Polyethylene Glycol Functionalized Magnetic Dicationic lonic Liquids as a Novel Catalyst and Their Application in Ring Opening of Epoxides in Water

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A simple and environmentally benign protocol for the aqueous synthesis of 1,2-azidoalcohols via regioselective ring opening of 1,2-epoxides using PEG-MDIL as a novel magnetic phase transfer catalyst is described. The catalyst was studied by UV spectroscopy, IR spectroscopy, and thermogravimetric analysis. The reactions occur in water and furnish the corresponding azidoalcoholes in high yields. No evidence for the formation of by-product and the products were obtained in pure form without further purification.

Keywords: Azidoalcohol; Ring opening; Epoxide; Phase transfer catalyst.

INTRODUCTION

The development of simple and efficient chemical processes or methodologies for the synthesis of biologically active compounds in water is one of the major challenges for chemists. Furthermore, using water as a solvent offers many advantages, such as safe, very cheap, readily available, and environmentally benign solvent.¹ Although today's environmental consciousness imposes the use of water as a solvent on both industrial and academic chemists, however, organic solvents are still used instead of water for mainly two reasons. First, most organic substances are insoluble in water, and as a result, water does not function as a reaction medium. Second, many reactive substrates, reagents, and catalysts are decomposed or deactivated by water.²

One of the most important strategies to overcome this limitation is the utilization of phase transfer catalyst such as ionic liquid (IL).

In 1971, Starks introduced the term "phase-transfer catalysis" to explain the critical role of tetraalkylammonium or phosphonium salts (Q^+X^-) in the reactions between two substances located in different immiscible phases.³

Since then, the chemical community has witnessed an exponential growth of phase-transfer catalysis as a practical methodology for organic synthesis. The advantages of this method are its simple experimental procedures, mild reaction conditions, inexpensive, environmentally benign, and the possibility of conducting large-scale preparations.⁴ Nowadays, it appears to be the most important synthetic

method used in various fields of organic chemistry, and has also found widespread industrial applications.

In recent yeas, the design of efficient and recoverable phase-transfer catalysts has become an important issue for reasons of economic and environmental impact. In particular, PEG based dicationic ionic liquid has considerable advantages, including easy catalyst recovery and product isolation, and employment of a continuous flow method owing to the two-phase nature of the system, which make the technique attractive for industrial applications. Although many phase-transfer catalysts are known, functionalized ionic liquids such as polyethylene glycol functionalized dicationic ionic liquids are practically important and used in many of organic reactions. High polarity and ability to dissolve organic and inorganic compounds increases the reaction rate and selectivity higher than with traditional methods has been reported.⁵⁻⁸

Recently, magnetic ionic liquids are attracting increasing interest as environmentally benign reaction media for various organic synthesis, catalysis, etc.⁹⁻¹¹ Further, magnetic ionic liquid offers several advantages, such as extremely low volatility, high thermal stability, non flammability and high ionic conductivity. These advantages and nontoxic nature of magnetic ionic liquid show its potential as a catalyst in organic synthesis. It is also reported that magnetic ionic liquids could be separated from other solvents by a combination of magnetic field and conventional methods such as filtration, ultracentrifugation, and adsorption.^{12,13}

Epoxides are often used as starting materials and in-

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termediates in organic synthesis partly because their opening leads to vicinal azidoalcohols are an important class of organic compounds and they serve as precursors in the synthesis of vicinal aminoalcohols, carbohydrates, nucleosides,¹⁴⁻¹⁶ lactames,¹⁷ and oxazolines.¹⁸ Optically active β-azido alcohols are of great significance as potential precursors for non-racemic aziridines and β-amino alcohols.^{19,20} The latter compounds are not only a common structural component in a vast group of naturally occurring and synthetic molecules, but also can be widely used as versatile chiral building blocks and chiral catalysts in organic synthesis.²¹ In particular, chiral 2-amino-1-arylethanols are important structural elements in pharmaceuticals such as-or-adrenergic blockers and agonists in the treatment of cardiovascular disease, cardiac failure, asthma and glaucoma.22

