



Full paper/Mémoire

Synthesis of 1,2-azidoalcohols from epoxides using a task-specific protic ionic liquid: 1-hydrogen-3-methylimidazolium azide

Fariba Heidarizadeh^{*}, Ali BeitSaeed, Eshagh Rezaee-Nezhad

Department of Chemistry, Faculty of Sciences, Shahid Chamran University, Ahvaz 6135743169, Iran

ARTICLE INFO

Article history:

Received 21 June 2013

Accepted after revision 12 August 2013

Available online 7 October 2013

Keywords:

Protic ionic liquid

Ionic liquid

[Hmim]N₃; 1,2-azidoalcohol

Epoxide

Ring opening

ABSTRACT

A task-specific ionic liquid as an environmentally eco-friendly green catalyst has been synthesized and used in the ring opening of epoxides under green conditions. In order to use protic ionic liquids (PIL), we decided to synthesize 1,2-azidoalcohols via a ring opening reaction of epoxides with 1-hydrogen-3-methylimidazolium azide ([Hmim]N₃), which actually acts as a solvent, a reagent and an activator of the epoxide ring. The reaction was carried out in short times (50–70 min) at 70 °C to give 1,2-azidoalcohol in 80–94% isolated yields.

© 2013 Published by Elsevier Masson SAS on behalf of Académie des sciences.

1. Introduction

1,2-azidoalcohol has been considered increasingly, since this compound is very important in both organic chemistry – for the synthesis of amino sugars, carboxylic nucleosides, lactams, and oxazolines [1]– and in medical chemistry – for the synthesis of β -blockers and its presence in various natural products and different bioactive compounds [2–4]. The ring opening of epoxides, which have been innovative ways to obtain direct azidolysis of epoxides in the presence of sodium azide, are frequently performed under several different conditions [5–9].

The ring cleavage of epoxides with azide [10–14] generally requires a long reaction time (12–48 h) and is often accompanied by isomerization, epimerization, rearrangement of the products [15], and tedious work-up. 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 [6]. But development of a new and efficient protocol for this transformation under mild and more convenient conditions is still needed.

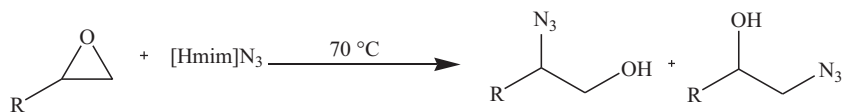
Herein we report an efficient method for the conversion of epoxides to 1,2-azidoalcohols. In this method we used a triple-function protic ionic liquid that contains an azide nucleophile for ring opening of epoxides. Various aliphatic and aromatic epoxides were converted into their azidoalcohols derivatives in excellent yields and in short time (Scheme 1).

PILs are a class of ionic liquids which are formed by mixing equimolar amounts of Brønsted acids and bases [16,6]. The strength of the acid/base combination determines the degree of the proton activity.

Recently, Welton et al. described the conversion of biomass to fuels and chemical products by ionic liquids [17]. On the other hand, Wasserscheid et al. studied the surface and the near-surface region of ionic liquid systems with a clear focus on reactions [18]. Finally, Davis Jr. et al. reported, for the first time, task-specific ionic liquids [19], non-toxic ions in the formulation of ionic liquids [20], and “boronium-ion”-based ionic liquids [21].

^{*} Corresponding author.

E-mail address: heidarizadeh@scu.ac.ir (F. Heidarizadeh).



Scheme 1. Preparation of azidohydrines in the presence of TSIL.

2. Results and discussion

Task-specific protic ionic liquids combine the advantageous characteristics of solid acids and mineral acids, and can be good candidates for traditional mineral liquid acids, such as sulfuric acid and hydrochloric acid, in chemical processes [22,23]. Thus, as a part of our continuing interest in the development of clean chemical processes, we synthesized a task-specific protic ionic liquid, [Hmim] N_3 . This ionic liquid has an acidic hydrogen that catalyzes the reaction and has an azide anion that takes part in the reaction. In this process, the remaining part of [Hmim] N_3 is methylimidazole, which can be used in the preparation of any other ionic liquids without any more purification, and this is in agreement with the atomic economy of green chemistry principles. We believe that this paper is the first report of this kind of task-specific protic ionic liquid.

In a typical experiment, phenyl glycidyl ether and [Hmim] N_3 was selected. The effect of the amount of ionic liquid on the reaction time was studied by varying the quantity of ionic liquid (1, 1.2, 1.5, 2, and 3 mmol/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 3 mmol/1 mmol epoxide (Table 1).

