{-}C_4H_9)_4N]_7P_2W_{17}FeO_{61}\cdot 3H_2O$, as an efficient catalyst. The reaction was performed under neutral condition at room temperature and afforded the corresponding products in high to excellent yields.

Introduction

Polyoxometalate as an inorganic metal oxygen cluster anions, because of unique and intriguing properties including sizes, shapes, the variety of compositions, redox potentials, acidity and solubility, has attracted much attention in the recent decades. They have been covering a large area studied in the fields of chemistry, physics, biology and material science [1]. Up to the present, the Keggin $\{XM_{12}O_{40}\}$ and Wells–Dawson $\{X_2M_{18}O_{62}\}$ (where $M=W$, Mo, less frequently V and most common $X=P$, Si) structures have been most studied [1,2]. Among diver applications of POMs, their catalytic activity is the most important and much conspicuous. Various catalytic reactions in the presence of Keggin type polyoxometalates as catalyst have been reported [1]. However, the Wells–Dawson type heteropoly compounds had a relatively poor study in the catalytic reactions. So, in the context of our works [3] on the catalytic applications of polyoxometalates, the transition metal substituted Wells–Dawson type polyoxometalates were used as catalyst in the ring opening of epoxides by amines.

The oxygen-containing heterocycles are well-known carbon electrophiles capable of reacting with several nucleophiles to provide 1,2-difunctional products [4]. Ring opening reaction of epoxides with amines gave ß-aminoalcohols that are extensively used in the synthesis of neutral products [5] and biologically active compounds [6], as pharmaceuticals and medicine [7], as a powerful source of chirality and also as insecticidal agents [8]. Due to the direct aminolysis of epoxides perform with a large excess of amines at elevated temperatures, several profitable promoters or catalysts for ring opening epoxides have been reported such as: phosphomolybdic acid (PMA)-Al_2O_3 [9], $(TBA)_4PFeW_{11}O_{39}\cdot 3H_2O$ [10], silica and alumina/modified alumina [11], zinc(II) and copper(II) [12], N,N-bis[3,5-bis(trifluoromethyl) phenyl]-thiourea [13], [Ti(o-i-pr)$_4$] [14], trifluoroethanol [15], metal triflates such as $Sn(OTf)_2$ [16], $Cu(OTf)_2$ [17], $Sm(OTf)_3$ [17], $Al(OTf)_3$ [18], $Er(OTf)_3$ [19], metal halides such as $InCl_3$ [20], $BiCl_3$ [21], $SbCl_3$ [22], $ZnCl_2$ [23], $InBr_3$ [24], $CoCl_2$ [25] and $Y(NO_3)_3\cdot 6H_2O$ [26]. In spite of a broad set of available activators, because of the existence of some defects in this methods such as high temperatures, low yields, rearrangement of epoxides and by-products, long reaction times, and high amount of catalysts, it is necessity to most study modification of methods for the synthesis of β-aminoalcohols.

In this work, for the first time we were interested to investigate the catalytic application of transition metal substituted Wells–Dawson type polyoxometalate in the ring opening reaction of epoxides with amines at room temperature. Thus, we report Fe(III) substituted polyoxometalate α_2-$[(n\text{-}C_4H_9)_4N]_7P_2W_{17}FeO_{61}\cdot 3H_2O$ as an efficient, inexpensive and useful catalyst for the synthesis of β-aminoalcohols.

Experimental.

General

The tetrabuthylammonium salts of Wells–Dawson type polyoxometalates were prepared according to the literature [27]. All catalysts were characterized by UV–vis and IR spectroscopy and TG analysis. Infrared spectra were recorded on a Shimadzu IR-435 spectrophotometer. The UV–vis spectra were recorded on a Variane Carey-5A

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http://dx.doi.org/10.1016/j.inoche.2012.11.005

instrument. The GC analyses were performed on a Shimadzu GC-16A instrument with a flame-ionization detector using silicon DC-200 column. ^{1}H NMR spectra were recorded on a Bruker AW 300 (300 MHz) spectrometer. Products were characterized by comparison of their spectral and physical data with those of known samples. All yields refer to isolated products. Chemicals were purchased from Fluka and Merck chemical companies. The chemical purities of all epoxides were checked by gas chromatography and confirmed to be higher than 98%.

