Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Molecular Catalysis A: Chemical 214 (2004) 155–160
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Room temperature ionic liquid promoted regioselective synthesis of 2-aryl benzimidazoles, benzoxazoles and benzthiazoles under ambient conditions

R.N. Nadaf, S.A. Siddiqui, Thomas Daniel, R.J. Lahoti, K.V. Srinivasan*

Division of Organic Chemistry, Technology, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India

Received 31 July 2003; accepted 13 October 2003

Abstract

A regioselective one-pot synthesis of 2-aryl benzimidazoles, benzoxazoles and benzthiazoles has been achieved in excellent isolated yields under ambient conditions using the ionic liquids, 1-butylimidazolium tetraflouroborate ([Hbim]BF_4) and 1,3-di-*n*-butylimidazolium tetrafluoroborate ([bbim]BF_4) as reaction media and promoters. There was no need for the use of an additional catalyst normally employed in the methodologies reported so far.

Keywords: Ionic liquids; 2-Aryl benzimidazoles; Benzoxazoles; Benzthiazoles; Benzoyl chlorides

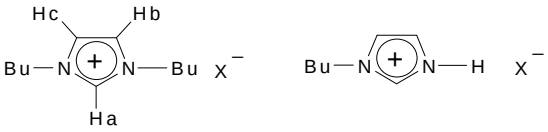
1. Introduction

The heterocycles 2-aryl benzimidazoles, benzoxazoles and benzthiazoles have received considerable attention in diverse areas of chemistry [1–5]. Some of these nuclei are found in a variety of naturally occurring compounds and are of significant importance in medicinal chemistry. Synthetic routes that are common to the preparation of these heterocycles typically involve the reaction of a carboxylic acid or its derivative with an appropriate 1,2-phenylenediamine, 2-aminophenol or 2-aminothiophenol in the presence of a strong acid at elevated temperatures [6,7]. Alternatively, a two-step procedure is employed wherein the 1,2-phenylenediamine, 2-aminophenol or 2-aminothiophenol are treated with one equivalent of an acid chloride, and the resulting mono-acylated product is subjected to cyclodehydration under a variety of conditions such as heating in aqueous acids [8] or by pyrolysis at 200–350 °C [9,10]. In addition to the harsh conditions employed in these cases, some side reactions such as Friedel–Crafts acylation [11] and Fries rearrangement [12] also take place leading to lowering of selectivities. The use of room temperature ionic liquids in the present work has circumvented all the above mentioned limitations.

In recent times, the use of room temperature ionic liquids (ILs) as 'green' solvents in organic synthetic processes has gained considerable importance due to their solvating ability, negligible vapour pressure, easy recyclability and reusability [13]. They have the potential to be highly polar yet non-coordinating solvents. In addition to the above mentioned salient features, we have shown recently the ILs can be used as promoters and catalysts for effecting organic transformations of commercial importance under ambient conditions. Thus, Heck and Suzuki reactions proceed at ambient temperature with considerably enhanced reaction rates through the formation of Pd–biscarbene complexes in the presence of ionic liquids under ultrasonic irradiation [14,15]. The nitration of phenols using ferric nitrate and clays in ionic liquid under ultrasonic irradiation has not only exhibited significant enhancement in reaction rates but also higher para selectivity than hitherto reported [16]. Aromatic substrates were mono-brominated in just 5 min at ambient conditions in the IL 1,3-di-*n*-butylimidazolium tetrafluroborate in excellent isolated yields in the absence of a catalyst [17]. The reaction of *o*-phenylenediamines with both acyclic and cyclic ketones in the IL 1,3-di-*n*-butylimidazolium bromide afforded 1,5-benzodiazepines in excellent isolated yields in the absence of a catalyst at ambient temperature [18]. In

* Corresponding author. Tel.: +91-20-588-9089; fax: +91-20-589-3614.
E-mail address: kvsri@dalton.ncl.res.in (K.V. Srinivasan).

1381-1169/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2003.10.064



[bbim]X [Hbim]X

X = Br, Cl, BF_4, PF_6, ClO_4

Fig. 1. Ionic liquids synthesized, characterized and screened.

continuation, we wish to report for the first time, a novel regioselective one-pot synthesis of 2-aryl benzimidazoles, benzoxazoles and benzthiazoles in excellent isolated yields promoted by imidazolium based ionic liquids under ambient conditions without the need for any added catalyst.