The effect of the reaction temperature on the reaction time of phenyl glycidyl ether azidolysis was investigated at reaction temperatures ranging from 25 to 70 °C. The results show that the suitable reaction temperature is 70 °C (Table 2).

After optimizing the conditions, we examined the generalization of these conditions to other substrates using several epoxides. Table 3 shows the results that clarify the fact that the reaction proceeds very efficiently in all cases. Different epoxides underwent ring opening easily in the presence of [Hmim] N_3 at 70 °C. The products were formed in excellent yields. The conversion was complete in 50–70 min.

Table 1

Optimization study of azidolysis reaction of phenyl glycidyl ether with different amounts of [Hmim] N_3 at 70 °C.

Entry	[Hmim] N_3 (mmol)	Reaction progress	Time (min)
1	1	–	–
2	1.2	–	–
3	1.5	Complete	100
4	2	Complete	85
5	3	Complete	55

Considering the emerging importance of [Hmim] N_3 as novel reactions media, we wish to report the use of task-specific ionic liquids as efficient promoters for the ring opening of various epoxides. The procedure gives products in good yields and short reaction times and avoids using organic solvents (handling, cost, safety, pollution). Environmental-friendly ionic liquid afforded a valuable alternative to promote numerous efficient catalytic systems that have already been proposed for the ring opening of epoxides. As it can be seen in Table 3, [Hmim] N_3 as a catalyst afforded good results in comparison to the other catalysts. In order to evaluate the efficiency of the method we introduce, more recently developed methods were compared with our present one on the basis of the yields and reaction times parameters; the results are given in Table 4.

Scheme 2 shows a plausible mechanism for the ring opening of epoxides in the [Hmim] N_3 as reagent, catalyst, and solvent.

3. Experimental

Products were characterized by comparison of their spectroscopic data (1H NMR, ^{13}C NMR, and IR) and physical properties with those reported in the literature. NMR spectra were recorded in $CDCl_3$ on Bruker Avance DPX 500 and 400 MHz spectrometers using TMS as an internal standard. FTIR spectra of KBr powder-pressed pellets were recorded on a BOMEM MB-Series 1998 FT-IR spectrometer. All yields refer to isolated products.

3.1. Procedure for the preparation of task-specific ionic liquids [Hmim] N_3 from [Hmim]Cl

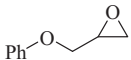
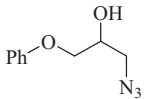
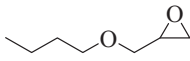
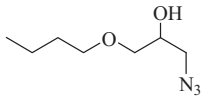

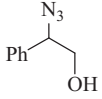
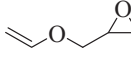
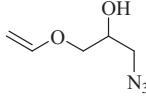
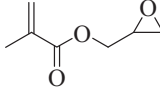
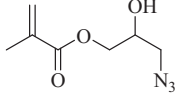

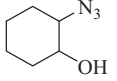
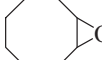
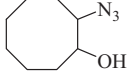
1-hydrogen-3-methylimidazolium chloride was prepared according to [24]. [Hmim]Cl (11.80 g, 0.1 mol) was dissolved in dry acetonitrile (25 mL) and stirred at room temperature for 25 min; NaN_3 (0.1 mol) dissolved in dry acetonitrile (40 mL) was added dropwise to [Hmim]Cl

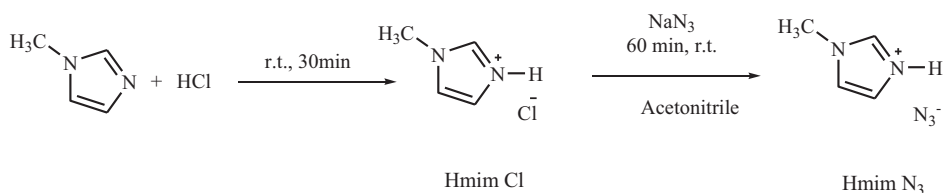
Table 2

Optimization study of azidolysis reaction of phenyl glycidyl ether (mmol) with [Hmim] N_3 (3 mmol) at different temperatures.

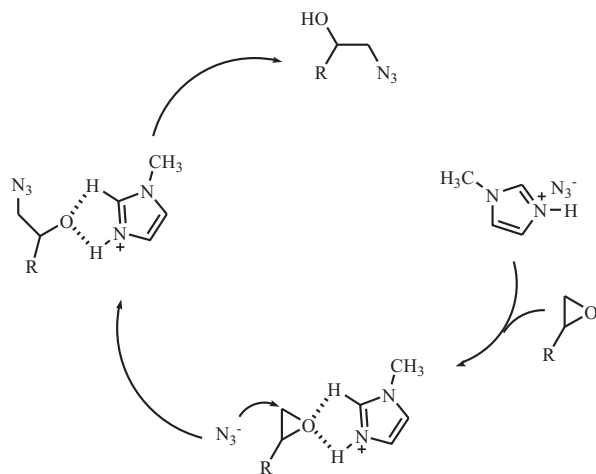
Entry	Temperature (°C)	Reaction progress	Time (min)
1	25	–	–
2	40	–	–
3	50	completed	85
4	60	completed	60
5	70	completed	55

Table 3
Preparation of 1,2-azidoalcohols using [MIM]N₃.

