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Ammonium decatungstocerate (IV): an efficient catalyst for ring opening of epoxides with aromatic amines

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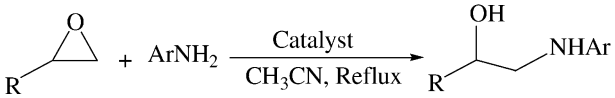
A mild, convenient and efficient ring opening of oxiranes with aromatic amines was catalyzed by ammonium decatungstocerate (IV) in acetonitrile. The reaction afforded the corresponding products in 92–100% yields. The catalyst was reused for several times with consistent activity.



KEY WORDS: ring opening; epoxides; catalysis; aromatic amines; aminolysis.

1. Introduction

Epoxides are well-known carbon electrophiles capable of reacting with various nucleophiles, and their ability to undergo regioselective ring opening reactions contributes largely to their synthetic value [1]. The epoxide ring opening with certain nucleophiles is generally carried out using either acid or base catalysis to produce ring-opened products. β-Aminoalcohols are an important class of organic compounds [2], which have found much use in neutral product synthesis and are also used as building blocks for the synthesis of pharmaceuticals [3], as insecticidal agents [4], and as chiral ligands for asymmetric catalysis [5]. The most practical and widely used route for the synthesis of these compounds is the direct aminolysis of 1,2-epoxides; however, these reactions, which are usually carried out with a large excess of ammonia or amines at elevated temperatures, often fail when poorly nucleophilic amines are concerned [6]. Since the high temperature may not be ideal for certain functional groups, many variety of activators/promoters have been developed and used to carry out epoxide opening at room temperature [7]. These include $CoCl_2$ [7a], $Ti(o\text{-}i\text{-}Pr)_4$ [7b], SmI_2 [7c], basic metal amides [7d], $SnCl_3$ [7e], metal triflates such as $Sn(OTf)_2$ [7f], $Cu(OTf)_2$ [7f], LiOTf [7g], $Yb(OTf)_3$ [7h], $La(OTf)_3$ [7i], and Pb_4SbOTf [7j], cyclodextrin [7k], and $CeCl_3$ [7l]. Although a wide choice of activators or promoters is available, many are associated with one or other drawback. These include the failure of deactivated aromatic amines, use of anhydrous organic solvents, moisture sensitive catalysts, expensive and hazardous reagents and etc. Hence, there is a need for newer versatile methods, which could be of great benefit.

In conjunction with the ongoing work in our laboratory on the application of polyoxometalates in organic synthesis [8], we investigated for the first time the applicability of a novel stable and recyclable catalyst, ammonium decatungstocerate (IV), for the efficient activation of oxirane ring opening with aromatic amines.

Heteropoly compounds 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 [9a, 9b]. 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. Their acid–base and redox properties can be varied over a wide range by changing the chemical composition. On top of that, heteropoly compounds have a very high solubility in polar solvents and fairly high thermal stability in the solid state. These properties

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render heteropoly compounds potentially promising acid, redox, and bifunctional catalysts in homogeneous as well as in heterogeneous systems. Heteropoly compounds are widely used as model systems for fundamental research, providing unique opportunities for mechanistic studies on the molecular level. At the same time, they have become increasingly important for applied catalysis. 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 [9]. However, there has been very little exploitation of their catalytic reactivity in nucleophilic ring-opening of epoxides.

2. Experimental

Products were characterized by comparison of their physical data with those of known samples. All yields refer to isolated products. The ammonium decatungstocerate (IV) icosohydrate was prepared according to the literature [10]. All catalysts were characterized by UV–Vis and IR spectroscopy and elemental analysis. Infrared spectra were recorded on a Philips PU-9716 or Shimadzu IR-435 spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker AW 80 (80 MHz) spectrometer. All analyses were performed on a Shimadzu GC-16A instrument with a flame-ionization detector using silicon D.C.-200 or carbowax 20-M columns. Mass spectra were recorded on a Shimadzu GCMS-QP 1000 EX. Microanalysis were carried out by the Research Institute of Petroleum Industry. 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%.