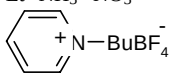
2. Results and discussion

Two sets of new ILs based on *N*,*N*-di-*n*-butyl imidazolium (bbim) and *N*-butyl imidazolium (Hbim) salts with varying basicity of the anions were synthesized (Fig. 1).

They were fully characterized by ^{1}H NMR, ^{13}C NMR and mass spectral analysis. For the [Hbim] ILs, ^{1}H NMR spectra were recorded neat using $CDCl_3$ as external lock wherein the NH proton chemical shifts were observed as broad singelets. In mass spectra, all the ILs showed [M–X] as the base peak and peaks corresponding to the molecular ion were not observed. The elemental analysis of the ILs were in conformity with their structures. The densities and viscosities of the ILs were determined and along with the ^{1}H NMR chemical shifts for the most acidic proton for the series of ILs screened are recorded in Table 1.

The ILs along with two nonimidazolium ILs such as ethyl ammonium nitrate and *n*-butylpyridinium tetrafluoroborate were then tested as solvents and promoters for the typical reaction of 1,2-phenylendiamine with benzoyl chloride under ambient conditions in the absence of any added catalyst to afford 2-phenyl benzimidazole (**3a**). The time for complete conversion and yield data are recorded in Table 2. The ILs, [Hbim]BF_4 among the monoalkyl imidazolium salts and [bbim]BF_4 among the dialkyl imidazolium salts, respectively, afforded the best results for this reaction. It is worth noting the non-imidazolium ILs took much longer time (5.3 h) to afford **3a** in relatively lowered yields (70–73%).

Table 2
Synthesis of 2-phenyl benzimidazole (**3a**) in different ILs

Entry	IL	Time of completion	Yield[a] (%)
1	[bbim]Br	40 min	90
2	[bbim]Cl	45 min	93
3	[bbim]BF_4	40 min	92
4	[bbim]PF_6	110 min	90
5	[bbim]ClO_4	130 min	87
6	[Hbim]Br	18 min	92
7	[Hbim]Cl	18 min	92
8	[Hbim]BF_4	10 min	95
9	[Hbim]PF_6	60 min	93
10	[Hbim]ClO_4	90 min	84
11	$Et^{\oplus}NH_3{}^{\ominus}NO_3$	5.3 h	70
12		5.3 h	73

[a] Isolated yield after column chromatography.

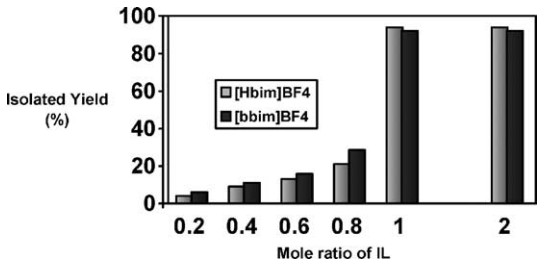


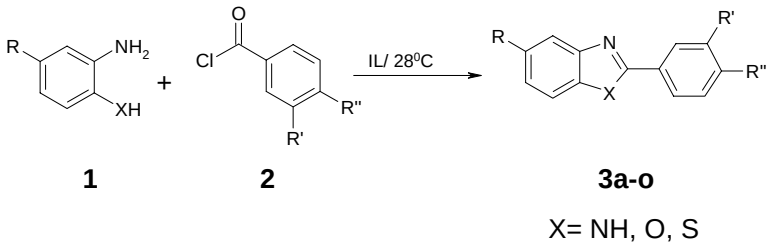
Fig. 2. Effect of mole ratio of IL on yield of **3a**.

The effect of mole ratio of these selected ILs with respect to the reactants was investigated (Fig. 2). It can be observed that a minimum of equimolar proportion of the IL is required for optimum results beyond which there is no further increase.