The most common method for the preparation of azidohydrins is the ring opening of epoxides by using different azides in suitable solvents. The reactions often carried out under either alkaline or acidic conditions and several different methods have been devised in order to obtain the direct azidolyses of epoxides in the presence of sodium azide.²³ Under these conditions, azidolyses are usually carried out over a long reaction times and azidohydrin is often accompanied by isomerization, epimerization, and rearrangement of products.²⁴ Unfortunately, some of these methods are not always fully satisfactory and suffer from disadvantages such as these methods require hazardous or toxic reagents high reaction temperature or relative long reaction times, difficulty in preparation and/or storage of reagents or catalysts, difficulty in work-up and isolation of products or low regioselectivity. Consequently, it seems that there is still a need for development of newer methods that proceed under mild and economically appropriate conditions. In order to overcome some of these limitations, a number of alternative procedures have been reported over the past few years using a variety of catalysts.²⁵⁻³¹

As a part of our program aiming at developing selective and environmental friendly methodologies for the preparation of fine chemicals and in continuation of our interest in magnetic ionic liquid promoted organic reactions, in this paper, we report on the evaluation of ring opening epoxide reaction in the H_2O -PEG-MDIL system.

RESULTS AND DISCUSSION

Polyethylene glycol functionalized magnetic dica-

tionic ionic liquid (PEG-MDIL) was synthesized as shown in Scheme 1. Polyethylene glycol dicholorid was prepared in high yield following a literature method.³² They were further treated with two equivalents of 1-methylimidazole, respectively, under neat reaction conditions, to form dicationic cholorid bridged by polyether linkage chains in high yields. With the exception of one compound containing one ether linkage chain (solid), the diimidazolium cholorid derivatives is sticky colorless liquid.





In the latest step, the anions of imidazolium based dicationic room temperature ionic liquid, Cl⁻, were easily changed with $FeCl_4$ anions by the simple mixing with $FeCl_3$ under neat conditions.

Due to the paramagnetic nature of the Polyethylene glycol functionalized magnetic dicationic ionic liquid, nuclear magnetic resonance technique could not be used to confirm its structure. Instead, UV, IR and Raman spectroscopes were used to characterize the PEG-MDIL structure.

The UV–vis absorption spectra of PEG-MDIL in acetonitrile consist of two main bands at 310–425 nm and 240–300 nm (see Fig. 1a). The shorter wavelength band is attributed to the π - π * transition in the imidazole ring, and the longer wavelength band was found to be due to the n- π * transition.

PEG-MDIL spectra exhibited absorption bands in the visible region at 534, 473 nm which are characteristic for

the FeCl₄ anion (Fig. 1b).

The thermal gravity analysis curve of catalyst under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹ is shown in Figure 2. There were three main steps of weight loss, and the decomposition events took place at 220 °C, 310 °C and 400 °C. On the base of weight changes, the first process PEG-MDIL spectra exhibited absorption bands was attributed to the loss of ether linkage (found 37% calc.



Fig. 1. Visible spectrum of PEG-MDIL (200-400 nm) (a), UV spectra of PEG-MDIL, PEG-DIL, and Cl-PEG-Cl (400-700 nm) (b).



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39%). The second event corresponded to the loss of FeCl₄ (found 40% calc. 42%). The weight loss (about 15%) during 400 °C to 500 °C was attributed to the decomposition of 1-methylimidazole.

To characterize the PEG-MDIL, we used the FT-IR spectrum. The FT-IR spectrum of native Cl-PEG-Cl and PEG-MDIL sample are shown in Fig. 3.

There are peaks at about1165 cm⁻¹, which were assigned to the characteristic absorption of N-CH₂ in functionalized PEG-MDIL. The absorption bands at 3152 and 3013 cm⁻¹ (imidazolium CH stretching modes), presented in the inset of Fig. 3 demonstrate modification of the PEG. The absorption at 2911cm⁻¹ is usually assigned to C-H stretching of the polyether linkage chains. The absorption observed at 1571 cm⁻¹ is also characteristic of the imidazolium ring and is assigned to imidazolium ring stretching.

In a typical experiment, phenyl glycidyl ether, and NaN₃ was selected. The effect of the amount of PEG-MDIL on the reaction time was studied by varying the quantity of ionic liquid (0, 0.05, 0.1, 0.15, and 0.2 gr/1 mmol phenyl glycidyl ether). The reactions were carried out under similar reaction conditions. It was observed that, with an increase in the proportion of ionic liquid, the azidolysis of phenyl glycidyl ether increases. The highest conversion of epoxide was obtained when the amount of ionic liquid used was 0.05 gr./1 mmol epoxide.