2.1. Preparation of the catalyst

Ammonium decatungstocerate icosahydrate was prepared according to Peacok's procedure [10]. $Na_2WO_4 \cdot 2H_2O$ (25 g, 75 mmol) was dissolved in 100 mL of ion-exchange water, the pH of which was adjusted to 7.2 by the addition of acetic acid. After heating at 90 °C with stirring, an aqueous solution containing $(NH_4)_2Ce(SO_4)_2 \cdot 2H_2O$ (4.75 g, 7.5 mmol) and a 1 equiv H_2SO_4 solution were added to make CeW_{10} form in the solution. This solution was obtained after filtration and used as catalyst. The structure of catalyst confirmed by IR, magnetic susceptibility, thermal gravimetric analysis (tga) and elemental analysis.

2.2. Aminolysis of epoxides: general procedure

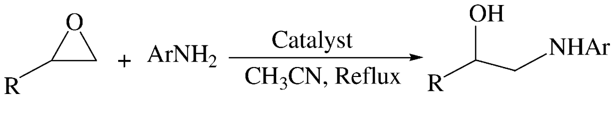
To a solution of oxiranes (1 mmol) and amine (1.2 mmol) in acetone (3 mL) was added the $(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$ (0.04 mmol). The reaction mixture was stirred under reflux condition for the appropriate time according to table 1. The progress of the reaction followed by TLC or GC. After completion of the reaction, the suspension was filtered and washed with ether. Evaporation of the solvent followed by chromatography on a short column of silica gel gave the pure product, yields 92–100% (table 1).

3. Results and discussion

We will describe below our results on the use of ammonium decatungstocerate (IV) polyoxometalate, $(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$, as catalyst for the aminolysis of epoxides to β-aminoalcohols in acetonitrile (Scheme 1).

In this paper, we wish to report that $(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$ can act as a mild and highly effective heterogeneous catalyst for the efficient ring opening of epoxides with various aromatic amines. This catalyst is readily available and easily prepared by the previously reported method [10]. The formation of polyoxometalate structure and composition of the compound was confirmed by IR, NMR and elemental analysis. Thermal gravimetric analysis was performed on the catalyst (between 40 and 240 °C). The results indicated that the hydration numbers are between 18 and 21.

From initial studies carried out with cyclohexene oxide, we found the best reaction condition. We initially by using the cyclohexene oxide and catalytic amount of ammonium salt of decatungstocerate (IV) in acetonitrile searched the optimum conditions of reaction. The reactions were conducted at reflux with magnetic stirring. The aminolysis was efficiently achieved under this condition (table 1, entry 6), and the presence of the catalyst was crucial to obtain full conversion of the β-aminoalcohol. After studied the various amount of the catalyst, we found that the 0.04 equivalent from catalyst is the best. We chose the CH_3CN as solvent and lower catalytic activities were observed with other solvents such as CH_2Cl_2, $CHCl_3$, CCl_4 and n-C_6H_6. The optimum amount of aromatic amine in this system was found 1.2 mmol and when the higher amount of amine was employed, a significant



Scheme 1

Table 1
Aminolysis of various epoxides catalyzed by decatungstocerate (IV)^{a}

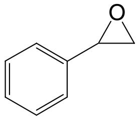
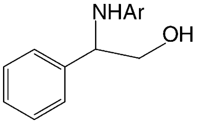
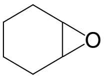
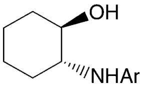
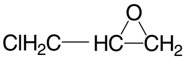
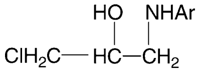
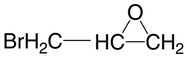
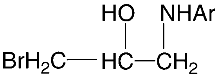
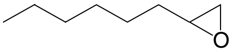
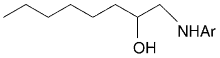
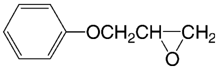
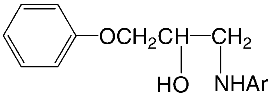
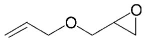
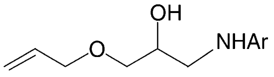
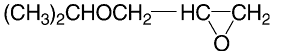
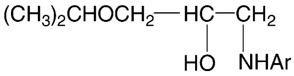
Entry	Epoxide	$ArNH_2$	Time (min)	Product/Yield (%)^{b,c}
				