Consequently, these two ILs were used to generate a variety of 2-aryl benzimidazoles, benzoxazoles and

Table 1
Significant characterization data for the ILs

Entry	IL	Density at 28 °C g/cm^3	Viscosity at 28 °C (cP)	Chemical shift δ (ppm)	
				Ha	NH
1	[bbim]Br	1.23	373.1	10.08	–
2	[bbim]Cl	1.02	1179.6	10.38	–
3	[bbim]BF_4	1.15	105.6	9.20	–
4	[bbim]PF_6	1.23	132.0	8.86	–
5	[bbim]ClO_4	1.19	57.6	9.02	–
6	[Hbim]BF_4	1.20	68.8	–	14.59
7	[Hbim]Br	1.21	98.6	–	12.22
8	[Hbim]Cl	1.11	149.6	–	12.17
9	[Hbim]ClO_4	1.29	28.2	–	11.83



Scheme 1.

Table 3
Synthesis of **3a**–**3o** in $[Hbim]BF_4$

Product **3**	X	R	R_1	R_2	Time (min)	Yield[a] (%)		
						First	Recycle I	Recycle II
3a	NH	H	H	H	10	95	95	93
3b	NH	H	H	NO_2	20	85	85	82
3c[b]	NH	H	F	CF_3	15	90	89	87
3d	NH	Me	H	H	10	96	96	94
3e	NH	Me	H	NO_2	20	84	84	82
3f[b]	NH	Me	F	CF_3	15	91	91	87
3g	O	H	H	H	10	96	95	93
3h	O	H	H	NO_2	20	82	81	79
3i[b]	O	H	F	CF_3	15	91	91	88
3j	O	Cl	H	H	10	89	88	87
3k	O	Cl	H	NO_2	25	79	79	77
3l[b]	O	Cl	F	CF_3	15	92	92	89
3m	S	H	H	H	10	96	96	94
3n	S	H	H	NO_2	25	80	78	77
3o[b]	S	H	F	CF_3	15	93	91	87

[a] Isolated yield after column chromatography.
[b] New compounds.

benzthiazoles by the reaction of 1,2-phenylenediamines, 2-aminophenols and 2-aminothiophenol with benzoyl chlorides, respectively, as shown in Scheme 1.

The time for complete conversion and the yield data for the 2-aryl heterocycles **3a**–**3o** in the respective ILs $[Hbim]BF_4$ and $[bbim]BF_4$ are recorded in Tables 3 and 4. All the known compounds were well characterized by melting point, IR, ^1H NMR and mass spectral analysis. Selected data for new compounds **3** are given in Table 5. In all cases, the IL could be recovered almost completely and

Table 4
Synthesis of **3a**–**3o** in $[bbim]BF_4$

Product **3**	X	R	R_1	R_2	Time (min)	Yield[a] (%)		
						First	Recycle I	Recycle II
3a	NH	H	H	H	40	92	90	90
3b	NH	H	H	NO_2	110	90	89	88
3c	NH	H	F	CF_3	80	91	89	89
3d	NH	Me	H	H	45	92	90	90
3e	NH	Me	H	NO_2	110	85	84	83
3f	NH	Me	F	CF_3	85	91	89	89
3g	O	H	H	H	40	92	90	90
3h	O	H	H	NO_2	110	86	85	84
3i	O	H	F	CF_3	85	91	89	87
3j	O	Cl	H	H	80	90	89	88
3k	O	Cl	H	NO_2	120	79	79	77
3l	O	Cl	F	CF_3	90	91	89	88
3m	S	H	H	H	40	94	93	92
3n	S	H	H	NO_2	120	82	81	80
3o	S	H	F	CF_3	85	91	89	89

[a] Isolated yield after column chromatography.