The effect of the reaction temperature on the reaction time of phenyl glycidyl ether azidolysis was investigated at



Fig 3. Comparison between FT-IR spectra of PEG-MDIL (b) and Cl-PEG-Cl (a).



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reaction temperatures ranging from 25 to 90 $^{\circ}$ C. The results show that the suitable reaction temperature is 90 $^{\circ}$ C.

The reaction was carried out in diethyl ether, n-hexane, acetonitrile, dichloromethane, ethyl acetate and water. From the results given in Table 1, it fallows that the best solvent for this reaction is water. Thus, water is an excellent solvent in terms of cost, availability, and environmental impact and shorter reaction times.

Epoxides bearing activated and deactivated groups were quickly and efficiently converted to the virtually pure azidohydrine and β -hydroxy azidoalcoholes products in high isolated yields (Table 2, Scheme 2). No evidence for the formation of α -azidoalcoholes as by-products of the reactions was observed and the products were obtained in pure form without further purification. Furthermore, cyclic epoxides, such as cyclohexene oxide reacted smoothly in SN₂ fashion to afford the corresponding 1, 2 azidoalcohols (Table 2, entries 3). The stereochemistry of the ring opening products was found to be in the trans-configuration as determined from the coupling constants associated with the ¹H NMR spectral resonances of the ring protons.





In the next step, the scope and efficiency of the catalyst were explored under the optimized reaction conditions for the substituted aromatic compounds, unsaturated aliphatic compounds, and aromatic heterocyclic compounds (Table 2, entries 8-10).

All the products were characterized and identified by comparison of their spectral data (IR, ¹H NMR and ¹³C NMR) with those of authentic samples. After completion of the reaction (Table 2), the mixture was cooled and organic phase was extracted with diethyl ether. Evaporation of organic solvent the desired products.

PEG-MDIL showed remarkable reactivity as a Lewis acid reagent and considerably accelerated the reactions. It seems that polyethylene glycol unitts in PEG-MDIL encapsulate alkali metal cations, much like crown ethers, and these complexes cause the anion to be activated. The 1-methylimidazol-3-ium units introduced ionic liquid property to the catalyst. In addition, FeCl₄⁻ groups at the IL,

Entry	Solvent	Time (min)	Yield (%)		
1	Et ₂ O	180	20		
2	CH_2Cl_2	180	25		
3	n-hexane	180	20		
4	EtOAc	180	40		
5	DMSO	20	85		
6	H_2O	15	94		

Table 1. Efficiency of solvents on azidolysis of epxides^a

^a 2,3-Epoxypropyl phenyl ether (1 mmol), NaN₃ (3 mmol), and 0.05 gr of PEG-MDIL were used under reflux conditions.

probably, facilitates the ring opening of epoxide (Scheme 3).



Scheme 3 Plausible mechanism for the ring opening of epoxide catalyzed by PEG-MDIL.

The success of the above reactions prompted us to investigate the recyclability of catalyst. We carried out our study by using the reaction 2,3-epoxypropyl phenyl ether with NaN₃ and under optimal conditions as a model study. The aqueous phase was then subjected to distillation at 80 °C under reduced pressure (10 mm Hg) for 4 h to recover the PEG-MDIL almost completely. It was found that the catalyst could be reused five times with slightly decreasing catalytic activity (Fig. 4).

The advantage of using this magnetic phase transfer catalyst for the synthesis of 1,2-azido-alcohols using azide ion is shown by comparing our results with those previously reported in the literature (Table 3).

EXPERIMENTAL

Material and Methods: Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. ¹H & ¹³CNMR spectra were recorded on a Bruker Advanced DPX 400 MHz instrument spectrometer using TMS as the internal standard in CDCl₃. IR spectra were recorded on a BOMEM MB-Series 1988 FT-IR spectrometer. Raman spectroscopy were recorded on

Entry	Substrate	Product	Time (min)	Yield(%)
1	pho	phO N ₃	15	94
2	ph	ph N ₃	15	92
3	○		20	84
4	\sim	OH N3	20	85
5	\sim \sim \sim		20	87
6	γ°		20	85
7	\checkmark	OH N3	20	80
8	CI	CI N3	20	89
9	$\operatorname{res}^{\circ}$	OH O N ₃	20	86
10	s S	OH N ₃	30	85

Table 2. Reaction of different epoxides with NaN3 using PEG-MDIL





a Bruker RFS 100/s Raman spectrometer. Epoxides, and PEG-400 were purchased from Merck Company in high purity. Products were characterized by comparison of their physical and spectroscopic data with those of known samples. The purity of products and reaction monitoring was accomplished by TLC on silica gel Poly Gram SILG/UV 254 plates.