1		$PhNH_2$	180	92
2		$2\text{-}ClPhNH_2$	30	100
3		$2\text{-}MeOPhNH_2$	45	100
4		$4\text{-}MeOPhNH_2$	60	100
5		$4\text{-}BrPhNH_2$	30	95
				
6		$PhNH_2$	30	100
7		$2\text{-}ClPhNH_2$	30	100
8		$2\text{-}MeOPhNH_2$	15	100
9		$4\text{-}MeOPhNH_2$	180	98
10		$4\text{-}BrPhNH_2$	30	100
				
11		$PhNH_2$	30	97
12		$2\text{-}ClPhNH_2$	30	100
13		$2\text{-}MeOPhNH_2$	60	100
14		$4\text{-}MeOPhNH_2$	45	100
15		$4\text{-}BrPhNH_2$	45	100
				
16		$PhNH_2$	30	96
17		$2\text{-}ClPhNH_2$	45	100
18		$2\text{-}MeOPhNH_2$	60	100
19		$4\text{-}MeOPhNH_2$	75	100
20		$4\text{-}BrPhNH_2$	45	100
				
21		$PhNH_2$	180	95
22		$2\text{-}ClPhNH_2$	45	95
23		$2\text{-}MeOPhNH_2$	90	98
24		$4\text{-}MeOPhNH_2$	240	95
25		$4\text{-}BrPhNH_2$	90	95
				
26		$PhNH_2$	60	100
27		$2\text{-}ClPhNH_2$	15	98
28		$2\text{-}MeOPhNH_2$	45	100
29		$4\text{-}MeOPhNH_2$	60	100
30		$4\text{-}BrPhNH_2$	45	98

Table 1
Aminolysis of various epoxides catalyzed by decatungstocerate (IV)[a]

Entry	Epoxide	$ArNH_2$	Time (min)	Product/Yield (%)[b,c]
				
31		$PhNH_2$	180	100
32		$2\text{-}ClPhNH_2$	45	95
33		$2\text{-}MeOPhNH_2$	45	100
34		$4\text{-}MeOPhNH_2$	240	98
35		$4\text{-}BrPhNH_2$	45	98
	 $(CH_3)_2CHOCH_2—HC—CH_2$ (with O bridging HC and CH_2)			 $(CH_3)_2CHOCH_2—\underset{HO}{HC}—\underset{NHAr}{CH_2}$
36		$PhNH_2$	180	100
37		$2\text{-}ClPhNH_2$	30	98
38		$2\text{-}MeOPhNH_2$	45	100
39		$4\text{-}MeOPhNH_2$	240	95
40		$4\text{-}BrPhNH_2$	15	98

[a] Catalyst 0.04 molar amount.
[b] All products were identified by comparison of their physical and spectral data with those of authentic samples [7].
[c] Yields refer to isolated products.

increase in the β-aminoalcohols was not observed. Separate experiments showed that at the time sited in table 1, there is little reaction without catalyst. From the results as summarized in table 1, catalytic reactions and substrate/amine ratios of 1/1.2 yield aminoalcohols with selectivities of 92–100%.

Cyclohexene oxide was treated with 1.2 equiv of aniline and 4 mol% of catalyst at reflux and after 30 min, there was formation of quantitative yield of aminoalcohol (table 1, entry 6). 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 ^1H-NMR spectrum.