Table 5
Selected data for new compounds

New compounds	Melting point (°C)	IR (cm^{-1})	^1H NMR ($CDCl_3$) δ (ppm)	Mass (*m*/*z*)
3c	166	1641 (C=N), 3253 (NH)	4.84 (brs, NH), 8.09 (s, 1H, Ar–H), 7.68 (d, 1H, $J = 8.5$ Hz, Ar–H), 7.51 (d, 1H, $J = 8$ Hz, Ar–H), 7.19–7.68 (m, 4H, Ar–H)	280
3f	174	1645 (C=N), 3252 (NH)	2.38 (s, 3H, Ar–CH_3), 4.64 (brs, NH), 7.87 (s, 1H, Ar–H), 7.58 (d, 1H, $J = 9$ Hz, Ar–H), 7.61 (d, 1H, $J = 8.5$ Hz, Ar–H), 7.01–7.63 (m, 3H, Ar–H)	294
3i	168	1648 (C=N)	8.14 (s, 1H, Ar–H), 7.69 (d, 1H, $J = 8.5$ Hz, Ar–H), 7.64 (d, 1H, $J = 8$ Hz, Ar–H), 7.25–7.58 (m, 4H, Ar–H)	257
3l	177	1643 (C=N)	8.30 (s, 1H, Ar–H), 7.82 (d, 1H, $J = 8.5$ Hz, Ar–H), 7.60 (d, 1H, $J = 8$ Hz, Ar–H), 7.50–8.15 (m, 4H, Ar–H)	311
3o	186	1648 (C=N)	8.13 (s, 1H, Ar–H), 8.11 (d, 1H, $J = 8.5$ Hz, Ar–H), 7.95 (d, 1H, $J = 8$ Hz, Ar–H), 7.27–7.53 (m, 4H, Ar–H)	293

recycled twice with only a very marginal loss in yield (∼2%) in the recycle batch II. As is evident, all the reactions proceed to completion under ambient conditions in both ILs without any catalyst. The respective 2-aryl benzimidazoles, benzoxazoles and benzthiazoles were obtained in high regioselectivity and could be isolated in excellent yields in all cases. However, reactions in [Hbim]BF_4 are much faster (10–25 min) in comparison to those in [bbim]BF_4 (40–120 min). This may be attributed to the higher Brønsted acidity conferred by the –NH proton of [Hbim]BF_4 as compared to the most acidic Ha proton of [bbim]BF_4 which is also evident from the chemical shifts (Table 1). For both the ILs, electron-withdrawing groups in the aryl rings of the reactants, make the reactions relatively sluggish.

The efficacy of the ILs to promote these heterocyclization reactions was correlated to the basicity of the anions of the ILs. It was assumed that the nature of the anion will govern the electrophilicity of the imidazolium cation, which in turn has a bearing on the acidity of the ILs. Thus, the time for complete conversion in the synthesis of 2-phenyl benzimidazole (**3a**) in different ILs (Table 2) was plotted against the pK_a values of the corresponding acids of the anion (Fig. 3). The pK_a values were obtained from literature [19]. It was observed that with decreasing pK_a or decreasing basicity of the anion (conjugate base), there is an increase in time for complete conversion making the reaction progressively sluggish. This correlation was more evident in the case of [Hbim] ILs when the time for complete conversion (Table 2) was plotted against –NH proton chemical shifts (Table 1) indicative of some inherent Brønsted acidities of the ILs as

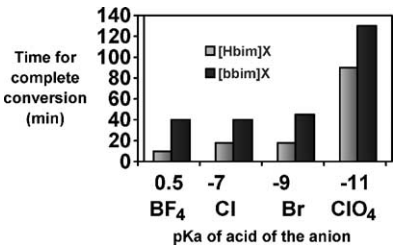


Fig. 3. Efficacy of ILs for heterocyclization in relation to the basicity of the anions.

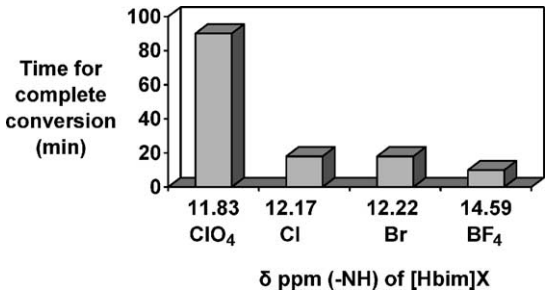


Fig. 4. Efficacy of ILs for heterocyclization in relation to Brønsted acidity of [Hbim]X (–NH proton chemical shifts).

shown in Fig. 4. The reaction becomes progressively faster with increasing downfield shift of the NH proton indicating that some acid catalysis from the IL is contributing. In all probability, the hydrogen bond interaction of the most acidic hydrogen (NH and Ha) of the imidazolium cations of the ILs with the carbonyl oxygen both during the acylation step and cyclodehydration of the mono-acylated product step may have promoted the overall reaction. Further work is in progress to obtain deeper insights into the role of the ILs in promoting the heterocyclization reaction.