Transition metal substituted polyoxometalates, $[P_2W_{17}MO_{61}]^{n-}$ (M = Mn, Fe, Co, Cu, Ni, Zn), prepared according to the literature [27].

Aminolysis of epoxides

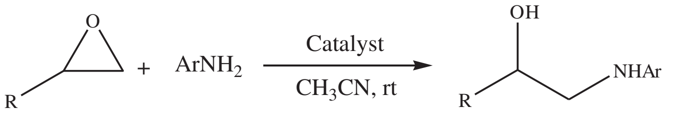
To a solution of epoxides (1 mmol) and amines (1.1 mmol) in acetonitrile (3 mL) were added the α_2-$[(n\text{-}C_4H_9)_4N]_7P_2W_{17}FeO_{61}\cdot 3H_2O$ (0.03 mmol). The reaction mixtures were stirred at room temperature for the appropriate time according to Table 2. TLC or GC indicated progress and the completion of the reaction. Evaporation of the solvent followed by plate chromatography on a plate of silica gel gave the pure product (Table 2). All of the compounds were fully characterized by IR, ^{1}H NMR, and ^{13}C NMR by comparison with the known compounds.

Results and discussion

In this paper, the catalytic effects of transition metal substituted Wells–Dawson type polyoxometalates, $[P_2W_{17}MO_{61}]^{n-}$ (M = Mn, Fe, Co, Cu, Ni, Zn), in aminolysis of epoxides to β-aminoalcohols in acetonitrile have been reported (Scheme 1). These catalysts are readily available, and the structure and composition of them confirmed by IR, UV–vis and elemental analysis [27]. The results of thermal gravimetric analysis (between 40 and 600 °C) on these catalysts indicated that the hydration numbers are about 3.

The best reaction conditions were found by study on cyclohexene oxide as a model substrate. At first, to obtain the best catalyst, the aminolysis of cyclohexene oxide in the presence of catalytic amounts of various polyoxometalates $[P_2W_{17}MO_{61}]^{n-}$ (M = Mn, Fe, Co, Cu, Ni, Zn) was performed. All of the reactions were carried out in acetonitrile at room temperature with magnetic stirring. Although the reaction without catalyst after 24 h gave a trace amount of product (below 5%), it was preceded catalytically upon addition of polyoxometalates. Among the catalysts tested, TBA salt of $[P_2W_{17}FeO_{61}]^{7-}$ was found to be highly active for this reaction (Table 1, entry 7). In this catalyst, Fe(III) acts as a good Lewis acid and so it can play a very important role in catalytic performance compared with the other metals. The catalytic activity for the other catalysts appeared in Table 1.

In the next step various amounts of the catalyst (10, 5, 3, 2.5, and 2 mol%) were investigated and 3 mol% of the catalyst gave the best result in the aminolysis of cyclohexene oxide. Among various solvents tested, we chose the CH_3CN as the best solvent for the ring opening of epoxides. Lower catalytic activities were observed with other solvents such as CH_2Cl_2, CH_3Cl, THF, and n-C_6H_{12}. The optimum amount of amine in this system was found 1.1 mmol and when the higher amount of amine was employed, a significant increase in the β-aminoalcohol was not observed. The catalytic reaction with substrate/amine ratios of 1/1.1, in proper reaction times gave β-aminoalcohol with high to excellent yields.



Scheme 1. Catalytic conversion of epoxides to β-aminoalcohols in the presence of transition metal substituted polyoxometalates.

Table 1
Aminolysis of cyclohexane oxide catalyzed by transition metal Wells–Dawson polyoxometalates.