As shown in table 1, aminolysis of various epoxides with aniline, 2-chloro aniline, 2-methoxy aniline, 4-methoxy aniline and 4-bromo aniline were investigated. In all cases, the reactions required reflux temperature in MeCN. In the reaction of cyclohexen oxide, except 4-methoxy aniline aminolysis were performed in a short time with quantitative yields (table 1, entries 6–10). Because of the predominant attack of amine on the less hindered carbon of the epoxide, all the terminal epoxides gave highly regioselective β-aminoalcohol in quantitative yields. The reaction of styrene oxide as an active epoxide (table 1, entries 1–5) has been completed with all of amines in 30–60 min. As expected in the case of styrene oxide α-amino was obtained as the major product (α/β = 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 reactions of (chloromethyl)- and (bromomethyl)-oxirane with amines were studied (table 1, entries 11–20). These reactions were performed in short times with excellent yields. In case of acyclic terminal olefins such as 1-octene oxide (table 1, entries 21–25) the major product resulting from the attack of nucleophile at the less substituted carbon to give the β-aminoalcohol in 87% yield.

4. Conclusion

The use of heterogeneous catalysts in different areas of the organic synthesis has now reached significant levels, not only for the possibility to perform environmentally benign synthesis, but also for the good yields frequently accompanied by excellent selectivities that can be achieved. In fact, the advantages of these catalysts are (i) the easy workup (separation of the catalyst simply by

Table 2
The results of $(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$ catalyst recovery in the aminolysis of cyclohexane oxide with aniline under reflux

Entry	Conversion/%[a]	W leaching/%[b]
1	100	0
2	100	0
3	100	0
4	99	0
5	98	< 1%
6	95	1%
7	91	1.5%
8	89	1.7%
9	87	1.8%

[a] All reactions carried out in 30 min.
[b] Reaction solutions assayed for leached tungsten using atomic adsorption spectrometer and based on initial tungsten concentration.

filtration), (ii) the high purity of the products, (iii) and the possibility of recycling catalysts, as well as avoiding the use of noxious substances [11]. In this case, we have found that $(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$, could be reused different times without loss of the activity, simply by filtering the catalyst, washing with acetone, drying and immediately reusing. After each reaction, the concentration of catalyst (tungsten) in solution was determined and it was very low (table 2). Therefore, the stability and reusability of the catalyst could be observed.

In this catalytic system, we have introduced $(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$ as a non-hygroscopic, non-toxic, available, stable, reusable and heterogeneous catalyst for the reactions of oxiranes with aromatic amines. In addition, the advantages such as mild, ease of preparation, simple filtration at the end of reaction, cheapness of the catalyst, high yields give a new synthetic application for $(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$ in organic synthesis. Even though the reaction mechanism is interesting, at the present time it is obscure to us, and we have not been able to assign any reasonable mechanism for them in our studies.

In summary, we have demonstrated a mild, efficient and convenient method for the ring opening of epoxides with aromatic amines using a stable, reusable and heterogeneous catalyst. Work on other reactions promoted by $(NH_4)_8[CeW_{10}O_{36}] \cdot 20H_2O$ and related compounds are currently underway in our laboratory.

Acknowledgments

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References

[1] (a) C. Bonini and G. Righi, Synthesis (1994) 225. (b) J.G. Smith, Synthesis (1984) 629.

[2] (a) D.J. Ager, I. Prakash and D. Schaad, Chem. Rev. 96 (1996) 835. (b) B.L. Chng and A. Ganesan, Bioorg. Med. Chem. Lett. 7 (1997) 1511. (c) G.A. Rogers, S.M. Parsons, D.C. Anderson, L.M. Nilsson, B.A. Bahr, W.D. Kornreich, R. Kaufman, R.S. Jacobs and B. Kirtman, J. Med. Chem. 32 (1989) 1217.

[3] (a) D. Roemer, H.H. Buescher, R.C. Hill, J. Pless, W. Bauer, F. Cardinaux, A. Closse, D. Hauser and R. Huguenin, Nature 238 (1977) 547. (b) C. Auvin-Guette, S. Rebuffat, Y. Prigent and B. Bodo, J. Am. Chem. Soc. 114 (1992) 2170.

[4] S. Wu, R. Takeya, M. Eto and C. Tomizawa, J. Pestic. Sci. 12 (1987) 221.