The synthesis of dichloro substituted (CI-PEG-CI): PEG-400 (15 g, 0.025 mol) and pyridine (5 mL, 0.0625 mol) was dissolved in tolue.ne (20 mL), stirred at 87 °C, thionyl chloride (5 mL, 0.0625 mol) as added slowly, and the resultant reaction mix-

Entry	Reaction conditions	Time (h)	Yield(%)	Ref.
1	NaN ₃ /PEG-MDIL/H ₂ O/Reflux	0.25	94	-
2	NaN ₃ /PEG/60 °C	1	90	26
3	[Bmim]PF ₆ /NaN ₃ /H ₂ O/65 °C	3	95	27
4	SiO ₂ -PEG/NaN ₃ /H ₂ O/reflux	2	95	28
5	TMSN ₃ / β -CD/H ₂ O/r.t.	5	45	29
6	[Hmim]N ₃ /70 °C	1	94	30
7	[Pbmim](FeCl ₄) ₂ /NaN ₃ /H ₂ O/reflux	1	92	31

Table 3. Comparison of efficiency of various catalysts in synthesis of 1,2azidoalcohol (Table 2, Entry 1)

ture was stirred for 15 h at 87 °C. Then the resulting solid was removed by filtration. After removal of the solvent under reduced pressure a viscous liquid residual was collected as dichloro substituted PEG-400 (91.6%).

Procedure for preparation of Poly(ethylene glycol) bis-(methylimidazolium chloride)(PEG-DIL): 1-Methylimidazole (2 mmol), and polyethylene glycol dicholoride (1 mmol) were placed in a Pyrex glass tube, sealed and heated at 80 °C for 16 h or 110 °C for 20 h, respectively. The organic solvent was removed and extracted with ethyl acetate (3×20 mL) which was then washed with water (2×20 mL) and ether (2×10 mL), and dried over anhydrous magnesium sulfate. The solvent was removed under vacuum at 65 °C overnight to give colorless

Procedure for preparation of PEG-MDIL: PEG-MDIL, was prepared by mixing PEG-DIL (1 mmol) with anhydrous FeCl₃ (2 mmol) at room temperature for 3 h, a dark brown liquid was obtained. The obtained PEG-MDIL was extracted with small amount of ethyl acetate. The solvent was evaporated and the resulting clear brown liquid was dried in vacuum oven at 60 °C for 24 h. The PEG-MDIL was obtained in high yield (83%).

General procedure for the preparation of 1,2-azidoalcohols in water: A solution of epoxide (1 mmol), NaN3 (3 mmol), PEG-MDIL (0.05 gr), and water (5 ml) were heated and stirred under reflux conditions for appropriate time (Table 2). The progress of the reaction was monitored by TLC (eluent: n-hexane-EtOAc 80:20). After completion of the reaction, the mixture was extracted with ether (2×10 ml). The combined organic extracts (dried over CaCl₂) were evaporated under reduced pressure. The desired azidohydrin was obtained in good to excellent isolated yields. For styrene oxide, further purification was achieved by column chromatography.