3. Experimental

3.1. General remarks

NMR spectra were recorded on Bruker AC-200 spectrometer in $CDCl_3$ with TMS as an internal standard. Density was measured using an Anton Paar vibrating tube densimeter (DMA 602/60). Viscosity was measured using a Brookfield Digital Viscometer model DV-I. Mass spectra were obtained with Finnegan MAT mass spectrometer. Infra red spectra were recorded with ATI MATT-SON RS-1 FTIR spectrometer. Melting points were recorded in open capillary and were uncorrected. Column chromatography was performed using silica–gel (60–120 mesh size) purchased from Thomas Baker and TLC was carried out using aluminium sheets pre-coated with silica gel $60F_{254}$ purchased

from Merck. All solvents and chemicals used were reagent grade procured from Merck and Lancaster and used without further purification unless otherwise stated. *N*-Butyl imidazole was prepared as per reported method [20].

3.2. Preparation of different ionic liquids

The ILs [bbim]Br, ethyl ammonium nitrate and *n*-butylpyridinium tetrafluoroborate were prepared as per methods reported in literature [14,21].

3.2.1. Preparation of 1-butylimidazolium tetrafluoroborate [Hbim]BF_4

Tetrafluoroboric acid (1 mol, 40% solution in water) was added slowly over a period of 30 min to 1-butyl imidazole (1 mol) at 0 °C under stirring. The reaction mixture was stirred for an additional period of 2 h at the same temperature. Water was removed from the reaction mixture by subjecting it to evaporation for 4 h at 80 °C under reduced pressure (10 mmHg) to give the product as colourless liquid (20 g; yield, 96%).

Viscous oil (20 g; yield 96%)–IR (KBr) $\nu = 3607, 3153, 2876, 1580, 1466, 894, 762\,cm^{-1}$–^{1}H NMR δ = 0.56 (s, 3H, CH_3), 0.95 (s, 2H, $CH_3CH_2(CH_2)_2N$), 1.47 (s, 2H, NCH_2CH_2), 3.87 (s, 2H, NCH_2), 7.12 (s, 2H, NC*H*C*H*N), 8.16 (s, 1H, NC*H*N), 14.59 (brs, 1H, NH)–^{13}C NMR δ = 13.1, 19.2, 32.1, 48.5, 120.9, 122.8, 135.2–MS: *m*/*z* (%): 124 (M–X, 26), 109 (3), 97 (92), 81 (100), 68 (26), 55 (56)–$C_7H_{13}N_2BF_4$ (211): calcd. C, 39.81; H, 6.16; N, 13.27. Found C, 39.81; H, 6.05; N, 13, 18.

All other ionic liquids such as [Hbim]PF_6, [Hbim]Br, [Hbim]Cl and [Hbim]ClO_4 were prepared as above using the corresponding acid of the anion.

3.2.2. Preparation of 1,3-di-n-butylimidazolium chloride [bbim]Cl

A mixture of 1-*n*-butyl imidazole (12.4 g, 0.1 mol) and *n*-butyl chloride (10.17 g, 0.11 mol) was heated with stirring at 70 °C for 4 h. Excess *n*-butyl chloride was distilled off at 80 °C under reduced pressure (10 mmHg) over 2 h leaving behind the pure IL [bbim]Cl (20.56 g; yield, 95%).

3.2.3. A typical procedure for 1,3-di-n-butylimidazolium tetrafluoroborate [bbim]BF_4

A mixture of 1-*n*-butyl imidazole (12.4 g, 0.1 mol) and *n*-butyl bromide (15.0 g, 0.11 mol) was heated with stirring at 70 °C for 4 h. Excess *n*-butyl bromide was distilled off at 80 °C under reduced pressure (10 mmHg) for 2 h. Water (100 ml) was added to the resulting thick liquid consisting of 1,3-di-*n*-butylimidazolium bromide ([bbim]Br), under stirring. A solution of sodium tetraflouroborate (22 g, 0.2 mol) in water (80 ml) was then added to the above solution and the mixture was stirred at 30 °C for 5 h. The ionic liquid [bbim]BF_4 separates out as an immiscible layer. The mixture was extracted with dichloromethane (3 × 30 ml). The combined DCM layer, which was separated, was washed with 2% hydrochloric acid, water, brine and dried over anhydrous sodium sulphate. The solvent DCM was distilled off under reduced pressure leaving behind the pure IL [bbim]BF_4 (23.0 g; yield, 85%).