Entry	Catalyst[a]	Yield[b]
1	α_2-$[K_7P_2W_{17}O_{61}(Fe^{3+}\cdot OH_2)]\cdot 8H_2O$	4
2	α_2-$[K_7P_2W_{17}O_{61}(Mn^{3+}\cdot OH_2)]\cdot 12H_2O$	14
3	α_2-$[K_8P_2W_{17}O_{61}(Co^{2+}\cdot OH_2)]\cdot 16H_2O$	13
4	α_2-$[K_8P_2W_{17}O_{61}(Ni^{2+}\cdot OH_2)]\cdot 17H_2O$	7
5	α_2-$[K_8P_2W_{17}O_{61}(Cu^{2+}\cdot OH_2)]\cdot 16H_2O$	5
6	α_2-$[K_8P_2W_{17}O_{61}(Zn^{2+}\cdot OH_2)]\cdot 8H_2O$	3
7	α_2-$[(n\text{-}C_4H_9)_4N]_7P_2W_{17}FeO_{61}\cdot 3H_2O$	96
8	α_2-$[(n\text{-}C_4H_9)_4N]_7P_2W_{17}MnO_{61}\cdot 3H_2O$	15
9	α_2-$[(n\text{-}C_4H_9)_4N]_8P_2W_{17}CoO_{61}\cdot 3H_2O$	13
10	α_2-$[(n\text{-}C_4H_9)_4N]_8P_2W_{17}NiO_{61}\cdot 3H_2O$	8
11	α_2-$[(n\text{-}C_4H_9)_4N]_8P_2W_{17}CuO_{61}\cdot 3H_2O$	4
12	α_2-$[(n\text{-}C_4H_9)_4N]_8P_2W_{17}ZnO_{61}\cdot 3H_2O$	3

[a] 3 mol% of catalyst was used.
[b] Yields refer to isolated product.

Cyclohexene oxide (1 mmol) was treated with 1.1 mmol of aniline and 0.03 mmol of catalyst at room temperature and after 40 min a quantitative yield of corresponding β-aminoalcohol was performed (Table 2, entry 1). To show the scope of the reaction, we extended it to a variety of aromatic amines and epoxides. In all cases, a very clean reaction was observed and the aminoalcohols had trans stereochemistry. The trans-configuration of aminoalcohols was assigned by ^{1}H NMR spectrum.

In all cases, the reactions are performed at room temperature in MeCN. In the reaction of cyclohexene oxide (Table 2, entry 1), except 2-nitroaniline, aminolysis was performed in a short time with quantitative yields. The reaction of styrene oxide as an active epoxide (Table 2, entry 2) has been completed with all of amines in 100–180 min. As expected in the case of styrene oxide α-amino was obtained as the major product ($\alpha/\beta = 95/5$) due to the formation of the stabilized benzylic cation during the reaction. In order to see the effect of polar electron-withdrawing groups adjacent to the epoxide's ring, the reaction of chloromethyl oxirane with amines was studied (Table 2, entry 6). In comparison with 1-hexene epoxide, which have an electron-donating group adjacent to the epoxide's ring (Table 2, entry 4), longer times for chloromethyl oxirane show the effect of polar electron-withdrawing groups. Sterically more hindered anilines such as 2-methylaniline led to the β-aminoalcohols still in excellent yields and not have any profound effect on their reactivity toward ring opening of epoxide. As shown in Table 2, the reaction was also efficient with the secondary N-methylaniline.

Finally, in comparison between two types of polyoxometalates, the Wells–Dawson type has larger molecular size than the Keggin type polyoxometalates and shows higher potential for coordination to transition metals. In literatures, a few works about the catalytic effect of Wells–Dawson type polyoxometalates are reported. For this reason and in comparison between catalytic effects of transition metal substituted Keggin and Wells–Dawson type polyoxometalates, the aminolysis of epoxides was performed. Our results showed that Fe(III) substituted Wells–Dawson type polyoxometalate can act very well and lesser catalytic amount of polyoxometalate is needed.

Conclusion

In this report, we have developed an efficient approach for the preparation of β- aminoalcohols. We have introduced α_2-$[(n\text{-}C_4H_9)_4N]_7P_2W_{17}FeO_{61}\cdot 3H_2O$ as a efficient, non toxic, available, and stable catalyst in the ring opening reaction of various epoxides with aromatic amines. This method is also usable for deactivated and sterically hindered amines in good yields.