Selected spectroscopic data: 1-Azido-3-phenoxypropan-2-ol (Entry 1): IR (neat): vmax N₃ (2100 cm⁻¹); ¹H NMR (400 MHz, CDCl₃): 3.51 (d, 2H), 3.88–3.98 (m, 1H), 4.00 (d, 2H), 4.16 (s, 1H), 6.93–7.00 (m, 2H), 7.01–7.06 (m, 1H), 7.26–7.36 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): 53.50, 69.23, 69.20, 114.29, 121.15. 2-Azido-2-phenyl-1-ethanol (Entry 2): IR (neat): vmax N³ (2103 cm⁻¹); ¹H NMR (400 MHz, CDCl₃): 3.36 (s, 1H), 3.73 (m, 2H), 4.65 (m, 1H), 7.33–7.44 (m, 5H). ¹³C NMR (100 MHz, CDCl₃): 66.27, 68.03, 127.47, 128.40, 128.51, 136.27 ppm. 1-Azido-3-propoxypropan-2-ol (Entry 4): IR (neat): vmax N₃ (2102 cm⁻¹); ¹H NMR (400 MHz, CDCl₃): δ:1.07 (t, 3H), 1.70-1.78 (m, 2H), 3.82 (s, 1H), 3.30 (m, 2H), 3.38 (t, 2H), 3.42 (d, 2H), 3.86 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ: 19.15, 31.74, 53.50, 69.73, 70.59, 71.71 ppm. 1-Azido-3-Allyloxypropan-2-ol (Entry 5): IR (neat): vmax N₃(2103 cm⁻¹); ¹H NMR (400 MHz, CDCl₃): δ: 3.45-3.54 (m, 2H), 3.8 (m, 1H), 3.96-4 (m, 2H), 4.18 (sbr, 1H), 3.7 (m, 2H), 5.2 (dd, 1H), 5.3 (dd, 1H), 5.8 (dd, 1H). ¹³C NMR (100 MHz, CDCl₃): 8: 53.37, 69.87, 71.32, 72.07, 117.36, 134.36 ppm. 1-Azido-3-isopropoxypropan-2-ol 9 (Entry 6): liquid; IR (neat): vmax N₃ (2103 cm⁻¹); ¹H NMR (CDCl₃, 400 MHz): δ : 1.40 (d, **J** = 6.5 Hz, 6H), 3.01 (m, 1H), 3.20 (dd, J = 7.0, 11.5 Hz, 1H), 3.25 (dd, J = 4.0, 11.5 Hz, 1H), 3.30–3.50 (m, 2H), 3.96 (brs, 1H, OH), 3.97-4.0 (m, 1H). ¹³C NMR (CDCl₃, 100 MHz) δ: 72.1, 71.3, 70.3, 53.4, 25.7 ppm. 1-Azidobutan-2-ol (Entry 7): IR (neat): vmax N3 (2098 cm⁻¹); ¹H NMR (400 MHz, CDCl₃): δ: 0.96 (t, 3H), 1.48(m, 2H), 3.2 (m, 1H), 3.4 (d, 2H), 3.97 (br, 1H). ¹³C NMR (100 MHz, CDCl₃): δ: 8.1, 27.7, 71.2, 53 ppm. 2-Azido-1-(p-chlorophenyl) ethanol (Entry 8): IR (neat); v_{max} (cm⁻¹): OH (3416), N₃ (2098); 1H NMR (400 MHz, CDCl3): δ: 2.55 (br s, 1H); 3.41 (d, 2H, J = 5.80 Hz), 4.85 (t, 1H, J = 5.95 Hz), 7.26–7.38 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ: 58.4, 73.1, 128.0, 129.4, 134.6, 139.4 ppm. 2-Methyl acrylic acid-3azido-2-hydroxy propyl este (Entry 9): IR (neat, cm-1) v_{max} (cm⁻¹): OH (3415), N₃ (2102); 1H NMR (400 MHz, CDCl3): δ: 1.8 (m, 3H), 3.2 (br s, 1H), 3.71 (d, 2H), 3.90 (d, 2H), 4.14 (m, 1H), 5.52 (m, 1H), 6.15 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ: 17.22, 56.42, 68.65, 70.46, 124.14, 136.72, 169.80 ppm. 2-Azido-1-(2'-thienyl)ethanol (Entry 10): IR (neat); v_{max} (cm⁻¹): OH (3416), N₃ (2103); 1H NMR (400 MHz, CDCl3): δ: 2.66 (d, 1H, J = 3.66 Hz); 3.40-3.64 (m, 2H), 5.14 (m, 1H), 6.96-7.04 (m, 2H),

7.29 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ: 58.42, 70.21, 125.34, 126.21, 127.60, 144.63 ppm.

CONCLUSIONS

In summary, we have successfully developed a novel magnetic polymer-supported catalyst as an efficient, inexpensive and non-corrosive catalyst for synthesis of 1,2-azidoalcohols via regioselective ring opening of their epoxides under reflux conditions. This operationally simple method does not require the use of toxic organic solvents. Moreover, this recyclable catalyst offers advantages like its ease of operation, high efficiency, and low cost. Current efforts in our research group are attempting to expand the application of PEG-MDIL for catalyzed organic reactions.

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