Entry	Epoxide	Product	Time (min)	Yield (%)
1			55	94
2			70	89
3			50	88
4			60	80
5			60	87
6			65	83
7			70	82



Scheme 2. Mechanism of the epoxide ring opening reaction by a task-specific ionic liquid.



Scheme 3. Synthesis of a task-specific ionic liquid.

over a period of 60 min at room temperature. The reaction mixture was magnetically stirred for 24 h at room temperature. The obtained white solid was washed with acetonitrile and the ionic liquid present in the filtrate was obtained by evaporation of the solvent under reduced pressure (Scheme 1).

3.2. General procedure for the preparation of 2-azidoalcohols

A mixture of epoxide (1 mmol) and [Hmim]N₃ (3 mmol) was heated at 70 °C under stirring for the time shown in Table 1 (Scheme 3). Progress of reaction was monitored by TLC using ethyl acetate:*n*-hexane (1:5). After reaction completion, the mixture was extracted with ethyl ether (10 mL × 3), washed with brine, dried with CaCl₂ and evaporated under reduced pressure. The desired azidoalcohols were obtained in good to excellent isolated yields (80–94%).

Table 4
Comparison of efficiency of various catalysts in synthesis of 1,2-azidoalcohol.

Entry	Catalyst/reagent/solvent	Temperature	Time (min)	Yield (%)	References
1	[Hmim]N ₃	70 °C	55	94	This work
2	Network Polymer/NaN ₃ /water	80 °C	90	89	[5]
5	SiO ₂ -PEG/NaN ₃ /H ₂ O	Reflux	120	95	[7]
2	β-cyclodextrine/TMSN ₃ /H ₂ O	r.t.	300	45	[25]
3	CeCl ₃ /NaN ₃ /(CH ₃ CN\H ₂ O)	Reflux	180	99	[26]
4	[Bmim]PF ₆ /NaN ₃ /H ₂ O	65 °C	180	95	[27]
6	PEG-300/NaN ₃ /Solvent free	60 °C	60	90	[28]
7	MPTC/NaN ₃ /H ₂ O	Reflux	30	85	[29]
8	Er(OTf) ₃ /TMSN ₃ /Solvent free	r.t.	400	86	[30]

4. Conclusion

The use of [Hmim]N₃ in the azidolysis of epoxides can be considered as an interesting new alternative to the existing nucleophile and homogeneous catalysts. It is possible to obtain high conversions and very high selectivities in a variety of reactions. Short reaction times, simple work-up in isolation of the products with high purity, and mild reaction conditions are the features of this new procedure.

Acknowledgments

The authors gratefully acknowledge the financial support of this work by Shahid Chamran (Ahvaz) University Research Council.