[5] (a) S. Masamune and R.P. Short, J. Am. Chem. Soc. 111 (1989) 1892. (b) H.C. Brown, U.S. Racherla and P.J. Pellechia, J. Org. Chem. 55 (1990) 1868. (c) R. Berenguer, J. Garcia and J. Vilarrasa, Tetrahedron Asymmetr. 5 (1994) 165. (d) J. Takehara, S. Hashiguchi, A. Fujii, S.I. Inoue, T. Ikaria and R. Noyori, Chem. Commun. (1996) 233.

[6] (a) M. Mousseron, J. Jullien and Y. Jolchine, Bull. Chem. Soc. Jpn. (1952) 757. (b) J.A. Deyrub and C.L. Moyer, J. Org. Chem. 34 (1969) 175.

[7] (a) J. Iqbal and A. Pandey, Tetrahedron Lett. 31 (1990) 575. (b) S. Sagava, H. Abe, Y. Hase and T. Inaba, J. Org. Chem. 64 (1999) 4962. (c) P. Van de Weghe and J. Collin, Tetrahedron Lett. 36 (1995) 1649. (d) J. Yamada, Y. Yumoto and Y. Yamamoto, Tetrahedron Lett. 30 (1989) 4255. (e) X.-L. Fu and S.-H. Wu, Synth. Commun. 27 (1997) 1677. (f) G. Sekar and V.K. Sing, J. Org. Chem. 64 (1999) 267. (g) S. Sagava, H. Abe, Y. Hase and T. Inaba, J. Org. Chem. 64 (1999) 4962. (h) M. Meguro, N. Asao and Y.J. Yamamoto, J. Chem. Soc., Perkin Trans. 1 (1994) 2597. (i) M. Chini, P. Crotti, L. Favero, F. Macchina and M. Pineschi, Tetrahedron Lett. 35 (1994) 433. (j) M. Fujiwara, M. Imada, A. Baba and H. Matsuda, Tetrahedron Lett. 30 (1989) 739. (k) L.R. Reddy, M.A. Reddy, N. Bhanumathi and K.R. Rao, Synlett. (2000) 339. (l) L.R. Reddy, M.A. Reddy, N. Bhanumathi and K.R. Rao, Synlett. (2001) 831.

[8] V. Mirkhani, S. Tangestaninejad, B. Yadollahi and L. Alipanah, Tetrahedron 59 (2003) 8213.

[9] (a) I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171. (b) N. Mizuno and M. Misono, J. Mol. Catal. 64 (1990) 1. (c) Y. Ono, in: Perspective in Catalysis, (eds.), J.M. Thomas and K.I. Zamaraev (Blackwell, London, 1992), p. 431. (d) I.V. Kozhevnikov, Catal. Rev. Sci. Eng. 37 (1995) 311. (e) M. Misono, Catal. Rev. Sci. Eng. 29 (1987) 269; 30 (1988) 339. (f) N. Mizuno and M. Misono, Chem. Rev. 98 (1998) 199. (g) N. Nojori and M. Misono, Appl. Catal. 95 (1993) 559. (h) Y. Izumi, K. Urabe and M. Onaka, Zeolite, Clay and Heteropoly Acid in Organic Reactions, (Kodansha/VCH, Tokyo, 1992), p. 99. (i) T. Okuhara, N. Mizuno and M. Misono, Adv. Catal. 41 (1996) 113. (j) C.L. Hill and C.M. Prosser-McCartha, Coord. Chem. Rev., 143 (1995) 407.

[10] (a) R.D. Peacock and T.J.R. Weakley, J. Chem. Soc. A (1971) 1836. (b) R. Shiozaki, H. Goto and Y. Kera, Bull. Chem. Soc. Jpn. 66 (1993) 2790.

[11] (a) G.H. Posner, Angew. Chem. Int. Ed. Engl. 17 (1978) 487. (b) D.C. Bailey and S.H. Langer, Chem. Rev. 81 (1981) 109. (c) P. Laszol, Acc. Chem. Res. 19 (1986) 121.