Viscous oil (23.0 g; yield 86%)–IR (KBr) $\nu = 3401, 3067, 2874, 1635, 1563, 1465, 1167, 753\,cm^{-1}$–^{1}H NMR δ = 0.96 (t, J = 7.0 Hz, 6H, CH_3), 1.40 (sept, J = 7.6 Hz, 4H, $CH_3CH_2(CH_2)_2N$), 1.97 (pent, J = 7.5 Hz, 4H, NCH_2CH_2), 4.41 (t, J = 7.0 Hz, 4H, NCH_2), 7.87 (s, 2H, NC*H*C*H*N), 9.20 (s, 1H, NC*H*N)–^{13}C NMR δ = 12.9, 18.9, 31.6, 49.3, 122.2, 135.2–MS: *m*/*z* (%): 181 (M–X, 100), 165 (15), 151 (12), 138 (61), 124 (40), 107 (33), 97 (65), 81 (62), 68 (16), 57 (42)–$C_{11}H_{21}N_2BF_4$ (268): calcd. C, 49.25; H, 7.83; N, 10.44. Found C, 49; H, 7.71; N, 10.21.

Similarly other ionic liquids such as [bbim]PF_6 and [bbim]ClO_4 were prepared as above using the corresponding acid of the anion.

3.3. Synthesis of heterocycles **3a**–**3o**

The 2-aryl benzimidazoles, benzoxazoles and benzthiazoles were prepared as per the typical procedures described below for 2-phenyl benzimidazole (**3a**) in [Hbim]BF_4 and [bbim]BF_4, respectively.

3.3.1. Typical procedure for synthesis of 2-phenyl benzimidazole (**3a**) in [Hbim]BF_4

A mixture of *o*-phenylenediamine (4.6 mmol) and benzoyl chloride (4.6 mmol) in [Hbim]BF_4 (4.6 mmol) was stirred at room temperature (28 °C). The completion of reaction was followed by TLC using 35% EtOAc in petroleum ether as eluent. After completion (10 min), the reaction mixture was diluted with water (25 ml) and the separated product was filtered. It was washed thoroughly with water and dried. The product, thus isolated, was pure enough (single spot on TLC). It was subjected to further purification by chromatography through a column of silica–gel using 20% EtOAc in petroleum ether as eluent and fully characterized. The aqueous layer consisting of the IL was subjected to distillation (80 °C at 10 mmHg) for 2 h to remove water, leaving behind the IL [Hbim]BF_4 (recovery 96%), which was recycled.

3.3.2. Typical procedure for synthesis of 2-phenyl benzimidazole (**3a**) in [bbim]BF_4

A mixture of *o*-phenylenediamine (4.6 mmol) and benzoyl chloride (4.6 mmol) in [bbim]BF_4 (4.6 mmol) was stirred at room temperature (28 °C). The completion of reaction was followed by TLC using 35% EtOAc in petroleum ether as eluent. After completion (40 min), the reaction mixture was extracted with 35% EtOAc in pet ether (2 × 15 ml). The product comes in 35% EtOAc in pet ether leaving behind [bbim]BF_4. The organic layer was separated, dried over anhydrous sodium sulphate and the solvent evaporated under reduced pressure to afford the crude **3a**. The crude product was subjected to column chromatography through a column

of silica–gel using 20% EtOAc in petroleum ether as eluent to isolate pure product. The [bbim]BF_4 left as the immiscible layer (recovery 97%) was used as such for the recycle studies.