References

- [1] S.W. Chen, S.S. Thakur, W. Li, C.K. Shin, R.B. Kawthekar, G.J. Kim, J. Mol. Catal. A: Chem. 259 (2006) 116.
- [2] A.G. Habeeb, P.N.P. Rao, E.E. Knaus, J. Med. Chem. 44 (2001) 3039.
- [3] S. Piantadosi, C.J. Marasco, E.J. Modest, J. Med. Chem. 34 (1991) 1408.
- [4] H.C. Kolb, M.G. Finn, K.B. Sharpless, Angew. Chem. Int. Ed. 40 (2001) 2004.
- [5] A. Mouradzadegan, A.R. Kiasat, P. Kazemian Fard, Catal. Commun. 29 (2012) 1.
- [6] F. Heidarizadeh, A. Zarei, J. Chem. Soc. Pak. 34 (2012) 593.
- [7] A.R. Kiasat, M. Zayadi, Catal. Commun. 9 (2008) 2063.
- [8] F. Kazemi, A.R. Kiasat, S. Ebrahimi, Synth. Commun. 33 (2003) 999.
- [9] J.S. Yadav, B.V. Reddy, B. Jyothirmai, M.S.R. Murty, Tetrahedron Lett. 46 (2005) 6559.
- [10] M. Chini, P. Crotti, F. Macchia, Tetrahedron Lett. 31 (1999) 5641.
- [11] M. Chini, P. Crotti, L.A. Flippin, C. Gardelli, E. Giovani, F. Macchia, M. Pineschi, J. Org. Chem. 58 (1993) 1221.
- [12] P. Serrano, A. Llebaria, A. Delgado, J. Org. Chem. 70 (2005) 7829.
- [13] P. Crotti, V. Di Bussolo, L. Favero, F. Macchia, M. Pineschi, Tetrahedron Lett. 37 (1996) 1675.
- [14] S.S. Palimkar, S.A. Siddiqui, T. Daniel, R.J. Lahoti, K.V. Srinivasan, J. Org. Chem. 68 (2003) 9371.
- [15] E.F.V. Scriven, K. Turnbull, Chem. Rev. 88 (1988) 297.
- [16] (a) T.L. Greaves, C.J. Drummond, Chem. Rev. 108 (2008) 206; (b) T.L. Greaves, A. Weerawardena, C. Fong, I. Krodkiewska, C.J. Drummond, J. Phys. Chem. B 110 (2006) 22479; (c) Z. Duan, Y. Gu, J. Zhang, L. Zhu, Y. Deng, J. Mol. Catal. A: Chem 250 (2006) 163; (d) A.R. Hajipour, F. Rafiee, Org. Prep. Proced. Int. 42 (2010) 285; (e) J. Akbari, A. Heydari, L. Ma'mani, H. Hassan, C.R. Chimie 13 (2010) 544.
- [17] (a) A. Brandt, M.J. Ray, T.Q. To, D.J. Leak, R.J. Murphy, T. Welton, Green Chem. 13 (2011) 2489; (b) M. Schrems, A. Brandt, T. Welton, F. Liebner, T. Rosenau, A. Potthast, Holzforschung 65 (2011) 527; (c) A. Brandt, J. Gräsvik, J.P. Hallett, T. Welton, Green Chem. 15 (2013) 550.
- [18] (a) J.M. Gottfried, F. Maier, J. Rossa, D. Gerhard, P.S. Schulz, P. Wasserscheid, H.-P. Steinrück, Z. Phys. Chem. 220 (2006) 1439; (b) C. Kolbeck, M. Killian, F. Maier, N. Paape, P. Wasserscheid, H.-P. Steinrück, Langmuir 24 (2008) 9500.
- [19] (a) E.D. Bates, R.D. Mayton, I. Ntai, J.H. Davis Jr., J. Am. Chem. Soc. 124 (2002) 926; (b) J.H. Davis Jr., Chem. Lett. 33 (2004) 1072; (c) A.E. Visser, R.P. Swatloski, W.M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J.H. Davis Jr., R.D. Rogers, Environ. Sci. Technol. 36 (2002) 2523.
- [20] J.H. Davis Jr., K.J. Forrester, T.L. Merrigan, Tetrahedron Lett. 39 (1998) 8955.
- [21] (a) J.H. Davis Jr., J.D. Madura, Tetrahedron Lett. 37 (1996) 2729; (b) M.D. Soutullo, C.I. Odom, A.B. Smith, D.R. McCreary, R.E. Sykora, E.A. Salter, A. Wierzbicki, J.H. Davis Jr., Inorg. Chim. Acta 360 (2007) 3099.
- [22] J.S. Wilkes, J. Mol. Catal. A: Chem. 214 (2004) 11.
- [23] A.C. Cole, J.L. Jensen, I. Ntai, K.L.T. Tran, K.J. Weaver, D.C. Forbes, J.H. Davis Jr., J. Am. Chem. Soc. 124 (2002) 5962.
- [24] R. Kore, R. Srivastava, Tetrahedron Lett. 53 (2012) 3245.
- [25] A. Kamal, M. Arifuddin, M.V. Rao, Tetrahedron: Asymmetry 10 (1999) 4261.
- [26] G. Sabitha, R.S. Babu, M. Rajkumar, J.S. Yadav, Org. Lett. 4 (2002) 343.
- [27] J.S. Yadav, B. Reddy, B. Jyothirmai, M.S.R. Murty, Tetrahedron Lett. 46 (2005) 6559.
- [28] A.R. Kiasat, M. Fallah-Mehrjardi, J. Iran. Chem. Soc. 6 (2009) 542.
- [29] A.R. Kiasat, R. Mirzajani, H. Shalhaf, T. Tabatabaei, M. Fallah-Mehrjardi, J. Chin. Chem. Soc. 56 (2009) 594.
- [30] A. Procopio, P. Costanzo, R. Dalpozzo, L. Maiuolo, M. Nardi, M. Oliverio, Tetrahedron Lett. 51 (2010) 5150.