4. Conclusion

A novel one-pot regioselective synthesis of 2-aryl benzimidazoles, benzoxazoles and benzthiazoles in excellent isolated yields has been developed under ambient conditions using room temperature ionic liquids as reaction media and promoters. For this procedure, there was no need for any additional catalyst, which are generally required in the methodologies reported so far. Several new ILs were synthesized, characterized and screened for these heterocyclization reactions. The efficacy of the ILs for the heterocyclization reaction has been correlated to the acidity of the ILs in terms of basicity of the anions and ^{1}H NMR chemical shifts. The ambient reaction conditions, absence of a catalyst and recyclability of the non-volatile ILs makes this an environment friendly methodology amenable for scale up.

Acknowledgements

The authors acknowledge financial assistance from Department of Science and Technology, New Delhi, vide Project No. SP/S5/OC-23/02.

References

[1] W.A. Denny, G.W. Rewcastle, B. Baguley, J. Med. Chem. 33 (1990) 814.
[2] J. Kondo, N. Suzuki, T. Imaoka, T. Kawasaki, A. Nakanishi, Y. Kawahara, Anal. Sci. 10 (1994) 17.
[3] M. Zhao, M. Samoc, P.N. Prasad, B.A. Reinhardt, M. Sinky, Chem. Mater. 2 (1992) 670.
[4] P.E. Cassidy, Thermally Stable Polymers, Marcel Dekker, New York, 1980.
[5] G. Frachy, C. Crestini, R. Berini, R. Salidino, E. Micione, Heterocycles 38 (1994) 2621.
[6] P.N. Preston, in: A. Wiessberger, E.C. Taylor (Eds.), Benzimidazoles and Congenetic Tricyclic Compounds. Part 1. The Chemistry of Heterocyclic Compounds, Wiley, New York, 1981, p. 5.
[7] M. Terashima, M. Ishii, Synthesis (1982) 1484 and references cited therein.
[8] M.A. Philips, J. Chem. Soc. (1928) 2839.
[9] N. Kudryashova, L.B. Piotrovskii, V.A. Naumov, N.B. Brovtsyna, N.V. Khromov-Borisov, Zh. Org. Khim. 10 (1974) 1542.
[10] D.V. Ramana, E. Kantharaj, Tetrahedron 50 (1994) 2485.
[11] G.M. Tseitlin, B.V. Tokarev, V.N. Kulagin, Zh. Org. Khim. 18 (1982) 931.
[12] Y. Kanaoka, T. Hamada, O. Yonemistu, Chem. Pharm. Bull. 18 (1970) 587.
[13] (a) T. Welton, Chem. Rev. 99 (1999) 2071;
(b) P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. Engl. 39 (2000) 3772;
(c) M.J. Earle, K.R. Seddon, Pure Appl. Chem. 72 (2000) 1391;
(d) C.M. Gordon, Appl. Catal. A: Gen. 222 (2001) 101;
(e) R. Sheldon, Chem. Commun. (2001) 2399.
[14] R.R. Deshmukh, R. Rajagopal, K.V. Srinivasan, Chem. Commun. (2001) 1544.
[15] R. Rajagopal, D.V. Jarikote, K.V. Srinivasan, Chem. Commun. (2002) 616.
[16] R. Rajagopal, K.V. Srinivasan, Ultrasonics Sonochem. 10 (2003) 41.
[17] R. Rajagopal, D.V. Jarikote, T. Daniel, R.J. Lahoti, K.V. Srinivasan, Tetrahedron Lett. 44 (2003) 1815.
[18] D.V. Jarikote, S.A. Siddiqui, R. Rajagopal, T. Daniel, R.J. Lahoti, K.V. Srinivasan, Tetrahedron Lett. 44 (2003) 1835.
[19] (a) D.D. Perrin, Ionisation Constant of Inorganic Acids and Bases in Aqueous Solution, second ed., Pergaman Elmsford, New York, 1982;
(b) R.P. Bell, The Proton in Chemistry, second ed., Cornell University Press, Ithaca, NY, 1973.
[20] (a) M. Haring, Helv. Chim. Acta 42 (1959) 1845;
(b) L.J. Mathias, D. Burkett, Tetrahedron Lett. 20 (1979) 4709.
[21] P. Walden, Bull. Acad. Imper. Sci. (St. Petersburg) (1914) 1800;
(b) J. Peng, Y. Deng, Tetrahedron Lett. 42 (2001) 403.